STABILIZATION OF FLY-ASH CONTAINING HEAVY METALS BY ALKALI ACTIVATION

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ABSTRACT

The immobilization of waste materials is receiving increasing attention from scientists all over the world. Alkali activation of fly ash or blast furnace slag is a method that successfully stabilizes these waste materials in a solidified matrix. Fly ash (FA) from Czech power plant Počerady and blast furnace slag (BFS) from Ostrava contain except the mains compounds also small amount of heavy metals – Ba^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Cr. The aim of this work is to find out the ability of aluminosilicate matrix (ASM) and matrix reinforced by wollastonite micro-fibre to stabilize and immobilize heavy metals which originate from raw materials. Amount of heavy metals in raw materials was investigated by XRF. Phase composition was determined by XRD. The ability of matrix to fix and immobilize heavy metals was investigated by leaching tests. These tests were based on the law 383/2001 Sb. and ČSN EN – 12457- 4. The concentration of heavy metals in eluate was analysed by ICP-MS. The addition of wollastonite improved the ability of alkali activated AMSs to fix Ba, Zn and Ni. Fixation of Cu and Cr wasn't influenced by addition of wollastonite.

KEYWORDS:

Heavy metals, fixation, wollastonite reinforcement

INTRODUCTION

Millions of tones of waste materials are generated each year all over the world. Most of them contain trace concentration of heavy metals. These metals can contaminate underground water or soil. Nowadays researchers all over the world try to find new methods and materials, which enable safety storage of the waste materials. Good possibilities to fix and immobilize heavy metals and other waste materials show alkali activated aluminosilicate matrixes (ASMs).

Structure of ASMs can be described as a sialate network of connected SiO_4 and AlO_4 tetrahedra. Negative charge of Al^{3+} is balanced by presence of positive ions Na^+ or K^+ (Komnitsas 2007). Fly ash and blast furnace slag are sources of silica and alumina. The ability of AMSs to fix and immobilize heavy metals has been investigated all over the world. Immobilization depends on many various factors as a composition of raw materials, pH, curing conditions, form of fixed element etc. AMSs are good for fixation of Ba and Pb, on the other hand fixation of As, Mo, Se and Cr is not so successful (Álvarez-Ayuso 2007; Izquierdo 2009; Zhang 2008). Mechanism of inhibition of heavy metals in AMSs hasn't been described precisely yet and depends on the element to be immobilized. Both chemical and physical interactions are expected to affect the immobilization. Chemical interactions mean, that metal cation can replace Na^+ or K^+ in the cavities and play the role of charge balancing ion or it can be incorporated within newly formed amorphous or crystalline aluminosilicate phases (Phair 2004). Physical encapsulation is linked with size and quantity of pores and their connection to the outside (van Jaarsveld 1999).

The addition of fibres or micro-fibres as a reinforcement element is used to improve toughness and other mechanical properties of cementious materials. Fibres also provide stabilization of matrixes. Wollastonite micro-fibres are commonly used as a reinforcement in many ceramic and cementious products. Using of wollastonite micro-fibres to reinforce AMSs results in improvement of their mechanical properties (Silva 2003).

EXPERIMENTAL

Materials and preparation

Fly ash used in the synthesis was of coal origine and obtained from power plant Počerady, Czech Republic. Blast furnace slag was obtained from Ostrava, Czech Republic. As alkali activator was used 16M KOH and K- water glas. The main chemical composition of raw materials is listed in Table 1. Wollastonite used for reinforcement was obtained from Ankerpoort, NB: The mineral company, Netherlands. Five types of AMSs with addition 0 wt.% , 2.5 wt.%, 5 wt.%, 7.5 wt.% and 10 wt.% of wollastonite were prepared. The ratio ash/slag was 3.6. The ratio dry matter/activator was 3.14. The concentration of heavy metals in raw materials was determined by X-ray Fluorescence (XRF). The phase composition of AMSs was determined by X-ray Diffraction Analysis (XRD) using Siemens D5005 diffractometer.

