



## Evaluation leaching of Fine-Grained converter Sludges stabilized by Portland slag Cement

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### Abstract

Main goal of the study was to describe properties of sludge stabilized by Portland slag cement. Prepared products of stabilized/solidified waste with three different contents 12 wt. %, 20 wt. % and 30 wt. %, respectively, of Portland slag cement were evaluated in accordance with valid waste legislation, mobility of monitored elements and from the aspect of development of mechanical strength after 2, 7 and 28 days of hydration. Leaching tests including procedures of sequential extraction and X-ray diffraction were the main techniques and evaluation methods used in the research. Obtained results of sequential extraction providing information about mobility potential and bioavailability of studied metals revealed that the Zn content of untreated sample in the most accessible ionto-exchange and carbonate fraction reached 8 x higher concentration than the appropriate concentration limit for hazardous waste. Results of determined compressive strengths of the S/S products indicated increasing of compressive strength with time and amount of added Portland slag cement. After 28 days of hydration the products contained phase of gismondine, independently on a quantity of the added binder. Immobilization of metals monitored by procedure used occurred already within two days in the process of solidification of the wastes and binder mixture and it was even more distinct with higher amount of added binder.

**Keywords:** Sludge, sequential extraction, stabilization, leaching, cement.

### Introduction

Traditionally, agglomeration process to recycle a secondary products generated in integrated metallurgical plant was used. Recycling of such materials, especially with content of Zn, alkali (sodium and potassium) and hydrocarbons is possible merely on the assumption of keeping the concentration limit of introduced harmful substances in accordance with operation requirements of individual production aggregates<sup>1</sup>. During the steel making process, approximately 15 - 16 kg of sludge is generated per ton of steel produced while applying scrubbing of furnace gas. Composition of these sludges strongly depends on charge composition and type of steel being produced. Majority of such wastes represent interesting source of Fe and C, but also a source of potentially hazardous metals as Zn, Pb, Cd and As on the other hand<sup>2</sup>. The most considerably represented Zn occurs in wastes as ZnO (spartalite) and ZnO.Fe<sub>2</sub>O<sub>3</sub> (franklinite) which is stable and insoluble in most acid and alkaline solvents<sup>3,4</sup>. According to present legislation of the Czech Republic (CR) and European Union (EU)<sup>5</sup> the converter sludges are classified as a hazardous waste. Such wastes are possible to deposit on a landfill only after application of some of the physico-chemical methods of the waste treatment. Implementation of the waste disposal European directive in 2009 leads to the effort to achieve appropriate treatment of given waste, reduction of volume as well as dangerous properties.

The most widespread technology of the waste treatment prior to final landfill deposit is stabilization/solidification (S/S). This technology features mixing of wastes with binding material (additive) reaching reduction of contaminants elutriation, their conversion into stable forms and encapsulation in monolithic part of high structural integrity. For application of the S/S technology for industrial wastes the Portland cement<sup>6</sup>, fly-ashes from incineration plants<sup>7</sup> or combination of Portland cement and lime<sup>8</sup> are used as a binders. The S/S process was applied for various kinds of industrial wastes containing heavy metals such as galvanic sludges<sup>9</sup>, dusts from electric arc furnace<sup>10</sup>, foundry sludges<sup>11</sup>.

Evaluation of wastes from the dangerousness toward environment point of view is based on leaching tests and determination of selected harmful substances in dry matter. Waste products treated by S/S method are evaluated only on the basis of leaching test before deposition on a landfill<sup>12</sup>. Such procedure enables to determine solely the total content of monitored metals which can be released when in contact with water, thus does not enable to obtain sufficient information leading to the assessment of potential bioavailability of heavy metals in various environmental conditions.

In an effort to describe in detail a distribution of metal forms and determine their potential bioavailability and mobility in the environment a series of methods of sequential extraction with a

view to simulate potential changes of environmental conditions which can affect the bioavailability of heavy metals was developed. The fundamental and widely used process of sequential extraction was proposed by Tessier<sup>13</sup> and with using of different extracting agents subsequently applied provides to determine distribution of observed heavy metals from the aspect of their presence in five distinguishable forms: ionto-exchange fraction where the heavy metals are present as exchangeable ions, carbonate fraction where the heavy metals are bonded to carbonates, reducible fraction where the heavy metals are bonded to ferrum and manganese oxides, oxidable fraction where the heavy metals are bonded to organic matter and sulphides, residual fraction where the heavy metals are bonded in silicate matrix. Technique of Tessier was modified as well by several authors<sup>14-16</sup> aiming to closer specify the portion of heavy metals bonded to iron and manganese oxides. In the work of Leinz<sup>17</sup> a modified procedure of Tessier's sequential extraction of purpose to determinate the individual forms of heavy metals in wastes from ground mining was applied. Compared with the Tessier's technique, the ionto-exchange fraction was further divided into soluble and sorbed fraction and also heavy metals bonded to chromium oxides (VI) were determined in the mentioned research. Method according to Leinz was used in work<sup>18</sup> onto dusts from electric arc furnace for description of mobility and bioavailability of Cr, Pb, Zn and Ni.

