Pergamon

Cement and Concrete Research 32 (2002) 1971–1979

CEMENT AND CONCRETE RESEARCH

Immobilization of Cr^{6+}, Cd^{2+}, Zn^{2+} and Pb^{2+} in alkali-activated slag binders

Jan Deja*

Faculty of Materials Science and Ceramics, University of Mining and Metallurgy, Al. Mickiewicza 30, 30-059 Cracow, Poland

Received 15 August 2001; accepted 14 June 2002

Abstract

Granulated blast furnace slag is the main component of alkali-activated slag cementitious materials (AASCs). Calcium silicate hydrates with a low Ca/Si ratio, hydrotalcite-type phase, some amounts of hydrogarnets and sodium zeolites form as main AASC hydration products. The microstructure of alkali-activated slag pastes shows a higher amount of gel pore content compared to OPC pastes and, simultaneously, significantly lower amount of capillary pores. The microstructure and phase composition of hydrated slag indicate that they can play an essential role in the immobilization of heavy metals. The properties of alkali-activated slag pastes in the presence of Zn, Cd, Cr and Pb ions were studied. The leaching TANK test was used to evaluate the level of immobilization of particular elements in mortars made containing these elements. It was found that the degree of Cd, Zn and Pb ion immobilization was very high (exceeding 99.9%). The values for Cr^{6+} were lower (ca. 99.0%). The strength development as well as microstructure observations are presented in the paper.

Keywords: Alkali-activated slag cement; Heavy metals; Compressive strength; Microstructure; Leaching

1. Introduction

With the increasing contamination of the natural environment, the problem of heavy metal immobilization becomes more and more significant. Several technologies will develop only when heavy-metal-containing by-products can be sufficiently and safely disposed of. In many research centres studies are being carried out to solve this problem.

Cementitious materials play an important role in the immobilization of heavy metals. They can be used not only in the construction of waste dumps and concrete shields but also as immobilizing agents, forming a matrix incorporating the heavy metals in a physical or chemical way. Cements are particularly useful in the processing of wet wastes; it is important in view of the fact that the wastes occur predominantly as slurries (e.g., galvanic wastes containing Cr^{+6}) [1–4].

The efficiency of the heavy metal immobilization is strongly related to the microstructure of the hardened paste, particularly to the pore size distribution and porosity. It is commonly known that capillary pores of diameters >100 nm decisively influence paste tightness and permeability [5]. On the other hand, the apparent diffusion coefficient of ions through porous materials has a close relation to the volume of very small pores with a radius less than 2 nm, and not to the total pore volume [6].

The pores in hardened alkali-activated slag (AAS) binders are distinctly smaller than those in Portland cement concretes, and the presence of capillaries is suppressed. Therefore, the migration of solutions in the hardened AAS concrete is hindered [7–9]. Many researches have confirmed that alkali activation of slag results in both reduced total porosity and median pore size [10–12].

Roy et al. [11] have found that median pore size for alkali-activated slag paste was only 1.8 nm.

Similar results were obtained by Cho et al. [12] who determined the micropore volume (< 5 nm) in alkali-activated slag pastes. The micropore volume of these pastes established ca. 78% of their total pore volume.

Beside microstructure, the pH values of the pastes also play an important role in the immobilization process. High pH values ensure the neutralising properties of the pastes. In an environment with high pH (>12) the heavy metal hydroxides of very low solubility precipitate. While pH

---

* Tel.: +48-12-617-2459; fax: +48-12-633-1593.

E-mail address: deja@uci.agh.edu.pl (J. Deja).

0008-8846/02/$ – see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0008-8846(02)00904-3

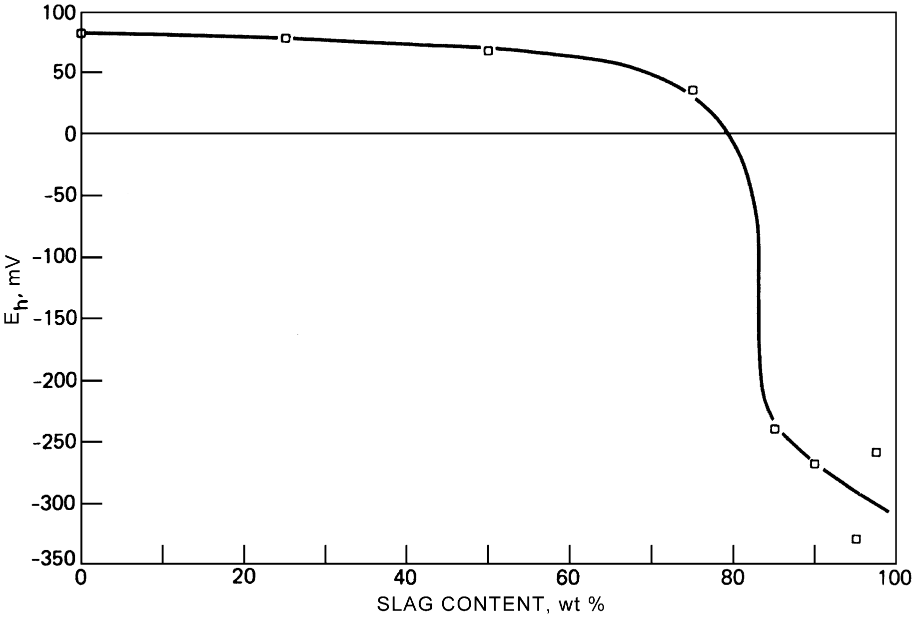

Fig. 1. Redox potentials of slag cements [28].

12.6 in Portland cement concrete mixture is given by the solubility of calcium hydroxide, in AAS mixtures, due to alkaline activators, the pH value is included in the range 12.0–13.7 [7,12–15]. Exact pH value is influenced by the type of activator (NaOH, Na_2CO_3, waterglass, etc.) and its concentration. It is believed, that most sodium in the AAS pastes is present in pore solution, and that sodium cations may have the effect of balancing and maintaining OH^- anions during AAS hydration [24].