Table 1 – Chemical composition of raw materials (wt.%)

	SiO_2	Al_2O_3	CaO	Na_2O	K_2O	MgO	SO_3	Fe_2O_3	TiO_2	P_2O_5
FA Počerady	53.9	29.8	2.13	0.24	2.66	0.93	0.76	7.18	1.75	0.13
BFS Ostrava	34.7	9.05	41.1	0.41	0.90	10.5	1.46	0.25	0.96	0.02

Leaching tests

Leaching tests were based on ČSN EN 12457 – 1 and the law 383/2001 Sb. AMSs were used for leaching tests after 28 days of curing at room temperature. Samples were crushed and separated and for test was used undersize 10 mm. As a leachant was used distilled water. Solid/liquid ratio was 10 l/kg. Leaching tests proceeded for 24 hours. After the test, pH had been measured and the eluate was filtered through membrane filters. The concentration of all heavy metals was determined by Inductively coupled plasma mass spectroscopy (ICP-MS) using Thermo X Series II.

RESULTS

XRF

The concentration of selected heavy metals in raw materials is listed in Table 2. Heavy metals are presented in FA and BSF only in trace concentration. Only Cr and Ni are included in both of them. The element with highest concentration is Zn.

Table 2 – Concentration of heavy metals (wt.%)

	Ba	Cr	Cu	Ni	Zn
FA Počerady	0.0000	0.0239	0.0175	0.0153	0.0762
BFS Ostrava	0.1496	0.0071	0.0000	0.0017	0.0000

XRD

The XRD diffractogams of AMSs reinforced with wollastonite are shown in Figs. 1 and 2. Quartz and mullite were detected in all samples as main crystalline phases. All samples also contain another crystalline phase as ankerite, akermanite, calcite, merwinite and anatase. Contrary to pure AMS reinforced AMSs include wollastonite. Instead of crystalline phases diffractograms show a relatively large amorphous content between 15 and 40 degrees 2θ.

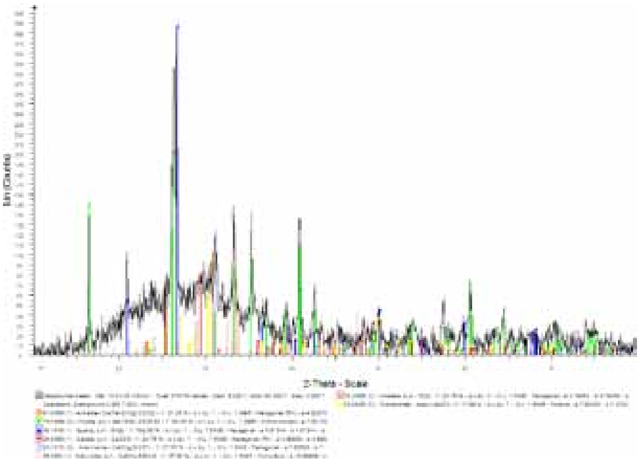

Fig. 1 - XRD spectrum of matrix with 2.5% wollastonite

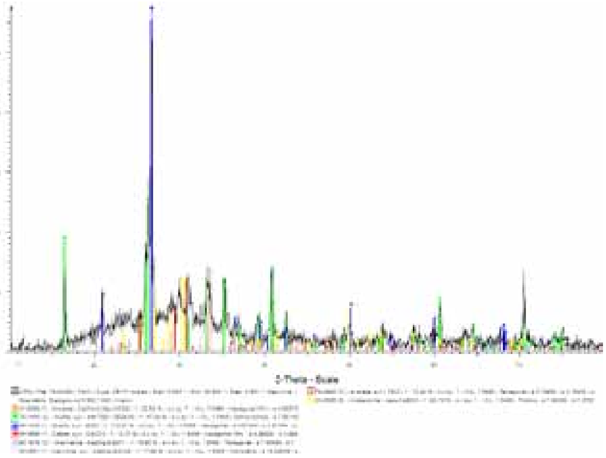

Fig. 2 - XRD spectrum of matrix with 10% wollastonite

Different addition of wollastonite didn't change the phase composition of AMSs, it means no new crystalline phases were determined in AMSs with different addition of wollastonite. Only low decrease of amorphous content can be observed linked with increasing of wollastonite.