The goal of the work was to evaluate present legislation of EU with regard to the waste leach, products of stabilization/solidification process of fine-grained metallurgical metallic sludges, simultaneously, with using of sequential extraction, to describe the measure of fixation of monitored heavy metals Zn, Cd, Pb in stabilized metallurgical wastes with possibility to predict their potential mobility and bioavailability in the environment. Furthermore, the strength as prerequisite for the feasibility of recycling of fine-grained sludges and thus use min. 60 wt. % of Fe was studied at stabilization products.

## Material and Methods

**Samples:** Fine-grained converter sludge was collected after its filtration on filter press in metallurgical plant in the Czech Republic. Production of such wastes in this plant is 50 000 tons per year. After the sampling completion the converter sludge with total weight of 5 kg was dried at laboratory temperature and homogenized by quartation to an average sample. For the purpose of waste solidification and stabilization commercially obtainable Portland slag cement CEM II/B-S 32,5 R containing 6 up to 20 wt. % of granulated blast-furnace slag was selected as a binder.

**Determination of chemical composition of solid phase of converter sludge and Portland slag cement:** Analysis of solid phase of the fine-grained converter sludge after total decomposition of samples was performed by means of atomic absorption spectrometer with flame atomization (F-AAS) on the

equipment Avanta (GBS Scientific Equipment Ltd.). The content of metallic iron was determined by titration after the sample dissolution into solution of FeCl<sub>3</sub> in carbon dioxide environment. Determination of concentration of iron in oxidation degree II was performed by titration in CO<sub>2</sub> atmosphere after the sample decomposition in acids mixture (HCl, HF). Iron concentration in oxidation degree III from the balance of iron forms and total content was calculated. Total concentration of carbon was determinate by instrument LC-144 (LECO Corporation). Silicium from the charge of converter sludge was determinate gravimetrically. The sample dissolved in mixture of acids (HCl, HNO<sub>3</sub>) subsequently by evaporation of solution with perchloric acid the silicic acid was separated followed by annealing and weighting of silicon dioxide. Oxides of major components of Portland slag cement specimen after melting with sodium peroxide and treating by acids mixture (HNO<sub>3</sub>, HCl) were determined photometrically and by complexometric methods. Alkali were converted into solution by the help of HCl and determined by F-AAS method. Concentration of sulphates was determined gravimetrically and expressed as SO<sub>3</sub>.

### Determination of leaching of waste converter sludge:

Treatment of the samples and preparation of aqueous leach was performed according to legislation of the CR and EU in force. To the quantity of the original sample corresponding to 100 g of sample dry residue 1000 ml of distilled water was added. After 24 hours of agitation ensuring the rotation of sample tubes head-heel at rotational speed of 10 rpm the leach was separated from solid phase by filtration with the aid of membrane filter (Millipore Nylon) with pore size of 0,45 µm. Thus prepared leachates were analysed by recommended methods for water analysis according to regulation 294/2005 Sb. Concentration of fluorides, chlorides and sulphates by means of ionic chromatograph with conduction detector Waters 431 (Waters Corporation) was determined. Phenolic index after the distillation with 4-aminoantipyrine was determined spectrophotometrically using UV/VIS spectrometer LAMBDA 11 (Perkin Elmer). The atomic absorption spectrometer AMA 254 (LECO Corporation) applying technique of generation of metallic mercury vapours with subsequent capture and enrichment on gold amalgam was used for determination of concentration of mercury in aqueous leach. Ba, Cr, Cu and Zn determination was done by the help of atomic emission spectrometer with inductance-coupled plasma Spectro Vision EOP (AES-ICP) from the SPECTRO Analytical Instruments GmbH. Furthermore, Cd, Ni, Pb was determined by the equipment Avanta (F-AAS). Method AAS with electrothermal atomization by instrument UNICAM 989 QZ (Analytik Jena AG) was used for determination of As, Mo, Se, Sb concentration. Determination of dissolved organic carbon (DOC) was performed on the analyzer MULTI N/C 3100 (Analytik Jena AG).

