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POSSIBILITY OF SECONDARY LEAD SLAG STABILIZATION IN CONCRETE WITH PRESENCE OF SELECTED ADDITIVES

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Abstract

A comparative technical and environmental evaluation of products arising from the stabilization/solidification of secondary lead metallurgical slag into a cement matrix was performed. Provided samples of an industrial slag generated in the process of recovery of lead from automotive batteries (Engitec CX process), were used in experimental work. Characterization of slag by X-ray Diffraction (XRD), Atomic Absorption Spectrometry (AAS) and Optical Microscopy (OM) revealed that slag contains a certain percentage of sodium and lead, in the form of oxides and sulphides, as well as unreacted coke and iron compounds. Dissolving of the slag components causes migration of ions into water what can induce a significant pollution of environment. Processing options for stabilization/solidification of secondary lead metallurgical slag into cement matrix with barium hydroxide and gypsum as selected additives due to possibility of forming insoluble forms of slag compounds were determined. The influence of concrete composition on the compressive strength, in the presence of selected additives, was also studied. Toxicity characteristics leaching procedure (TCLP) was conducted to evaluate the leaching behaviour. The results revealed that with careful control of the solidification process in presence of selected additives, slag could be used as a partial aggregate replacement in the concrete production.

Key words: secondary lead, slag, stabilization, solidification, leaching, TCLP

Introduction

Lead is one of the essential and most widely used metals in the world. From the whole lead production in Europe up to 70 % of lead is used in battery industry and scrap automotive batteries are a major source of secondary lead. Also, the secondary refining

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industry supplies more than 50 % of lead consumed. In the same time, lead is of a great environmental concern, i.e. many lead compounds and products which contain lead are classified as hazardous (toxic) materials [1]. Because of this fact the industry is responding to ecological concern by recovering ever increasing amounts of lead so that secondary production of lead is steadily on the raise.

The treatment of waste lead batteries is mainly based on pyrometallurgical processes in furnaces with chemical reduction of all metallic compounds to their metalic form by means of heating and providing adequate trapping and reducing substances [2]. Nowadays, one of the processes used for lead recovery from exhausted batteries is the Engitec Integrated CX process, which crushes the whole batteries, separates battery components and desulphurisates the battery paste. Paste desulphurisation, prior to smelting, can reduce the quantity of slag produced, the amount of sulphur dioxide released to the air. Also, removing polypropylene (PP) decreases emission of volatile organic compounds (VOC), including dioxins [1]. Plant data also indicates an increase in furnace productivity of about 25 – 30 %, using feed from the CX system [3]. The sodium carbonate is most frequently used reagent for desulphurization of damped Pb paste. Many technologies suggest processing of paste by NaOH, the $PbSO_4$ being transformed into $Pb(OH)_2$ [4] for production of Na_2SO_4, supplied to detergent industry.

The production of metals is related to the generation of slag as by-product that is generated by the reaction of slag forming accompanying elements (e.g. Fe) with added fluxes [1]. The physical and chemical properties of this slag, which are important to its later treatment, are entirely dependent on the chemical composition of the used fluxes. Depending to added flux in process, different types of slags can be obtained. Calcium slags are produced by adding $CaCO_3$ and they are least dangerous for environment, but during the process a huge amount of slag is produced. Sodium slags are produced by adding Na_2CO_3 and they contain lead (approximately 5 wt. %) and soluble alkalies. Also, this slag decomposes in contact with the air and due to its solubility there is possibility of migration of its constituents in the environment [5]. Industry mainly uses sodium slags from rotary furnace due to smaller amount of total slag which are viscous at lower temperature, reduced energy and gas consumption. Energy savings in the production of lead alloys from secondary raw materials and introduction of cleaner production in metallurgical industry are of a great importance from economic and ecological aspects [6,7]. While slags which contain certain amounts of lead in the elementary state could be mostly valorizated with recovery within the process, final slag with a low metal content requires disposal. All kinds of slags from secondary lead smelters are classified as hazardous waste in the European Waste Catalogue [8].

