



## Review

# Immobilization of heavy metals (Pb, Cu, Cr, Zn, Cd, Mn) in the mineral additions containing concrete composites

Zbigniew Giergiczny, Anna Król\*

Opole University of Technology, Faculty of Mechanical Engineering, Department of Environmental Engineering,  
ul. Mikołajczyka 5, 45-271 Opole, Poland

## ARTICLE INFO

## Article history:

Received 10 March 2007  
Received in revised form 11 November 2007  
Accepted 4 March 2008  
Available online 18 March 2008

## Keywords:

Cement  
Binder  
Fly ash  
Slag  
Immobilization  
Porosity  
Leaching  
Heavy metals  
Hazardous waste

## ABSTRACT

The presented work determines the level of heavy metals ( $Pb^{+2}$ ,  $Cu^{+2}$ ,  $Zn^{+2}$ ,  $Cr^{+6}$ ,  $Cd^{+2}$ ,  $Mn^{+2}$ ) immobilization in the composites produced using Ordinary Portland Cement (OPC) as well as of binders containing large amount of mineral additives in its composition—siliceous fly ash (FA), fluidized bed combustion ash (FFA) and ground granulated blast furnace slag (GGBFS). Heavy metals were introduced to cementitious materials in the form of soluble salts as well as components of hazardous wastes (medical ash, metallurgical dust).

It has been stated, that the level of heavy metals immobilization is combined with composites composition. Majority of analyzed heavy metals, added to binders' composition in the form of heavy metal salts achieves high level of immobilization, in mortar based on binder with 85% GGBFS and 15% OPC. The lowest immobilization level was reached for chromium  $Cr^{+6}$  added to hardening mortars as  $Na_2Cr_2O_7 \cdot 2H_2O$ . The level ranges from 85.97% in mortars made on blended binder (20% OPC, 30% FFA and 50% GGBFS) to 93.33% in mortar produced on OPC.

The increase of the so-called immobilization degree with time of hardened material maturing was found. This should be attributed to the pozzolanic or pozzolanic/hydraulic properties of components used; their effect on microstructure of hardened material is also important. Mineral additions enter the hydration reactions in the mixtures and favor the formation of specific microstructure promoting the immobilization of hazardous elements.

© 2008 Elsevier B.V. All rights reserved.

## Contents

1. Introduction .....	247
2. Materials and methods .....	248
2.1. Materials .....	248
2.2. Methods .....	248
3. Results and discussion .....	248
4. Conclusions .....	254
Acknowledgment .....	255
References .....	255

## 1. Introduction

Solidification of heavy metals containing inorganic materials in mortars and concretes produced using OPC is an effective way of immobilization. Mechanism of the processes occurring on

immobilization, as well as the assessment of the effectiveness of solidification has been widely studied and discussed in many reports [1–3].

Significant role in the immobilization process is attributed to the so-called C–S–H phase (calcium silicate hydrates)—the main component of hardened paste [4,5]. Absorbability, low permeability preventing the migration of liquids and the presence of small gel pores (micropores) are among the decisive factors affecting high immobilization potential of C–S–H [6].

\* Corresponding author. Tel.: +48 77 4006396; fax: +48 77 4006192.  
E-mail address: [a.krol@po.opole.pl](mailto:a.krol@po.opole.pl) (A. Król).

The properties and amount of C–S–H are highly bound with the content of mineral additions in cementitious material. The positive effects of mineral additions on the properties of solidifying composites are listed below [7–9]:

- Additional amount of C–S–H with lower C/S is formed, as well as calcium aluminates and sulfoaluminates filling the pores; these are the products of reactions between active components of mineral additions and  $\text{Ca}(\text{OH})_2$  evolved on calcium silicate phases hydration (from cement).
- Modification of microstructure owing to the presence of mineral addition (dense, compact C–S–H of low porosity, presence of addition in form of small particles acting as fillers).

The role of calcium aluminate and sulfoaluminate hydrates in the immobilization process should not be ignored. In the structure of calcium sulfoaluminates the incorporation of mono- and bi-valent ions is possible. This relates both to anions and cations [10]. Calcium sulfoaluminates play an exceptional role as Cr and Mo immobilizers, forming solid solutions with these elements [11]. According to Gougar et al. [12], aluminium in ettringite may be replaced synthetically by  $\text{Ni}^{3+}$ ,  $\text{Co}^{3+}$ ,  $\text{Cr}^{3+}$  and  $\text{Ti}^{3+}$ . Instead of sulfate,  $\text{AsO}_4^{3-}$ ,  $\text{CrO}_4^{2-}$ ,  $\text{SeO}_4^{2-}$  or  $\text{MoO}_4^{2-}$  are incorporated. It is also possible to replace  $\text{Ca}^{2+}$  by  $\text{Sr}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$ .

The precipitated, insoluble hydroxides of heavy metals, such as Cr(III), Pb, Zn modify the porosity of cement matrix—the total porosity is reduced and the gel pores ratio increases [2,13,14].

The level of heavy metals immobilization in the cementitious composites produced using mineral additions, such as fly ash from black coal combustion, fluidized bed brown coal combustion ash and ground granulated blast furnace slag was investigated. Heavy metals were introduced to cementitious materials in the form of heavy metal salts as well as components of hazardous wastes (material from metallurgical furnace de-dusting installation and fly ash from the medical wastes incineration).

## 2. Materials and methods

### 2.1. Materials

The following heavy metals ions, in the form of soluble salts, were added into binder composition:  $\text{Pb}^{+2}$  as  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Zn}^{+2}$  as  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cu}^{+2}$  as  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Cr}^{+6}$  as  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ ,  $\text{Mn}^{+2}$  as  $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Cd}^{+2}$  as  $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ .

Two types of waste materials were used as a source of heavy metals:

- Fly ash from the medical wastes incineration PUROTHERM–PYROLISE system technology (medical ash, MA).
- Material from metallurgical arc furnace de-dusting installation (metallurgical dust, MD)—dust originates from arc furnace de-dusting for steel melting process from scrap.

The binders tested in his work were produced using OPC, fly ash from the black coal combustion, and ground granulated blast furnace slag from the pig iron production and ash from the brown coal combustion in fluidized bed. Chemical composition of particular components and physical properties are given in Table 1.