The properties of alkali-activated slag concretes have been studied at the University of Mining and Metallurgy Cracow for many years [8,16–19]. According to Małolepszy and Deja [8], besides C-S-H phase small amounts of hydrogehlenite, hydrogarnets and sodium zeolites exist in AAS pastes. Similar results were obtained in many other works [7,20–22]. A recent research work carried out by Wang and Scrivener [23] shows that regardless of the activator used, the main hydration product of alkali-activated slag cementitious materials (AASCs) is gel-like calcium silicate phase with a low Ca/Si ratio. A hydrotalcite-type phase is also formed in the pastes activated with both NaOH and waterglass. Formation of zeolites in AASC pastes is strongly dependent on the chemical composition of the slag and requires a system with relatively high Al/Si ratio and a sufficiently low Ca/Si ratio [24].

Hydration products of AASCs can incorporate the part of heavy metals to the structure [25–27].

The reducing conditions in the hydrated slag pastes (presence of S^{2-} ions) also play a positive role in the immobilization process (for example: partial reduction of Cr^{6+} to Cr^{3+}, reduction of the pertechnetate ion to Tc dioxide). The redox potential of mixtures containing granulated blast furnace slag has been reported in the literature [28,29]. Redox potentials of slag cements are presented in Fig. 1 [28].

Therefore, the presented properties of alkali-activated slag pastes and the results of previous works [12,27,28,30,31] confirm their good conditions for immobilization of heavy metals.

2. Characteristics of starting materials

The following materials have been used to produce pastes and mortars:

Granulated blast furnace slag, ground in a ball mill to the specific surface of 360 ± 5 m^2/kg. The chemical analysis and physical properties of the slag are provided in Table 1.

Aggregate. Standard quartz sand of the granulation 0 to 2 mm was used as aggregate in mortar preparation.

Table 1
Chemical composition of slag

Component	Weight percent
CaO	41.10
SiO_2	38.10
Al_2O_3	9.60
MgO	8.40
Fe_2O_3	0.40
SO_3	1.10
$Na_2O + K_2O$	1.20
Residuum	0.10
Glassy phase content	80%
Specific gravity	2.95 g/cm^3

Table 2
Concentration of Zn, Cd, Cr, and Pb ions in the mortars

Type of activator	Ion concentration (mg/kg)							
	Mortar	Zn	Mortar	Cd	Mortar	Cr	Mortar	Pb
Na_2CO_3	A	491	C	1385	E	765	G	1701
	B	811	D	2761	F	1485	H	3365
	I	34	I	2	I	23	I	23
Waterglass	K	230	M	1370	O	764	R	1696
	L	420	N	2730	P	1484	S	3357
	J	33	J	2	J	22	J	22

Alkaline activators. Sodium carbonate (Na_2CO_3) and waterglass (silicate modulus $M_s = 2.0$) have been used as alkaline activators.

Heavy metals. The following heavy-metal-containing compounds have been used in sample preparation: $Zn(NO_3)_2$, $Pb(NO_3)_2$, $CdCl_2$ and Na_2CrO_4. Their amounts added to the hydrating samples were on level 1% and 2% of slag weight. Only for $Zn(NO_3)_2$ (taking into account the strong retardation effect of Zn ions), additions of this salt were reduced to the level 0.5% and 1% (in the case of sodium-carbonate-activated samples) and 0.25% and 0.5% in samples activated with waterglass. The samples, denoted as I and J, were not doped—only traces of heavy metals originating from the slag have been detected. Detailed information about Zn, Cd, Cr and Pb ion concentrations in the mortars can be seen in Table 2.

3. Preparation of mortars and pastes

The mortars were prepared at water to cementitious material ratio equal to 0.36. The ratio of ground granulated blast furnace slag to sand was 1:3.

The amount of alkaline activator in the activated slag mixes differs according to the alkalinity and fineness of the slag and according to the required strengths of hardened concretes. Usually, 2% to 7% of Na_2O (calculated) of the slag content is necessary [7,10]. Małolepszy has found that Na_2CO_3 is especially suitable for slags rich in C_2MS, and NaOH is a good activator for slags rich in C_2AS [32]. Małolepszy and Deja have found that for Polish granulated blast furnace slag (taking into account chemical and mineralogical composition of the slag) 5% addition of Na_2CO_3 or 15% addition of waterglass is optimum [8,17,18,33].

The mortars denoted as A–I were prepared using sodium carbonate as an alkaline activator (5% of slag weight) whereas those denoted as J–S were activated by waterglass (15% of slag weight). The samples denoted as I and J were prepared as reference alkali-activated slag pastes without addition of heavy metal compounds. The alkaline activators and heavy metals compounds were fully dissolved in water and after that mixed with slag. The mortars were mixed in a standard laboratory mixer, cast into molds for ISO 40 × 40 × 160-mm bars and shaken in a laboratory shaker.

The pastes for mineralogical and porosity investigations, with water to solid ratio equal to 0.28, were mixed in the laboratory mixer for 180 s. The heavy metal compounds and alkaline activators were dissolved in water. The 10 × 10 × 60-mm bars were made with the pastes using a vibrating table with a frequency of 3000 vibrations per minute.

4. Curing of pastes and mortars

After the preliminary consolidation, all the samples were matured in the molds for the first 24 h, at 20 °C and 100% RH. Subsequently, the pastes and mortars activated by waterglass were stored at 20 °C, 100% RH up to 720 days. The mortars and pastes activated by sodium carbonate were subjected to low-pressure steam curing at 85 °C for 4 h and subsequently stored at 20 °C, 100% RH. In the case of Na_2CO_3 activation, low-pressure steam curing gives higher hydration rate of slag and, consequently, better early-strength development [8,17,18].