Stabilization is a pre-landfill waste treatment proces, which has been used for different types of industrial waste, but is particularly suited to those containing heavy metals. The continuing need to develop economical and improved waste management techniques has increased the potential importance of solidification technology throughout the world, in a process defined as the best demonstrated available technology (BDAT) [9]. The performance of products, arising from the stabilization/solidification of slags from lead batteries recycle into a Portland cement matrix, has been evaluated not only in order to get a stabilized waste to be disposed of according to the current regulation, but also to obtain a recyclable material, with both economic and environment benefits [2]. Angelis and other [10] concluded that secondary lead metallurgical slag can be used as inert materials in a cement mortar under careful control of the conditions, so only a limited amount of slags can replace siliceous sand, if the troubles caused by the interactions of lead with cement components are to be avoided.

The aim of this paper is the assessing the performance of the product obtained by the stabilization/solidification of lead slags with cement matrix in the presence of selected additives, barium hydroxide and gypsum. An evaluation of physico-chemical, mineralogical and technical characteristics of the slag, as well as its reactivity in cement, is reported and evaluated. The leachability of lead from prepared concrete blocks was also carried out in order to determine its toxicity.

Experimental work

Materials and preparation

Provided samples of an industrial slag generated in the process of recovery of lead from automotive batteries (Engitec CX process), were used in experimental work. Slag was generated in short rotary furnace, fed with desulphurized paste. When slag was delivered, its particle size varied from 50 to 500 mm. Standing on the air, so called “aging“ of slag was followed by decomposing and forming finer fraction and powder. From the total amount of delivered slag, a coarse fraction (about 15 wt. %) could be returned in the process, while finer (about 85 %) may be used as experiment material, prepared by sieving through sieve, opening 1 mm, and drying to constant weight. Also, used aggregates were prepared by sieving through sieve, opening 5 mm (coarse aggregate) and 0.5 mm (fine aggregate). Portland cement (PC 35M (V-I) 32.5 R) and powder form of additives (pro analysi) were used without preparation.

The fraction of slag used in this study was in the range 0-1 mm. It was mixed with cement, additive (barium hydroxide or gypsum), fine and coarse aggregates in corresponding proportions. The 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. After mixing of dry components with barium hydroxide, hot water was added in order to increase solubility of barium hydroxide, while in mixture with gypsum, cold water was added. Also, one control concrete cube without slag and additive was prepared by the recipe for a concrete mark 30, which compressive strength was expected as 30 MPa according to standard JUS U.M1.020. All samples were made using water to binder with the ratio (w/b) of 0.60 by weight, where the workability requirements were met. The mixtures were cast into molds (edge length 100 mm) and vibrated to reduce the volume of entrapped air. Mold was removed after 24 h and castings were cured in a humidity chamber.

The samples were prepared in Laboratory for Extractive Metallurgy of the Faculty of Technology and Metallurgy in Belgrade.

Characterization of the materials

The characteristic of the slag have been evaluated on the basis of chemical composition and grain size distribution. Solubility of slag in water at 20 and 55 °C, as well as increase of weight and change of granulometric size distribution of slag during “aging” was determined. Chemical and mineral compositions of slag samples were determined by X-ray Diffraction (XRD), Atomic Absorption Spectrometry (AAS) and Optical Microscopy (OM).

Characterization of concrete blocks has been done after 28 days in order to determine mechanical and leaching behaviour.

Compressive strength was determinated according to standard JUS U.M1.020 with servohydraulic testing machine, Instron 1332, loading capacity 100 kN, control module Fast track 8800, fast moving clips 1mm/min. Determined values for cubes with edge length 100 mm were calculated taking into account compressive strength for cubes with edge length 200 mm, according to the valid legal regulations for concrete. Ratio of cube used in this experiment and cube with edge 200 mm was 0.90. Measured compressive strength of control sample was smaller than expected value (30 MPa), probably due to production in laboratory conditions without adequate industrial equipment. Due to this reason measured values of compressive strengths of all prepared samples were calculated by multiplying with a coefficient 2.6, which represents the ratio between expected and measured values of the control concrete sample.

Leaching behaviour of all concrete cubes was evaluated by modified toxicity characteristics leaching procedure (TCLP) [11], in order to examine the leachability of lead from fragmented samples with size 100 % less than 9.5 mm. While contact time and rotating speed for TCLP test are 18 h and 30 rpm, due to limited laboratory conditions these parameters in this research were maintained as 14 h and 80 rpm. During the test, leach liquor was filtered and used for analysis of lead by AAS.