### 2.2. Methods

Water eluats of binders and waste were prepared according to the procedure specified in EN 12457-1-4:2002 [16]. This procedure is also quoted by Council Decision 2003/33/EC [17] when talking about characteristic (categorization) of waste received in on storage areas. According to EN 12457-1-4:2002 [16] water extracts were

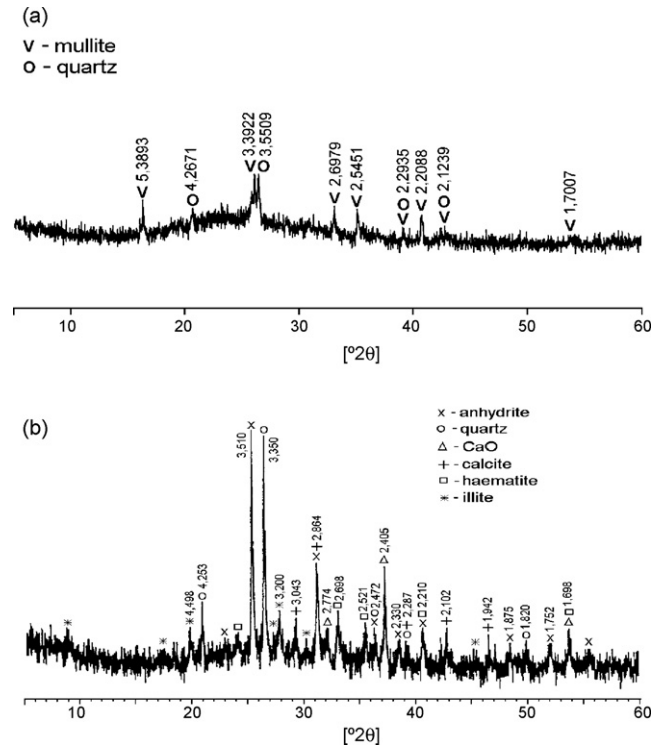


Fig. 1. XRD pattern of siliceous fly ash (a) and fluidized bed combustion fly ash (b).

made on 100-g samples (mortar or waste), reduced to particle grain size under 10 mm. The material was flooded with leaching liquid (distilled water with pH 7) and subjected to the process of leaching (agitation) for 24 h [16]. Weight ratio of water (L) to solid mass (S) was 10 (L/S = 10) [16]. Such method was used to prepare water extracts from mortars and wastes used in the study (MA, MD).

Heavy metal concentrations in water eluats as well as in dry samples were determined with help of emission spectrometer ICP-AES "Plasma 400" manufactured by PerkinElmer company.

Setting time was measured according to the standard EN 196-3:2005 *Methods of testing cement—Part 3: Determination of setting time and soundness*. Strength of mortars was tested according to the standard EN 196-1:2005 *Methods of testing cement—Part 1: Determination of strength*.

XRD studies were done on powdered samples, using Philips X'change X-Ray diffraction spectrometer.

The heat of hydration was measured with help of differential calorimeter ToniCAL III.

The microstructure of hardened samples was observed under the scanning electron microscope JEOL 5400 with energy dispersive LINK ISIS microanalyzer. The chemical analysis in order to identify the particular components of samples was thus carried out.

Tests of microporosity of hardened mortars were carried using mercuric porosimetry method on apparatus Carlo Erba S 200.

## 3. Results and discussion

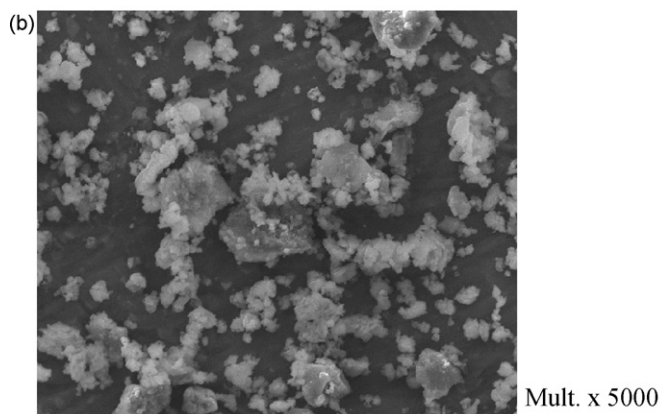
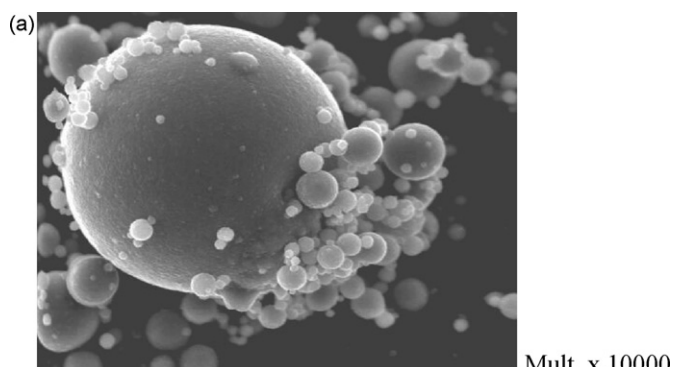
Siliceous fly ash used in this study shows high  $\text{SiO}_2$  content and substantial amount of glassy phase. Therefore, the percentage of active  $\text{SiO}_2$  can exceed 25%. The crystalline components are quartz, mullite, haematite, magnetite (Fig. 1a), practically inactive on hydration. In the fly ash from the combustion in fluidized bed the glassy phase and mullite are not present because the temperature in the furnace is too low (800–900 °C) (Fig. 1b). In these samples the anhydrite, formed as a product of desulfurization, is detected.

**Table 1**  
Chemical composition and properties of components used in binder production

Type of material	Notation	Specific surface area (cm <sup>2</sup> /g)	Density (g/cm <sup>3</sup> )	Chemical composition (mass %)								
				Loss on ignition	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	SO <sub>3</sub>	Na <sub>2</sub> O <sub>eq</sub> <sup>a</sup>	
Ordinary Portland cement	OPC	3150	3.10	2.5	64.2	20.1	5.9	3.4	1.5	2.8	0.8	
Siliceous fly ash	FA	3450	2.13	1.8	3.7	51.5	27.8	7.5	2.5	0.7	3.0	
Ground granulated blast furnace slag	GGBFS	3900	2.90	0.0	45.2	36.5	9.1	1.4	6.1	0.4	0.9	
Fluidal fly ash	FFA	6322	2.67	3.2	18.7 <sup>**</sup>	33.9	17.9	6.7	3.1	9.0	2.8	

<sup>a</sup> Na<sub>2</sub>O<sub>eq</sub> = Na<sub>2</sub>O + 0.658 K<sub>2</sub>O [15].

