Application of fly ash /granulated blast-furnace slag cementing material for immobilization of Pb2+

Li Chao[1], Zhao Feng-qing[1,2,*]

[1] Department of Chemical Engineering, Hebei University of Science & Technology, Shijiazhuang, 050018, China
[2] Hebei Engineering Research Center of Solid Waste Utilization, Shijiazhuang, 050018, China

Abstract. Based on activation and synergistic effect among various materials, a low-cost cementing material, FGC binder, was prepared by using fly ash, granulated blast-furnace slag (BFS), carbide slag and compound activator. The results showed that the immobilization efficiency of FGC binder for Pb^{2+} is higher than that of OPC cement. The hydration products and mechanism of immobilization were analyzed by using XRD. The major products of FGC binder are C-S-H, C-A-H, ettringite and zeolite-like materials. Under the experimental conditions, the Pb2+ curing efficiency of FGC binder is 1.04 ~ 1.24 times that of ordinary Portland cement.

1 Introduction

At present, an effective method to deal with Pb^{2+} contained waste is cement immobilization [1-3]. However, OPC cement generally has poor immobilization effect on lead-containing waste, resulting in a high exudation rate of Pb^{2+}. In addition, the cost and carbon dioxide emission related with cement production is high, and the application is limited. It is imperative to develop high-performance and low-cost cementing material for this purpose [4-6].

The main approach to reduce the cost of cementitious materials is to maximize the use of industrial waste [7-9]. Fly ash is a fine particulate solid waste with pozzolanic properties. Under certain conditions, when fly ash is mixed with lime and other alkaline substances, hydrated calcium silicate, ettringite and zeolite substances form in the hardened paste, resulting in bonding strength [10-12]. Another industrial by-product is BFS in iron-making process. Just as cement, BFS has undergone a similar high temperature process. Its main components are di-calcium silicate, tri-calcium silicate and RO phase, which have potential cementing activity. Experiments showed that there is a certain synergistic effect between fly ash and granulated BFS in hydration. The synergistic combination of both materials can help to improve the performance of cementing materials and reduce cost [13-15].

In this study, fly ash, granulated BFS and carbide slag are used as the main raw materials to prepare FGC binder. The performance of FGC binder in immobilization of Pb^{2+}, instead of ordinary Portland cement, is investigated and the hydration products are analyzed.

2 Experimental

2.1 Materials

Anhydrous sodium sulphate and anhydrous calcium chloride are bought from market. CF activator is provided by Hebei Zhongke Environmental Protection Co. Ltd. Modified gypsum is the desulfurized gypsum calcined at 650-700 ℃. OPC cement (42.5#), Fly ash, BFS, carbide slag, tailings are provided by Shijiazhuang Jingxing Construction Material Corp. Ltd. Table 1 shows the main chemical compositions of some raw materials.

Table 1. Main chemical composition of raw materials（%）.

Material	SiO_2	MgO	CaO	Al_2O_3	Fe_2O_3	SO_3
Fly ash	49.82	0.66	5.96	33.90	4.40	2.05
BFS	39.05	8.47	30.98	2.53	13.65	—
Modified gypsum	2.05	1.20	42.37	44.45	0.35	—
Carbide slag	3.82	0.14	92.02	2.72	0.50	—
Tailings	64.92	3.51	12.05	6.10	9.76	—

2.2 Method

2.2.1 Preparation of samples

In order to study the effect on Pb^{2+} immobilization, pure lead nitrate was dissolved in deionized water to prepare lead nitrate solutions of different lead concentrations, which is mixed with FGC binder to prepare lead cured samples according to GB / T17671-1999. The control samples with P•O 42.5 ordinary Portland cement are also prepared in the same method.

2.2.2 Leaching test

[*] Corresponding author: zhaofq3366@126.com

© The Authors, published by EDP Sciences. This is an open access article distributed under the terms of the Creative Commons Attribution License 4.0 (http://creativecommons.org/licenses/by/4.0/).

Leaching test was performed in reference to HJ557-2010 (Solid waste-Extraction procedure for leaching toxicity-Horizontal vibration method). Put 100 g paste sample into 2L extraction flask. Then the extractant was added in solid-liquid ratio of 10: 1 ($L\cdot kg^{-1}$). After the extraction flask was tightly capped, it was fixed on the reciprocating horizontal oscillator and shaken at room temperature for 8 hours. During the shaking process, the extraction bottle was opened in a fume hood at regular intervals to release excessive pressure caused by gas generation and allowed to stand for 16 h. A vacuum filter was used to collect leachate for further analysis.

2.2.3 Determination of Pb^{2+} and hydration products

The lead content in leachate was determined by UV1900 UV spectrophotometer. The mineral composition of FGC cement after hydration was determined by D/ MAX2500PC X-ray diffractometer.

