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Immobilization of zinc from metallurgical waste and water solutions using geopolymerization technology

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Abstract. Geopolymeraization technology is recognized as a promising method for immobilization of heavy metals by the stabilization or solidification process. This process involves the chemical reaction of alumino-silicate oxides with highly alkaline activator yielding the new material with amorphous or semi-amorphous structure, called geopolymer. Fly ash and blast furnace slag were mainly used as a raw material for geopolymerization process. In this paper we have investigated the possibility of immobilization of Zn from electric arc furnace dust (EAFD) through geopolymerization of fly ash and possibility of Zn^{2+} adsorption from waste waters using fly ash based geopolymers. Efficacy of Zn immobilization from electric arc furnace dust was evaluated by TCLP test while the immobilization of Zn^{2+} ions from the water solution was evaluated through the removal efficiency. The results have shown that geopolymerization process may successfully be used for immobilization of Zn by stabilization of EAFD and for production of low cost adsorbent for waste water treatment.

Keywords: zinc, geopolymerization, fly ash, adsorption, water solutions, electric arc furnace.

Introduction

Geopolymerization technology is recognized as promising waste minimization technology. Fly ash, blast furnace slag are mainly used as a raw material for a geopolymerization process This process involve reaction of alumosilicate source with a highly alkali solutions followed by the dissolution of Al and Si from the source materials in the alkali and formation of gel by the polycondesation of Al and Si complexes. The final step is hardening of gel. As a result of geopolymerization process, inorganic polymer called geopolymer, with amorphous or semi-amorphous structure is formed. The empirical formula of geoplymer is:

$$M\,[(-SiO_2)z - AlO_2]n{\cdot}wH_2O$$

where M is a cation, usually an alkali (Na, K, Ca), n is a degree of polycondensation, $w \leq 3$ and z is 1, 2 or 3, (Davidovits, 1991). Properties of geopolymers manly depend of the choice of alumosilicate source and reaction parameters such as temperature and time of curing, type and concentrations of alkali solution and solid/liquid ratio. Fly ash is widely used as a raw material for a geopolymerization process and fly ash based geopolymers are currently recognised as a promising replacement for cement as binders for mortar and concrete.

Moreover, fly ash geopolymerization is considering as a possible way of heavy metals immobilization. Immobilization may proceeds by the solidification/stabilization process (Luna at al., 2009, Fernández Pereira et al., 2009) and by adsorption (Wang et al., 2007). Solidification is conversion of liquid in the solid while stabilization present fixation of hazardous materials by the chemical reaction or physical encapsulation making them less mobile. Immobilization of heavy metals by adsorption is related to the removing heavy metals from the waste waters. In this sense, geopolymerization of fly ash may be a promising

technology for immobilization of heavy metals from industrial waste waters and the metallurgical wastes.

In this paper we have investigated possibility of immobilization of Zn from electric arc furnace dust (EAFD) through geopolymerization process and possibility of usage of fly ash based geopolymers as low-cost adsorbent for Zn^{2+} removal from waste waters. Electric arc furnace dust is a metallurgical waste generating by remelting of iron and steel scrap and it is classified as a hazardous waste due to the leaching of heavy metals in the environment. Currently, EAFD is recycling by hydro and pyrometallurgical processes or by returning them in the furnace, but none of these processes is not commercialised. Besides, recently a special attention is given to the investigation of possibility of immobilization of EAFD through stabilization process in the useful products that can be used in construction.

Materials and Methods

Fly ash and EAFD were supplied from coal faired power station in Pljevlja and steel factory Niksic in Montenegro. Chemical compositions of fly ash and heavy metals content in EAFD are given in the table 1. Fly ash (FA) is activated by alkaline solution prepared by mixing sodium water glass (Na_2O = 8.5%, SiO_2 = 28.5%, density of 1.4 kg/m^3) and NaOH solution.

Table 1. Chemical composition of fly ash and heavy metals content in EAFD

FA		EAFD	
Content %		Heavy metals content, %	
SiO_2	49.45	Zn	26.6
Fe_2O_3	5.23	Pb	3.45
Al_2O_3	21.77	Cr	0.52
TiO_2	0.66	Cu	0.56
CaO	13.34	Cd	0.096
Na_2O	0.46		
ZnO	$4.5 \cdot 10^{-3}$		
MgO	1.29		
MnO	0.02		
P_2O_5	0.24		
K_2O	1.4		
LOI*	4.35		

*Loss on ignition.

In order to investigate the possibility of zinc immobilization, geopolymers were prepared using mixture of EAFD and fly ash in a ratio 1 : 9 and mixing with a alkali solution at the solid to liquid ratio 1. Alkali solutios were prepared by mixing of sodium water glass (Na_2SiO_3) with 7, 10 and 13 M NaOH solutions at the Na_2SiO_3/ NaOH ratio of 1, 1.5 and 2. Geoplymers were synthetised in the way that EAFD was mixed with NaOH solution for 10 min, than water glass and fly ash were adedd and mixing was continued in addtition 5 minutes. As a result, geopolymer paste was formed. The paste were casted in the cylindric mould and curred in a oven at 65^{0}C for 48 h. After this time, the specimens were allowed to cool, removed from mould and left to stay additional 28 days at ambiental temperature. Efficiency of Zn immobilization was evaluated using TCLP (toxic characteristc leaching procedure) method 1311. During TCLP test, the solid was pulverized and mixed with a extraction fluid (acetic acid solution pH = 2.88 ±0.5) at the solid:liquid ratio 1:20 for 18 h. After the tests, solid and liquid phases were separated by filtration and the eluates are acidified with nitric acid to the value of pH less than two. Metals content was determined using ICP-OES (Spectro Arcos). TCLP test simulates more aggressive leaching conditions than those in a environment, and pulverization of sample may leads to overestimation.

