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LEACHING PROPERTIES OF SECONDARY LEAD SLAG STABILIZED/SOLIDIFIED WITH CEMENT AND SELECTED ADDITIVES

Sodium lead slag, generated during secondary lead production, is characterized as hazardous waste. The aim of the study was to investigate leaching mechanism and behaviour of lead and arsenic from sodium lead slag previously stabilized/solidified in concrete using additives: MgO, CaO, Ba(OH)$_2$ and gypsum. The influence of selected additives on pollutant release was also investigated. The results of the NEN 7375 leaching test indicate dissolution of lead and arsenic from the outer layer of specimens, followed by depletion of possible mobile forms. Analysis of leachates from samples with various compositions showed that proper selection of additives may reduce leaching of Pb and As below the specified limits.

1. INTRODUCTION

Lead, well-known and widely used heavy metal, represents a serious pollutant for the environment due to its toxicity and bioaccumulation. The growth in lead consumption can be almost entirely attributed to the demands of the battery market, which has increased almost seven-fold since 1960 [1]. About 50% of total lead production worldwide is based on secondary refining of lead, mainly from waste lead-acid batteries [2]. The Engitec Integrated CX System, which involves crushing of the whole batteries, separation of battery components and the battery paste desulphurisation prior

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smelting, has been recognized as the best available technology (BAT) for lead recycling [3].

Slag is an inevitable waste from secondary lead smelting process. Depending on added flux during the battery paste smelting, various types of slag can be obtained: silica slag, calcium slag and sodium slag (produced by adding Na_2CO_3 as flux). Although sodium slag contains lead (approximately 5 wt. %), soluble alkalis and decomposes in contact with air, Na_2CO_3 is mainly used in industry due to generated amount of total slag, as well as reduced energy and gas consumption [4]. Secondary lead slag is characterized as hazardous waste in European Waste Catalogue due to content of hazardous substances in concentrations that higher than those allowed and possible cumulative effects of multiple pollutants such as lead, arsenic and antimony [5]. Each year, the treatment of waste batteries in Europe produces 200 000 tones of toxic and unstable secondary lead slag [6].

As a hazardous waste, secondary lead slag should be treated and disposed of in safe and designated dumping sites. Cementitious stabilization/solidification (S/S) processes of waste containing inorganic materials can be an effective technique for reducing the mobility of heavy metals. According to Hills and Pollard [7], the compressive strength and leaching of pollutants are the basic parameters for assessing the effectiveness of waste treatment by the S/S technique. Chemical and physical immobilization of metals depends on successful hydration of the binders (cement) when mixed with water to form minerals characteristic for cement-based systems [8]. Significant role in the immobilization is attributed to the calcium silicate hydrates (C–S–H) as the main component of hardened paste.

Lassin et al. [6] found that the secondary lead slag could not be stabilized due to the extent of soluble fraction of the waste. Chemical and physical characteristics of the sodium slag are the reason of its spontaneous decomposition in air, which increases its polluting potential. Stabilization/solidification of secondary lead slag by incorporating the slag into concrete mixture was performed in previous study done by authors [9]. The amount of the secondary lead slag in concrete and proper selection of additives had a significant influence on the properties of S/S waste. Stabilized material had compressive strength above required, as well as reduced leaching of Pb and Zn.

The release of pollutants from waste in contact with the atmospheric water is the main potential hazardous source, due to the leaching phenomenon. The leaching of the contaminant from S/S waste forms is mostly a diffusion-controlled process [10] which may be influenced by many factors: chemical composition of the waste, pH, redox potential, complexation, liquid-to-solid ratio, contact time, etc. [11]. The most common experimental tools for studying the leaching phenomenon are leaching tests, developed especially for mineral waste materials. Batch leaching tests are used to determine pollution potential of raw or treated waste, and dynamic tests provide information about the release dynamics. Diffusion-leaching test EA NEN 7353 [12] is a dynamic test that has been used in several studies [13, 14] for determination of

leaching characteristics of pollutants from stabilized/solidified waste. According to NEN 7375 test, different release rates of components during test period could indicate the predominant leaching mechanism from matrices: dissolution, diffusion controlled release and surface wash of or depletion of the component.

The aim of this study was to investigate leaching mechanism and behavior of pollutants from sodium lead slag generated during CX process stabilized/solidified in concrete using cement as hydraulic binder and selected additives (magnesium oxide, calcium oxide, barium hydroxide and gypsum). Inorganic additives are used to improve the performance of concrete [15], but there are no available data in literature on their effect on leaching of certain elements from S/S lead slag. Content of CaO determines the thermodynamics and kinetics of the S/S process, i.e. formation, structure and morphology of C–S–H gel [16]. Oxides of calcium and magnesium were used in order to investigate the possibility of using dolomitic lime (calcium-magnesium oxide) as a potential natural additive in the manufacture of concrete. Barium(II) hydroxide was used to increase the stabilization of sulfates in concrete [17]. Gypsum was selected for its influence on mechanical properties of concrete. Previous studies have shown that the addition of up to 5% of gypsum improves compressive strength and reduce leaching of lead from materials [18].

