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Edited by

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Igor Miljanović, Ivana Simović

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Foreword

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The XVI BMPC Chair

LEACHING BEHAVIOR OF SULFUR CONCRETE WITH FLY ASH USED FOR REMOVAL OF HEAVY METALS FROM WASTEWATER

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Abstract: When considering the materials that have become waste in a technological process, one way of their immobilization is for the production of certain new materials. The basic fact is to provide the environmentally acceptable level of the produced material. In this research fly ash from ''Power Plant Nikola Tesla'' Obrenovac was used as an sorbent for removal of heavy metals from flotation wastewater originating from artificial lake ''Cerovo''. After the sorption, fly ash was used as filler for the production of sulfur concrete. Sulfur concrete samples with standard dimensions were subjected to leaching tests by immersion in distilled water during the period of up to six months. Leaching is the process by which different contaminants are released from the solid phase into the water phase. The process itself is universal, as any material exposed to contact with water will leach components from its surface or its interior depending on the porosity of the material considered. Results of examining leaching degree of heavy metals from the sulfur concrete samples with fly ash as filler showed that the leaching degree of all metals (copper, cadmium, zinc, iron, nickel) except manganese was negligible. It can be concluded that in the sulfur concrete samples with fly ash as filler, immobilization of heavy metals occurred.

Keywords: fly ash, sulfur concrete, leaching.

INTRODUCTION

During the mining process of copper exploitation, large amount of waste water generate. At the Cerovo and Krivelj deposits, RBB-RTB, one of the biggest problems presents the generated lake at the open pit. At this moment, the estimated amount of the “Cerovo lake” is 600.000.000 dm^3 (and it grows every day) of this water with the average content of 200 mg Cu^{2+}/dm^3. Concentrations of copper and other heavy metals in the wastewater and water-streams have to be reduced in order to satisfy rigid legislative standards. They can be removed by various technologies, most often expensive or inefficient and technically complicated especially because of limited maximal accepted concentrations required by the EPA (Environmental Protection Agency) (Milicevic et al. 2012, Papandreou et al. 2007, Pentari et al. 2009). The conventional techniques for heavy metals removing from aqueous solutions include oxidation, reduction, chemical precipitation, filtration, ion exchange, adsorption, membrane techniques, electrolytic or liquid extraction, reverse osmosis, biological process (Pentari et al. 2009, Babel et al. 2003). Fly ash has potential application in wastewater treatment because of its major chemical components (alumina, silica, ferric oxide, calcium oxide, magnesium oxide and carbon), and its physical properties such as porosity, particle size distribution and surface area. Besides, the alkaline nature of fly ash makes it a good neutralizing agent (Milicevic et al. 2012, Papandreou et al. 2007). Namely, fly ash as a potential hazardous solid waste produced like a by-product in power plants worldwide in million tonnes has attracted researches interest for years. The objective of this study is possibility of using domestic fly ash on ability for removing the heavy metals from acid waste drainage water. Beside that, large amount of secondary sulfur is produced during the oil refining whereby the amount of this by-product daily increasing because of the rigid requirements of EPA legislative.

Since fly ash is widely used as filler in Portland cement concrete, the idea was to apply contaminated fly ash after the sorption of heavy metals from the wastewaters in preparation of sulfur polymer concrete as a filler component. Namely, sulfur concrete uses secondary sulfur which is a by-product from the oil refining as a binder instead of Portland cement (Vlahovic et al. 2013, Vlahovic et al. 2012). Since previous experience has shown that sulfur concrete is inert with no leaching of heavy metals, it can be expected that leaching of hazardous components would be negligible. Therefore, obtained concrete belongs to the eco-friendly material. Also, sulfur concrete is resistant to salty and acidic environments, while the mechanical properties are satisfactory.

Industrial by-products are almost zero-cost materials and in the same time their utilization can contribute to the solution of their management problem improving the material efficiency within several industrial activities. Therefore, usage of those two by-products that are obviously hazardous materials for disposal to the landfill as well as treating of wastewater would solve several environmental problems.