Results and discussion

Properties of slag

The chemical composition of the slag is shown in *Table 1* and *Figure 1*. It contained high amounts of Na (Na_2O, Na_2SO_4) and Fe (FeS, Fe_2O_3) along with considerable amounts of lead (PbS, PbO), Si (SiO_2) and Ca (CaO). Also, trace amount of Cr (Cr_2O_3), Cu (CuS), Zn (ZnO) and Ti (TiO_2) were present in the slag. High contents of sodium and lead, 43.20 and 7.43 wt. %, respectively, indicate that the selected slag sample was more alkaline and lead "reach". Also, high contents of carbon in the slag, as residual reducing substance, and sulphur from paste, were presented in the slag.

Table 1 Chemical composition of slag

Constituent	Amount, wt. % on dry basis
Na (Na_2O and Na_2SO_4)	43.20
Fe (FeS and Fe_2O_3)	20.10
Pb (PbS and PbO)	7.43
Si (SiO_2)	4.71
Ca (CaO)	3.42
Cr (Cr_2O_3)	0.13
Cu (CuS)	0.25
Zn (ZnO)	0.12
Ti (TiO_2)	0.60
C	9.40
S (total)	9.54

As the chemical characterization of the slag confirmed the presence of lead and traces of other metals without content of arsenic, it can be concluded that the studied slag was a by-product of melting electrode paste (fine particles of lead oxide and lead sulphate) from waste lead-acid batteries. Slag formed in the process of melting metallic components such as grids, poles together with paste, contains a higher percentage of lead as well as arsenic and other metals. Mixing of slags is desirable in order to avoid the occurrence of cumulative adverse effects on the environment. Namely, lead and arsenic compounds are "ecotoxic" (H14) and may cause the long-term adverse effects in the aquatic environment (R50-53) if concentration of this metals are higher than concentration limit (0.25 %) [12]. Thus, slag with higher than prescribed content of lead is defined as hazardous waste. Also, secondary lead metallurgical slag with the similar content of lead [15] was defined as hazardous waste with lead concentration in slag leachate much higher than limit value for performing TCLP test.

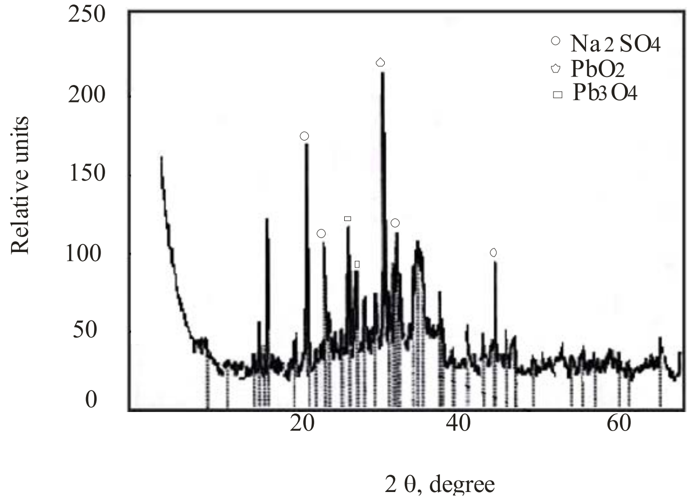


Figure 1 X-ray diffraction pattern of raw slag

Figure 2 Optical micrograph of slag macrostructure (fraction – 1 mm)

Analysis performed by optical microscope confirmed the presence of residual reduction agent (coke) and conglomerates of hematite (Fe_2O_3) or hydro-hematite ($Fe_2O_3 \cdot H_2O$), as well as reduced lead balls in the slag. A higher amount of silicate phases was observed with a piece of foam of hydro-hematite, with individual grains of galena (PbS) cylindrical in shape and without reflection (Figure 2).

The obtained high water solubility in the slag (fraction 0-1 mm), 22.4 and 24.0 wt. % at 20 °C and 55 °C, respectively, is probably a consequence of high sodium content. This fraction is also very important from the environmental point of view, because it is known that tiny particles may contain high amount of potentially leachable elements due to their high sorption capacity. Dissolving of the slag components causes migration of ions into water inducing a significant pollution of environment.

During contact with the air, the weight of slag was increased, with average increase of 23 % during ten days. This “aging“ of slag is probably due to the reaction of Na_2O with CO_2 and moisture from the air. In contact with the air formed Na_2CO_3 crystallizes as monohydrate.