2. EXPERIMENTAL

Sodium lead slag. During the process of lead recovery from automotive batteries, charge for rotary furnace consisted of desulfurized paste, metals from grid, Na_2CO_3, Fe^0 and reducing agent (coke). Samples of sodium slag, generated in short rotary furnace, were collected after each charge throughout 20 days of campaign. Collected samples were mixed to form one representative sample of sodium slag and left to age on air.

After ageing period of ten days [9], total amount of delivered slag was prepared by drying to constant weight and sieving. A coarse fraction >1 mm (ca. 15 wt. %) was rejected and returned to smelting, while fraction <1 mm (ca. 85 wt. %) was used as an experiment material. Chemical compositions of prepared slag, determined by atomic absorption spectrometry (AAS) and typical composition of sodium lead slag [19] are presented in Table 1. The slag contained high amounts of Na and Fe, considerable amounts of Pb, Si and Ca, trace amount of Cr, Cu, Zn and As, as well as Cr from refractory lining. Residual carbon, as reducing substance, and sulphur from paste and coke, were also present in the slag.

The pollution potential of the slag was evaluated by the European standard test, EN 12457-2 [20]: powdered slag (<1 mm fraction) was agitated in distilled water for 24 h at 10:1 liquid-to-solid ratio.

Chemical composition of the secondary lead slag [wt. %]

Constituent	Composition of prepared slag	Typical composition of sodium lead slag [19]
Na (Na$_2$O and Na$_2$SO$_4$)	34.60	20.00–35.00
Fe (FeS and Fe$_2$O$_3$)	20.10	2.00–20.00
Pb (PbS and PbO)	7.43	5.00–10.00
Si (SiO$_2$)	4.71	2.00–12.00
Ca (CaO)	3.42	1.00–9.00
Cr (Cr$_2$O$_3$)	0.13	–
Cu (CuS)	0.25	–
Zn (ZnO)	0.12	0.00–0.50
As (As$_2$O$_3$)	0.078	0.01–0.2
C	9.40	5.00–10.00
S (total)	3.30	3.00–6.00

Stabilization/solidification of sodium lead slag. The cement mixtures were made using commercial Portland cement (PC 35M (V-I) 32.5R), aggregates (coarse aggregate <5 mm; fine aggregate <0.5 mm), water, slag (<1 mm faction) and powdered additives: magnesium oxide (p.a.), calcium oxide (p.a.), barium hydroxide (p.a.) and gypsum (technical grade). Additives replaced 5 wt. % of cement, slag replaced 15 and 30 wt. % of aggregates, making 10 and 20 wt. % of the total concrete mixture, respectively. All samples were made using water to binder (cement) ratio (w/b) of 0.60 by weight, where the workability requirements were met. Compositions of the mixtures are presented in Table 2.

Proportions of concrete mixtures [wt. %]

Constituent	M1	M2	C1	C2	B1	B2	G1	G2
Cement	22	22	22	22	22	22	22	22
MgO	1	1	–	–	–	–	–	–
CaO	–	–	1	1	–	–	–	–
Ba(OH)$_2$	–	–	–	–	1	1	–	–
Gypsum	–	–	–	–	–	–	1	1
Coarse aggregates	21	21	21	21	21	21	21	21
Fine aggregates	33	23	33	23	33	23	33	23
Slag	10	20	10	20	10	20	10	20
Water	13	13	13	13	13	13	13	13

The mixtures were cast into moulds and cured for 28 days in order to determine leaching behaviour. The leachability of elements from the concretes was evaluated by modified EA NEN 7375 diffusion-leaching test [12]. The monolithic concrete cubes

(40 mm × 40 mm × 40 mm), after curing for 28 days, were immersed in leaching agent (distilled water, pH = 4 with HNO_3), for the test period of 64 days, with sequential total renewal of leachant after a fixed period time, with 8 extractions (0.25, 1, 2.25, 4, 9, 16, 36, 64 days). A liquid/solid ratio was 5. The eluate was collected in separate fractions after a fixed period of time and analysed. For all experimental assays, the eluates were analysed for pH, *Eh* and concentrations of elements and presented results were the main value of three. After determination of pH and *Eh*, a portion of the leachate obtained after each renewal was collected for the determination of the sulphates by ion chromatography (IC). The remaining eluate samples were filtered and acidified at pH 2 with HNO_3 and then analysed for cations by inductively coupled plasma mass spectrometry (ICP-MS) on Agilent ICP-MS 7500ce device.

Cumulative leaching according to NEN 7375 was calculated from [12]:

$$\varepsilon_n^* = \sum_{i=1}^{n} E_i \qquad \text{for} \qquad n = 1, ..., N \tag{1}$$

where ε_n^* is the measured cumulative leaching of a component for period *n* comprising fractions $i = 1$ to n, in mg/m^2 of sample surface area, E_i is the measured leaching of the component in fraction *i* in mg/m^2 and N is the total number of leachant renewal periods.