EXPERIMENTAL

Synthetic aqueous solution was prepared with the concentration of heavy metals as appeared in ``real`` wastewater from the generated lake at open pit of Cerovo deposit, RBB-RTB. The synthetic aqueous solution was prepared by dissolving the appropriate amount of different salts in deionized water. All chemicals were of analytical reagent grade. The solution was chemically analyzed due to determination of metal's and trace elements content with atomic adsorption spectrophotometry (AAS) using Spekol 1300 instrument (Analytic Jena, Jena, Germany).

The fly ash used as a sorbent of heavy metals from the wastewater was collected in power plant Nikola Tesla, Obrenovac, without any pre-treatment. It remains as a residue from lignite combustion recovered from cyclones and electrostatic filters of the power plant. Namely, hydraulic and pozzolanic properties of power plant fly ash can be utilized in order to develop non-conventional sorption media for industrial effluents treatment. All fly ashes contain the same basic chemical elements but in different proportions. The main constituents of fly ash are silicon, aluminum, iron, and calcium with smaller amounts of sulfur, magnesium, alkalis, and tracers of many other elements. The results of chemical analysis showed that the main and most important components of the fly ash are silica, alumina, as well as calcium and iron oxides.

Chemical analysis of synthetic aqueous solution that imitated the real wastewater is given in Table No. 1. Chemical composition of filtrate after the sorption is shown in the same table. The value of the synthetic aqueous solution pH was 2.87. Sorption was carried out by mixing of 2 l of solution and 200 g of fly ash with the frequency of rotation of 800 rpm/min during 1 hour. After the sorption, mixture was filtered. Filtrate and solid residue (loaded or contaminated fly ash) were analyzed by chemical analysis.

Table 1, Chemical composition of solution before and after sorption.

Solution Content (mg/l)	Before sorption	After sorption
Fe	9.56	< 0.01
Mn	34	12.7
Cd	0.37	0.06
Zn	49.5	0.25
Ni	0.7	0.1
Cu	167	<0.01

It is obvious that all monitored metals were removed from the solution to the maximum acceptable concentration given by EPA standard. Exception is manganese where the concentration decreased twice but it was still above the allowable limit in waste water.

Content of heavy metals in the fly ash before and after the sorption is shown in Table No. 2. As expected, the content of heavy metals in the sorbent that is fly ash increased in proportion to their reduction in the wastewater solution.

Table 2, Chemical analysis of fly ash before and after the sorption.

Fly ash Content (%)	Before sorption	After sorption
Fe	-	3.59
Mn	0.045	0.066
Cd	0.005	0.008
Zn	0.021	0.048
Ni	0.03	0.09
Cu	0.005	0.168

After the sorption and filtration, solid residue that is fly ash contaminated or loaded with heavy metals was subjected firstly to the drying at ambient air and temperature for 24 hours, and then in the laboratory drier for another 24 hours at 50°C. Dried loaded fly ash was further used for preparation of sulfur polymer concrete as filler.

Sulfur which is the basic component for the preparation a modified sulfur binder, originates from oil refining process by Clauss procedure in Oil Refinery Pancevo with high purity of 99.9 %.

River sand was used as an aggregate. Chemical analysis indicated that the aggregate mainly consists of oxide of silica (88.98 %), aluminium (3.61%) calcium (0.84 %), iron (0.62 %), potassium (0.59 %), sodium (0.57 %), and magnesium (0.19 %).

The aim of this study was the stabilization of metal loaded fly ash and obtaining eco friendly building material. Namely, the stabilization procedure took place in the structures made of sulfur polymer concrete, where the Portland cement was replaced by modified sulfur and saturated fly ash was used as filler (5 wt. % of dry mix). The procedure of preparation of sulfur concrete included several operations: homogenization of dry mixture of aggregate and filler at sulfur melting temperature, 132-141°C, admix with melted and modified sulfur for another 2 minutes, cast into the molds preheated at 120°C and vibrated for 10 s. The samples were left to harden inside molds at room temperature for 3 hours. Samples were removed from the mold and cured at room temperature for 24 hours.