<sup>\*\*</sup> Free CaO = 3.1%

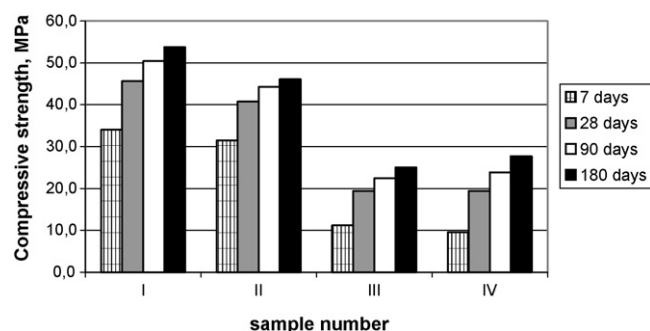


**Fig. 2.** Microstructure of siliceous fly ash grains (a) and fly ash from fluidized bed combustion (b).

Residual sorbent—calcite, free CaO and dehydrated illite are also present [18,19].

Fly ash samples used in the studies exhibit different morphology, because of different origin (different installation and parameters of combustion) (Fig. 2 a and b). Siliceous fly ash occurs in the form of spherical grains with 3–40 μm diameter. The particles of fly ash from the fluidal process, being mainly the products of clayey minerals de-hydroxylation, are of irregular character (Fig. 2b).

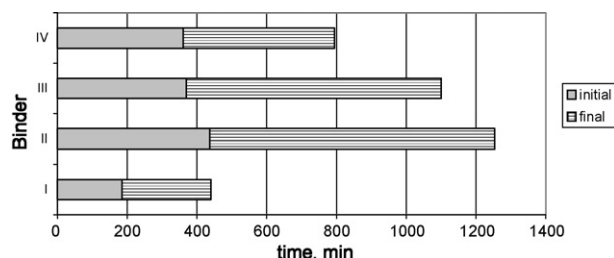
Ground granulated blast furnace slag is classified as a material of hydraulic character, with glassy phase as a main constituent. Glassy phase content in the ground granulated blast furnace slag is higher than 90% [20], and therefore this material reveals hydraulic activity (the additive, which activated by grinding process or alkaline materials, e.g. Ca(OH)<sub>2</sub>—the result of the process of siliceous



**Fig. 3.** Compressive strength of mortars.

phase hydration from cement composition, hardens and sets under water analogously as Portland cement) [15,20]. The crystalline components of slag are as follows: melilite (solid solution between gehlenite and akermanite) in significant amount and in lower amount monticellite and merwinite [21]. In particular, components of binders, the heavy metal contents were analyzed (Table 2), and the water extracts were prepared according to the procedure given in the EN 12457-1-4:2002 [16]. The data are presented in Table 3. The leachability of heavy metals is low. In many cases the values are within the limits given in the standards as acceptable for surface water used as a source of drinking water, according to the Council Directive 75/440/EEC [22] or even directly for drinking water (Council Directive 98/83/EC) [23].

The components of binders were matched with aim to produce a hardened matrix of high calcium silicate hydrate content, showing low C/S ratio. Thus, binders' composition consisted of secondary industrial materials (FFA, FA, GGBFS), in order to limit the clinker amount and achieve low C/S ratio in C–S–H phase, essential for the immobilization of heavy metals [4]. OPC was used as a binder and as a reference in the heavy metal immobilization experiments.



**Fig. 4.** Setting time of binders.

**Table 2**  
Heavy metals contents in the components of mineral binders

Type of material	Content (mg/kg)											
	As	Hg	Cr	Cd	Pb	Co	Ni	Mn	V	Cu	Zn	Tl
OPC	5	3	29	4.5	42	6	7	244	10	17	198	56
FA	140	7	97	11	34	32	41	482	176	71	142	160
GGBFS	5	3.5	12	3	<5	6	<2.5	1978	10	22	36	22
FFA	183	8	63	16	35	67	48	402	143	136	209	24

**Table 3**  
Heavy metals contents in water extracts from binder components

Type of material	Concentration of chemical element (mg/dm <sup>3</sup> )											
	As	Hg	Cr	Cd	Pb	Co	Ni	Mn	V	Cu	Zn	Tl
OPC	<0.05	0.0003	0.542	<0.001	0.072	0.009	0.022	<0.0004	0.092	0.005	0.054	<0.003
FA	<0.05	0.0003	0.148	0.001	0.026	0.080	0.019	0.004	0.112	0.001	0.016	<0.003
GGBFS	<0.05	0.0004	0.007	0.002	0.030	0.045	0.028	0.016	0.034	0.004	0.011	<0.003
FFA	<0.05	0.0001	0.035	0.002	0.011	0.050	0.024	<0.0004	0.031	<0.0004	0.018	<0.003
CD (75/440/EEC)	0.05	0.0005	0.05	0.005	0.05	–	–	0.05	–	0.02	0.5	–
CD 98/83/EC	0.01	0.001	0.05	0.005	0.01	–	0.02	0.05	–	2.0	–	–

**Table 4**  
Properties and composition of mineral binders

Sample number	Percentage of particular components (mass %)				Specific surface area (m <sup>2</sup> /kg)	Density (g/cm <sup>3</sup> )
	OPC	FFA	FA	GGBFS		
I	100	–	–	–	315	3.10
II	20	30	–	50	395	2.86
III	30	30	40	0	410	2.58
IV	15	–	–	85	395	2.92

Composition of binders and their physical properties are shown in Table 4.

The compressive strength and setting time of materials produced as binders are shown on Figs. 3 and 4. Mortar made of Portland cement (OPC–binder I) characterizes with the shortest setting time with the simultaneous highest compressive strength. Similar strength level was reached by mortar made on binder II; however, its setting time is the longest among all tested binders. The analysis of physical–mechanical parameters is important considering the durability of produced mortars and may affect the application method of studied mortars (binders).

Standard mortars were prepared basing on I–IV binders according to the procedure given in the standard EN 196-1:2005 *Methods of testing cement—Part 1: Determination of strength*. They were the heavy metals ions solidifying matrices. The mortars were stored in standard conditions (temperature 20 ± 2 °C; RH > 95%).