5. Results and discussion

5.1. Mechanical strength of mortars

The compressive strength of alkali-activated slag mortars was measured after 3, 28, 180, 360 and 720 days curing. The 40 × 40 × 160-mm bars were used. The results are shown in Tables 3 and 4.

As can be seen from the data thus obtained, the type of activator strongly influenced the compressive strength of mortars. Waterglass-activated samples generally show significantly higher compressive strength. These differences are particularly evident in early stages of hydration. After 3 and 28 days of curing, the compressive strength of mortar I (waterglass activated) was two times higher than that of sample J (sodium carbonate activated). Significant reduction of these differences was observed for long-cured samples—after 2 years of hydration the compressive strength of mortar

Table 3
Compressive strength of Na_2CO_3-activated slag mortars

Type of mortar	Compressive strength (MPa)				
	3 days	28 days	180 days	360 days	720 days
A (0.5% Zn)	26.2	30.1	34.1	50.5	52.1
B (1.0% Zn)	27.1	32.1	36.2	49.5	53.1
C (1.0% Cd)	26.2	36.6	42.1	54.1	63.1
D (2.0% Cd)	25.1	33.2	41.1	53.3	61.2
E (1.0% Cr)	27.2	35.6	46.1	61.2	70.1
F (2.0% Cr)	28.2	47.2	57.2	64.6	72.1
G (1.0% Pb)	27.4	36.2	42.1	59.1	66.2
H (2.0% Pb)	28.5	34.1	41.2	51.3	59.7
I[a]	28.7	38.6	46.3	52.9	66.2

[a] No heavy metal addition.

Table 4
Compressive strength of waterglass-activated slag mortars

Type of mortar	Compressive strength (MPa)				
	3 days	28 days	180 days	360 days	720 days
J[a]	54.5	74.3	78.3	84.1	90.1
K (0.25% Zn)	43.2	54.2	60.1	70.1	77.2
L (0.5% Zn)	41.2	57.8	63.3	69.5	73.5
M (1.0% Cd)	37.2	42.1	46.1	57.2	56.2
N (2.0% Cd)	31.6	36.3	40.2	46.2	47.1
O (1.0% Cr)	53.2	64.1	69.1	74.1	96.2
P (2.0% Cr)	54.1	69.3	73.5	82.1	99.7
R (1.0% Pb)	52.1	68.8	71.2	80.1	92.1
S (2.0% Pb)	50.9	60.2	65.7	74.1	85.2

[a] No heavy metal addition.

J was 90.1 MPa, whereas that of mortar I was 66.2 MPa. After 28 days of curing, compressive strength values measured for the zinc-nitrate-containing samples were about 20% lower than for reference samples. However, important is that during next 23 months of curing, strength increase for these samples was observed, and after 2 years of hydration strength reduction of samples containing Zn ions was stable (ca. 20%).

Decrease in compressive strength (compared to the control samples without heavy metals) was observed when $CdCl_2$ was added. An interesting phenomenon was observed for waterglass-activated samples containing 2% of cadmium chloride (N)—after 720 days of curing ca. 50% decrease in strength (in comparison to reference samples) was measured.

On the other hand, at sodium chromate addition, in both cases, significant increase in compressive strength in comparison to the control samples (I and J) was observed.

Influence of Pb ions on the compressive strength of alkali-activated slag mortars is not very significant.

One can say that addition of heavy-metal-containing salts to the alkali-activated slag mortars influences their compressive strength development; however, no strength decrease with time is observed.

5.2. Leaching tests

To measure the amount of Zn^{2+}, Cd^{2+}, Cr^{6+} and Pb^{2+} ions leached from the AASC mortars, the TANK method was used in presented work [34]. After 3 days of preliminary curing alkali-activated slag mortars (40 × 40 × 160-mm bars) were placed in polyethylene containers filled with 2 dm^3 of distilled water. After 1, 4 and 12 months, the concentrations of Zn^{2+}, Cd^{2+}, Cr^{6+} and Pb^{2+} in the water were measured.

Chromium (VI) and total chromium content after the oxidation of Cr(III) to Cr(VI) was analysed by the following methods:

- spectrophotometrically, as a red-violet complex of chromium with benzocarbazide ($\lambda_{max} = 545$ nm at 5-cm-thick cuvette),
- impulse polarography using sodium hydroxide or sodium hydroxide and triethanolamine as basic electrolyte [35].

Table 5
Concentration of heavy metal ions in water (determined by TANK test)

Sample	Ion concentration (mg/dm^3)		
	1 month	4 months	12 months
A (0.5% Zn)	0.020	0.059	0.073
B (1.0% Zn)	0.027	0.062	0.074
C (1.0% Cd)	0.008	0.019	0.020
D (2.0% Cd)	0.016	0.038	0.042
E (1.0% Cr)	0.362	1.321	1.325
F (2.0% Cr)	1.967	4.731	4.971
G (1.0% Pb)	0.054	0.146	0.172
H (2.0% Pb)	0.071	0.212	0.215
K (0.25% Zn)	0.019	0.042	0.057
L (0.5% Zn)	0.012	0.072	0.092
M (1.0% Cd)	0.031	0.035	0.047
N (2.0% Cd)	0.012	0.081	0.085
O (1.0% Cr)	0.088	1.320	1.351
P (2.0% Cr)	3.725	4.780	4.811
R (1.0% Pb)	0.034	0.048	0.049
S (2.0% Pb)	0.037	0.039	0.041

The cadmium, lead and zinc content were determined by atomic absorption spectrometry using air–acetylene flame or by emission spectroscopy with plasma flame. Alternatively, traces of zinc were analysed by derivative impulse polarography in the basic solution of acetate buffer. Results of these chemical determinations are presented in Table 5.

At some simplified assumption (among other things that the leaching process is of linear character, irrespective of the concentration in the solution) the "degrees of immobilization" have been calculated. The results are presented in Table 6.