Cumulative derived leaching is also calculated according to the formula [12]:

$$\varepsilon_n = E_i \frac{\sqrt{t_i}}{\sqrt{t_i} - \sqrt{t_{i-1}}} \tag{2}$$

where ε_n is the derived cumulative leaching of a component for period *n* comprising fraction $i = 1, ..., n$, in mg/m^2, E_i is the measured leaching of the component in fraction *i*, in mg/m^2, t_i is the replenishment time of fraction *i* in *s* and t_{i-1} is the replenishment time of fraction $i - 1$. Derived leaching values can be used to evaluate leaching behaviour, mobility and mechanism of pollutants leaching [12]. *Eh* and pH data were used in *Eh*–pH diagrams for further investigation of leaching mechanism.

3. RESULTS AND DISCUSSION

3.1. POLLUTION POTENTIAL OF SECONDARY LEAD SLAG (EN 12457-2 TEST)

The leachability of selected elements (Cr, Fe, Zn, As, Pb) from the slag was examined using the EN 12457-2 leaching test [20]. Iron was not detected in the leachate. Cr and Zn concentrations were below the limits. The concentrations of Pb and As were higher than the specified limit values for those elements (Table 3), which confirmed

classification of secondary lead slag as hazardous waste. pH of the leachates was 12.00, which indicated the alkaline nature of waste.

Pollution potential of secondary lead slag determined by the EN 12457-2 leaching test [mg/kg of dried material]

Element	Cr	Fe	Zn	As	Pb
Concentration	0.10	n.d.[a]	0.10	12.0	21.6
Limit value[b] [20]	10.0	–	50.0	2.0	10.0

[a] n.d.– not detected, under detection limit.
[b] For non-hazardous waste.

3.2. LEACHING PROPERTIES OF STABILIZED WASTE (NEN 7375 TEST)

The alkaline nature of the S/S matrix could significantly change the initial pH of the leachant. Dissolution of hydroxides and hydrates in acidic medium increases pH (ca. 12) of the leachates [21]. pH and conductivities of leachates, measured during 64 days, showed the same trend for all cement mixtures (Fig. 1).
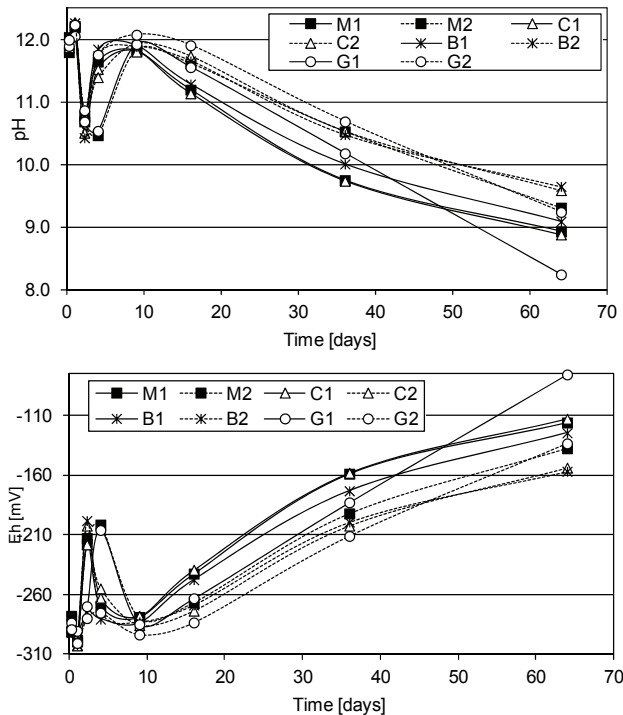

Fig. 1. pH and *Eh* values during 64 days of the leaching test

pH values at the end of each extraction were much higher than initial pH (4.0) of the leachate. The maximum pH occurred on the first day of the leaching test, followed by slight decrease on 2.25th day and renews increase on the 4th and 9th day. After 9 days of leaching, pH displayed steady decrease until the end of the test.

Comparing mixtures with same additives, pH values were higher in samples containing 20% of the slag (M2, C2, B2, G2) than in samples with 10% due to more alkaline nature of the waste. The highest pH on the first day (12.28) was found in the mixture C2 with CaO as additive and 20% slag. pH decreased with progressive extraction and the lowest value of pH after 64 days was found in the mixture prepared with gypsum and 10% slag (G1).

Cumulative concentrations of selected elements (Cr, Fe, Zn, As, Pb) and SO_4^{2-} ions, calculated according to Eq. (1) for all mixtures after 64 days are presented in Table 4. Concentrations of Cr leached were in the range from 3.59 (G2) to 7.85 (B1) mg/m^2 and they were well below the limit value of 150 mg/m^2. Concentrations of SO_4^{2-} *Eh* ions were in the range from 3240 (B2) to 18 020 (G2) mg/m^2, below the concentration limits of 25 000 mg/m^2. Zinc ions were not detected in M1 mixture, whereas the maximum concentration of 14.96 mg/m^2 was measured in B1 sample, also well below 200 mg/m^2 as limit. There are no limitations for leaching of Fe which concentrations reached 79.16 mg/m^2 (G2). Leaching of As and Pb will be discussed in more detail.