### Mineralogical, microscopical and granulometric analysis:

Mineralogical analysis was performed by the method of X-ray

pulverized diffraction analysis on apparatus Bruker D8 Advance type (theta/2theta) equipped by positional sensitive detector VANTEC from the Bruker corporation company. As a source of X-ray radiation cobaltic lamp ( $\lambda = 1,78897 \text{ \AA}$ ) heated at conditions of  $U = 35 \text{ kV}$ ,  $I = 25 \text{ mA}$  was used. Divergence of primary beam was limited by 2 mm crevice. During the analysis the sample was rotated in order to eliminate the effect of preferential orientation of phase's crystals. Identification of present phases was done with using of PDF-2 (release 2004) database. Microscopical analysis of converter sludge and Portland cement was performed by scanning electron microscopy (SEM) on device QUANTA FEG 450 from the FEI Company. Pictures were obtained with usage of backscattered-electrons at accelerating potential of 15 kV. Particles size of converter sludge sample was measured by instrument Partica LA950 of Horiba Scientific company which provides very wide range of measurement (from 0,01  $\mu\text{m}$  to 3000  $\mu\text{m}$ ).

**Evaluation of pollutants mobility in sample of converter sludge:** Sequential extraction being the scale of mobility of heavy metals in studied waste was performed on non-treated sample of converter sludge in ratio of solid and liquid phase 1:10. Such sequential extraction procedure includes seven steps in total listed in table-1. The individual steps of sequential extraction and thus forms in which the selected heavy metals were analysed, are marked as S1 – S7. Extraction solutions were treated to required pH by using of  $\text{CH}_3\text{COOH}$ . After each step of sequential extraction performed the solid phase was separated by vacuum filtration with membrane filter with mean pore's size of 0,45  $\mu\text{m}$ . The solid phase was dried and used in following step of sequential extraction, thus seven extracts samples in total (S1-S7) were obtained. At retrieved extracts the determination of Zn by AAS-ICP method and Cd, Pb by F-AAS method was done.

**Procedure of stabilization of converter sludge, evaluation of strength of stabilization product and mobility of Zn, Cd, Pb in S/S sludges:** In the first phase, three mixtures of converter sludge and cement (with content of cement 12 wt. %, 20 wt. % and 30 wt. %) were prepared. Afterwards, mixing water in the amount corresponding to 50 wt. % of Portland slag cement's sample was added to the each mixture. Such prepared pastes were placed into cylindrical forms with inner diameter of 42 mm and high of 54 mm. Formed mixtures were stored in moisture for 24 hours then removed from the forms and leaved freely in laboratory conditions (20 °C temperature and 60 wt. % of relative air humidity). In appropriate time intervals after 2, 7 and 28 days of the storage, respectively, the compressive strength tests of cylindrical samples were performed by Tira Test 2300 (TIRA GmbH) testing machine. Specimens after determination of the compressive strength were further treated by grinding and quartation for subsequent evaluation of chemical specialization described above. Steps S1, S2 and S3 by stabilized samples were used. These fractions were selected by reason of identification of their most significant potential bioavailability and mobility in the environment with regard to other fractions<sup>19,20</sup>. In retrieved solutions after mentioned sequential extractions Zn, Cd and Pb elements were determined

with usage of F-AAS.

## Results and Discussion

**Characterization of fine-grained converter sludge:** Table-2 represents chemical composition of the fine-grained converter sludge determined by AAS method. Major share of determined forms of iron in fine-grained converter sludge sample confirms its potential of using in iron and steel production. On the other hand, the presence of zinc and other nonferrous metals (Pb, Cd) including alkali make such using impossible though. In compliance with evaluation of wastes leaching according to valid European legislation the monitored parameters values did not exceed given maximum permissible concentrations (table-3) above which it is necessary to consider the waste as hazardous. Thus assessed waste does not require before landfill deposition the physico-chemical treatment (solidification / stabilization) according to legislation<sup>20</sup> from the aspect of prevention of pollutants relieving into the environment. Chemical analysis of Portland slag cement is shown in table-4. The results enable to classify the Portland slag cement CEM II/B-S 32,5 R as low-alkali ASTM type of cement<sup>21</sup>.

**Table-1**  
**Scheme of sequential extraction**

Fraction	Step	Phases	Operational condition
Exchangeable fraction	(S1)	Soluble	25 g of sample and silica gel was extracted in 250 ml of water
	(S2)	Sorbed species	250 ml 1 M $\text{CH}_3\text{COONa}$ at rotation of container with rotational speed of 10 rpm at ambient temperature
Acido-soluble fraction	(S3)	Hydroxides and carbonates	at rotation of container for a period of 2 h with 250 ml 1 M $\text{CH}_3\text{COONa}$ , pH 5
Reducible fraction	(S4)	$\text{Fe-MnO}_{x\text{am}}$	250 ml 0,25 M $\text{NH}_2\text{OH.HCl}$ in 0,25 M HCl for a period of 30 min. on water bath at temperature of 50 °C
	(S5)	$\text{FeO}_{x\text{cryst}}$	250 ml 4 M HCl for a period of 30 min. on water bath at temperature of 94 °C
Oxidable fraction	(S6)	Sulphide	20 g of sodium chlorate and 100 ml conc. HCl, after a period of 45 min. Residue was extracting for a period of 40 min. with 25 ml 4 M $\text{HNO}_3$ on water bath at boiling temperature. Thus prepared extracts were analysed individually and received results were summed.
Residual fraction	(S7)	Silicate	150 ml conc. $\text{HNO}_3$ at 200 °C, added 70 ml HCl and 70 ml HF at 200 °C