The results obtained confirm the high "immobilization potential" of alkali-activated slag mortars. The level of heavy metal concentration in water was very low (only for

Table 6
Degrees of heavy metals immobilization (determined by TANK test)

Sample	Immobilization degree (%)		
	1 month	4 months	12 months
A (0.5% Zn)	99.986	99.959	99.949
B (1.0% Zn)	99.988	99.974	99.969
C (1.0% Cd)	99.998	99.995	99.995
D (2.0% Cd)	99.998	99.995	99.995
E (1.0% Cr)	99.837	99.405	99.403
F (2.0% Cr)	99.543	98.901	98.845
G (1.0% Pb)	99.989	99.970	99.965
H (2.0% Pb)	99.993	99.978	99.978
K (0.25% Zn)	99.971	99.937	99.914
L (0.5% Zn)	99.990	99.941	99.925
M (1.0% Cd)	99.992	99.991	99.988
N (2.0% Cd)	99.998	99.990	99.989
O (1.0% Cr)	99.960	99.404	99.390
P (2.0% Cr)	99.135	98.890	98.882
R (1.0% Pb)	99.993	99.990	99.990
S (2.0% Pb)	99.996	99.996	99.996

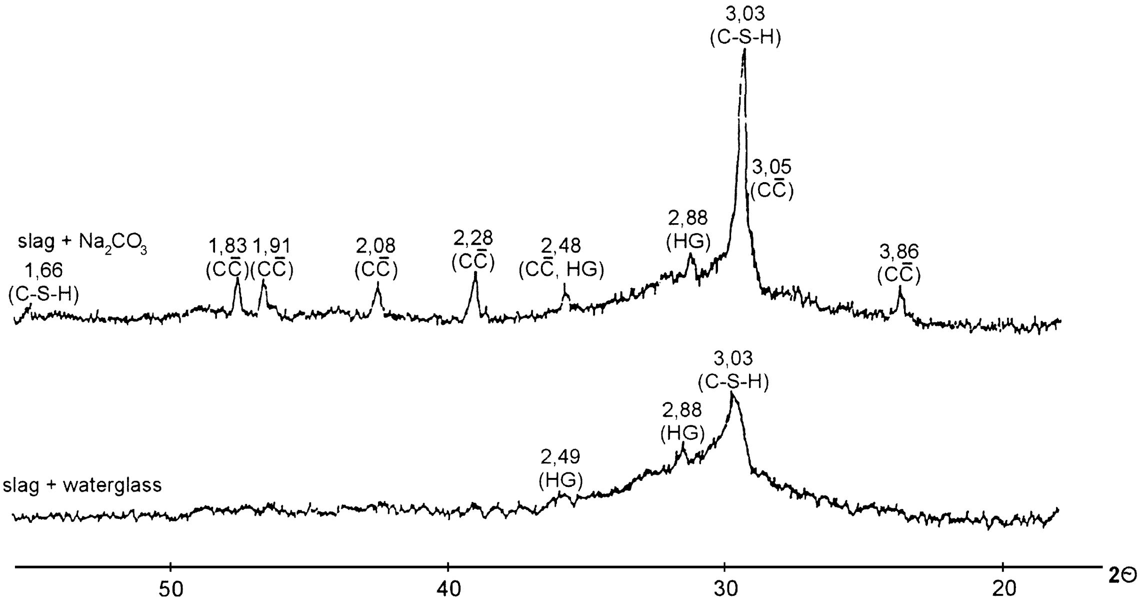

Fig. 2. XRD patterns of AAS pastes after 720 days of hydration.

samples containing Cr^{6+} ions concentrations were higher). It is evident that the “leaching rate” of heavy metal ions in the 4- to 12-month curing period is significantly lower than in the initial period of hydration. In a few cases, no concentration changes were observed between 4 and 12 months of samples curing.

In all cases (except of Pb^{2+}-containing samples) the degree of heavy metal immobilization in Na_2CO_3-activated mortars was higher than in those mortars produced with waterglass.

Irrespective of very high levels of heavy metal immobilization, there are differences between the results achieved for different ions:

(a) For Zn^{2+}-ion-containing samples high immobilization degree was observed (over 99.9% after 12 months storage in water).

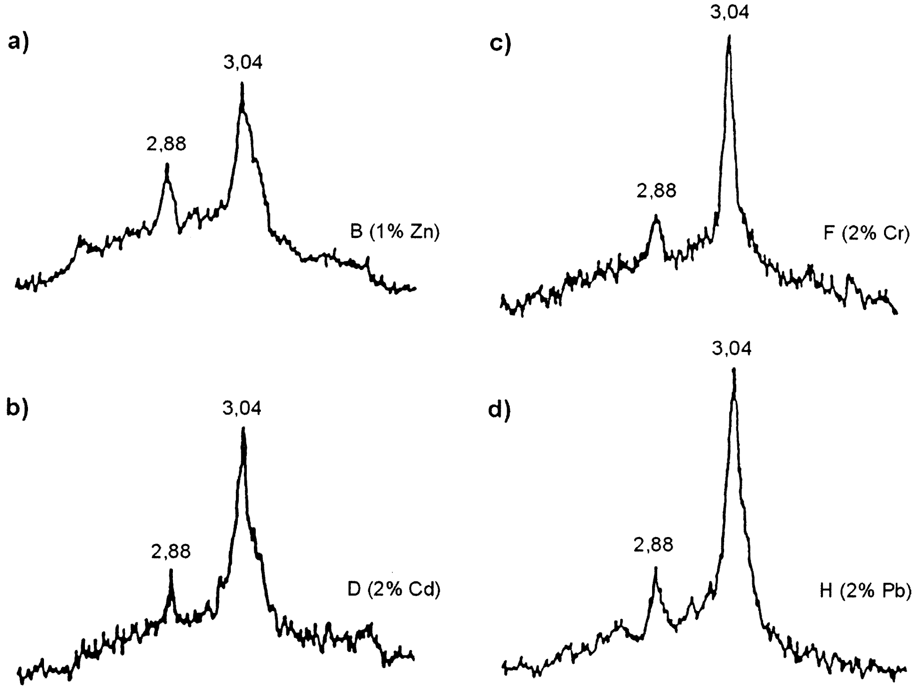

Fig. 3. Influence of heavy metals on the phase composition of the pastes after 720 days of hydration (samples activated with sodium carbonate).