T a b l e 4

Cumulative metal leached in NEN 7375 test [mg/m^2]

Sample	Cr	Fe	Zn	As	Pb	SO_4^{2-}
M1	6.46	13.99	0.00	5.79	40.88	6350
M2	4.62	5.10	1.47	8.00	63.96	8650
C1	6.98	20.98	0.95	5.88	40.01	6140
C2	4.27	11.62	0.84	8.96	77.99	8690
B1	7.85	14.59	14.96	12.87	60.89	3470
B2	4.89	8.46	1.99	12.01	42.99	3240
G1	4.45	51.99	1.84	4.00	102.13	10 660
G2	3.59	79.16	2.86	13.78	115.89	18 020
Limit value [12]	150		200	27	100	25 000

Cumulative concentrations of As and Pb (mg/m^2) and measured pH values after each extraction period during 64 days were plotted together against time for all investigated systems (Figs. 2 and 3, respectively). During 64 days of the leaching test several regimes of lead leaching could be observed that were accompanied by changes in the pH value of leachates (Fig. 2). pH of the system influences leaching, fixation and speciation of metals in the stabilized/solidified matrix [22].
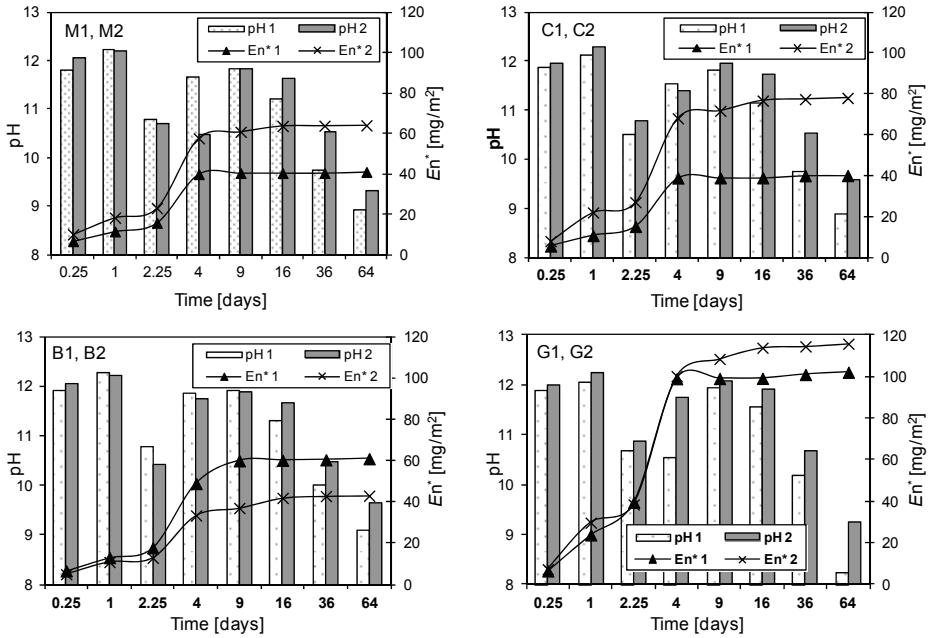
Fig. 2. Lead cumulative concentration and measured pH values during 64 days
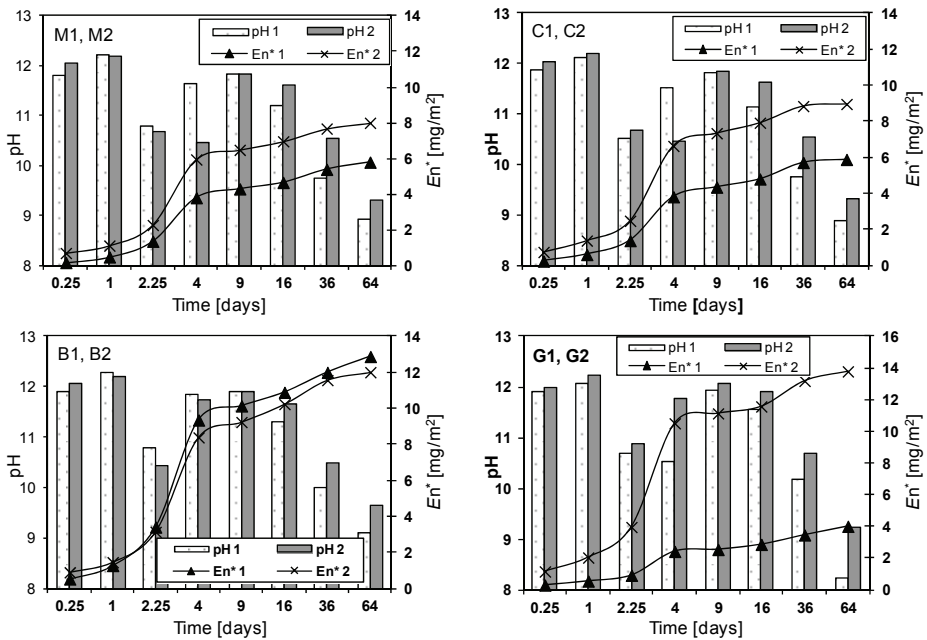of the leaching test for various systems

Fig. 3. Arsenic cumulative concentration and measured pH values during 64 days
of the leaching test for various systems

Lead is amphoteric in nature and its theoretical lowest solubility point occurs at pH 8.5. Leaching rate increases as the pH deviates from this pH. Decrease of pH value on the 2.25th day caused slight delay in Pb release. After that point, further pH increase up to the 4th day is followed by increased release of lead. Around 95% of leached lead has been released during the period of the first 4 days. Steady pH decrease after the 9th day is accompanied with almost constant amount of leached Pb.

