Detoxification of a highly toxic lead-loaded industrial solid waste by stabilization using apatites

T.A. Ioannidis, A.I. Zouboulis*

Department of Chemistry, Division of Chemical Technology, Aristotle University of Thessaloniki, Box 116, GR-541 24 Thessaloniki, Greece

Received 28 December 2001; received in revised form 14 August 2002; accepted 3 September 2002

Abstract

Apatites are known for their properties to immobilize lead contained in aqueous solutions or contaminated soils. In this study, apatites were examined as stabilization additives for lead-loaded industrial solid toxic wastes. The specific waste was the residue, obtained after thermal treatment of sludges (incineration), which was derived from tetraethyl lead fuel storage tanks. It was found to contain around 30 wt.% lead and 33 wt.% iron. Standard leaching tests (according to DIN 38414 S-4) were applied for the determination of leachability of metals from the ash and, thus, of chemical toxicity; the proposed leaching tests examined both initial and stabilized products in order to evaluate the effectiveness of the applied additives. The results obtained demonstrate the fact that lead concentrations in leachates, after the application of the proposed leaching tests using apatites as additives and with a ratio of 50% solid waste–50 wt.% apatite, could be reduced to the range of 1 mg/l.
© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Stabilization; Industrial solid waste; Leaching; Lead; Apatite; Thermal treatment

1. Introduction

Solidification/stabilization (S/S) is an established technology that has been used for almost 20 years to treat a variety of toxic industrial wastes [1]. Historically, S/S was placed among the top five source control treatment technologies, as they were applied to Superfund remedial sites in the USA [2]. For this purpose, a number of inorganic additives can be applied, such as silicates, cement, apatites (synthetic and natural), etc. This study presents the treatment process of lead-rich thermal residues, after appropriate incineration of sludges

* Corresponding author. Tel./fax: +30-310-997794.
E-mail addresses: ioannidisthem@yahoo.co.uk (T.A. Ioannidis), zoubouli@chem.auth.gr (A.I. Zouboulis).

derived from storage tanks, containing tetraethyl lead. The initial sludge was found to contain large quantities of various harmful organic compounds, such as tetraethyl lead (TEL), ethylene dibromide, ethylene dichloride, as well as oxidized derivatives of iron and lead. Initially, the sludge was subjected to incineration (under reduced conditions), producing a lead-rich ash, which is still highly toxic. The highly toxic properties of ash prohibit its direct disposal or landfilling. Therefore, effective stabilization is essential, before its final disposal, in order to avoid severe environmental pollution.

Alternatively, the recycling of lead contained in the toxic material could be considered; however, it has been estimated that the total quantity of the waste was not sufficient, in order to apply such a treatment technology that focuses on lead recovery. It must be pointed out that hydrometallurgical experiments concerning lead recovery are currently in progress, mainly for research purposes. Preliminary results demonstrate that although most lead quantity can
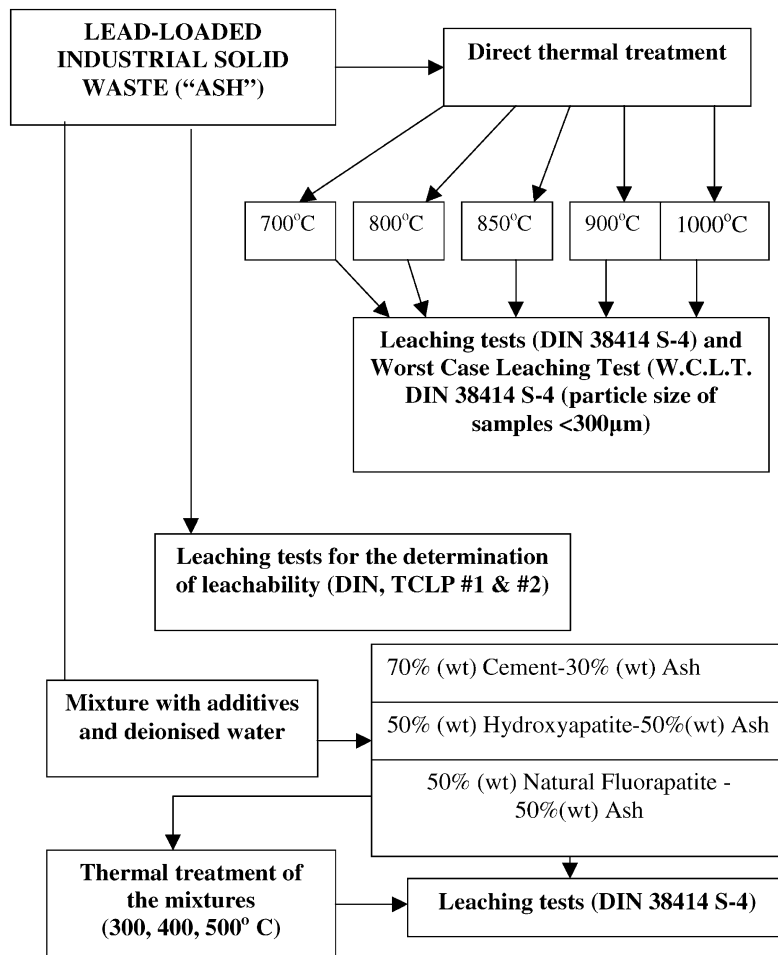

Fig. 1. Conceptual diagram of the performed experimental study.

be removed/recovered efficiently from the waste, the solid residue remains still toxic and further treatment is required. As a result, the stabilization of the initial waste provides a challenge, especially after considering the fact that the proposed technique could be also applied (after the appropriate modifications) to the stabilization of similar, less toxic wastes.

The chemical durability of the derived stabilized products was determined by the application of the appropriate leaching tests. Leaching tests are used to assess: (a) whether a waste should be classified as a hazardous one, (b) the effectiveness of the solid waste treatment process, and (c) whether land disposal may be an appropriate way of managing the stabilized wastes. During the last few years, standardization and harmonization of available leaching/extraction tests, has been an important issue [3]. Most investigations were carried out according to the experimental conditions of the DIN 38414 S-4 method [4], as well as of the toxicity characteristic leaching procedure (TCLP) [5]. The DIN method uses deionized water, and certain physicochemical parameters, such as pH value, can be also examined in order to interpret the experimental results. The TCLP method uses acetic acid; acid attack enhances lead and iron solubilities.

Apatites have been used for a number of years in environmental technology to treat a variety of aqueous wastes [6–9] and were also extended to contaminated soils [10,11]. In this paper, apatites are examined as stabilizing additives for lead-loaded, highly toxic, industrial solid wastes. An additional aim of the proposed work was to control and compare the chemical durability of the derived stabilized products. An overview of the proposed experimental study is presented schematically in Fig. 1.