**Table 5**  
Chemical composition with heavy metals contents and specific surface of wastes

Component	Content in waste (mass %)	
	Medical ash	Metallurgical dust
Loss of ignition	21.35	4.05
SiO <sub>2</sub>	24.71	8.05
Al <sub>2</sub> O <sub>3</sub>	12.76	8.00
Fe <sub>2</sub> O <sub>3</sub>	5.83	40.20
CaO	20.54	10.20
MgO	2.30	10.45
SO <sub>3</sub>	4.76	1.57
Cr	0.032	0.65
Pb	0.023	3.75
Mn	0.065	9.10
Zn	0.59	3.45
Cd	0.0034	0.013
Cu	0.14	0.29
Blaine specific surface (m <sup>2</sup> /kg)	806 <sup>a</sup>	594

<sup>a</sup> After grinding.

Binders mixed with heavy metals addition (1% by mass of binder) were marked by putting the symbol of heavy metal next to binder mark, for example: I Pb or IV Cr.

Wastes were introduced as 20% by mass of binder. Chemical composition and heavy metal contents in the wastes used in this work are shown in Table 5. In Table 6 the concentrations of heavy metals in water extracts are given together with upper limit values; the latter ones relate to the wastes classified as “other than hazardous or inert”. These values have been found too high for cadmium (in medical ash) and lead (in metallurgical dust). Therefore, the wastes should be subjected to de-activation process prior to the deposition on the storage dump, in order to reduce the heavy metals leaching and to achieve safe deposition.

Medical ash was preliminary ground to the specific surface given in Table 5. Blended materials were denoted using symbols MA or MD added to the number of binder, e.g. II MA or III MD.

**Table 6**  
Heavy metals contents in water extracts from wastes

Type of waste	Heavy metals contents (mg/kg)					
	Cr	Cd	Pb	Mn	Cu	Zn
Medical ash	3.30	2.48	5.70	1.51	2.70	3.20
Metallurgical dust	7.67	0.88	18.89	9.16	0.82	1.95
Permissible value according to Council Decision 2003/33/EC	10.0	1.0	10.0	–	50.0	50.0

**Table 7**

Leaching and immobilization level of heavy metals

Binder sample notation	Leaching of heavy metals (mg/kg) and immobilization degree (%)			
	28 days		90 days	
	mg/kg	%	mg/kg	%
<b>Lead, Pb (Pb<sup>2+</sup>)</b>				
I Pb	4.06	99.82	3.54	99.84
II Pb	0.64	99.97	0.54	99.98
III Pb	3.00	99.86	2.90	99.87
IV Pb	0.96	99.96	0.75	99.97
<b>Zinc (Zn<sup>2+</sup>)<sup>a</sup></b>				
I Zn	1.95	99.91	2.07	99.91
III Zn	3.20	99.85	3.02	99.86
<b>Chromium (Cr<sup>6+</sup>)</b>				
I Cr	148.08	93.33	156.79	92.94
II Cr	311.47	85.97	255.55	88.50
III Cr	250.02	88.74	229.60	89.66
IV Cr	225.34	89.85	190.99	91.40
<b>Cadmium (Cd<sup>2+</sup>)</b>				
I Cd	0.01	99.99	0.01	99.99
II Cd	0.09	99.99	0.09	99.99
III Cd	0.02	99.99	0.01	99.99
IV Cd	0.05	99.99	0.05	99.99
<b>Copper (Cu<sup>2+</sup>)<sup>a</sup></b>				
I Cu	0.08	99.99	0.07	99.99
III Cu	0.06	99.99	0.06	99.99
IV Cu	0.99	99.96	0.76	99.97
<b>Manganese (Mn<sup>2+</sup>)</b>				
I Mn	0.004	99.99	0.004	99.99
II Mn	0.004	99.99	0.004	99.99
III Mn	0.01	99.99	0.01	99.99
IV Mn	0.09	99.99	0.07	99.99

<sup>a</sup> Composites II Zn, IV Zn and II Cu collapsed at early age of hardening.

After 28- and 90-day curing the water extracts were produced from the mortars prepared with heavy metal salts and subsequently the heavy metal concentrations were determined. In Table 7 the concentration of heavy metals is given together with degrees of their immobilization in cement matrix, calculated according to the following formula:

$$I_n = 100 - W_n \quad (1)$$

where  $I_n$  is the immobilization of heavy metal, % and  $W_n$  leaching factor (%).

Leaching was expressed in the following way:

$$W_n = \frac{m_{n,e}}{m_{n,z}} \times 100 \quad (2)$$

where  $m_{n,e}$  is the mass of heavy metal in water extract (mg) and  $m_{n,z}$  the mass of heavy metal introduced to the mortar subjected to the extraction process (mg).

Immobilization level of particular heavy metal ions depends strongly on the hydration time. It becomes higher with time or

attains early high values and does not show any further change (see Table 7). Chromium in Portland cement (binder I) is here an exception—after 28 days of maturing the immobilization degree is 93.33%, while after 90 days it slightly decreases, up to 92.94%.

The immobilization level is strongly affected by the composition of binder. In all 28 days stored materials produced in this work the degree of immobilization was higher than 99.8%. For every binder–metal couple, a different value of immobilization degree was found. The relation between heavy metal immobilization and composition of binder is particularly well visible for lead and chromium. The lowest lead immobilization level has been found for binder I (OPC), the highest—for binder II (with fly ash) and IV (with GGBFS added as 85% by mass). Chromium is effectively stabilized in the matrix produced from binder I and IV; the lowest values are found for binder II (see Fig. 5 a and b).

High level of lead immobilization in the matrix produced using ground, granulated blast furnace slag is in good agreement with the data reported by Thevenin and Pera [14] and Cho et al. [24].

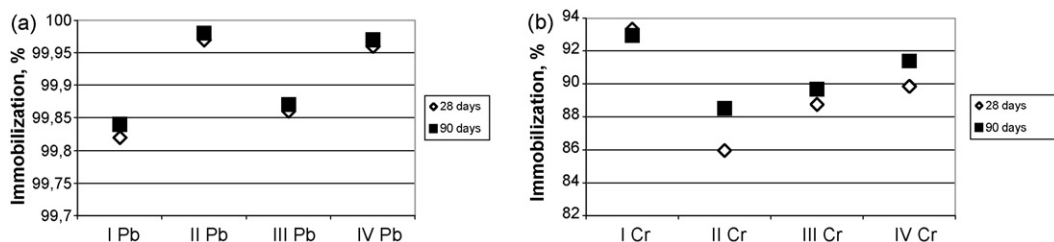


Fig. 5. Immobilization degree of lead (a) and chromium (b) in hardened matrices.