Geopolymers used as a low cost adsorbent were prepared by mixing of fly ash with alkali solution at solid to liquid ratio 0.75, at the water glass/NaOH ratio of 1.5 but using a 10 M NaOH. Mixing was conducted for 5 minutes and geopolymer paste was casted in mould, and cured at the same conditions as in previous case. After 28 day of storage at the ambiental temperature the samples are crusshed to the size below 400 μm and used as adsorbent for Zn^{2+} removal from water solution. Solutions containining Zn^{2+} were prepared by dissolving $ZnSO_4$ in a distilled water to obtain concentration of 100 mg Zn^{2+} per litter. The adsorption was conducted in a batch experiments. One litter of Zn^{2+} solution were poured in 2 litter balloon with 10 g of adsorbent and mixed at 100 rpm for 24 h. Initial pH of suspension was 9.8. In a second case, prepared suspension was blowed with CO_2 in order to decrease the pH of suspension to the value of 7.5 and mixing was continued for 24 h.

Results and Discussion

Immobilization of Zn from EAFD

Immobilization of Zn from EAFD may proceeds by chemical bonding, adsorption or physical encapsulation. We have investigated the influence of pH alkali solution on the Zn immobilization from EAFD. Alkali solution pH may be changed by the change of Na_2O content in the geopolymer matrix. It may be changed by the change of NaOH concentration or by the change of Na_2SiO_3/NaOH ratio in alkali solution. Results of investigation of influence of NaOH solution concentration and Na_2SiO_3/NaOH ratio on the immobilization of zinc are given in the Table 2 and 3, respectively. It is evident that the Zn leaching from geopolymer decrease with increase of NaOH solution concentration used for geopolymer synthesis and with decrease of Na_2SiO_3/NaOH in alkali solution. In a both cases the alkali solution pH is increased and pH of suspension (pulverised geopolymer and TCLP fluid) is increased, as well. It is evident that

dissolution of Zn from geopolymers is strongly affected by the pH of alkali solution used for the geopolymer synthesis. Increase of pH result in better Zn immobilization in a geopolymer matrix.

Table 2. pH and Zn^{2+} concentration in TCLP eluates in a function of NaOH concentration used for geopolymer synthesis (Na_2SiO_3/NaOH =1.5)

C(NaOH) mol/dm^3	pH	TCLP, (mg/L)
7	8.30	0.327
10	8.54	0.191
13	8.75	0.133

eluates in a function of water glass/NaOH ratio prepared with 13 M NaOH

Table3. pH and Zn^{2+} concentration in TCLP

Na_2SiO_3/NaOH	pH	TCLP, (mg/L)
1	8.60	0.149
1.5	8.54	0.191
2	7.90	0.485

Adsorption o f Zn^{2+} from waste waters

Results related to the investigation of possibility of use fly ash based geopolymers as potential low cost adsorbent for Zn^{2+} removal from waste water are given in the Fig. 1.

As in a previous case, it s evident that pH of suspension has a significant influence on the adsorption of Zn^{2+} on the fly ash based geopolymers. The higher removal efficiency of Zn^{2+} from the water solution is achieved in the case of blowing suspension with CO_2. In a both cases, (with and without blowing) the highest adsorption of Zn^{2+} is achieved after 2 h. Prolongation of adsorption after 2 h has no influence on the Zn^{2+} removal efficiency in the case of suspension blowing while in another case (without blowing) desorption of Zn^{2+} is evident.

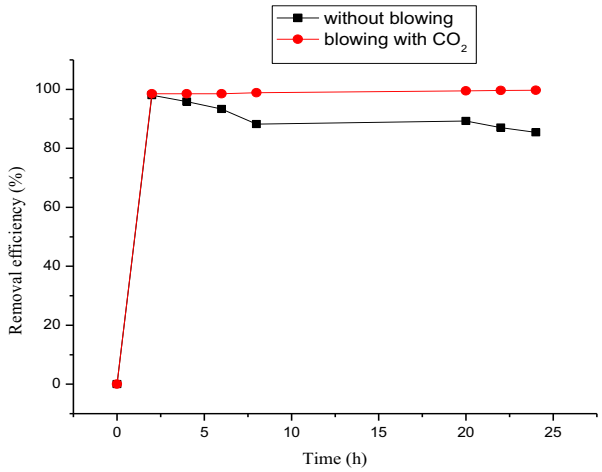

Fig. 1. Change of Zn^{2+} removal efficiency in a function of time.

Conclusions

The results have shown that possibility of immobilization of Zn from electric arc furnace dust is strongly dependent on the pH of alkali solution used for a geopolymer synthesis, i.e. on the Na_2O content in a geopolymer matrix. Increase in Na_2O content in a geopolymer mixture result in increase of alkali solution pH, and better Zn immobilization from electric arc furnace dust.

Results of investigations Zn^{2+} adsorption from waste waters have shown that fly ash based geopolymers may be used as potential low cost adsorbent. The highest Zn^{2+} removal efficiency is achieved after 2 hours.

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