2. Materials and methods

2.1. Sample characterization

The ash produced after the preliminary incineration process retains the major part of its initial high toxicity, as it still contains large quantities of lead oxides (and bromides). The elemental and chemical composition of this ash, as found by the application of AAS, is depicted in Table 1. The ash was also characterized by XRD (as shown in Fig. 2) in order to reveal the respective crystalline phases; hematite (Fe_2O_3) and PbBr(OH) were found (as shown in Table 1). The toxic compound PbBr(OH) concentration was found to be at 37.4 wt.% of this ash and this high concentration suggests that further stabilization seems to be necessary.

Ash composition is a highly heterogeneous system; some of the particles appear to be particularly rich in iron, whereas the rest are rich in lead, as verified by microanalysis using an X-ray energy dispersive system (EDS). Moreover, the chemical analysis performed for the initial solid waste produced results that presented significant variations, especially for lead (12–34 wt.%) and for iron (22–40 wt.%). Particle size of the initial ash varied from 250 μm to more than 1000 μm. A 30 wt.% ash had more than 1000 μm average particle size. For this purpose, a large quantity of ash was initially grounded, homogenized and sieved to produce a fine solid with particle size smaller than 300 μm. This procedure is expected to improve the reactivity with additives and, thus, to increase the stability of obtained product against leaching tests.

Table 1
Elemental and chemical composition of initial solid waste (ash)

Composition	wt.%	Chemical forms	wt.% of total
Fe	33	Fe_2O_3	47
Pb	29.6	PbBr(OH)	37.4
Br_2	10.1	$PbSO_4 \cdot PbO$	4.3
Si	1	SiO_2	2.2
S (total)	0.25	Al_2O_3	1.5
Al	0.8	SbO	0.3
Sb	0.3	Other oxides	3
C (total)	0.75		
Other elements (oxygen, etc.)	20.2		
H_2O	4		
Total	100		

2.2. Leaching tests

Standard leaching methods (according to DIN 38414 S-4 and TCLP) were applied in order to determine the leachability of metals from the ash; the main experimental conditions for each method are summarized in Table 2. TCLP may utilize two different extraction fluids. Extraction fluid #1 contains 5.7 ml of glacial CH_3COOH, diluted in 500 ml of reagent water, with the addition of 64.3 ml of NaOH (1N); this solution was diluted with deionized water to 1 l yielding a final pH value 4.93 ± 0.05. Extraction fluid #2 contains 5.7 ml of glacial CH_3COOH, diluted with deionized water to the volume of 1 l, yielding a pH value 2.88 ± 0.05.

The DIN 38414 S-4 method was applied for the determination of metals leachability, regarding the treated (stabilized) samples; the permissible particle size for these samples
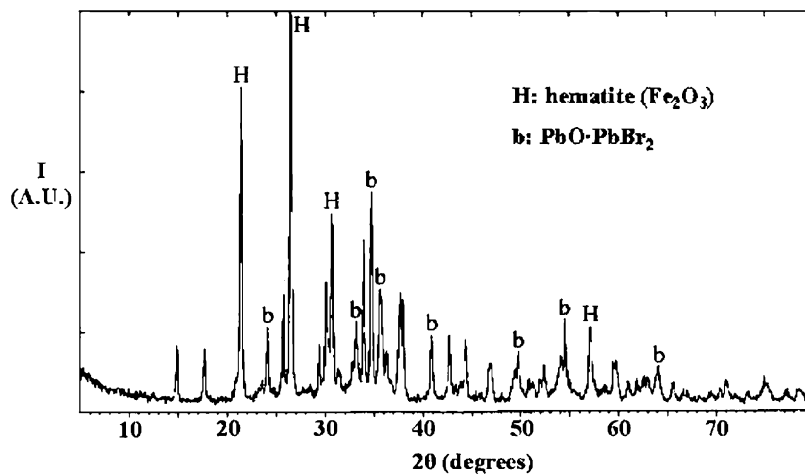

Fig. 2. X-ray diffractogram of the initial ash.

Table 2
Experimental conditions of DIN or TCLP leaching test methods

Method	Elution agent	pH value	Elution time	Sample preparation	Eluate/solid ratio	Movement
Standard leaching test (DIN 38414-S4)	Deionized water (pH 5.7–6.5)	No control	24 h	<10 mm or particle distribution curve	10:1	Overhead circulation (10 rpm)
Worst case leaching test (WCLT)	Deionized water (pH 5.7–6.5)	No control	24 h	<300 μm	10:1	Overhead circulation (10 rpm)
TCLP	Solutions of acetic acid	pH $\sim$ 5 (TCLP #1) or pH $\sim$ 3 (TCLP #2)	18 h	9.5 mm	20:1	NBS rotary tumbler (30 rpm)

is 10 mm (Table 2), whereas the particle size of all examined treated samples was below 10 mm. Therefore, grinding of samples is not required, since the DIN leaching protocol is followed. A more stringent modification of the DIN method can be introduced by crushing the samples in order to pass the particles through a 300 μm sieve and repeat the procedure under the same experimental leaching conditions. Due to the exponential increase of the total surface area, it is expected that dissolution phenomena will be increased. This procedure can be referred to as a worst case leaching test (WCLT) and it was used in order to reveal the effects of the hardened (stabilized) product break down in smaller pieces. This method (WCLT) was applied to the samples derived by the application of direct thermal treatment, i.e. without the use of additives (see also Fig. 1).

2.3. Stabilization method

The stabilization method proposed in this study involves the following steps: (a) The examined stabilization additive (synthetic hydroxyapatite or natural fluorapatite, respectively) together with the "ash" were placed in a conical flask. Characterization data for the examined additives (synthetic hydroxyapatite, natural fluorapatite or Portland cement) are presented in Table 3. The examined ratio for all samples was set to 50 wt.% ash–50 wt.% apatite, except for cement (70 wt.% cement–30 wt.% ash). The sample quantity was 5 g (i.e. 2.5 g ash–2.5 g additive). This ratio was determined based upon preliminary experiments and it was kept constant throughout all experiments, in order to compare the obtained results. Deionized