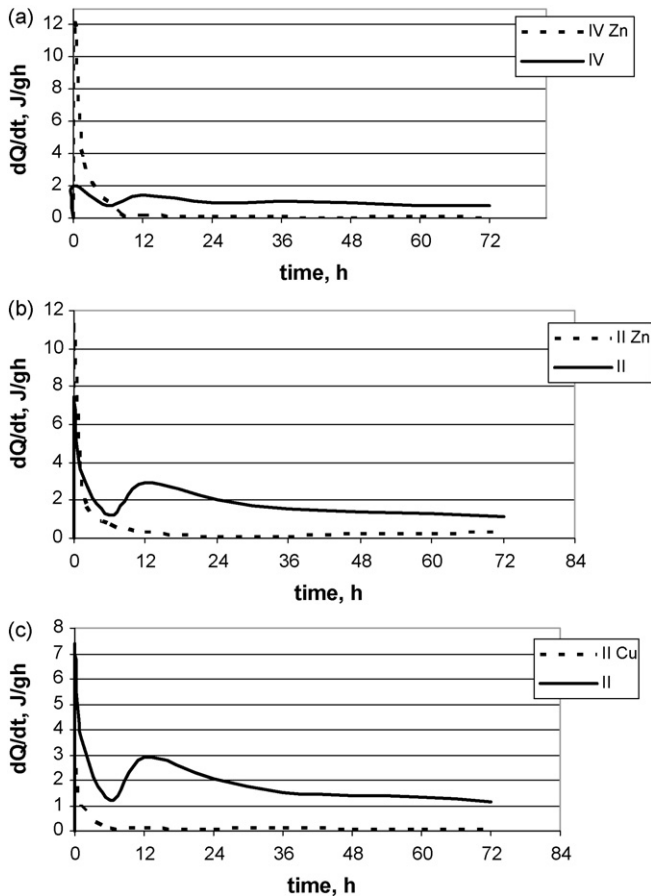


Fig. 6. Hydration heat of binder IV and IV Zn (a), II and II Zn (b), II and II Cu (c).

The lower immobilization degrees were found in OPC matrix and in cement with fly ash by Wang and Vipulanandan [25]. As the immobilization of chromium is concerned, binder I–OPC and binder IV (85%GGBFS) show similar immobilization degree. These data are close to those reported by Cho et al. [24] and Van der Sloot [26].

One can notice that among the heavy metals taken into account in this study there are two metals—manganese and cadmium, which exhibit very similar leachability, irrespective of binder matrix composition.

**Table 8**  
Immobilization level of heavy metals in matrices with MA or MD waste addition

Binder		Immobilization level of heavy metals (%)						
		Cr	Cd	Cu	Pb	Zn	Mn	
I MA		96.90	99.46	99.24	99.35	99.90	99.19	
II MA	28 Days	94.86	99.72	99.81	96.22	99.77	98.41	
III MA		88.53	99.78	98.59	96.71	99.86	99.46	
IV MA		98.03	99.77	99.79	99.45	99.83	99.52	
I MA		98.51	99.74	99.80	98.89	99.78	99.86	
II MA	180 Days	97.76	99.85	99.92	98.95	99.87	99.92	
III MA		91.32	99.82	99.84	99.33	99.92	99.89	
IV MA		99.46	99.91	99.82	99.95	99.95	99.95	
I MD		99.83	99.58	99.86	99.36	99.90	99.95	
II MD	28 Days	99.71	95.63	99.80	99.80	99.78	99.89	
III MD		99.32	96.00	99.80	99.77	99.81	99.90	
IV MD		99.78	97.02	99.84	99.79	99.83	99.92	
I MD		99.91	99.80	99.95	99.73	99.94	99.97	
II MD	180 Days	99.87	98.66	99.94	99.94	99.95	99.98	
III MD		99.77	98.07	99.92	99.95	99.97	99.99	
IV MD		99.90	98.33	99.95	99.90	99.94	99.97	

Some composites produced with heavy metal compounds—those denoted as II Zn, IV Zn and II Cu collapsed at early age of hardening and in this case the leaching tests were not carried out. Cu and Zn salts introduced to the paste hampered markedly hydration process, as it is documented by calorimetry (Fig. 6). The second heat evolution peak does not occur at the same time as in the paste without heavy metal salt—there is no co-called acceleration period within the first 3-day hydration. Summarized amount of isolated heat during the hydration process is for binder IV (15% OPC, 85% GGBFS) 85.78 J/g, whereas after the addition of salt containing  $Zn^{2+}$  ions, it drops to 25.36 J/g (significant slow down of hydration process). Similar relations were observed for binder II with the addition of Zn and Cu ions (Fig. 6b and c).

The studies of composites produced with heavy metal salts aimed in determination of immobilization level as well as the basic physical/mechanical properties characterization.

In practice, hazardous wastes originating from human activity are the source of heavy metals, usually more than one element, and the tests should include all of them. Therefore, in the subsequent part of the study the two waste materials were incorporated—fly ash from the medical wastes incineration (MA) and material from metallurgical furnace de-dusting installation (MD).

Achieved leachability level of heavy metal contents in water extracts produced from mortars is used for wastes stabilization (wastes added as 20% by mass of binder). The values characterizing leachability from these mortars are significantly lower than the maximum limits for “the wastes produced as a result of hazardous wastes processing into materials for storage of wastes other than hazardous or inert”, according to the Council Decision 2003/33/EC [17]. Calculated immobilization level (Table 8) shows high degree of immobilization of particular elements in composite matrices. After 28 days most of heavy metals were bound with effectiveness higher than 99%. However, this statement does not relate to chromium; Cr immobilization degree is the lowest—88.5% for III MA binder (cement + siliceous fly ash) and slightly rises with time (see Table 8).

The highest effectiveness of heavy metal immobilization, both in case of medical ash and metallurgical dust is found for binder IV (15% OPC and 85% GGBFS), as the immobilization of heavy metals vs. composition of binder matrix is analyzed. The immobilization level is similar to that for composite with Portland cement (binder I), plotted in Fig. 7, exemplifying the Cr and Pb stabilization. The trends marked in Fig. 7 are compatible to those observed in the studies with heavy metal salts (Fig. 5).