(b) About 99.99% immobilization degrees for cadmium ions were measured after 12 months.

(c) For mortars with Pb^{2+} ions, very high immobilization degrees were obtained (99.965–99.978% for samples activated with sodium carbonate and 99.990–99.996% for mortars activated with waterglass).

(d) The concentration of leached Cr^{6+} ions was very small in comparison with the concentration of Cr^{6+} ions in the mortars, but this ion is leached more easily than others. After 1 year, immobilization degrees of Cr^{6+} ions were on the level 98.845–99.403% for samples activated by sodium carbonate. For the same samples activated by waterglass, chromium ion binding was 98.882–99.390%. These results are in good agreement with the data obtained by Cho et al. [12].

5.3. Phase composition of slag pastes

The phase composition of the alkali-activated slag pastes was determined by XRD. The influence of hydration time (from 28 to 720 days) on the phase composition was limited. As an example, the XRD patterns for the pastes activated with Na_2CO_3 and waterglass after 720 days of hydration are shown in Fig. 2.

The broad and diffuse peaks from the original slag around 28–32° 2θ reflect the short-range order of the $CaO–Al_2O_3–MgO–SiO_2$ glass structure.

For both pastes a peak can be identified, superimposed on the amorphous hump, at about 3.03 Å. This is attributed to the (110) reflection of poorly crystalline C-S-H phase. For samples activated with waterglass, additionally only small amounts of hydrated gehlenite (stratlingite—C_2ASH_8) were detected. It is marked in Fig. 2 as HG. In the paste activated with sodium carbonate, besides C-S-H and hydrated gehlenite, a significant amount of calcium carbonate ($C\overline{C}$) was detected. The broader peak corresponding to the reflections of C-S-H in waterglass-activated samples suggests that the C-S-H phase thus formed has a lower crystallinity than C-S-H in slag activated with sodium carbonate. The addition of heavy metals did not significantly affect the phase composition of the pastes. The results are presented in Fig. 3.

Low crystallinity of the C-S-H phase and limited sensitivity of the XRD method make impossible the precise determination of differences concerning the rates of slag hydration in the pastes containing heavy metals. However, it seems that content of calcium carbonate in samples F and H (sodium-carbonate-activated samples containing Cr or Pb ions) is slightly higher (higher 3.04 Å peak). It is difficult to find the data relating to the equilibrium products in such complex systems. Undoubtedly, the carbonates are formed, as results from some published reports show [25,36].

Table 7
Porosity of the pastes

Type of paste	Total cumulative volume (mm^3/g)		Pore radius average (nm)	
	28 days	720 days	28 days	720 days
Na_2CO_3 activator				
A	36.4	17.8	17	11
B	48.5	26.2	16	9
C	39.5	21.7	13	9
D	47.3	20.6	35	17
E	44.6	27.4	38	20
F	38.6	21.7	10	9
G	38.2	17.1	20	10
H	38.9	24.8	13	11
I	36.4	18.9	12	8
Waterglass activator				
J	29.5	16.4	6	3
K	40.1	17.4	9	5
L	34.8	18.5	7	5
M	31.3	17.1	5	4
N	29.3	14.8	4	4
O	27.1	13.9	7	4
P	28.2	14.5	7	4
R	30.5	15.9	5	4
S	32.8	17.4	9	5

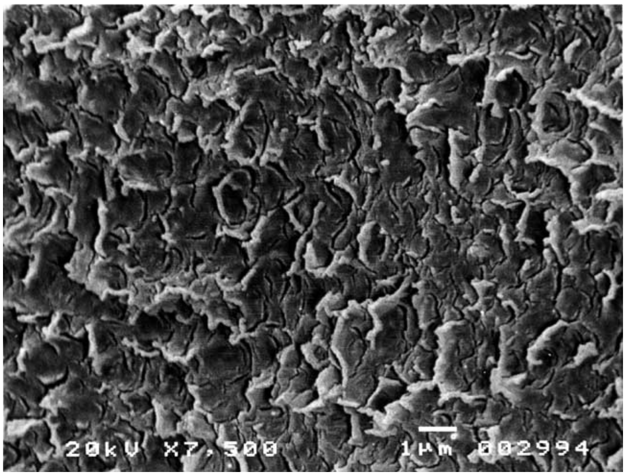

Fig. 4. Microstructure of AASC paste (without addition) activated by waterglass.

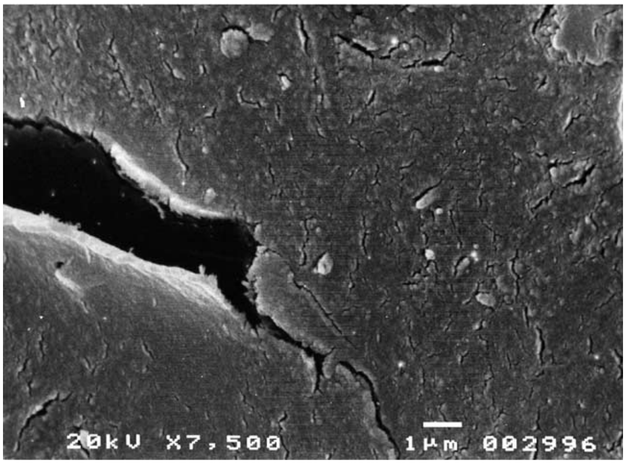

Fig. 5. Microstructure of AASC paste with Pb ions addition. Compact C-S-H Type IV phase with microcracks (waterglass activation).