Similar to lead, arsenic release is accelerated after the 2.25th day with the increase of pH value. Until the 4th day, around 70% of leached As has been released. During the next 60 days, there can be observed slow increase in As concentration with the decrease of pH value (Fig. 3).
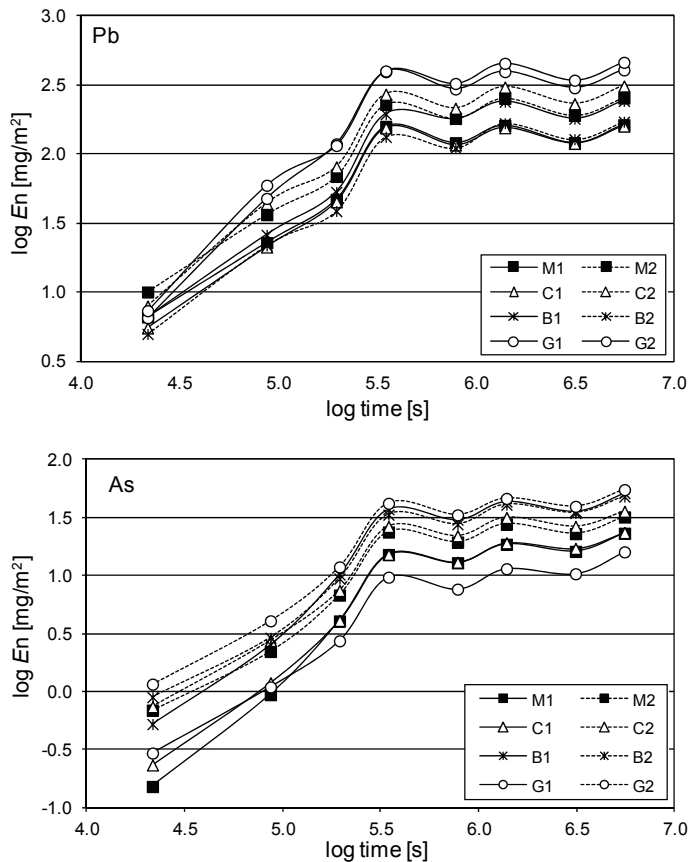

Fig. 4. Time dependence of derived cumulative leaching of Pb and As
for all investigated mixtures

The leaching of elements from the stabilized/solidified matrix is mostly diffusion controlled and a test like NEN 7375 characterizes detailed leaching mechanism and

rate of release under mass-controlled leaching scenario. For assessment of the leaching behaviour, the derived cumulative leaching ε_n of Pb and As for each individual mixture was calculated (Eq. (2)) [12]. The time dependences of derived cumulative leaching of Pb and As are presented in Fig. 4 as log–log plots.

According to NEN 7375 test the slope of linear regression of presented log–log plots indicates the predominant leaching mechanism. Following conditions are given for the different slope values [12]. The value less than 0.35 indicates surface wash or depletion of the component, the slope value between 0.35 and 0.65 indicates diffusion controlled release and the value greater than 0.65 indicates dissolution.

Leaching mechanisms of Pb and As were determined for all time intervals (increments) in a given order: 2–7, 5–8, 4–7, 3–6, 2–5 and 1–4. The eluate fraction for time increment 2–7 (from 24 h to 36 days) is considered as a "total increment" for the entire diffusion test. The first and the last fraction are not included in order to eliminate interpretative errors due to wash-off effects and possible depletion of a component during the test. Cumulative leaching ε_n^*, identified diffusion-controlled increment, calculated slope of linear regression of the derived cumulative 1–4 ε_n versus time (log–log plots) and standard deviation of slope for that increment as well as estimated 64 days release based on diffusion controlled interval (mg/m^2) [13] for Pb and As are presented in Table 5.

Table 5

Table 5. Cumulative measured release (ε_n^*) of lead and arsenic according to NEN 7375 test and estimated 64 day emission based on the diffusion controlled increment

Element	Mixture	ε_n^* [mg/m^2]	Diffusion controlled increment	Slope of logε_n–log$t$		Estimated 64 day release [mg/m^2]
				Value	Standard deviation	
Pb	M1	40.88	2–7	0.47	0.19	65.60
	M2	63.96	2–7	0.48	0.18	102.01
	C1	40.01	2–7	0.48	0.19	65.07
	C2	77.99	2–7	0.48	0.17	123.09
	B1	60.89	2–7	0.57	0.19	108.56
	B2	42.99	2–7	0.52	0.17	69.29
	G1	102.13	3–6	0.47	0.32	209.25
	G2	115.89	2–7	0.51	0.18	189.73
As	M1	5.79	3–6	0.63	0.33	12.36
	M2	8.00	2–7	0.63	0.21	14.37
	C1	5.88	3–6	0.64	0.33	12.81
	C2	8.96	2–7	0.62	0.20	16.08
	B1	12.87	3–6	0.59	0.33	27.21
	B2	12.01	3–6	0.61	0.32	25.64
	G1	4.00	2–7	0.62	0.18	5.84
	G2	13.78	2–7	0.61	0.21	23.81