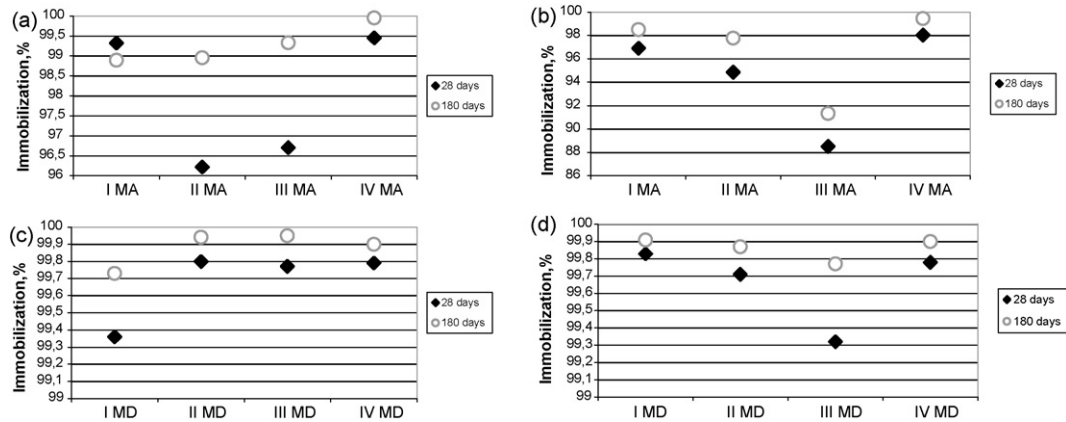


Fig. 7. Immobilization of Pb (a and c) and Cr (b and d) in the composites with metallurgical and medical wastes.

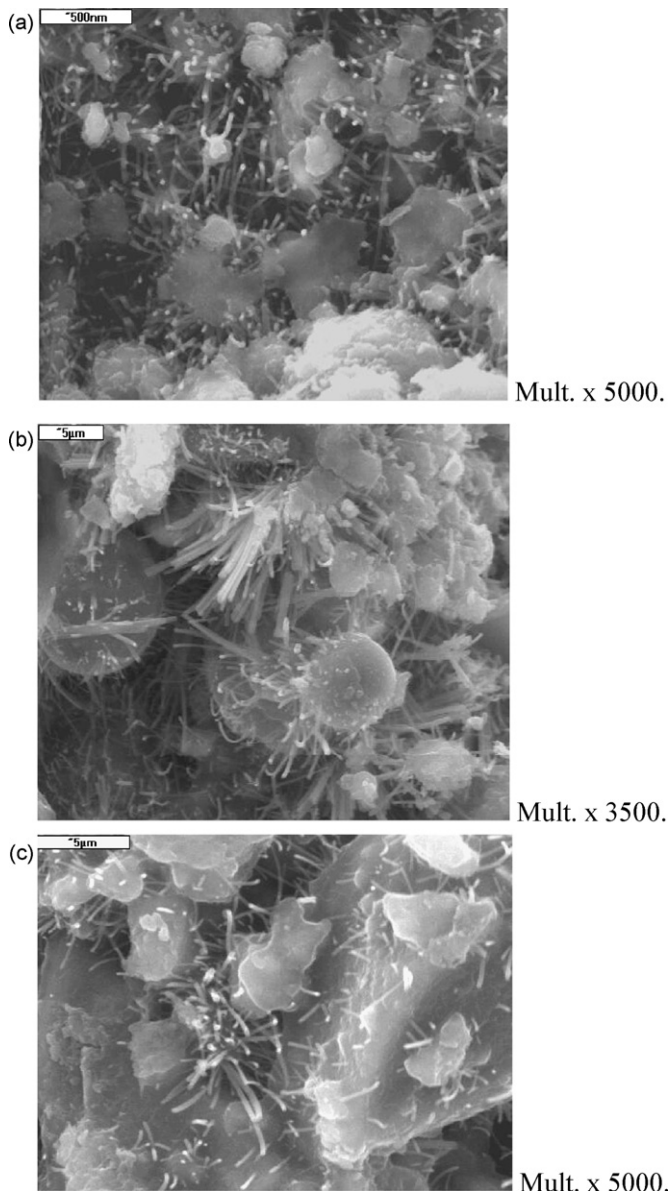


Fig. 8. Microstructure of mortar produced using binder II (a and b) and IV (c)—28 days hydration.

The Pb immobilization depends on the type of Pb-bearing material. Similar values are found for the binders with  $\text{Pb}(\text{NO}_3)_2$  (Fig. 5a) and with metallurgical dust (Fig. 7c). The best immobilization after 28 days was achieved in composites produced from binders II and IV, the lowest—for binder I. In case of medical ash addition the Pb immobilization is the best for matrix produced using binder I and IV; the lowest—for fly ash composites (Fig. 7a and c).

The immobilization level of the other elements (Cd, Cu, Zn, Mn) is the function of cementitious matrix composition, curing time and the properties of waste being the source of heavy metals. It should be underlined that the multi-components matrix hampers very well the migration of heavy metals to the environment; the concentration values are significantly lower than the acceptable limits.