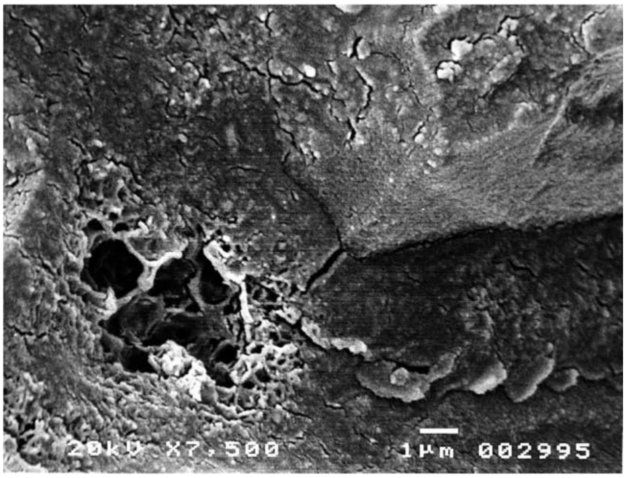

Fig. 6. Microstructure of AASC paste with addition of 0.5% of $Zn(NO_3)_2$. C-S-H phase "growing" in the pore (waterglass activation).

5.4. Microporosity of pastes

The microporosity of the pastes after 28 and 720 days of curing was determined by means of mercury porosimetry. The samples activated by Na_2CO_3 (A to I) as well as those activated by waterglass (J to S) were taken into account. The total porosity and the average pore diameter were determined. The results are shown in Table 7.

The total porosity of the pastes activated by waterglass is generally lower than for samples activated by sodium carbonate. The reduction of the total porosity with the age of the pastes was also observed. It can be the consequence of empty spaces being filled by the hydration products.

On the other hand, the influence of the activator type on the average pore diameters reveals remarkable differences. After 720 days of curing the average pore diameters for the pastes activated by waterglass were on the level 3 to 5 nm. For the same samples activated by Na_2CO_3 the average pore diameters were in the range 8 to 11 nm. Only for samples D and E pore radius was higher (17 to 20 nm). It seems that in all pastes (especially for those activated by waterglass) small gel pores dominate and the amount of capillary pores is significantly lower than in typical cement pastes.

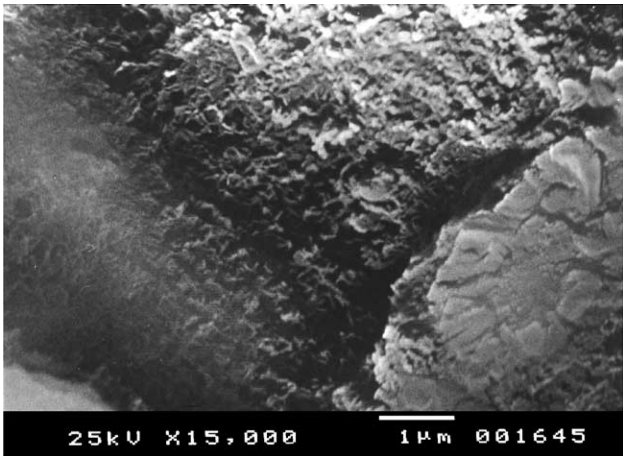

Fig. 7. Microstructure of AASC paste with addition of Cr ions (activated by sodium carbonate).

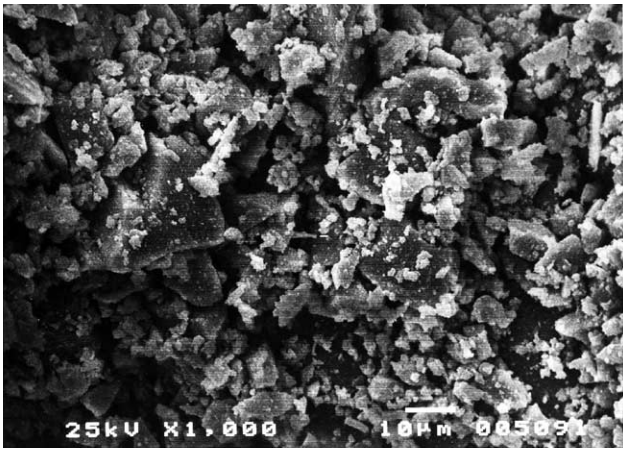

Fig. 8. Microstructure of AASC paste with addition of Cd ions (sodium carbonate activation). Poorly crystallized C-S-H phase.

The microporosity of the pastes is in good agreement with the results of previous works concerning the microporosity of Portland cement and alkali-activated slag mortars [9,10,33].

5.5. Microscopic observations of pastes

The microstructure of hardened alkali-activated slag pastes was investigated by SEM. All the samples were very compact, with the gel-like C-S-H phase as a main component occurring in two forms: C-S-H Type III and C-S-H Type IV, respectively, following Diamond's classification [37]. The significant differences between the samples doped with heavy metals and reference samples were not observed. In the samples activated by waterglass a higher amount of dense gel-like products was detected. In the sodium-chromate-doped samples, a C-S-H Type I phase increase was observed. On the other hand, higher amounts of small microcracks in the pastes activated with waterglass (see Figs. 4, 5 and 6) are well seen.

Examples of typical microstructure of the samples are presented in Figs. 4–8.

6. Conclusions

The influence of the addition of Zn^{2+}, Cd^{2+}, Cr^{6+}, Pb^{2+} ions on the phase composition and microstructure of alkali-activated slag pastes as well as the strength development and immobilization of heavy metals in AAS mortars were investigated. High concentrations of cadmium, zinc, lead and chromium ions were applied (up to 2% by weight of binder).

Based on the results the following conclusions can be drawn:

(1) Irrespective of the type of activator, poorly crystalline C-S-H phase was the main hydration product in the systems analysed. Small amounts of hydrated gehlenite were also present in both types of pastes (waterglass-activated and Na_2CO_3-activated). In the pastes activated with sodium carbonate, significant amounts of $CaCO_3$ were detected. The addition of heavy metals did not significantly affect the hydration products of AAS pastes.