The "total increment" (2–7) was identified as diffusion controlled increment of lead release for all systems, except for G1, indicating that Pb leaching from these matrices was most likely governed by diffusion. But, almost all Pb had been released during first 4 days of the test, which corresponded to 1–4 increment. The slopes of linear regression of the derived cumulative leaching ε_n calculated for 1–4 increment of all systems were greater than 0.65. If the slope is greater than 0.65 then there is a possibility of dissolution of the component although the test piece is not dissolving. In that case, according to NEN 7375 test, dissolution of the particular component has no permanent character and dissolution is only occurring from the outer layer of the test piece. For the rest of the test period (5–8 increment) calculated slope value was lower than 0.35. According to NEN 7375 test, if the slope is lower than 0.35, it can be explained by the fact that chemical conditions have changed, as a result of a different diffusion level, or that a mobile chemical form becomes depleted whilst a different leachable form of that component remains (more strongly) bonded in the matrix [12]. When there is an evidence of depletion, the calculated 64 days release based on diffusion controlled interval might provide an overestimate of the actual leaching. The upper limit of leaching in that case is the cumulative measured leaching over the test period [13].

Leaching mechanism of arsenic, identified by the slope of "total increment", was diffusion for M2, C2, G1 and G2 systems. In other systems the slope of the "total increment" was greater than 0.65 indicating dissolution of As. Similar to lead release, in first 4 days of the test period, leaching mechanism was most likely governed by dissolution of the component from the outer layer of the test piece, and in the second part of the test period (next 60 days, 5–8 increment), by depletion. The cumulative curves, (Fig. 3), indicate that the depletion of the available As is not complete by the end of the test, because no plateau was reached, and As release could continue after 64 days. Similar results were obtained by Coussy et al. [14].

Existence of different mobile chemical forms of Pb and As ions are confirmed in pH-*Eh* diagrams for metal (Pb, As)–Ca–S–H_2O systems according to concentration of ions in solutions of analyzed mixtures.

Figure 5 shows the *Eh*–pH diagram of Pb. Measured values of *Eh* and pH of all investigated mixtures are in the area of stable $3PbO \cdot PbSO_4$ form for pH between 8.8 and 11.6 and dissolved $Pb(OH)O^-$ ions for pH around 12. In G1 mixture, one measuring point (pH = 8.24) is in the area of dissolved $Pb(OH)^+$, which is consistent with the results of increased Pb leaching from this mixture. It can be seen that for high pH values, occurring during the first four days of the test period, Pb was in the form of dissolved ions. This is in good agreement with the dissolution mechanism determined based on the slope for 1–4 increment. Lower pH values, measured during the second period of the test (next 60 days), correspond to the area of stable $3PbO \cdot PbSO_4$ form,

which is consistent with the results of decreased Pb leaching and depletion of more mobile form.
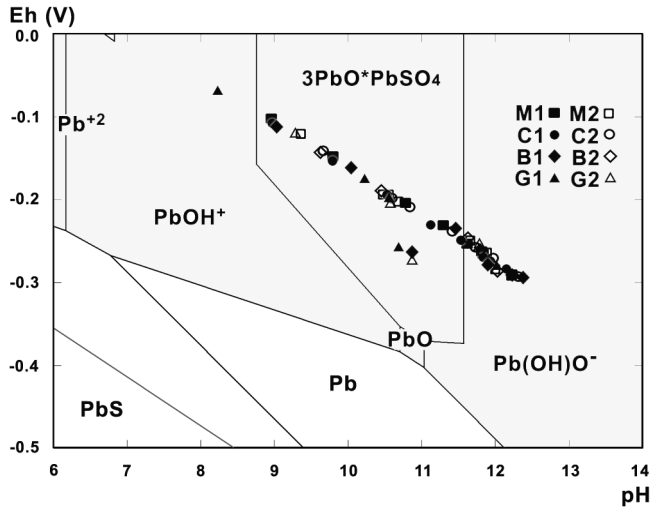

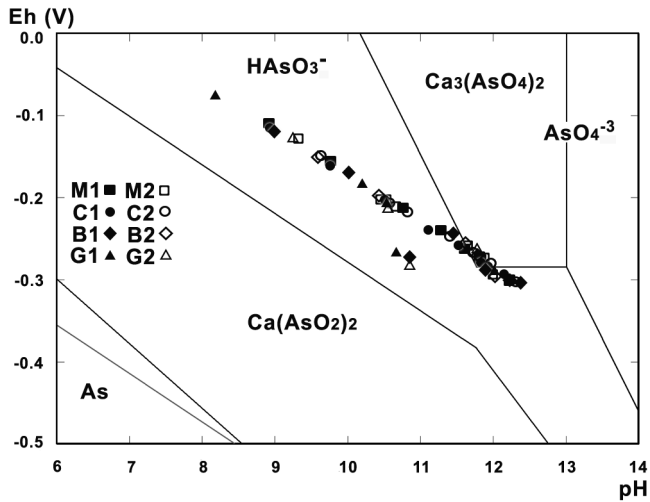Fig. 5. *Eh*–pH diagram of Pb for all analyzed systems