Table 3
Characterization of used inorganic additives

Component	wt.%	Specific surface area (m^2/g (%))	Particle size (μm)
Natural fluorapatite (source Kosmiras–Epirus region, Greece)			
40.0% $Ca_{9.25}Na_{0.35}Mg_{0.14}(PO_4)_{4.74}(CO_3)_{1.26}F_{2.50}$ and 52.9% $CaCO_3$		2.4 (±10)	<500
P_2O_5	13.92		
CaO	51.62		
MgO	0.39		
Al_2O_3	0.76		
Fe_2O_3	0.57		
Na_2O	0.53		
CO_2	23.25		
Synthetic hydroxyapatite			
$Ca_5(PO_4)_3OH$ (MERCK 2196)		46.5 (±10)	<50
Portland cement typical chemical composition			
SiO_2	17–24		
CaO	61–67		
MgO	0.1–4		
Al_2O_3	3–8		
Fe_2O_3	1–6		
$Na_2O + K_2O$	0.5–1.5		
SO_3	1–3		

water was added, in a ratio of 35–90 wt.% of dry weight of samples, depending on the specific moisture properties of the additives. The mixture (paste) was subsequently manually homogenized with a stirrer for 30 min. (b) The resulting product was dried at 105 °C until constant weight was obtained, as required by the experimental conditions of the DIN method. (c) The resulting dry product was placed in a laboratory press and cylindrical samples (10 mm × 10 mm) were produced, applying a 1.43 MPa pressure; lower pressure was insufficient for pelletization, whereas in most cases higher pressures crushed the samples. Pelletization was applied in order to produce uniform and reproducible samples for leachability studies, as it is known that leaching behavior can be affected by the specimen size and shape [3]. (d) Selected samples (mixtures of apatites and ash) were subsequently heated for 2 h at 300, 400, or 500 °C, respectively. The chemical toxicity of the produced samples was assessed by the application of the DIN method. Heating was used to investigate the formation of more stable phases containing lead. The selection of heating temperatures was based upon preliminary research findings, as results showed that temperatures higher than 500 °C could lead to substantial weight loss of hazardous ash, due to the volatilization of certain constituents.

It must be emphasized that the ratio of deionized water added during the first (homogenization) step, varies according to the (specific) chemical properties of examined additive. The chemical water demand for cement hydration lies close to the w/c ratio of 0.25, i.e. below the lower limit for fluidity [12]; in this study 0.4–1% w/c of water was added.

Apatites were introduced in order to facilitate the formation of insoluble phases, such as $Pb_5(PO_4)_3OH$ and $Pb_3(CO_3)_2(OH)_2$. The amount of water added during step (a) of the proposed stabilization method was 35 wt.% for fluorapatite and up to 90 wt.% for hydroxyapatite with respect to the total dry weight of mixture (ash and additive). These amounts of water kept constant for all experiments concerning natural fluorapatite and synthetic hydroxyapatite, respectively. The main reason for selecting these values was that the mixture started to exhibit sufficient fluidity properties, making the homogenization procedure better and easier.

2.4. Analytical determinations

Measurements of lead concentration in leachates (in the range of mg/l) were performed using a Perkin-Elmer 2380 AAS. A Perkin-Elmer 5100 ZL graphite furnace, fixed with a Perkin-Elmer 5100 atomic absorption spectrophotometer was used for the measurement of lower lead concentrations (in the range of μg/l). A METROM 632 pH-meter was used for pH measurements and the JULABO SW 21 shaking bath was used for agitation (leaching) at stable temperatures.

3. Results and discussion

Leaching tests were applied to initial "ash" samples. When the DIN method was used, lead concentrations in the leachates were 15.1 mg/l, whereas after the application of TCLP method, lead concentrations in leachates were found to be substantially higher, i.e. 2427.3 and 4381.8 mg/l for leaching solutions #1 (pH ∼ 5) and #2 (pH ∼ 3), respectively. The results showed that lead concentrations exceeded the maximum concentration limit, which

is 5 mg/l for lead (by TCLP), by orders of magnitude, therefore, rendering the initial ash highly toxic. The European Environmental Legislation intends to decrease this limit [13]. The increased lead concentrations, especially when TCLP was applied, were due to the increased lead solubility in acetic acid solutions [14], since lead acetate is one of the most soluble lead compounds (44.2 g/100 ml H_2O). Moreover, lead solubility increases at lower (acidic) pH values.

3.1. Thermal treatment

The thermal treatment of the initial ash (i.e. without the presence of additives) was examined under the application of various temperatures (500–1000 °C). It was observed that significant weight losses of ash occurs (11–27 wt.%), when heating at temperatures ≥700 °C is applied. The variation in weight loss for each temperature with the duration of heating is illustrated in Fig. 3. The chemical determinations and the EDS studies performed for the initial ash heated at 1000 °C, proved that the major part of losses can be attributed to lead and bromide. However, it must be stressed that when heating temperature of the initial ash were ≤500 °C, the total weight loss did not exceed 5.6 wt.%, although the humidity of the initial waste was 4 wt.%. Therefore, the total weight losses of the dry product, after heating at 500 °C, were insignificant (around 1.6 wt.%).

Sintering may also occur, especially when the applied temperatures exceed 800 °C. This observation is apparent in the respective SEM photographs, as illustrated in Fig. 4. Moreover, there was a significant change in the morphology of the sintered product at 900 °C, where dark hollows were revealed. A possible explanation may be due to the fact that lead and bromide content of the PbBr(OH) compound started to evaporate rapidly and the entrapped gases escaped from the sintered product. The resulting products derived by thermal treatment
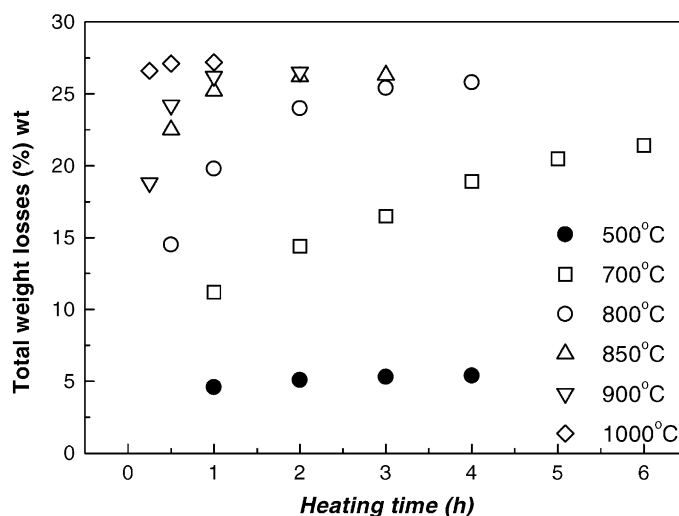