**Table-2**  
**Chemical composition of converter sludge**

Analysis	Concentration [Wt. %]
moisture	21,5
C	2,48
Fe <sub>c</sub>	60,0
Fe <sub>k</sub>	8,71
FeO	50,9
Fe <sub>2</sub> O <sub>3</sub>	16,9
Zn	1,6
Cd	0,003
Cr	0,06
Pb	0,21
Si	1,70
Ca	3,61
Mg	0,83
Mn	0,75
Al	0,10
Cu	0,02
K	0,1
Na	0,05

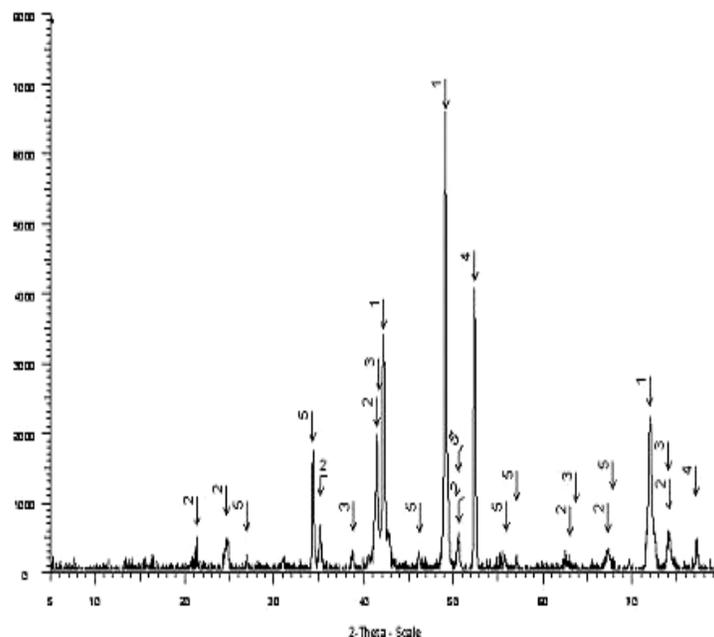
**Table-3**  
**pH and concentration of monitored parameters in aqueous leach of converter sludge**

Monitored parameter	Concentration [mg.l <sup>-1</sup> ]
pH	10,6
RL	288
Chlorides	70
Fluorides	6,20
Sulphates	78
Phenolic index	<0,05
DOC	1,87
As	<0,01
Ba	<0,02
Cd	<0,005
Cr total	<0,03
Cu	<0,03
Hg	<0,001
Ni	<0,02
Pb	<0,05
Se	<0,01
Sb	<0,01
Zn	0,088
Mo	0,019

**Table-4**  
**Chemical composition of cement**

Element	Concentration (Wt. %)
Moisture	0,7
CaO	46,2
Al <sub>2</sub> O <sub>3</sub>	3,63
Fe <sub>2</sub> O <sub>3</sub>	2,42
MgO	1,13
K <sub>2</sub> O	0,64
Na <sub>2</sub> O	0,24
SO <sub>3</sub>	2,54
SiO <sub>2</sub>	19,80

Mineralogical composition of the fine-grained converter sludge determined by XRD method (figure-1.) indicates onto presence of iron phases such as FeO (wustite), Fe<sub>2</sub>O<sub>3</sub> (hematite), α-Fe<sub>2</sub>O<sub>3</sub> (α-hematite), calcite (CaCO<sub>3</sub>) and metallic iron. X-ray diffraction analysis of used cement revealed the presence of tricalcium silicate (Ca<sub>3</sub>SiO<sub>5</sub>), tricalcium aluminate (Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>), calcium aluminium silicate Ca(Al<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>) and gypsum (CaSO<sub>4</sub>)·2H<sub>2</sub>O as solidification regulator (figure-2.) Intensities of all three crystalline phases were rather low (for instance, by comparison with intensities of diffraction lines at phases present in the sludge as seen in figure-1.) which corresponds to dilution of minerals by glassy phase present from granulated blast-furnace slag.