(2) The microstructure observations of hardened slag pastes show very dense gel-like C-S-H phase as the dominant product of hydration. Opposite to the pastes activated with sodium carbonate, in waterglass-activated samples small microcracks were well seen. The differences between the samples doped with heavy metals and reference samples were not significant.

(3) For slag used in this study, the waterglass-activated slag mortars gave much higher strength than Na_2CO_3-activated slag mortars. In both types of mortars, after 2 years of hydration, the addition of zinc ions brings about a decrease in compressive strength reaching 15% as compared to the reference value. The influence of cadmium ions on the sodium-carbonate-activated mortars is less pronounced—the compressive strength decrease does not exceed 5%. For waterglass-activated mortars, very significant strength decrease of the mortars containing Cd^{2+} ions was observed. On the other hand, in the mortars containing Na_2CrO_4, about 10% compressive strength increase was observed. The compressive strength decrease in the mortars containing Pb^{2+} ions was below 10%. It should be noted that the strength development between 28 and 720 days takes place in all mortars containing heavy metals.

(4) The microporosity of alkali-activated slag pastes varied with alkaline activators. Na_2CO_3-activated slag pastes exhibited slightly higher total porosity and significant higher average pore radius in comparison to the waterglass-activated pastes. Taking into account the results of previous works, it should be noted that both types of alkali-activated slag pastes exhibited a significantly lower porosity than typical OPC [9,10,33].

(5) It was found that the degree of Cd^{2+}, Zn^{2+} and Pb^{2+} ion immobilization was very high, exceeding 99.9%; only the values for Cr^{+6} were lower (over 98.8%). The "leaching rate" of heavy metals ions in 4–12 months of curing period was significantly lower than in the initial period of hydration. In a few cases, no concentration changes of the leached ions were observed between 4 and 12 months of sample curing.

Taking into account the results of microporosity measurements (finer pore structure in waterglass-activated pastes) it looks surprising that amounts of heavy metal ions leached from waterglass-activated mortars are in few cases higher than for Na_2CO_3-activated mortars. Presumably, this is the consequence of the microcracks present in the pastes activated with waterglass (Figs. 4–6) and formation of calcite in the system activated with sodium carbonate. The microcracks are the ways of faster migration. This problem was mentioned in previous works [8,38]. The formation of calcite in Na_2CO_3-activated slag pastes seals the microstructure and makes possible the incorporation of heavy metal ions in the $CaCO_3$ structure.

The results thus presented prove that alkali-activated slag cementitious material can be successfully used as a heavy metal immobilizing agent and can play an important role in waste management.

Acknowledgements

The author would like to acknowledge partial support from the Polish Scientific Research Committee (Grant No. 18. 160.248PBO764/S2/93/05).

References

[1] D.M. Roy, Cementitious materials in nuclear waste management, Proceedings of the 9th International Congress on the Chemistry of Cement, New Delhi, vol. VI, National Council for Cement and Building Materials, NCB, New Delhi, 1992, pp. 88–113.

[2] F.P. Glasser, Application of cements to the treatment and conditioning of toxic wastes, Proceedings of the 9th International Congress on the Chemistry of Cement, New Delhi, vol. VI, National Council for Cement and Building Materials, NCB, New Delhi, 1992, pp. 114–118.

[3] P. Krivenko, J. Skurchinskaya, L. Lavrinenko, O. Starkov, E. Konalov, Physico-chemical bases of radioactive wastes immobilization in a mineral-like solidified stone, in: P.V. Krivenko (Ed.), Alkaline Cements and Concretes, Proceedings of the 1st International Conference, VIPOL Stock Co., Kiev, Ukraine, VIPOL Stock Co., Kiev, Ukraine, 1994, pp. 1095–1106.

[4] D.M. Roy, Alkali-activated cements. Opportunities and challenges, Cem. Concr. Res. 29 (1999) 249–254.

[5] A.M. Neville, Properties of Concrete, Addison Wesley Longman, Harlow, UK, 1995.

[6] S. Goto, M. Daimon, Proceedings of the 8th International Congress on the Chemistry of Cement, Rio de Janeiro, vol. VI, Abla Grafica e Editora Ltda, Rio de Janeiro, Brazil, 1986, pp. 405–409.

[7] B. Talling, J. Brandstetr, Present state and future of alkali activated slag concretes, Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Proceedings of the 3rd International Conference, Trondheim, Norway, ACI SP114, vol. 2, American Concrete Institute, Detroit, USA, 1989, pp. 1519–1545.

[8] J. Małolepszy, J. Deja, The influence of curing conditions on the mechanical properties of alkali activated slag binders, Silic. Ind. 53 (11–12) (1988) 179–186.

[9] J. Deja, J. Małolepszy, Effect of cementitious material on the corrosion of steel development in the environment of high chloride content, Proceedings of the International Conference on Corrosion and Corrosion of Steel in Concrete, Sheffield, vol. II, Sheffield Academic Press Ltd., Sheffield, UK, 1994, pp. 684–697.

[10] C. Shi, Strength, pore structure and permeability of alkali-activated slag mortars, Cem. Concr. Res. 26 (12) (1996) 1789–1799.

[11] D.M. Roy, W. Jiang, M.R. Silsbee, Chloride diffusion in ordinary, blended, and alkali-activated cement pastes, Cem. Concr. Res. 30 (2000) 1879–1884.

[12] J.W. Cho, K. Ioku, S. Goto, Effect of Pb^{II} and Cr^{VI} ions on the hydration of slag alkaline cement, Adv. Cem. Res. 11 (3) (1999) 111–118.

[13] K. Byffors, G. Klingstedt, V. Lehtonen, H. Pyy, L. Romben, Fly Ash,

Silica Fume, Slag and Natural Pozzolans in Concrete, Proceedings of the 3rd International Conference, Trondheim, Norway, ACI SP 114, vol. 2, American Concrete Institute, Detroit, USA, 1989, pp. 1429–1466.