Leaching tests

All leachates had pH between 12.25 – 12.43. Concentrations of heavy metals in leachates are shown in Table 3. All determined elements are presented only in a trace concentration. The leaching results show, that Ni, Cu and Zn are leached from all matrixes in low concentrations, while Cr and Ba are leached from some matrixes in higher concentrations.

Table 3 – Concentration of heavy metals in leachates (μg/l)

Wollastonite addition (wt.%)	Cr	Ni	Cu	Zn	Ba
0.0	13.970	4.608	5.023	3.347	12.250
2.5	3.609	3.930	3.829	2.838	10.390
5.0	9.037	2.963	2.947	2.669	9.316
7.5	3.895	2.743	5.335	2.207	7.574
10.0	3.106	2.472	3.461	1.106	7.167

Fig. 3 shows dependence of concentration of leached heavy metals on the addition of wollastonite reinforcement into the AMSs. There is no dependence in leaching of Cr and Cu. Increasing addition of the wollastonite into the AMSs positively influences the ability of AMSs to fix Zn, Ni and Ba. The highest decrease in leaching shows Ba. This can be explained, that Cr and Cu are probably fixed in AMSs not only by physical encapsulation, but they can be chemically bonded to the structure. On the contrary Ba, Ni and Zn are mainly fixed by physical encapsulation. The addition of wollastonite improves mechanical properties and solidity of AMSs, so it can also improve physical encapsulation of heavy metals. The best properties show AMS with 10% addition of wollastonite.

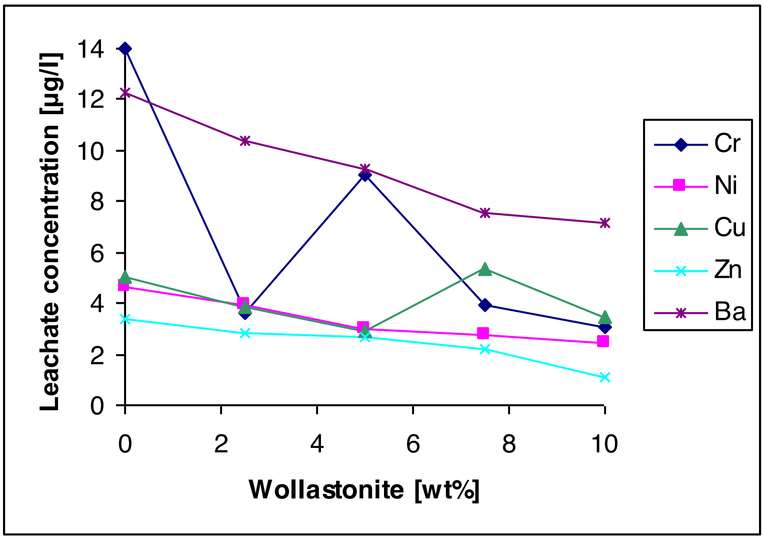

Fig. 3. Concentration of heavy metals in leachates from AMSs

CONCLUSION

Alkali activated AMSs has ability to fix and immobilize heavy metals. The addition of wollastonite to AMSs improved mechanical properties and also fixation of some heavy metals. Results showed, that releases of Ba, Ni and Zn from AMSs decreased with increasing addition of wollastonite in AMSs. Physical encapsulation is supposed to be main mechanism of fixation of these metals. On the other hand the addition of wollastonite had no influence on fixation of Cu and Cr. Cu and Cr suppose to be fix in AMSs both by physical encapsulation and chemical bonds. All heavy metals were presented in leachates only in a trace concentration. Phase composition is similar in all AMSs. Main crystalline phases are quartz, mullite, ankerite, akermanite, calcite, merwinite, anatase and wollastonite. XRD determined significant amorphous content.

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