Fig. 3. Total weight loss (wt.%) after thermal treatment of initial ash for different time periods, and different heating temperatures.
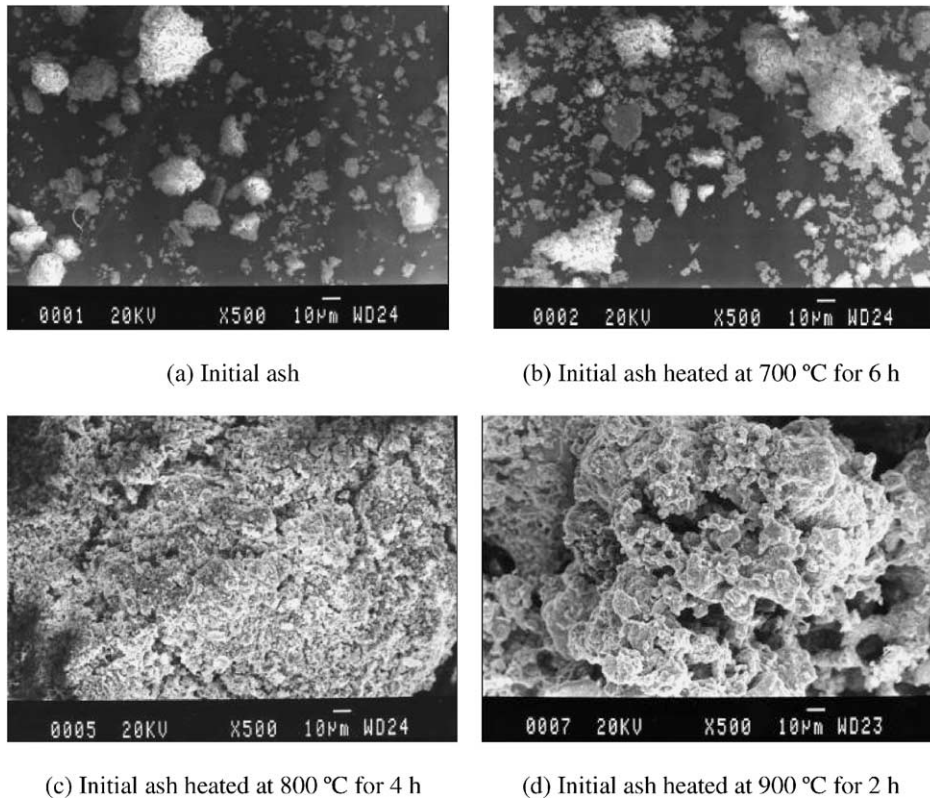
(a) Initial ash

(b) Initial ash heated at 700 °C for 6 h

(c) Initial ash heated at 800 °C for 4 h

(d) Initial ash heated at 900 °C for 2 h

Fig. 4. Ash morphology after thermal treatment in various temperatures (for different time periods).

at temperatures $\geq 900\,^\circ$C were much harder and more stable, both from a chemical and a physical point of view [15]. The average particle size values of sintered samples, derived after heating at 800, 850, 900 and 1000 °C, were measured to be approximately 0.2–0.4 mm, 0.2–0.6 mm, 0.4–0.8 mm and 5–10 mm, respectively.

In order to examine the chemical toxicity and the degree of stabilization of thermally treated samples, leaching tests were applied, according to the DIN method. Fig. 5 presents the average values of three separate experiments, performed under the same conditions. Measurements of final pH extract did not reveal any significant difference, as all pH values were similar to those of deionized water. $PbSO_4$ solubility in water is 0.0425 g/l H_2O, whereas the solubility of basic lead sulfate ($PbSO_4 \cdot PbO$) in water is also similar (0.044 g/l H_2O) [14]. Complex phase transformations between these phases are responsible for the observed leachabilities, as far as lead is concerned. It was found that the initial toxic ash was sufficiently stabilized, following thermal treatment at 1000 °C, because the measured lead concentrations in leachates were reduced from around 2 mg/l (for temperatures below 1000 °C) to 10–50 μg/l at 1000 °C. Losses in the gas phase, as well as the formation of a more stable phase containing lead and iron oxides, were the main reasons for this observation [15].
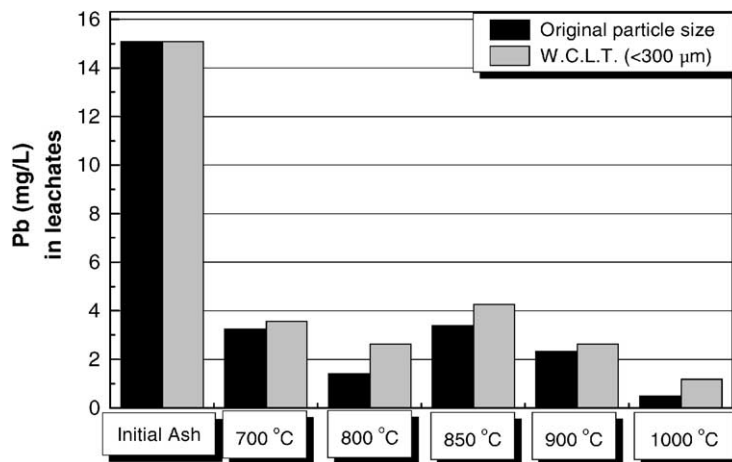
Fig. 5. Determination of lead leachability, applying the DIN 38414 S-4 method to the thermally treated samples of initial ash for various temperatures.

It has been suggested that ash consisting of small amounts (i.e. 0.5–2 wt.%) of heavy metals, treated at high temperatures (more than 1400 °C), can be transformed to a stabilized (non-toxic) product, as toxic metals content is not leachable [16]. The same observation was made during the aforementioned experiments, with the main difference that this ash was initially containing significant amounts of lead. The application of such high temperatures creates a significant amount of non-leachable vitreous phases. It has to be emphasized though, that the environmental pollution problem cannot be solved by the simple application of thermal treatment, due to major total weight losses (Fig. 3). Therefore, the specific type of losses should be further clarified.

For this purpose, when the initial ash was heated at 1000 °C, an amount of vapor phase was collected by condensation, using a metallic plate, and analyzed in order to obtain qualitative indications about the specific type of losses. The collected amount constituted mainly by lead and bromide. Moreover, after heating was terminated, chemical and SEM analyses were performed to the final product (i.e. to initial ash heated at 1000 °C). The results obtained showed that almost the entire amount of the initial bromide content and almost 42 wt.% of the initial lead content were evaporated. On the contrary, almost the entire amount of initial iron content remained in the final product.

Therefore, apart from the extensive energy cost to apply such high temperatures, the pollution problem was simply transferred to the subsequent toxic air treatment, which may present more difficulties; as a result, direct thermal treatment cannot be suggested as a valid option for the examined waste. Hence, the subsequent application of an appropriate stabilization method, focused on inorganic additives, seems to be necessary.