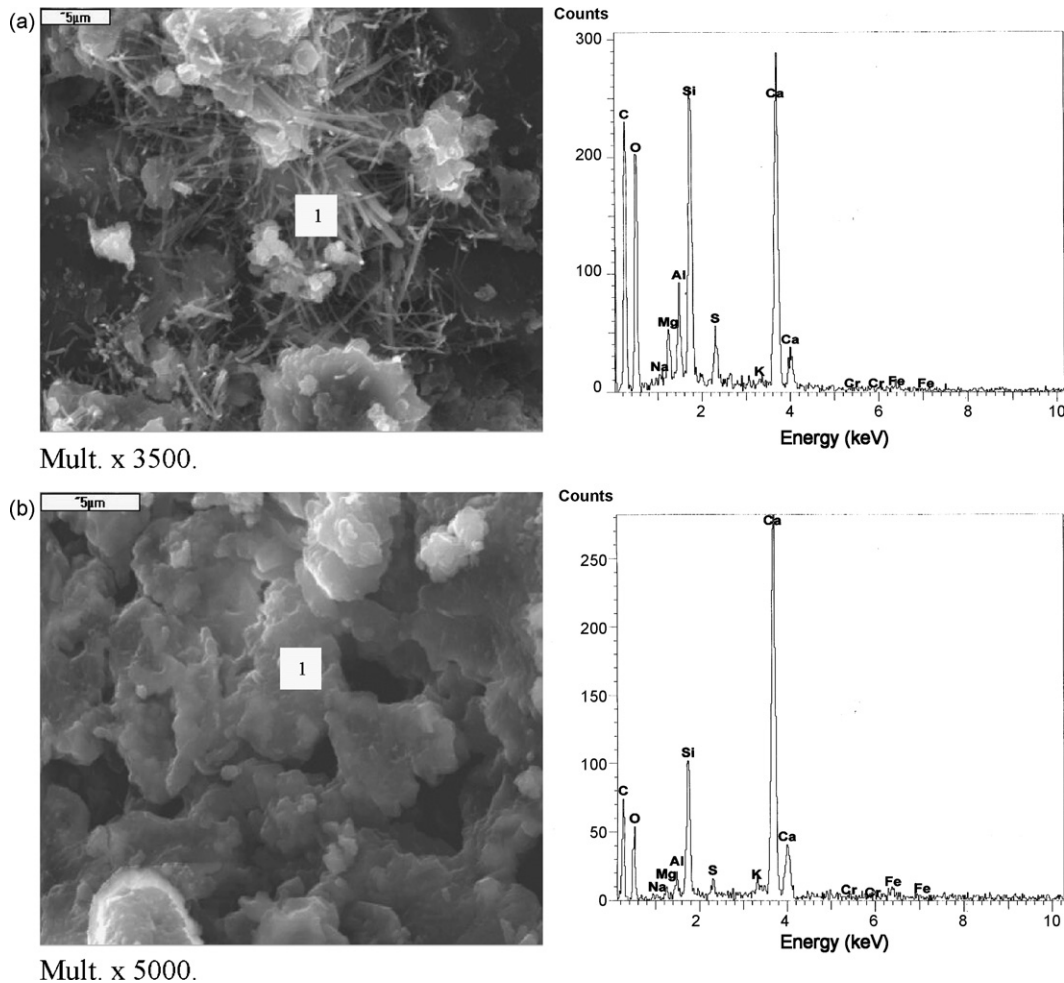
The heavy metal immobilization levels are high or grow up steadily with time (Table 8—see binders after 28 and 180 days). Growth of immobilization effectiveness at longer time should be bound with pozzolanic (siliceous fly ash) or pozzolanic/hydraulic activity (fluidal fly ash, ground granulated blast furnace slag), and consequently further hydration reaction progress in matrices with mineral additions. Composites with high mineral additions content show significant strength development at later age (Fig. 3), when the active components enter the reaction with  $\text{Ca}(\text{OH})_2$  and the calcium aluminate and silicate hydrates are formed. The examples of most characteristic microstructures for particular binders are presented in Fig. 8. The crystallization of these new products takes place in the pores of hardened composite matrix and thus the porosity is reduced and durability increases [7].

The formation of additional C–S–H with lowered C/S ratio and higher corrosion resistance are of special importance for immobilization [7,18,19]. The wastes to be stabilized can also take part at later age in the compact, dense, durable structure formation, because of their fineness (Table 5), chemical composition (Table 5) and high temperature origin. This was proved by porosity measurements for some selected composites produced using medical ash, tested after different time of hardening (Table 9). Total porosity decreases with time and the pore structure changes. The ratio of small gel pores augments while the capillary pores are reduced.

SEM observations reveal the gel-like C–S–H as a dominating component in the hardened samples produced with wastes; there is also fibrous ettringite present. The examples of observed, most characteristic microareas of hardened mortars on binders

**Table 9**  
Microporosity of mortars without and with MA waste

No. of binder	Pore volume (cm <sup>3</sup> /g)				
	Total porosity	<10 (nm)	10–100 (nm)	100–1000 (nm)	>1000 (nm)
II/28days	0.9094	0.1020	0.5418	0.2009	0.0647
II MA/28days	1.7368	0.2772	0.8797	0.4177	0.1622
II MA/180days	1.6234	0.2925	0.9338	0.264	0.1331
III/28days	1.492	0.1819	0.8757	0.327	0.1074
III MA/28days	1.5462	0.3245	0.761	0.3596	0.1011
III MA/180days	1.4578	0.397	0.888	0.1175	0.0553
IV/28days	1.3102	0.1796	0.9185	0.1484	0.0637
IV MA/28days	1.2361	0.2718	0.7076	0.1912	0.0655
IV MA/180days	1.209	0.3232	0.7392	0.0932	0.0534



**Fig. 9.** Microstructure of mortar produced using binder II MA (a) and IV MA (b)—after 180 days with EDS analysis in the spot 1.

II and IV with medical ash addition (MA) are described in Fig. 9. EDS analysis in some selected areas shows the presence of Cr<sup>+6</sup> incorporated to the structure of hydration products (Fig. 9).

#### 4. Conclusions

Heavy metals (Pb, Cu, Zn, Cd, Mn) added as salts are very effectively immobilized in hydrated matrices (from 99.82% to 99.99%); Cr is an exception immobilized with lower degree (from 85.97% to 93.33%). Immobilization is effected by the composition of solidifying binder and time of maturing. Among the mineral additions containing binders (II–IV), the binder IV, with high GGBFS content

(85%) appeared as a best one. It is as effective as Portland cement itself. In case of the other cementitious mixtures (binder II and III) a very high immobilization of such elements as Pb, Cu, Zn, Cd and Mn was found. Therefore, these binders can be used in the stabilization of elements mentioned above. Effect of percentage of heavy metal(s) containing waste on the hardening process (setting time, strength development) should be carefully controlled. In this work the hampering of hydration was found in the presence of zinc and copper nitrates. In the industrial wastes there are the other components hindering potentially hydration, e.g. soluble phosphates or fluorides.