[14] J. Małolepszy, J. Deja, Immobilization of heavy metal ions by the alkali activated slag cementitious materials, Stud. Environ. Sci. 60 (1994) 519–524.

[15] S. Song, H.M. Jennings, Pore solution chemistry of alkali-activated ground granulated blast-furnace slag, Cem. Concr. Res. 29 (1999) 159–170.

[16] A. Derdacka, J. Małolepszy, Application of ground granulated blast furnace slag in binding material production, Cem. Wapno Gips, (10) (1975) 291–296 (in Polish).

[17] J. Małolepszy, J. Deja, Slag binder with low energy consumption, Part I, Cem. Wapno Gips 4 (1983) 300–304 (in Polish).

[18] J. Małolepszy, J. Deja, Slag binder with low energy consumption, Part II, Cem. Wapno Gips 5 (1984) 138–142 (in Polish).

[19] J. Małolepszy, The role of alkalies in the hydration of vitrified calcium and magnesium silicates, Proceedings of the 9th International Congress on the Chemistry of Cement, New Delhi, vol. IV, National Council for Cement and Building Materials, NCB, New Delhi, 1992, pp. 118–123.

[20] V.D. Glukhovsky, Soil silicates: Properties, manufacturing technology and application, Doct. Tech. Sc. degree thesis, Civil Engineering Institute, Kiev, Ukraine, 1965 (in Russian).

[21] P.V. Krivenko, Alkaline cements, in: P.V. Krivenko (Ed.), Alkaline Cements and Concretes, Proceedings of the 1st International Conference, VIPOL Stock Co., Kiev, Ukraine, VIPOL Stock Co., Kiev, Ukraine, 1994, pp. 11–130.

[22] J. Pera, M. Chabannet, Durability of alkali-activated slag cements, in: K.L. Scrivener, J.F. Young (Eds.), Mechanisms of Chemical Degradation of Cement-Based Systems, E&FN Spon, London, 1997, pp. 281–288.

[23] S.D. Wang, K. Scrivener, Hydration products of alkali activated slag cement, Cem. Concr. Res. 25 (3) (1995) 561–571.

[24] S.D. Wang, The role of sodium during the hydration of alkali-activated slag, Adv. Cem. Res. 12 (2) (2000) 65–69.

[25] W. Nocuń-Wczelik, Hydrated calcium silicates formation in the presence of some additives, Proceedings of the 3rd International Conference Euro-Ceramics, Madrid, vol. 2, Faenza Editrice Iberica, S.L., Castellon de la Plana, Spain, 1993, pp. 1041–1049.

[26] D. Breck, Zeolite Molecular Sieves Structure, Chemistry and Use, John Wiley & Sons, New York, 1974.

[27] D.M. Roy, Concrete the gigaphase ceramic: Its role in environmentally friendly technology, in: S. Somiya, R.P.H. Chang, M. Doyama, R. Roy (Eds.), Proceedings of the 3rd Okinaga Symposium, Elsevier, Amsterdam, 1998, pp. 81–88.

[28] R.D. Spence, W.D. Bostick, E.W. McDaniel, T.M. Gilliam, J.L. Shoemaker, O.K. Tallent, I.L. Morgan, B.S. Evans-Brown, K.E. Dodson, Immobilization of technetium in blast furnace slag grouts, Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Proceedings of the 3rd International Conference, Trondheim, Norway, ACI SP 114, vol. 2, American Concrete Institute, Detroit, USA, 1989, pp. 1579–1596.

[29] F.P. Glasser, Progress in the immobilization of radioactive wastes in cement, Cem. Concr. Res. 22 (1992) 201–216.

[30] M.W. Grutzeck, Hazardous waste (organic, heavy metal): Cement disposal, Proceedings of the 9th International Congress on the Chemistry of Cement, New Delhi, vol. VI, National Council for Cement and Building Materials, NCB, New Delhi, 1992, pp. 119–125.

[31] E. Zamorani, I.A. Sheikh, M.D. Rossa, G. Serrini, Physical properties and leachability of MLW stream containing Cr, Ni and Cd immobilised in a cement matrix, Scientific Basis for Nuclear Waste Management XII, Proceedings of Materials Research Society Symposium vol. 127, (1989) 489–494.

[32] J. Małolepszy, Proceedings of the 8th International Congress on the Chemistry of Cement, Rio de Janeiro, vol. IV, Abla Grafica e Editora Ltda, Rio de Janeiro, Brazil, 1986, pp. 104–107 (108–111).

[33] J. Deja, Chloride resistance of pastes and mortars containing mineral additives, Proceedings of the 10th International Congress on the Chemistry of Cement, Gothenburg, vol. IV, Amarkai AB and Congrex Goteborg AB, Goteborg, Sweden, 1997, p. 4iv015.

[34] R.H. Rankers, I. Hohberg, Leaching tests for concrete containing fly ash—evaluation and mechanism, Stud. Environ. Sci. 48 (1991) 275–286.

[35] A. Bobrowski, B. Barchańska, Chem. Anal. 24 (1979) 857–863 (in Polish).

[36] W. Nocuń, J. Małolepszy, Studies on immobilization of heavy metals in cement paste—C-S-H leaching behaviour, Proceedings of the 10th International Congress on the Chemistry of Cement, Gothenburg, vol. IV, Amarkai AB and Congrex Goteborg AB, Goteborg, Sweden, 1997, p. 4iv043.

[37] S. Diamond, The microstructures of cement paste in concrete, Proceedings of the 8th International Congress on the Chemistry of Cement, Rio de Janeiro, vol. I, Abla Grafica e Editora Ltda, Rio de Janeiro, Brazil, 1986, pp. 122–147.

[38] J. Małolepszy, J. Deja, The effect of variable curing conditions on the properties of mortars with silica fume, Proceedings of 4th Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Istanbul, vol. II, (1992) 1075–1087.