**Figure-1**  
**X-ray diffraction of fine-grained metallic sludge (1 - FeO, 2 - Fe<sub>2</sub>O<sub>3</sub>, 3 - alfa-Fe<sub>2</sub>O<sub>3</sub>, 4 - Fe, 5 - CaCO<sub>3</sub>)**

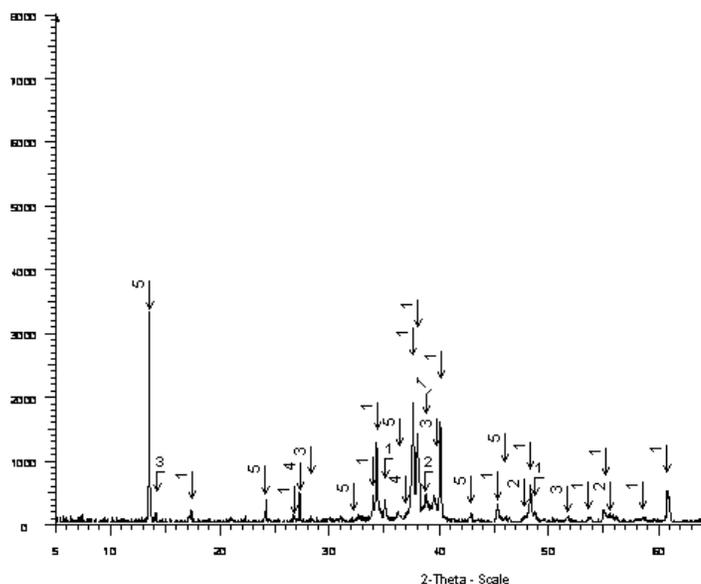


Figure-2

X-ray diffraction of Portland slag cement (1 -  $\text{Ca}_3\text{SiO}_5$ , 2 -  $\text{Ca}_3\text{Al}_2\text{O}_6$ , 3 -  $\text{Ca}_2\text{AlFeO}_5$ , 4 -  $\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8)$ , 5 -  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ )

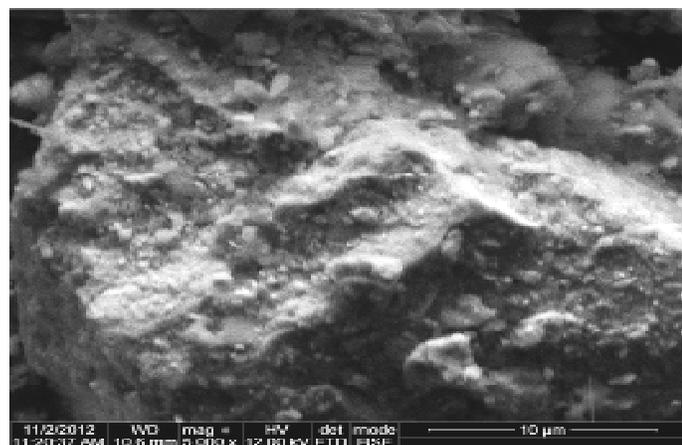
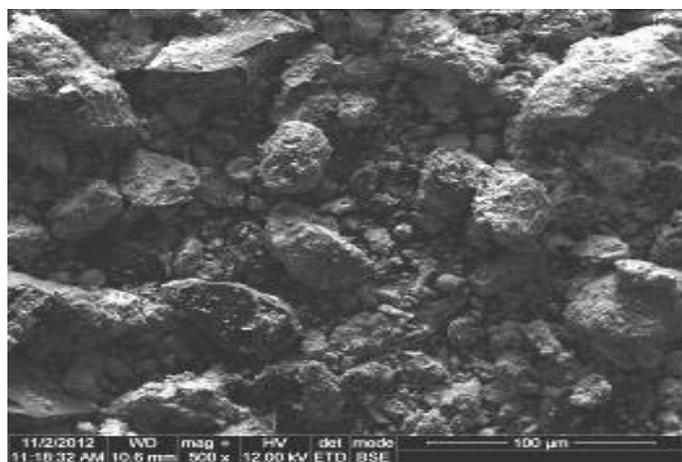


Figure-3

Pictures of converter sludge (magnification 500x, 5000x)

Figure 3 presents micrographs of converter sludge (BOF sludge) obtained by SEM at 500x and 5000x magnification. Granularity appearance of given material was heterogeneous with representation of the particles wide distribution where at magnification of 5000x was visible that smaller particles were fixed on the surface of bigger particles hence creating agglomerates. Distribution function of particles size of sludge (figure- 4.) shows to the most represented fraction from 0,25 to 6,72  $\mu\text{m}$ . It was observed from cumulative distribution function that 92 % of sludge had particle size less than 120  $\mu\text{m}$ .

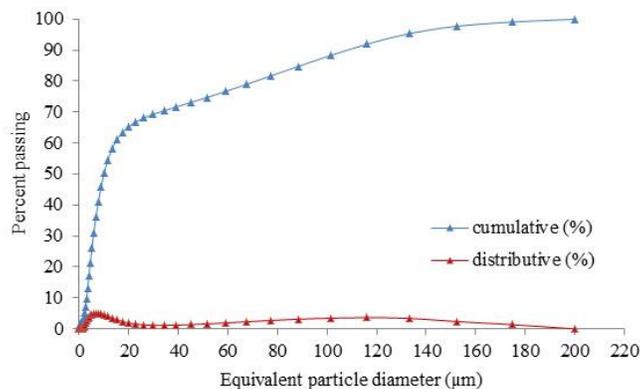


Figure-4

Particle size distribution of BOF sludge

**Sequential extraction:** Contents of Zn, Cd and Pb analyzed in the individual extracts obtained by sequential leaching are shown in table 5. Beside of elements contents in the particular extracts expressed in mg/l the percentages of extracted element in given fraction to the total element content in the sample are introduced. Results in table-5 show that all monitored elements are predominantly fixed to crystalline iron oxides (S5). Pb was extracted predominantly between steps (S4) till (S7) and compared to Zn (88,0 %) and Cd (88,4 %) was fixed on stable phases (98,3 %).