3 Results and discussion

3.1 Proportioning of FGC Binder

On the basis of single factor experiment, CF activator (A), sodium sulphate (B), calcium chloride (C) and modified gypsum (D) are used as design variables, the mechanical strength of the binder being the response value. Therefore, the response surface analysis experiment of 4 factors and 3 levels is designed, to optimize the composition of compound activator. The result is obtained: CF activator 1%, sodium sulphate 1.5%, calcium chloride 0.51%, and modified gypsum 6%, thereby obtaining the proportioning of FGC binder [15]: compound activator 10 %, carbide slag 8 %, slag 57.4 % and fly ash 24.6 %.

3.2 Immobilization characteristics of Pb^{2+}

In reference to HJ557-2010, the performance of FGC binder and OPC cement for Pb^{2+} immobilization were tested. See Table 2.

Table 2. Immobilization of Pb^{2+} with different binder.

Binder	Before curing/ ($mg\cdot L^{-1}$)	After curing/ ($mg\cdot L^{-1}$)	Immobilization efficiency ratio (%)
FGC binder	0.5	0.2260	1.24
	1.0	0.3360	1.06
	1.5	0.6211	1.04
	2.0	0.4474	1.24
	2.5	0.7020	1.05
Portland cement	0.5	0.2786	1
	1.0	0.3755	1
	1.5	0.6528	1
	2.0	0.7518	1
	2.5	0.7864	1

Note: Immobilization efficiency ratio is the ratio of the solidified Pb^{2+} amount with FGC binder and that of OPC cement.

As can be seen from Table 5, FGC binder is superior to ordinary Portland cement in immobilization of Pb^{2+}. Under the experimental conditions, the Pb^{2+} curing efficiency of FGC binder is 1.04 ~ 1.24 times that of ordinary Portland cement.

Compared with ordinary Portland cement, the FGC binder can reduce the cost of the cementing material by more than 30 %. Meanwhile, as the main raw materials are industrial waste (fly ash and carbide slag) and by-products (BFS), the use of FGC binder is favourable for reducing carbon dioxide emission.

4 Analysis of hydration products and Pb^{2+} Immobilization Mechanism

4.1 XRD analysis

It can be seen from the XRD spectrum of the hydration products in Figure 1 that at the hydration age of 3 days, the main hydration products are C-S-H gel, C-A-H gel and a small amount of ettringite (AFt). Besides, incomplete reaction of anhydrite, phase mullite and quartz diffraction peaks can also be observed. With the increase in hydration age, at the hydration age of 28 days, the hydration product C-S-H increases, C-A-H disappears with the enhancing in the diffraction peak of ettringite. At the same time, the diffraction peaks of zeolite (mordenite) appear [16].

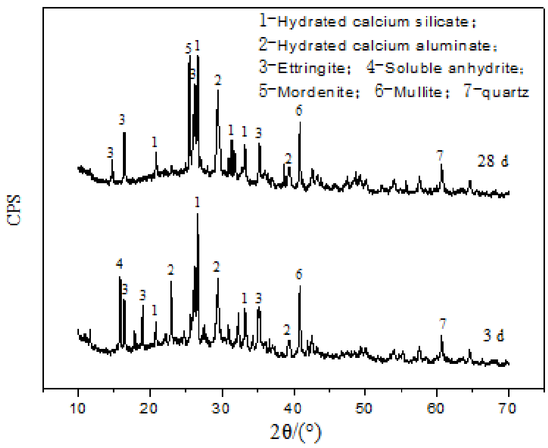

Figure 1. XRD spectrum of the hydration products.

4.2 Pb^{2+} immobilization mechanism

The immobilization performance of Pb^{2+} with FGC binder is closely related to the hydration products as C-S-H gel, C-A-H gel, ettringite and zeolites. During the hydration reaction, the active SiO_2 and Al_2O_3 dissolve rapidly in alkaline environment, and combine with Ca^{2+} in the system to form C-S-H and C-A-H. With the increase in hydration age, dense network structure gradually formed and Pb^{2+} is encapsulated in the inner part of these materials. At the same time, the modified gypsum and sulphates in the activator of FGC binder provide enough SO_4^{2-} for the system to react with hydrated C-A-H gel and $Ca(OH)_2$ to produce more ettringite than OPC cement. When SO_4^{2-} exists in the solution, Pb^{2+} can enter the lattice of ettringite to form Ca-Pb type of ettringite, with the chemical formula of $\{(Ca, Pb)_6[Al(OH)_6]_2 \cdot 3SO_4 \cdot 26H_2O\}$.

The zeolite structure of the material also contributes to the immobilization of Pb^{2+}. Zeolite is of three-dimensional grid composed of silica tetrahedron (or alumina tetrahedron) in which there are variety of micro-holes and channels of different size. These micro-holes and channels have physical adsorption for heavy metals. At the same time, the aluminum of '+3' valence state in the aluminoxane tetrahedron structure is bound to four oxygen atoms, so that the overall alumina tetrahedron exhibits negative charge. In order to balance the electrovalency, the cation (Na^+, K^+) is needed. The radius of Pb^{2+} happens to be between Na^+ and K^+, so it is easy to replace Na^+ and K^+ in the structure of alumina tetrahedron, achieving the effect of Pb^{2+} stabilization.