3.2. Waste stabilization

The ratio between the hazardous ash and the inorganic additive was set to 50–50 wt.%, except in the case of cement addition, where the ratio was set to 70–30 wt.% (cement/solid

Table 4
Lead and iron concentrations and pH measurements of leachates, according to DIN 38414 S-4 method applied to the stabilized mixtures that contain additive and ash

Sample	Code	Additive–Ash (50–50 wt.%)	Pb (mg/l)	Fe (mg/l)	pH
1	C-w.t.t.	Cement 70%–ash 30% (w.t.t.)	1.95	<0.3	12.08
2	F-w.t.t.	Fluorapatite–ash (w.t.t.)	0.80	0.70	7.40
3	F-300	Fluorapatite–ash (300 °C)	0.97	0.55	7.21
4	F-400	Fluorapatite–ash (400 °C)	0.87	1.55	7.13
5	F-500	Fluorapatite–ash (500 °C)	0.65	<0.5	7.38
6	H-w.t.t.	Hydroxyapatite–ash (w.t.t.)	1.30	1.10	6.73
7	H-300	Hydroxyapatite–ash (300 °C)	0.75	0.63	6.21
8	H-400	Hydroxyapatite–ash (400 °C)	0.85	<0.50	5.82
9	H-500	Hydroxyapatite–ash (500 °C)	0.80	<0.50	6.74
10	Vitr	50–35–15 (vitrified)	0.046	<0.30	6.60
11	F-bl.	Fluorapatite blank experiment	N.D.	N.D.	8.01
12	H-bl.	Hydroxyapatite blank experiment	N.D.	N.D.	7.40

w.t.t.: without thermal treatment; N.D.: not detected.

waste). All samples were of the same quantity (5 g), constituted by 2.5 g of initial ash and 2.5 g of the examined additive. When thermal treatment of mixtures (ash–additive) was applied, temperatures ≤500 °C were selected, in order to avoid weight losses (see also Fig. 3). Table 4 and Figs. 7 and 8 present the respective experimental results for the stabilized products. Table 5 and Fig. 6 present selected SEM and EDS micrographs, as well as the elemental analysis, with respect to specific areas of interest. Sample 10 is a vitrified product, obtained during a previous study [15]; it is included here only for comparison reasons. The specific sample consists of 50 wt.% of the examined ash, 35% SiO_2 and 15% Na_2O; the mixture was heated at 1400 °C for 2 h, forming an amorphous glassy product.

It has to be mentioned that when a natural fluorapatite was utilized as an additive, an increase of iron concentrations in leachates was observed. This can be considered to be an indication of phase transformation in iron phases, since iron was present as hematite

Table 5
Detailed EDS analysis of specific areas of interest of Fig. 6

Area	Area ID	Element (wt.%)				
		Ca	P	Fe	Pb	Br
Gray (dominant)	F1	26.2	13.2	2.7	5.3	–
	H1	35.8	10.4	0.8	0.9	0.9
White needles	F2	10.3	4.9	2.7	23.3	8.7
	H2	10.4	2.0	18.2	16.3	6.6
White flat	F3	8.9	6.5	42.0	9.8	0.2
	H3	6.7	1.4	53.9	8.9	6.7
White particles	F4	14.5	7.4	21.9	13.8	3.6
	H4	10.7	2.5	30.3	6.2	2.3

(F) areas refer to fluorapatite–ash sample and (H) areas refer to hydroxyapatite–ash sample.
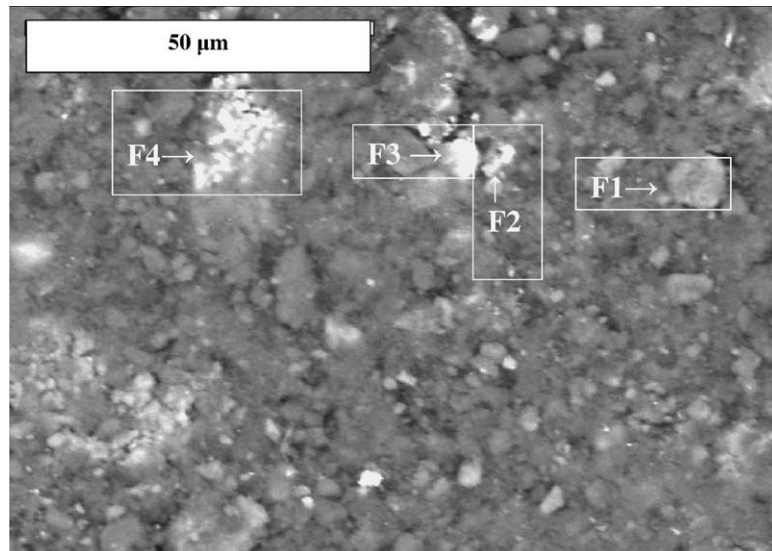
Fluorapatite 50%- Ash 50% (wt)
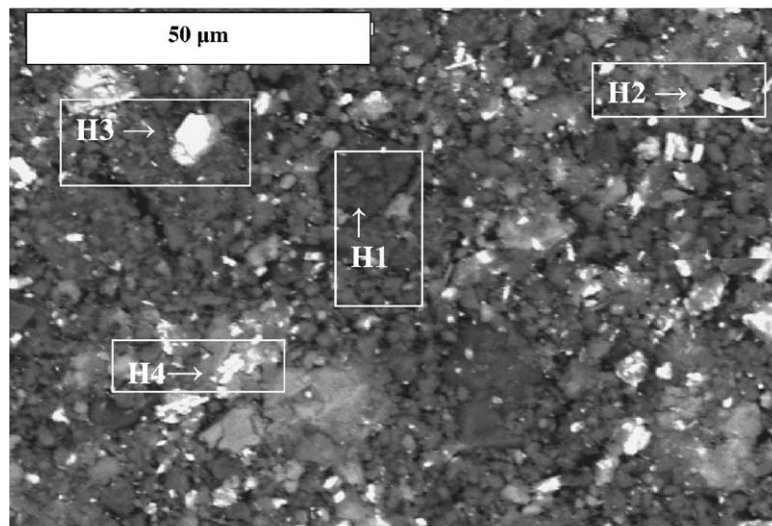
Hydroxyapatite 50% - Ash 50% (wt)

Fig. 6. SEM representative micrographs of sample no. 5 (fluorapatite–ash 50–50% without thermal treatment), and no. 9 (hydroxyapatite–ash 50–50% without thermal treatment).