**Ionto-exchange and carbonate fraction (S1, S2 and S3):** Soluble or sorbed specialties (S1 a S2) were determined only by Zn (0,1 % in total, see table 5). Elements bonded to carbonates and hydroxides (S3) are considered to be easily releasable into the environment at mild acid conditions. For these reasons the ionto-exchange (S1, S2) and carbonate (S3) fractions represent most significant risk of bioavailability and potential mobility of elements fixed in wastes which are landfill deposited. Determined content of Zn bonded to hydroxides and carbonates reached value of 164 mg/l (11,9 % - Table 5.) which is more than 8x higher than the maximum permissible concentration defined for hazardous waste (20 mg/l). Determined contents of Cd (0,29 mg/l; 12,8 %) and Pb (4,9 mg/l; 2,7 %) as seen in Table 5 did not exceed regulation defined limit concentrations for hazardous wastes (Cd 0,5 mg/l; Pb 5 mg/l – Table 5) 20.

**Reducible fraction (S4 a S5):** Heavy metals fixed onto amorphous oxides of iron and manganese, silicious particles, crystalline oxides of iron, can be extracted in case of the waste exposition under reduction conditions. By application of reducing agent  $\text{NH}_2\text{OHHCl}$  ( $E = -1,87 \text{ V}$ ) especially Cd (0,31 mg/l; 15,2 % - see table 5) bonded onto amorphous  $\text{Fe-MnO}_x$  were extracted. It was proved by application of step S5 of sequential extraction that the observed metals of Zn (850 mg/l; 61,56 % - table 5), Cd (1,2 mg/l; 58,82 % - Table 5), Pb (128,75 mg/l; 73,29 % - table-5) were most considerably fixed just onto crystalline oxides of iron.

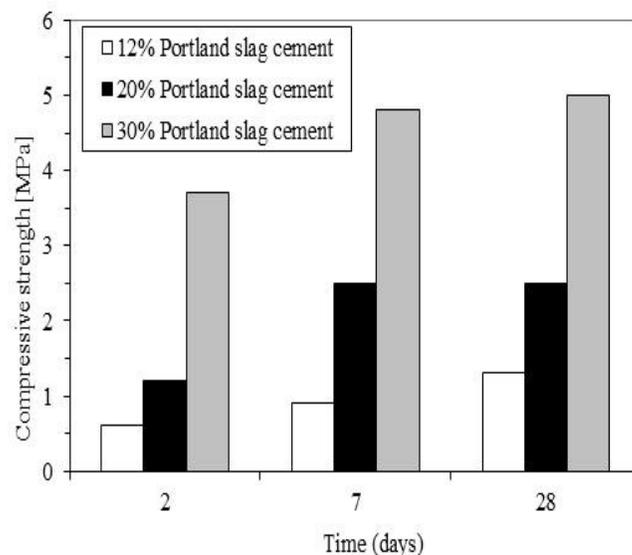
**Oxidable fraction (S6):** Fraction denotes the amount of heavy metals fixed onto organic material and sulphides which could be released into the environment in the case of oxidative conditions. After the step (S6) as mentioned in table 1 second most considerable representation of monitored heavy metals was determined: Zn (280 mg/l; 20,28 %), Cd (0,27 mg/l; 13,24 %) and Pb (25,81 mg/l; 19,40 %) - Table 5.

**Residual fraction (S7):** Metals contained in this fraction were bonded in crystalline structure of minerals and, thus represented fraction which was hardly extractable. The greatest representation of observed heavy metals in this fraction had Pb (0,2 mg/l; 4,05 %) in comparison with Zn (3,5 mg/l; 2,53 %) and Cd (<0,02 mg/l; 1,11 %) - table 5.