Fig. 6. *Eh*–pH diagram of As for all analyzed systems

Figure 6 shows *Eh*–pH diagram of As. For measured pH and *Eh* of analyzed systems, values around pH = 12 are in the area of stable $Ca_3(AsO_4)_2$ and the rest are in the area of dissolved $HAsO_3^-$ ions. Stable form will influence the fixation of arsenic, while mobile dissolved ions will result in increase of As leaching. It can be concluded

that during the first period of the test, leaching mechanism of As was probably controlled by the release of $HAsO_3^-$ ions and partially dissolved $Ca_3(AsO_4)_2$ from the surface, followed by diffusion and depletion of mobile $HAsO_3^-$ ions during the second period of the test. The cumulative curves, presented in Fig, 3, which have not reached a plateau, also indicate the existence of mobile form at the end of leaching period.

The effect of changes in pH values on the leaching rate of Pb and As is evident (Figs. 2 and 3). However, pH values of matrices with different compositions were very similar during 64 days of the leaching test, although the leaching of constituents differs. This indicates a significant effect of various additives on the leaching of metals from concrete matrices.

CaO and MgO as additives had very similar results in immobilization of Pb and As. The lowest concentration of leached Pb and low concentration of As were detected in systems with MgO and CaO as additives and 10% slag (M1 and C1).There are few papers dealing with the influence of MgO on S/S process of waste. It is assumed that its influence is mostly based on the control of pH in the range of minimal solubility of metals [23]. CaO is a constituent of cement which participates in hydration reaction during hardening of concrete and has positive influence on performances of solidified waste and stabilization of pollutants [21]. Its addition influences immobilization of As ions by precipitation of formed Ca-As salts [24] but could have reverse effect on Pb leaching due to the amphoteric nature of lead [25]. This was confirmed by increased leaching of Pb in system with CaO and 20% of slag. In systems with MgO, CaO and gypsum, release of Pb and As was higher with increased slag content (20%), which was expected. However, this was not the case in systems with Ba(OH)$_2$ as additive. In these samples, leaching of metals from B1 (10% of slag) were higher than from B2 (20% of slag). The reason for this could be the formation of BaSO$_4$ which was noted in the work done by Karatasios et al. [17] who investigated sulfate leaching from lime--based barium mortars, and also implied by the multiple reductions in SO_4^{2-} *Eh* ions leaching from these samples. New formed salt could increase densification of matrices and physical encapsulation of metal ions. The highest concentrations of leached Pb and As were in samples with gypsum as additive and 20% of slag. The reason for this could be poor bonding between cement and slag in the presence of gypsum which was confirmed elsewhere [9].

4. CONCLUSION

The paper presents an analysis of the leaching behaviour and mechanism of pollutants from sodium lead slag stabilized/solidified in concrete using cement as hydraulic binder and selected additives (magnesium oxide, calcium oxide, barium hydroxide

and gypsum). High pollution potential of the slag was confirmed by the EN 12457-2 leaching test due to release of Pb and As above specified limits for those elements.

During 64 days of the NEN 7375 leaching test there can be observed several regimes of lead and arsenic leaching that are accompanied by changes in pH values of leachates. According to NEN 7375 test, leaching of Pb and As for the first 4 days could be governed by dissolution of the component from the outer layer of the test piece followed by depletion of dissolved chemical form during the next 60 days of the test, whilst a different leachable form of that component remains (more strongly) bonded in the matrix. Existence of different mobile chemical form of Pb and As ions was confirmed in pH–Eh diagrams for the metal (Pb, As)–Ca–S–H_2O systems. At high pH values, during the first four days, Pb was probably in the form of dissolved ions. Lower pH values, measured during the next 60 days of the test period, corresponded to a stable $3PbO \times PbSO_4$ form, which is consistent with the results of decreased Pb leaching. Throughout the test period, As was probably in the form of dissolved $HAsO_3^-$ ions which depletion could be likely continued after the completion of the test.

Systems with 10% of slag and CaO and MgO as additives gave similar leaching results, while in systems with 20% of slag, the sample with CaO showed more significant lead release. With increased slag content, release of elements also increased, except from samples with $Ba(OH)_2$ as an additive, probably due to formation of $BaSO_4$. G1 and G2 samples did not meet leaching limitation as a result of poor bonding between cement and slag in the presence of gypsum as additive. Although the results of the leaching test indicate the same leaching mechanism of lead and arsenic from samples with different composition, proper selection of additives may reduce leaching of Pb and As below the specified limits. Best results in stabilization of Pb and As were obtained when using CaO as an additive and 10% of slag (C1 sample).