The effectiveness of immobilization was proved in solidification experiments with heavy metals containing hazardous wastes



(medical ash, metallurgical dust). Immobilization of particular elements is affected by the composition of solidifying binder and time of maturing (the highest after 180 days maturing; it relates particularly to Cr). When considering medical ash (MA) to solidifying mortars, the level of over 99% of  $Pb^{+2}$ ,  $Cu^{+2}$ ,  $Cd^{+2}$ ,  $Mn^{+2}$ ,  $Zn^{+2}$  ions immobilization (coming from its content) is possible to be achieved. However, the level of  $Cr^{+6}$  ions immobilization is lower and varies from 91.32% in mortar on binder III (30% OPC, 30% FFA, 40% FA) to 99.46% on binder IV (15% OPC, 85% GGBFS).

The level of immobilization of  $Pb^{+2}$ ,  $Cr^{+6}$ ,  $Zn^{+2}$ ,  $Mn^{+2}$ ,  $Cu^{+2}$  coming from steel dust exceeds 99.7% after 180 days of hydration. Only in case of  $Cd^{+2}$  the immobilization level is variable and amounts from 99.80% on binder I (OPC) to 98.07% in mortar on binder III (30% OPC, 30% FFA, 40% FA).

The solidification of heavy metal compounds in matrices produced using mineral additions is beneficial from the natural environment point of view in several aspects. The wastes from the other areas of human activity, e.g. from power industry (fly ash of different origin), metallurgy (GGBFS) can be very effectively adapted for this purpose. The materials thus produced are not detrimental for environment and can be stored or practically implemented, e.g. in road making.

### Acknowledgment

The current research was financially supported by research project by Ministry of Science and High Education no. PB-1493/T02/2006/30 (2006–2009).

### References

- [1] T. Astrup, H. Mosb c, T.H. Christensen, Assessment of long-term leaching from waste incineration air-pollution-control residues, *Waste Management* 26 (2006) 803–814.
- [2] D. Stephan, D. Kn fel, R. H rdtl, Influence of heavy metals on the properties of cement and concrete—binding mechanisms and fixation, in: *Proceedings of the 11th International Congress on the Chemistry of Cement “Cement’s Contribution on the Development in the 21st Century”*, Durban, South Africa, 2003, pp. 2178–2186.
- [3] K. Watanabe, K. Yokozeki, R. Ashizawa, N. Sakata, M. Morioka, E. Sakai, M. Daimon, High durability cementitious material with mineral admixtures and carbonation curing, *Waste Management* 26 (2006) 752–757.
- [4] W. Nocu n-Wczelik, J. Ma lepszy, Studies on immobilization of heavy metals in cement paste—CSH leaching behavior, in: *Proceedings of the 10th International Congress on the Chemistry of Cement*, vol. 4, G teborg, 4iv043 8, 1997.
- [5] H.F.W. Taylor, *Cement Chemistry*, Academic Press, London, 1990.
- [6] M.S.Y. Bhatti, Fixation of metallic ions in Portland cement, in: *Proceedings of the Fourth National Conference Hazardous Wastes and Hazardous Materials*, Washington, 1987, pp. 140–145.
- [7] J.D. Bapat, Performance of cement concrete with mineral admixtures, *Advances in Cement Research* 13 (2001) 139–155.
- [8] Z. Giergiczny, The properties of cements containing fly ash together with other admixtures, in: *Proceedings of Fourth International Conference “Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete”*, Istanbul, 1992, pp. 24–30.
- [9] E. Sakai, S. Miyahara, S. Ohsawa, S.-H. Lee, M. Daimon, Hydration of fly ash cement, *Cement and Concrete Research* 35 (2005) 1135–1140.
- [10] F.P. Glasser, Application of cements to the treatment and conditioning of toxic wastes, in: *Ninth International Congress on the Chemistry of Cement*, New Delhi, 1992, pp. 114–118.
- [11] F.P. Glasser, Immobilization potential of cementitious materials, in: *Proceeding of the International Conference on Environmental Implication of Construction Materials and Technology Developments*, Maastricht, 1994, pp. 77–86.
- [12] M.L.D. Gougar, B.E. Scheetz, D.M. Roy, Ettringite and C–S–H Portland cement phases for waste ion immobilization: a review, *Waste Management* 4 (1996) 295–303.
- [13] F.D. Tam s, L. Cset nyi, J. Tritthart, Effect of adsorbents on the leachability of cement bonded electroplating wastes, *Cement and Concrete Research* 22 (1992) 399–404.
- [14] G. Thevenin, J. Pera, Interactions between lead and different binders, *Cement and Concrete Research* 29 (1999) 1605–1610.
- [15] W.F. Locher, *Cement Principles of Production and Use*, Verlag Bau+Technik GmbH, Dusseldorf, 2006.
- [16] EN 12457-1-4:2002, Characterization of waste – leaching – compliance test for leaching of granular waste materials and sludges—Part 4: one stage batch at a liquid to solid ratio of 10 l/kg for materials with particle size below 10 mm (without or with size reduction).
- [17] Council Decision (2003/33/EC) of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC.
- [18] Z. Giergiczny, High calcium fly ash, *Cement Lime Concrete* 5 (2005) 271–282.
- [19] Z. Giergiczny, Effect of fly ash from different sources on the properties of hardened cement composites, *Silicates Industriels, Ceramic Science and Technology* 3–4 (2005) 35–40.
- [20] Z. Giergiczny, J. Ma lepszy, J. Szwabowski, J. Śliwiński, *Cements With Mineral Additives in Modern Concrete Technology*, G ra dzcze Cement, Heidelberg Cement Group, 2002 (in Polish).
- [21] J. Bijen, *Blast Furnace Slag Cement for Durable Marine Structures*, VCN/BetonPrisma, The Netherlands, 1998.
- [22] Council Directive (75/440/EEC) concerning the quality required of surface water intended for the abstraction of drinking water in the Member States.
- [23] Council Directive (98/83/EC) on the quality of water intended for human consumption.
- [24] J.W. Cho, K. Ioku, S. Goto, Effect of  $Pb^{II}$  and  $Cr^{VI}$  ions on the hydration of slag alkaline cement and the immobilization of these heavy metal ions, *Advances in Cement Research* 3 (1999) 111–118.
- [25] S.Y. Wang, C. Vipulanandan, Leachability of lead from solidified cement-fly ash binders, *Cement and Concrete Research* 26 (1996) 895–905.
- [26] H.A. Van der Sloot, Comparison of the characteristic leaching behavior of cements using standard (EN 196-1) cement mortar and an assessment of their long-term environmental behavior in construction products during service life and recycling, *Cement and Concrete Research* 20 (2000) 1079–1096.