(Fe_2O_3) in the initial ash. It is known that hematite is almost insoluble in water [14]. Moreover, it was proved that when the DIN method was applied to the initial ash, iron concentrations in leachates were found to be lower than the detection limit of the applied analytical determination method (AAS, i.e. lower than 0.3 mg/l). The complexity of this
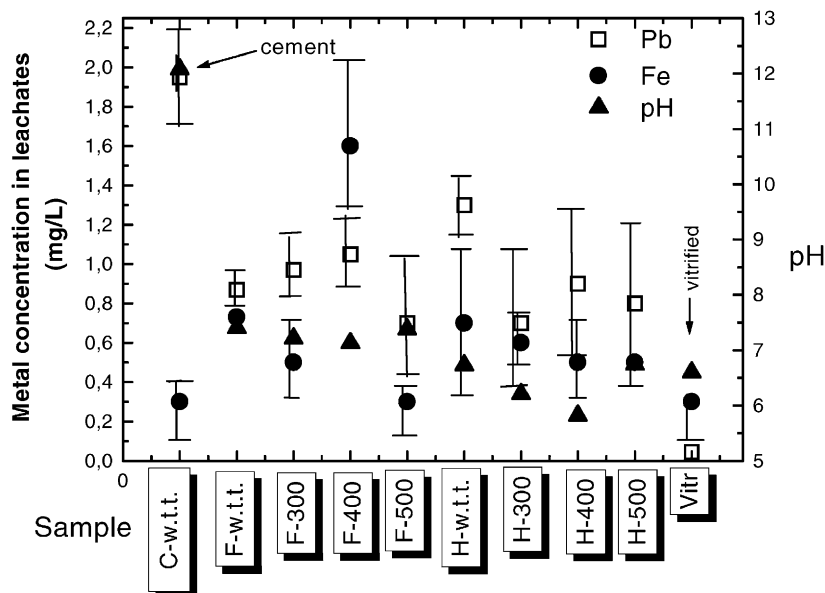
Fig. 7. Lead and iron concentrations and pH values of leachates after the application of standard leaching test DIN 38414 S-4 method to the stabilized products. The results are presented as average values of duplicate experiments.

system did not allow the characterization of a specific phase, which contained mainly iron and could be responsible for the observed increased leachability. Also, it has to be taken into consideration that the additive in this case was natural fluorapatite, therefore, it was possible that some impurities, contained in small amounts, could be also leachable and responsible for the obtained results.

Due to the system complexity, the interpretation of results should be careful. Fig. 6 presents representative SEM micrographs of stabilized samples, containing 50% of initial ash and 50% of the additive (hydroxyapatite or fluorapatite), without the application of thermal treatment. Although homogenization occurred, some differences can be observed in the micro-scale. Nevertheless, certain areas of interest seemed to be repeated and for this reason a detailed EDS analysis of these areas was performed, as depicted in Table 5.

The white, needle-like areas (F2, H2) showed increased concentrations of lead and bromide, whereas the white flat areas (F3, H3) showed increased concentration of iron, similar to those revealed in the SEM micrographs of the initial ash. Therefore, it could be assumed that these areas were not the result of chemical reactions, but more likely the result of initial ash particles forming a solid/liquid matrix (paste) during the homogenization step, when water was added. When these needle-like areas were decreased or disappeared, the results in Fig. 7 showed that there was an increase of metals leachability (Fe and Pb). Moreover, increased values for bromides were measured in the white needle areas (F2, H2). Although it was not identified by XRD, this could be an indication that small amounts of lead bromide may be formed. It is also known that lead bromide is more soluble in water (solubility: 4.554 g/l H_2O), than lead oxide (solubility: 0.023 g/l H_2O) and therefore, this compound

can be considered to be more leachable, increasing the concentration of lead in leachates [14].

The experimental results, after the application of the DIN method to the stabilized products, are presented in Fig. 7. These results indicate that significant stabilization has occurred, although certain differences may be noticed. The vitrified product yielded the best stabilization results, as far as physical and chemical durability is concerned [15]. When thermal treatment was applied, a significant deviation between the results can be noticed. Compared to the cement stabilization, apatites showed better stabilization results, i.e. lower leachability values for lead.

Additionally, it has to be considered that the cement-stabilized sample contained lower quantity (30 wt.%) of toxic ash, as compared to the other additives. Cement hydration reactions need more time and specific humidity conditions in order to increase the physical and chemical strength of produced samples [1,12]. Moreover, an increased pH value was measured (Table 4—sample 1); therefore, toxic metals release was more probable to occur. In this study, the experimental conditions did not allow the detailed examination of reactions, concerning cement addition as it was used only for comparison reasons, according to the applied stabilization procedure. Therefore, the relatively insufficient results obtained with cement addition refer to this specific application and not to its general use as a commonly applied stabilization additive.
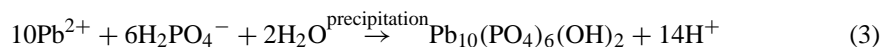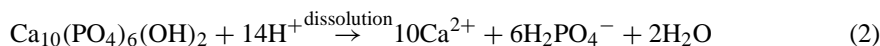
The possible stabilization mechanisms including the addition of apatites may be the following:

1. Ion exchange, according to the following general chemical reaction [17]:

$$\text{apatite–Ca}^{2+} + \text{M}^{2+} \rightarrow \text{apatite–M}^{2+} + \text{Ca}^{2+} \tag{1}$$
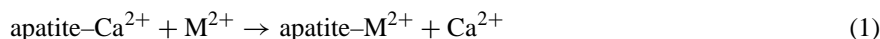
where M^{2+} is a divalent cation (Pb in this study).

2. Dissolution of apatite and precipitation of hydroxy-pyromorphite [8]:

$$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + 14\text{H}^+ \overset{\text{dissolution}}{\rightarrow} 10\text{Ca}^{2+} + 6\text{H}_2\text{PO}_4^- + 2\text{H}_2\text{O} \tag{2}$$

$$10\text{Pb}^{2+} + 6\text{H}_2\text{PO}_4^- + 2\text{H}_2\text{O} \overset{\text{precipitation}}{\rightarrow} \text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2 + 14\text{H}^+ \tag{3}$$

3. Surface sorption in the case of natural fluorapatite [18].
4. Solid phase transformation when thermal treatment was applied may be also possible in a smaller extent.

It has to be noticed that the respective main mechanism is difficult to be defined. According to certain literature reports, an ion exchange reaction was mainly responsible, when apatites were used in aqueous solutions containing heavy metals; it was also found that apatites present a significant selectivity for lead [7,17]. More recently, it was proposed that the responsible mechanism involves mainly dissolution and precipitation [8,9] or sorption reactions (following the previous mechanism), when natural apatites were applied [18]; these studies verified also the selectivity of apatite for lead. The formation of insoluble phosphates (containing lead) has been also achieved by the use of phosphoric acid as additive [19] or by the use of soluble phosphates in contaminated soils [20–22], showing very good stabilization results in both cases.