REFERENCES

[1] PAWLOWSKI L., *Effect of mercury and lead on the total environment*, Environ. Prot. Eng., 2011, 37 (1), 105.
[2] AGRAWAL A., SAHU K.K., PANDEY B.D., *Recent Trends and Current Practices for Secondary Processing of Zinc and Lead. Part I: Lead Recovery from Secondary Sources*, Waste Manage. Res., 2004, 22 (4), 240.
[3] LEWIS A.E., BEAUTEMENT C., *Prioritising objectives for waste reprocessing: a case study in secondary lead refining*, Waste Manage., 2002, 22 (6), 677.
[4] KAMBEROVIĆ Ž., RADOVIĆ N., KORAĆ M., JOVANOVIĆ M., *The strategy for cleaner production in the Metallurgy of Republic of Serbia*, Proc. 2nd Symposium Recycling Technologies and Sustainable Development Sokobanja, Technical Faculty in Bor, Bor, 2007, 284.
[5] *European Waste Catalogue (EWC)*, Commission Decision, 2000/532/EC.

[6] LASSIN A., PIANTONE P., BURNOL A., BODENAN F., CHATEAU L., LEROUGE C., CROUZET C., GUYONNET D., BAILLY L., *Reactivity of waste generated during lead recycling: An integrated study*, J. Hazard. Mater., 2007, 139 (3), 430.

[7] HILLS C.D., POLLARD S.J.T., *The influence of interference effects on the mechanical, microstructural and fixation characteristics of cement-solidified hazardous waste forms*, J. Hazard. Mater., 1997, 52 (2–3), 171.

[8] SHI C., *Hydraulic cement systems for stabilization/solidification*, [in:] *Stabilization/Solidification of hazardous, radioactive and mixed wastes*, R. Spence, C. Shi (Eds.), CRC Press, 2004, 49.

[9] KNEŽEVIĆ M., KORAĆ M., KAMBEROVIĆ Ž., RISTIĆ M., *Possibility of secondary lead slag stabilization in concrete with presence of selected additives*, Metallurgiya – J. Metallurgy, 2010, 16 (3), 195.

[10] DUTRÉ V., VANDECASTEELE C., *An evaluation of the solidification/stabilisation of industrial arsenic containing waste using extraction and semi-dynamic leach tests*, Waste Manage., 1996, 16 (7), 625.

[11] VAN DER SLOOT H.A., COMANS R.N.J., HJELMAR O., *Similarities in the leaching behaviour of trace contaminants from waste, stabilized waste, construction materials and soils*, Sci. Total Environ., 1996, 178 (1–3), 111.

[12] EA NEN 7375, *Leaching characteristics of moulded or monolithic building and waste materials; Determination of leaching of inorganic components with the diffusion test*, 2004.

[13] LAMPRIS C., STEGEMANN J.A., CHEESEMAN C.R., *Chloride leaching from air pollution control residues solidified using ground granulated blast furnace slag*, Chemosphere, 2008, 73 (9), 1544.

[14] COUSSY S., BENZAAZOUA M., BLANC D., MOSZKOWICZ P., BUSSIÈRE B., *Assessment of arsenic immobilization in synthetically prepared cemented paste backfill specimens*, J. Environ. Manage., 2012, 93 (1), 10.

[15] STARK J., *Recent advances in the field of cement hydration and microstructure analysis*, Cement. Concrete. Res., 2011, 41 (7), 666.

[16] BATCHELOR B., *Overview of waste stabilization with cement*, Waste Manage., 2006, 26 (7), 689.

[17] KARATASIOS I., KILIKOGLOU V., THEOULAKIS P., COLSTON B., WATT D., *Sulphate resistance of lime-based barium mortars*, Cement. Concrete. Comp., 2008, 30 (9), 815.

[18] CRANNEL B.S., EIGHMY T., KRZANOWSKI J.E., EUSDEM J.D., SHAW E.L., FRANCIS C.A., *Heavy metal stabilization in municipal solid waste combustion bottom ash using soluble phosphate*, Waste Manage., 2000, 20 (2–3), 135.

[19] ĐOKIĆ J., KAMBEROVIĆ Ž., KORAĆ M., Characterization of the slag in waste lead acid battery recycling, Proc. II International Symposium Environmental Protection in Industrial Areas, University in Pristina, Faculty of Technical Science, Kosovska Mitrovica, 2009, 449.

[20] EN 12457-2, *Compliance test for leaching of granular waste materials and sludges*, 2002.

[21] MALVIYA R., CHAUDHARY R., *Leaching behaviour and immobilization of heavy metals in solidified/stabilized products*, J. Hazard. Mater., 2006, 137 (1), 207.

[22] HEASMAN L., VAN DER SLOOT H.A., QUEVAUILLER P., *Harmonization of leaching/extraction Tests. Studies in Environmental Science*, Vol. 70, Elsevier, Amsterdam, 1997.

[23] CUBUKCUOGLU B., OUKI S.K., *Solidification/stabilisation of electric arc furnace waste using low grade MgO*, Chemosphere, 2012, 86 (8), 789.

[24] VANDECASTEELE C., DUTRE V., GEYSEN D., WAUTERS G., *Solidification/stabilisation of arsenic bearing fly ash from the metallurgical industry. Immobilisation mechanism of arsenic*, Waste Manage., 2002, 22 (2), 143.

[25] KOGBARA R.B., AL-TABBAA A., *Mechanical and leaching behaviour of slag-cement and lime-activated slag stabilised/solidified contaminated soil*, Sci. Total. Environ., 2011, 409 (11), 2325.