**Table-5**  
**Concentration of monitored metals after individual extraction steps**

Element	Step	Concentration [mg/l]	Concentration [%]
Zn	S1	0,37	0,03
	S2	0,83	0,06
	S3	164	11,88
	S4	50,65	3,67
	S5	850	61,56
	S6	280	20,28
	S7	3,5	2,53
Cd	S1	<0,02	<0,00
	S2	<0,02	<0,00
	S3	0,29	12,75
	S4	0,31	15,20
	S5	1,2	58,82
	S6	0,27	13,24
	S7	<0,02	1,11
Pb	S1	<0,1	<0,1
	S2	<0,1	<0,00
	S3	4,9	1,74
	S4	19,3	1,51
	S5	128,75	73,29
	S6	25,81	19,40
	S7	0,2	4,05

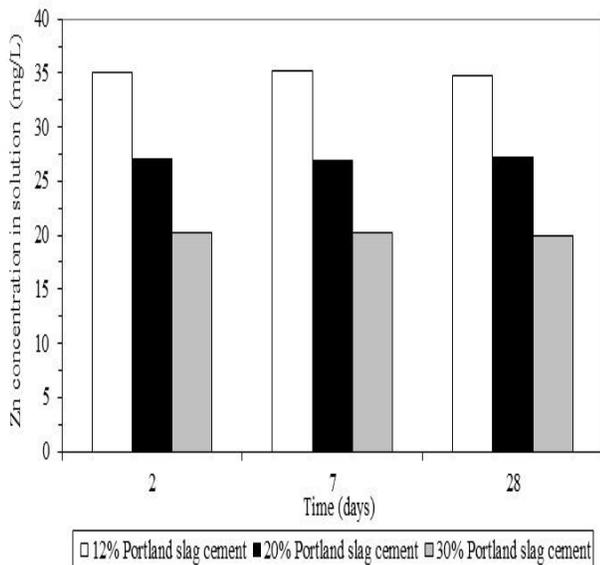
**Evaluation of S/S process with usage of Portland slag cement:** From figure-5 is marked obvious a positive influence of the cement content and sample maturing time period on compressive strength of test-pieces used.



**Figure-5**  
**Development of compressive strength of S/S products**

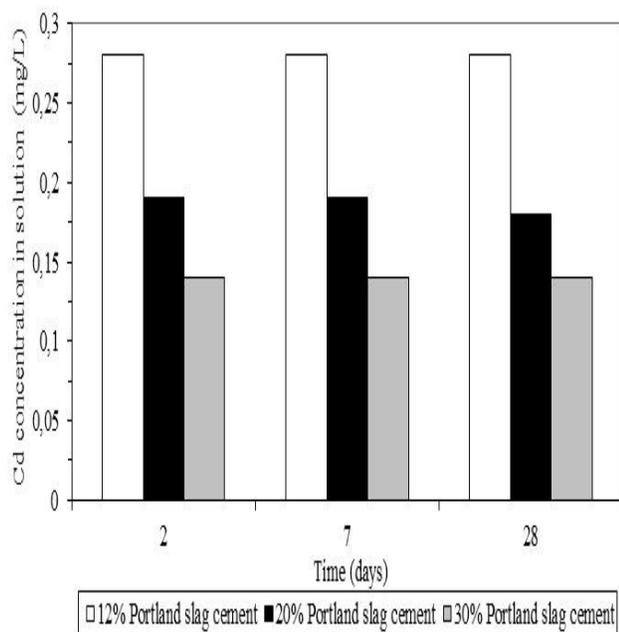
Increasing of the compression strength with the cement content relates to creation of higher amount of the main product of aqueous reaction CEM II/B-S which is C-S-H gel. Such amorphous phase represents the main binding phase formed during binders' hydration with content of Portland cement. C-S-H gel can be mostly proved only with difficulty by X-ray diffraction analysis<sup>22</sup>. Increasing of the strength by given content of cement with the time period (figure-5) was supposedly related to gradual hydration of tricalcium silicate due to which C-S-H gel grew as a hydration product and the strength contributor. X-ray diffraction analysis detected a fade away of diffraction lines of phases present in the cement used at the beginning of maturing process of the test-pieces (figure 6 a up to c). Furthermore, such method proved that during the hydration process there were not any changes of majority phases brought into the mixture by waste sample. After 28 day of maturing process a diffraction lines of gismondine phase which belongs to the group of zeolites appeared on X-ray diffraction records of all the studied samples.

Contents of Zn, Cd and Pb in extracts prepared from the samples of stabilized converter sludge are graphically compared for particular time periods of hydration in figure 6 – 8. The graphs show summation of concentrations obtained in the first three steps of used sequential extraction according to Leinz<sup>23</sup>.