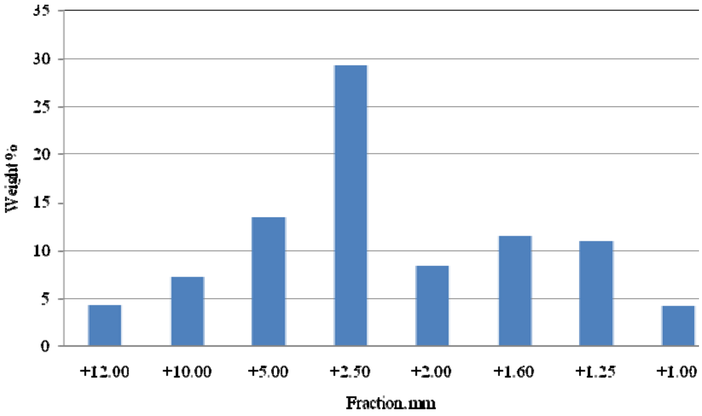
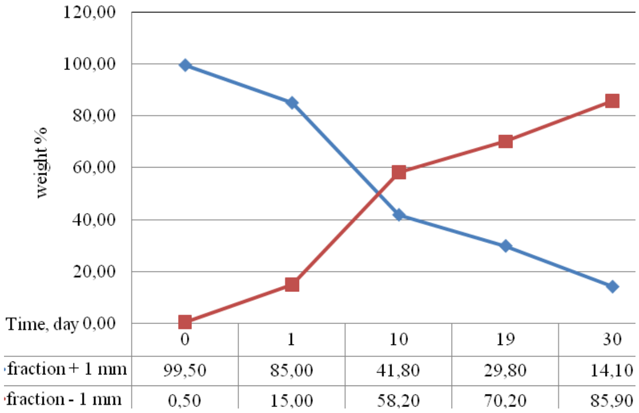


Figure 3 Grain size distribution of slag



Time, day	0	1	10	19	30
fraction + 1 mm	99,50	85,00	41,80	29,80	14,10
fraction - 1 mm	0,50	15,00	58,20	70,20	85,90

Figure 4 Change in grain size distribution of slag for fraction + 1 and -1 mm

The grain size distribution of the raw slag before and after contact with the air is shown in Figures 3 and 4, respectively. Raw slag contained only about 5 wt. % of fraction smaller than 1 mm. During contact with the air for 30 days the granulation has been significantly changed (*Figure 3*) as a consequence of the above mentioned reaction.

Properties of concrete cubes

Concrete cubes with slag were prepared using cement as the main binder and two selected types of additives as partial replacement of cement. Barium hydroxide was used for chemical fixation of sulphate ions into the solid phase in order to form water insoluble $BaSO_4$, while gypsum was used to increase strength of stabilized form of waste [13].

Properties of concrete cubes were determined after 28 days by measuring their compressive strength and amount of lead leached using TCLP test.

Compressive strength is determined in order to compare mechanical characteristics of stabilized waste with cement and selected additives. For the waste stabilized into cement like form, increase of strength characteristics are expected [14].

Strengths of all concrete cubes, prepared with slag and additives, were compared with compressive strength of control cube, prepared without slag and additives. Concrete cubes with 10 and 20 wt. % of slag, prepared with $Ba(OH)_2$ exhibited lower strength with similar values for both concentration of slag. It is assumed that this was a consequence of the formation of compounds with barium which position, size or shape had the significant influence on mechanical properties of concrete due to weak cement matrix and increased porosity of material.

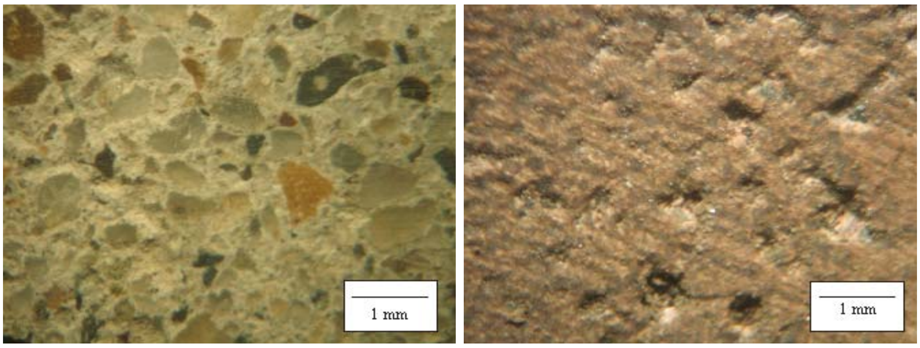
Concrete cubes manufactured with gypsum showed different strength for samples with 10 and 20 wt. % of slag. The sample with 10 wt. % of slag attained similar strength in comparison with the control cube, while the mechanical strength is reduced by an increasing quantity of slag to 20 wt. % (Table 2).