In order to evaluate the degree of metals immobilization after encapsulation of saturated fly ash in the sulfur polymer concrete, desorption experiments were carried out at 25 ˚C. Leaching tests were realized by immersing the samples of prepared sulfur concrete into the bucket with 5 l of deionized water for 1, 2, 7, 14, 21, 90, and 180 days (Papandreou et al. 2007, Papandreou et al. 2011). The % desorption of each metal was examined. After the each period of immersing, leachates were subjected to the chemical analysis due to determine content of heavy metals as the evidence weather the leaching from the sulfur concrete occurs. In order to check how hazardous are leachates, maximum acceptable concentration (MAC) according to the Environmental Protection Agency (EPA) is shown as well, Table No. 3.

Table 3. Maximal acceptable concentration of heavy metals in waste water.

Maximum Acceptable Concentration (mg/l)	Fe	1.0
	Mn	1.0
	Pb	0.1
	Cd	0.01
	Zn	1.0
	Ni	0.1
	Cu	0.1
	Cr	0.1
	Cl^-	250
	SO_4^{2-}	200

The results of leaching tests are shown in Figures No. 1 and No. 2. Obtained results from desorption experiments after encapsulation of metal saturated fly ash in concrete were excellent. After 6 months in deionized water none metal was desorbed in traceable amount indicating the excellent stabilization of heavy metals achieved by encapsulation in sulfur concrete. Namely, all monitored metals were desorbed generally in a very small amount into deionized water, much below the maximum acceptable concentration allowed in waste water by EPA. The exception is again evident in case of manganese, where increased leaching of manganese was observed.

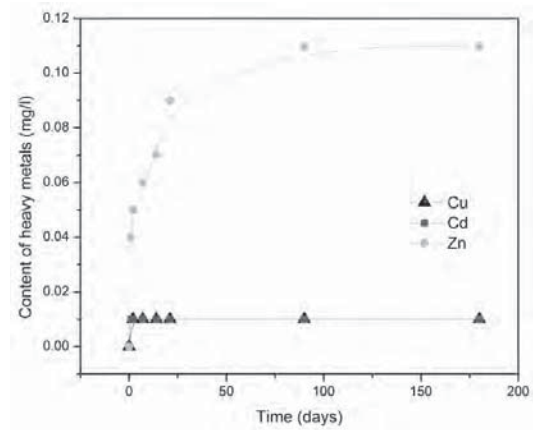

Figure 1, Copper, cadmium and zinc ions concentrations from the sulfur concrete.

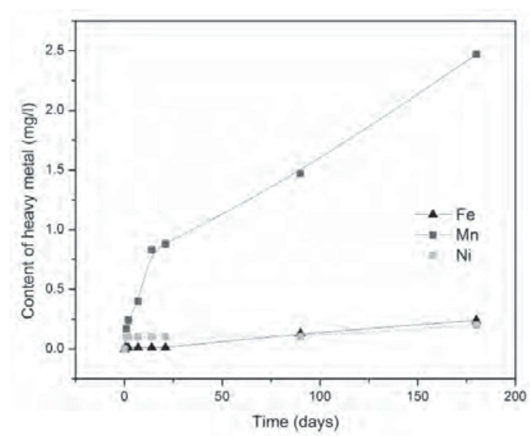

Figure 2, Iron, manganese, and nickel ions concentrations from the sulfur concrete.

It is evident that content of copper and cadmium in leachates after 6 month of testing is almost negligible while content of zinc is slightly higher but it is still not as high so it can be considered as a very small. It is noticed that only leaching of manganese increases with the time of immersing into the water, exceeding the MAC. Further studies will be focused on solving the problem of Mn immobilization in the sulfur concrete.

This study shown that immobilization of heavy metals except manganese into the sulfur concrete were satisfactory allowing the safely handling of these blocks and deposition in industrial landfills without risk for the environment.

CONCLUSION

The stabilization of metal saturated fly ash by encapsulation in sulfur polymer concrete, where modified sulfur from oil refining process was used as a binder and contaminated fly ash after the sorption of heavy metals from the waste water was used as filler, was excellent in neutral environment (deionized water). The stabilized concrete was almost inert since it did not show metal desorption except manganese under neutral solution for a period of 6 months indicating that the stabilized concrete can be almost safely disposed in industrial landfill and partly eliminating the risk of pollution for groundwater and other natural water receivers.

The aim of this procedure and technological scheme is to allow the exploitation of several by-products: fly ash from power plants, industrial wastewater, sulfur from oil refining process.

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