**Figure -6**

**Zn concentration in leachate S1-S3 prepared from S/S products**

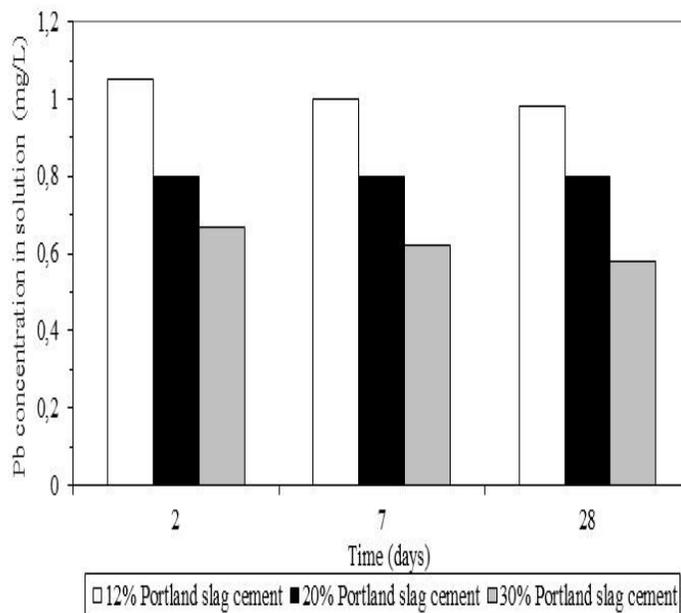


**Figure-7**

**Cd leaching from S/S products**

It can be claimed, from the comparison of contents of metals analyzed in solidified waste extracts after performing of the step S1- S3 of the extraction procedure (figures 7 – 9) that amount of monitored metals contained in the extracts decreased with amount of cement used. Higher amount of the cement led to higher quantity of C-S-H gel, therefore it can be assumed that the main cause of immobilization of observed heavy metals was bounding of these metals in the structure of C-S-H gel created

already in the incipient period of hydration (hence after 2 days). Thereupon is evident that the ability of metals immobilization by given mixture did not increase with the time period of hydration and obviously effective immobilization of such metals occurred already at the beginning of maturing process of prepared samples. By comparison of determined contents of Zn (11,97 %), Cd (12,75 %) and Pb (1,74 %) in sum of steps S1-S3 of sequential extraction of original sample and the products of S/S process (see Table 6) can be stated that already after two days the content reduction of observed heavy metals in ionto-exchange and carbonate fraction occurred. In the extracts prepared after steps (S1) and (S2) summarily representing the ionto-exchange fraction the presence of monitored metals was not determined (detection limit of Zn: <0,01 mg/l, Cd: <0,02 mg/l, Pb: <0,1 mg/l). The most significant decrease of Zn concentration related to the content of cement in stabilized products was achieved by 30 % of Portland slag cement (20,2 mg/l) and already after two days of hydration (figure-7). Determined value slightly exceeded the maximum permissible concentration of Zn and thus the waste is possible to classify as a hazardous waste. Determination of Cd contents in extracts of S/S products (figure-8) revealed the lowest determined content at 30 % of Portland slag cement. Its influence on the Cd immobilization was proved only by 20 % and 30 % considering the content of Cd in performed steps of sequential extraction by original sample. In case of Pb, as can be seen in figure-9. Likewise the most significant decrease in its concentration was at 30 % of Portland slag cement content. At all the tested stabilized products with different Portland slag cement content a reduction of Pb concentration regarding the original content was observed in ionto-exchange and acido-soluble fractions.



**Figure-8**

**Pb leaching from S/S products**

**Table-6**

**Determined contents of Zn, Cd and Pb in steps S1-S3 at different portions of Portland slag cement in 2, 7 and 28 day**

Element	Days	Portland slag cement		
		12 mass. %	20 mass. %	30 mass %
		[%]	[%]	[%]
Zn	2	2,6	2,0	1,5
	7	2,6	2,0	1,5
	28	2,5	1,9	1,4
Cd	2	12,3	8,4	6,2
	7	12,3	8,4	6,2
	28	12,3	7,9	6,2
Pb	2	0,4	0,3	0,2
	7	0,4	0,3	0,2
	28	0,4	0,3	0,2

## Conclusions

In the paper the evaluation of S/S products of fine-grained converter sludge from the aspect of both strength and mobility of Zn, Cd and Pb by methods of sequential extraction was done. The Portland slag cement mixed with the fine-grained converter sludge at content of 12 wt.%, 20 wt.% and 30 wt.%, respectively, was used for the stabilization. Products of hydration were evaluated after 2, 7 and 28 day, respectively. Obtained set of compressive strength results of the S / S products shows that the increase of the compressive strength occurs over time and with the amount of Portland-slag cement. Higher amount of cement and supposedly gradual hydration of tricalcium silicate enabled the development of C-S-H gel as hydration product and strength contributor. X-ray diffraction records of hydration products revealed that during the hydration there were not any changes of majority phases brought into the mixture by the waste sample. After 28 day hydration the products contained phase of gismondine from group of zeolites independently of the amount of added binder. From the comparison of the first three steps of sequential extraction, which enables to assess a mobility of Zn, Cd and Pb in original sample and in the S/S products, it results that with increasing quantity of added binder it decreases a quantity of monitored elements which are present in the S/S products in a bioavailable forms. Duration of hydration process has not a significant influence on the immobilization of monitored heavy metals present in the S/S products.

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