Table 2 Compressive strength of concrete cubes determined after 28 days

Sample	Additive	Slag content, wt. %	Measured compressive strength, MPa	Expected compressive strength, MPa
Control	-	-	11.68	30.00
B10	$Ba(OH)_2$	10	8.74	22.75
B20		20	8.77	22.80
C10	$CaSO_4 \cdot CaO$	10	11.70	30.42
C20		20	7.29	18.95

With careful control of the solidification process in presence of selected additives, slag could be used as a partial aggregate replacement in concrete production with application in production of low load-bearing surface (compressive strength 15 MPa) and load-bearing plates and columns (compressive strengths 30 MPa).

Presence of closed porosity, as the result of poor bonding between the cement and slag, caused a substantial reduction in strength of concrete samples prepared with 20 % of slag and gypsum (Figure 5).



(a) *(b)*

Figure 5 Porosity of concrete cubes (a) without slag and additive and (b) with 20 % of slag and gypsum as selected additive

Leaching behaviour was determined in order to evaluate stabilization/solidification of lead in concrete and a possible danger of concrete cubes with slag for the environment. Total content of lead in leach liquor from TCLP test is shown in Table 3.

Leaching of lead was the highest from concrete cubes prepared with 20 wt. % slag. The lowest amount of lead in leachate was obtained with the material prepared with 10% slag and barium hydroxide. However, significantly lower compressive strength of these cubes limits their application. Cement stabilization in presence of barium hydroxide was probably followed by the formation of insoluble compounds which presence in the cement matrix could decrease compressive strength of materials, regardless on the amount of slag.

Reduction of compressive strength and high release of lead from the solidification product prepared with 20% of gypsum are the limiting factors for a potential reuse of this material. Using gypsum with cement in concrete was followed by the formation of lower stabilized products for higher amounts of slag due to weaker slag binding with the cement matrix.

Table 3 Leached amounts of lead from concrete cubes obtained with TCLP test

Samples	Additive	Slag content, wt. %	Leached lead, mg/l
Control	-	-	0.03
B10	$Ba(OH)_2$	10	0.63
B20		20	1.26
C10	$CaSO_4 \cdot CaO$	10	1.27
C20		20	5.06
Limit value, mg/l			5.00

Conclusion

It can be concluded that the amount of the secondary lead metallurgical slag, by-product of Engitec CX process, as well as selected type of additives have a significant influence on the properties of prepared concrete.

Content of metals in waste depends on the process and management of waste received. Conducting a controlled process and separating generated slag obtained performing different melting processes; it is possible to extract slag with determined forms and contents of metals.

Slag containing metals (lead and arsenic) above concentration limits for corresponding metal compounds (0.25 %) have the characteristics of hazardous waste (eco-toxic) that require treatment (stabilization/solidification) before disposal.

Stabilization of slag in cement matrix with barium hydroxide was followed by the low release of lead from the solidification products, while the low compressive strength is a limiting factor for potential use of this material. Concrete blocks prepared with lower amount of slag and gypsum as an additive have the highest compressive strength and also the environmental performance of this material meets the required standards. Increasing of slag amount was followed with higher release of lead and lower mechanical properties.

Observed changes are the consequences of interactions of slag compounds with additives, as well as with cement components. Cement stabilization in presence of barium hydroxide was probably followed by the formation of insoluble compounds which presence in the cement matrix could decrease compressive strength of materials, regardless on the amount of slag. However, using gypsum with cement in concrete was followed by the formation of lower stabilized products for higher amounts of slag due to weaker slag binding with the cement matrix. Also, the increased porosity was one of the main factors influencing the decrease of the compressive strength.

With careful control of the solidification process in presence of selected additives, slag could be used as a partial aggregate replacement in concrete production with application in production of low load-bearing surface (compressive strength 15 MPa) and load-bearing plates and columns (compressive strengths 30 MPa).

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