Table 6
Existing and possible phases, recorded after the application of DIN method to the stabilized samples (mixtures of apatite and ash)

Sample	Thermal condition	Recorded phases	Possible phases	Comments
Natural fluorapatite–ash 50–50 wt.%	Without thermal treatment	$-CaCO_3$, $-Pb_3(CO_3)_2(OH)_2$—a variant of $Ca_5(PO_4)_3F$ similar (but not the same) to the initial phase[a]	$-Pb_5O_3(OH)_4$	Hydroceroussite formation is favored at similar pH values. Transformation of initial natural fluorapatite to a similar (undefined) phase. Significant phase transformation of initial PbBr(OH)
	Heated at 500 °C	$-Ca_5(PO_4)_3F$, $-Pb_5(PO_4)_3F$, $-Ca_2PbO_4$—a variant of $Ca_5(PO_4)_3F$ similar (but not the same) to the initial phase[a]	$-CaPbO_3-x$	Transformation of initial natural fluorapatite to a similar (undefined) phase. Significant phase transformation of initial PbBr(OH)
Hydroxyapatite–ash 50–50 wt.%	Without thermal treatment	$-Ca_5(PO_4)_3OH$, $-PbBr(OH)$, $-Pb_2HP_3O_{10}$, $-Pb_2P_4O_{12}\cdot3H_2O$	$-Pb_3O_2(SO_4)$	Hydroxyapatite structure was not disrupted. Small extent of phase transformation of initial PbBr(OH)
	Heated at 500 °C	$-Ca_5(PO_4)_3OH$, $-PbBr(OH)$, $-Pb_5(PO_4)_3OH$	$-PbO\cdot PbBr_2$, $-2PbO\cdot PbBr_2$	Hydroxyapatite structure was not disrupted. Small extent of phase transformation of initial PbBr(OH)

[a] See Table 3 for the initial composition of the natural fluorapatite.

In order to examine the solid phases of stabilized products, XRD studies were performed to the residuals of stabilized products, which formed after the application of DIN method. The formation of new phases is presented in Table 6. In another study, it was found that under usual environmental conditions, pyromorphites [$Pb_5(PO_4)_3(Cl, OH, F)$] are the most stable lead phosphate minerals; thermodynamics predict that other solid phases could be also converted to pyromorphite, following a dissolution–precipitation mechanism [11]. In this study, hydroxy-pyromorphite formation was observed, when hydroxyapatite was used as an additive. It must be emphasized that the treatment process did not change significantly the structure of hydroxyapatite, as only a small amount of it was dissolved.

It was also reported that pH values around 6.6–6.8 favor hydroxyl fluoropyromorphite formation as a new phase, while pH values around 7.1 favor the formation of hydrocerussite or carbonate hydroxyl fluoropyromorphite, when fluorapatites are utilized [18]. Hydrocerussite formation was also observed in this study, whereas the pH values varied between 7.2 and 7.6, in the case of natural fluorapatite–ash mixture (50–50 wt.%). It must be mentioned though, that natural fluorapatite structure may be changed significantly after stabilization treatment and the application of DIN method. The initial main peaks (XRD) were drifted, and a new (undefined) phase was formed, showing rather similar peaks, although not the same, with the $Ca_5(PO_4)_3F$ ones. This observation might suggest the formation of a new phase which contains $Ca_5(PO_4)_3F$ bonded with other phases. The peaks regarding PbBr(OH) were also changed, indicating a phase transformation.

Previous studies revealed that apatite solubility is minimum, when pH values vary between 5.7 and 7.2 [7]. The respective values of pH in this research varied from 5.8 to 7.4. Analytical determinations of calcium concentrations in leachates support also this option. In Fig. 8, it can be noticed that there was an increase of calcium concentrations in leachates,
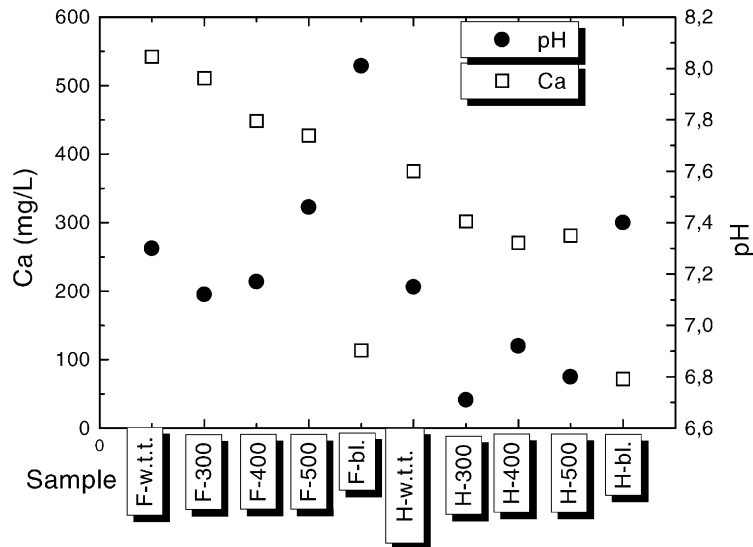

Fig. 8. Calcium concentrations and pH measurements of leachates after the application of DIN 38414 S-4 method. The experimental results are the average values of duplicate experiments.

when stabilized samples were examined, as compared to the respective blank experiments. This can be considered as an initial indication that at least part of the chemical form of apatites was transformed; transformation of calcium products occurred and as a result, an increase of calcium release in leachates can be observed. The decrease of pH measurements in the leachates of stabilized samples, as compared with the blank experiments (by the application of the DIN method to the additive only), can be explained by the fact that the main ionic species, contained in the leachates of blank experiments, are in the forms of Ca^{2+} and OH^- ions, therefore yielding higher (i.e. more alkaline) pH values (see also [23]).

As far as thermal treatment is concerned, certain other insoluble phases are expected to create, as phase transformation could possibly occur. It was found that thermal treatment did not change significantly the existing lead compounds, when hydroxyapatite was used, as possible interactions between lead and hematite did not occur. Phase stability diagrams can explain this observation [24]; the major constituents of the studied samples can be defined from these diagrams. $PbBr_2 \cdot PbO$ remains stable up to $500\,°C$, whereas at these temperatures other intermediate phases, such as $2PbO \cdot PbBr_2$, can be also formed, as indicated in Fig. 9. Moreover, interactions between PbO with Fe_2O_3 could be expected, although for temperatures higher than $600\,°C$.

The experimental results showed that there was not only one mechanism, which could sufficiently explain the respective stabilization phenomena, described in this study. Although the respective mechanisms were not fully understood or proved, the indications obtained lead to the suggestion that a multi-mechanism combination occurs, consisting mainly of
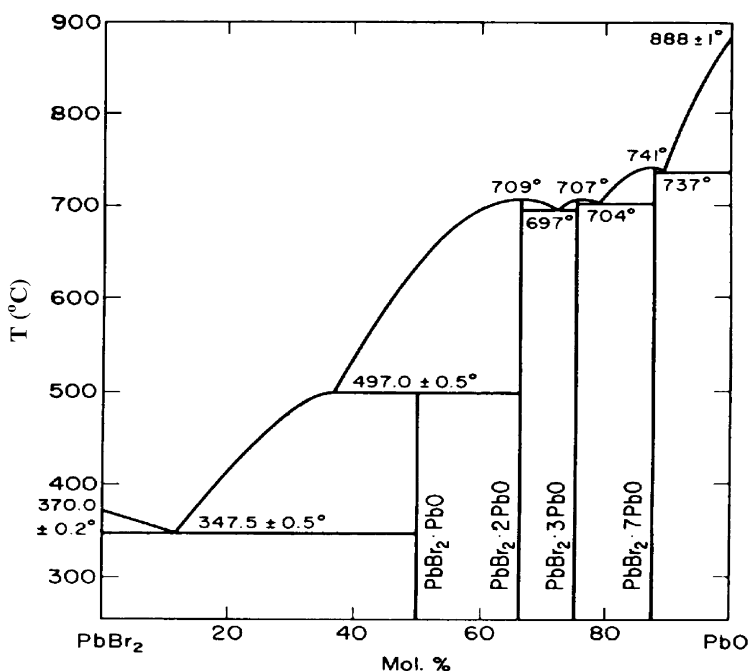