5 Conclusions

The synergistic effect of fly ash, slag, carbide slag and compound activator is the key to the performance of FGC binder. Compared with ordinary Portland cement, FGC binder can not only reduce the cost, consume large amount of solid wastes, but also reduce carbon dioxide emission.

Under the experimental conditions, the Pb^{2+} immobilization efficiency of FGC is 1.04~1.24 times that of ordinary Portland cement. That is to say, compared with ordinary Portland cement, FGC cement has stronger solidifying ability for Pb^{2+}.

XRD analysis shows that the hydration products of FGC binder are mainly C-S-H , C-A-H, AFt and zeolite like materials. The excellent performance of FGC binder for Pb^{2+} immobilization is due to the gelation physical encapsulation, physical adsorption and the requirement of chemical valence balance in structure of the hydration products.

References

1. GUO Xiao-lu, ZHANG Li-yan, SHI Hui-sheng. Effect factors and mechanism of solidification/stabilization of heavy metals by geopolymers [J].Journal of Function Materials, 2015 , 46(5): 5013-5018 (in Chinese)
2. ZHANG Yuan, LIU Ze, WANG Dong-min. Research progress of the stabilization of heavy metals using fly ash based geopolymer [J]. Bulletin of the Chinese Ceramic Society, 2016, 35(6):1751-1755(in Chinese)
3. QI Yi-jin, XU Zhong-hui, XU Ya-hong, et al. The effect on immobilization of MSWI fly ash with coal fly ash [J]. Environmental Science＆Technology, 2017,40(06):98-103 (in Chinese)
4. ZHANG Zhi-hong, GUO Jia-yu, GUO Guan-lin, et al. Engineering characteristics of stabilized contaminated soil with heavy metals by cement and SR[J]. Chinese Journal of Environment Engineering, 2017, 11(5):3172-3178(in Chinese)
5. MENG Jiu-ling, ZHANG Li-juan, CHEN Mian-biao, et al. Pollution Research of heavy metals from Soil-vegetable around a waste landfill plant[J]. Environmental Science & Technology, 2017 (3):182-189(in Chinese)
6. XIE Hua-ming, ZENG Guang-ming, LUO Wen-lian, et al. Stabilization /solidification of heavy metal contaminated sediment using cement, fly ash and DTCR[J]. Chinese Journal of Environment Engineering，2013, 7(3):1121-1127(in Chinese)
7. WANG Bin-yun, CHANG Jun, YE Zheng-mao，et al. Study on preparation of backfilling cementitious material with industrial waste [J].Metal Mine, 2011, 40(6):165-168 (in Chinese)
8. ZHOU Hui-qun, XIONG Jia-guo, ZHANG Yu-cai，et al. Research on characteristic of composite cement produced by industrial wastes [J].Journal of Wuhan University of Technology, 2008, 30(3):61-64(in Chinese)
9. Zhao F Q, Li H, Liu S J, Preparation and properties of an environment friendly polymer-modified waterproof mortar [J]. Construction & Building Materials, 2011, 25(5):2635-2638 (in Chinese)
10. ZHANG Lei, LV Xian-jun, JIN Zi-qiao. Study of application of fly ash to cemented backfilling in mine[J]. Mining R＆D, 2011(4):22-25(in Chinese)
11. LI Mao-hui, YANG Zhi-qiang, WANG You-tuan, et al. Experiment study of compressive strength and mechanical property of filling body for fly ash composite cementitious materials[J].Journal of China University of Mining＆Technology, 2015, 44(4):650-655(in Chinese)
12. YAN Pei-yu. Mechanism of fly ash’s effects during hydration process of composite binder [J]. Journal of the Chinese Ceramic Society, 2007, 35 (s1):171-175(in Chinese)
13. Zhao Feng-qing, Ni Wen, Wang Hui-jun, et al. Activated fly ash/slag blended cement [J]. Resources Conservation & Recycling, 2007, 52(2):303-313.
14. Zhao Feng-qing, Zhao Jing, Liu Hong-jie. Autoclaved brick from low-silicon tailings[J]. Construction & Building Materials, 2009, 23 (1):538-541.
15. Liu M C, Zhao F Q. Influencing Factors of Steel Slag/Blast Furnace Slag Based Solidifying Agents for Total Tailings Paste Backfill[C]// International Conference on Material Engineering and Application. 2016.
16. Liu Man-chao,Feng Yan-chao, Zhao Feng-qing, et al. Filling cementitious materials using steel slag and slag to produce fully-tailed sand [J].Iron and Steel,2017,52(07):89-95+103.