Fig. 9. Phase stability diagram of the system PbO–$PbBr_2$ [24].

dissolution and precipitation, but it also includes ion exchange, sorption and phase transformation (although the last two mechanisms were prevailing for the case of natural fluorapatite only).

This can be also supported by the fact that lead was not removed from an aqueous solution, whereas the respective chemical reactions took place during the initial admixture (homogenization) step of stabilization procedure. At this step the amount of added water (35 wt.% for natural fluorapatite and 90 wt.% for synthetic hydroxyapatite with regard to the dry sample) was less than that required in order to allow dissolution and precipitation reactions to take place sufficiently. The resulting paste, containing (in dry weight) 50 wt.% of initial ash and 50 wt.% of the additive, was agitated manually for 30 min, therefore allowing the respective rapid reactions to occur [6,7,25]. During this step, lead reacted with calcium and phosphates that were present in the structure of the apatites. These reactions were activated by the addition of water. Water was then removed (by heating at 105 °C) facilitating the production of cylindrical samples, since the initial plasticity of paste disappeared, and as it was proved by the obtained results, sufficient stabilization of solid waste was finally occurred.

4. Conclusions

The direct thermal treatment of the examined solid waste transfers the pollution problem to a waste air management problem, since significant amounts of lead can be evaporated when heated at temperatures higher than 700 °C. Therefore, the proposed method is not suitable for the treatment of this specific toxic waste. On the contrary, highly toxic waste, such as the ash used in the current study, can be effectively stabilized by the use of synthetic hydroxyapatite as well as of natural fluorapatite, applied as inorganic additives. The application of vitrification may produce the best results, but the use of the examined inorganic additives was also found to produce efficient results, although they cannot be characterized as "straightforward applicable", due to the significant amount of additives demanded for this purpose. Nevertheless, the results obtained regarding stabilization by addition of apatites can be characterized as particularly promising.

Acknowledgements

References

[1] M.D. LaGrega, P.L. Buckingham, J.C. Evans, Hazardous Waste Management, McGraw-Hill, New York, 1994.

[2] EPA Report, Solidification/Stabilization at Superfund Sites, EPA/542-R-00-010, Cincinnati, USA, September 2000.

[3] H.A. Van der Sloot, L. Heasman, Ph. Quevauviller, Harmonization of leaching/extraction tests, Studies in Environmental Science, vol. 70, Elsevier, Amsterdam, The Netherlands, 1997.

[4] Deutsche Norm, German standard methods for the examination of water, wastewater and sludge, DIN 38414, 1984.

[5] EPA Report, Stabilization/Solidification of CERCLA and RCRA Wastes, EPA/625/6-89/022, Cincinnati, USA, May 1989.

[6] J.C. Elliot, Structure and chemistry of the apatites and other calcium orthophosphates, Studies in Inorganic Chemistry, vol. 18, Elsevier, UK, 1994.

[7] Y. Takeuchi, T. Suzuki, H. Arai, J. Chem. Eng. Jpn. 21 (1988) 98.

[8] Q.Y. Ma, S.J. Traina, T.J. Logan, J.A. Ryan, Environ. Sci. Technol. 27 (1993) 1803.

[9] Q.Y. Ma, S.J. Traina, T.J. Logan, J.A. Ryan, Environ. Sci. Technol. 28 (1994) 1219.

[10] V. Dutre, C. Vandecasteele, Environ. Sci. Technol. 32 (1998) 2782.

[11] A.J. Ryan, P. Zhang, D. Hesterberg, J. Chou, E.D. Sayers, Environ. Sci. Technol. 35 (2001) 3798.

[12] F.P. Glasser, J. Hazard. Mater. 52 (1997) 151.

[13] EU Directive 98/83/EU, Drinking water quality indented for human consumption, 1998.

[14] R.D. Lide (Ed.), CRC Handbook of Chemistry and Physics, 81st ed., CRC press, Boca Raton, USA, 2000.

[15] P. Kavouras, G. Kaimakamis, T.A. Ioannidis, T. Kehagias, P. Komninou, S. Kokkou, E. Pavlidou, I. Antonopoulos, M. Sofoniou, A.I. Zouboulis, C.P. Hadjiantoniou, A. Prakouras, T. Karakostas, Waste Manage. (2002) in press.

[16] A. Ramesh, J.A. Kozinski, Environ. Pollut. 111 (2001) 255.

[17] T. Suzuki, T. Hatsushika, M. Miyake, J. Chem. Soc. Faraday Trans. 78 (1982) 3605.

[18] X. Chen, J.V. Wright, J.L. Conca, L.M. Peurrung, Environ. Sci. Technol. 31 (1997) 624.

[19] J. Yang, E.D. Mosby, W.S. Casteel, W.R. Blanchar, Environ. Sci. Technol. 35 (2001) 3553.

[20] T.T. Eighmy, B.S. Crannell, L.G. Butler, F.K. Cartledge, E.F. Emery, D. Oblas, J.E. Krzanowski Jr., D.J. Eusden, E.L. Shaw, C.A. Francis, Environ. Sci. Technol. 31 (1997) 3330.

[21] T.T. Eighmy, B.S. Crannell, L.G. Butler, F.K. Cartledge, E.F. Emery, D. Oblas, J.E. Krzanowski Jr., D.J. Eusden, E.L. Shaw, C.A. Francis, Waste Manage. 18 (1998) 513.

[22] B.S. Crannell, T.T. Eighmy, J.E. Krzanowski Jr., D.J. Eusden, E.L. Shaw, C.A. Francis, Waste Manage. 20 (2000) 135.

[23] L. Wu, W. Forsling, W.P. Schindler, J. Colloid Interface Sci. 147 (1991) 178.

[24] National Institute of Standards & Technology (NIST), Phase equilibria diagrams database, Version 2.1 for Windows 95, Am. Ceram. Soc., 1994.

[25] Y. Xu, W.F. Schwartz, J. Contam. Hydrol. 15 (1994) 187.