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ScienceDirect

Procedia Engineering 151 (2016) 162 – 169

Procedia Engineering

www.elsevier.com/locate/procedia

International Conference on Ecology and new Building materials and products, ICEBMP 2016

Immobilization of heavy metals in natural zeolite-blended cement pastes

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Abstract

The toxic wastes containing heavy metals are conducive to serious environmental problems at the contamination of water, air and soil. The ability of alumino-silicate systems to immobilize heavy metals from hazardous wastes by solidification process has been investigated since 1990s. Likewise, the efficiency of zeolites to fix heavy metals in their frameworks has relatively long been known. This paper deals with the investigation of efficiency of natural zeolite-blended cement pastes for the immobilization of heavy metals. Natural zeolite was used to partially replace ordinary Portland cement (OPC) at rates of 0% and 20% by weight of a binder and soluble heavy metal salts were added to a mixing water in an amount of 1% and 5% by weight of the binder. The flexural and compressive strength of the cement pastes were investigated, while the leachability of the heavy metals was determined. Additionally, scanning electron microscopy was performed to investigate the microstructure of the cement pastes, while the pore size distribution was analyzed with mercury intrusion porosimetry. The results indicated that the flexural and compressive strengths of the pastes containing 20 wt.% of natural zeolite were higher than those with OPC alone. It was also found out that the effectiveness in reducing the leachability of Ba, Cd, Cu, Ni and Pb was better for the natural zeolite-blended cement pastes.

Peer-review under responsibility of the organizing committee of ICEBMP 2016

Keywords: Heavy metals; immobilization; zeolite; cement paste; strength; porosity; microstructure

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Peer-review under responsibility of the organizing committee of ICEBMP 2016
doi:10.1016/j.proeng.2016.07.363

1. Introduction

With the increasing contamination of the natural environment, the problem of heavy metal immobilization becomes more and more significant. Various technologies have been develop to render a waste non-toxic or to reduce the potential for the release of toxic species into the environment. One of these technologies is solidification/stabilization (S/S) by cementitious binders. High pH of cement is effective in immobilizing many toxic metals by precipitation and sorption reactions and encapsulation of contaminated waste or soil [1,2]. Ordinary Portland cement (OPC) is widely used in these stabilization techniques due to its commercial availability and low cost. However, supplementary cementing materials such as granulated blast furnace slag, coal fly ash, condensed silica fume, rice husk ash and natural pozzolans are often used to replace OPC in S/S of wastes.

Slag-based cement effectively stabilizes chromates [3], which suggests that Cr^{VI} is reduced to Cr^{III}. The use of slag in cementitious binders can also greatly decrease the extracted amount of inorganic Hg compounds [3]. Many laboratory research projects and commercial applications have used Portland fly ash cement to stabilize/solidify hazardous, radioactive and mixed wastes [4,5]. A Portland cement/fly ash binder can be successfully use to solidify a heavy metal sludge containing Cd, Cr, Cs, Hg, Ni and Pb [5,6,7]. Other laboratory results [8] have indicated that the use of silica fume as an admixture in cement binder decreases the diffusion coefficient of contaminants very significantly, especially for organic contaminants, chromium and selenium [9,10]. Some results indicate that the use of silica fume is more effective than fly ash. Various investigators have used a cement-clay matrix to immobilize heavy metals in the composites, especially a cement-bentonite clay matrix [10,11], or a cement-kaolinite matrix [12]. Illite clay has proven to be an effective additive in cementitious waste forms for retarding the release of the soluble radioisotope ^{137}Cs [13].

Several natural pozzolans such as zeolites, calcined clays and volcanic ashes are used for production of natural pozzolan cements [14]. Only few publication can be identified on the direct use of blended or interground natural pozzolan cements for S/S. However, zeolites and several clay minerals have been widely used as sorbents for certain heavy metals [15–18]. Natural zeolites are microporous crystalline aluminosilicates containing clinoptilolite, with approximate empirical formula $(Ca, Fe, K, Mg, Na)_{3\text{-}6}Si_{30}Al_6O_{72}\cdot 24H_2O$, as the main mineral component. The structure of clinoptilolite is based on a 3-dimensional skeleton made of silicon tetrahedrons interconnected by oxygen atoms with a part of silicon atoms replaced by aluminum atoms. It forms through the devitrification of volcanic ash in lake and marine waters. It is the most studied of all zeolites and is widely regarded as the most useful. Clinoptilolite has a particularly high cation exchange capacity which provides many useful properties, mainly in chemical engineering as catalyst support [19], molecular sieves [20], or sorbents [21]. In civil engineering, their utilization as pozzolans dates back already to ancient times when the mixture of zeolites containing tuff and lime was used as hydraulic binder [22].

Ch. Napia et al. investigated the properties of solidified waste using OPC containing synthesized zeolite ($Na_{96}Al_{96}Si_{96}O_{384}$) and natural zeolite (clinoptilolite) as a binder [23]. They concluded that the use of zeolites to partially replace (20% and 40%) OPC as a solidification binder produced solidified waste with lower strength. However, it is more effectiveness in terms of leachability of Ni, Cr, Cu and Zn, than the use of OPC alone. The application of natural zeolite resulted in a better outcome than using synthesized zeolites.

Y.S. Ok et al. conducted studies to determine whether a granular material, formulated by mixing of zeolite with OPC, has a satisfactory efficiency for heavy metal removal from aqueous solutions [24]. Column experiments demonstrated that the material was more efficient and had a higher sorptive capacity than activated carbon for removing Cd, Cu, Pb and Zn from industrial wastewater.

W. Mozgawa et al. presented the results of application of natural clinoptilolite for immobilization of heavy metal cations (Ag^+, Pb^{2+}, Cd^{2+} and Cr^{3+}) from aqueous solutions and used zeolite to prepare autoclaved new building composites with relatively low bulk density (about 1.35 g/cm^3) and with the compressive strength on maximum value about 40 MPa [25]. The influence of heavy metal cations on the compressive strength values was insignificant (except for the Cr^{3+} ions). Amounts of Ag^+, Pb^{2+} and Cd^{2+} washed out with water from the prepared material were imperceptible.

The findings indicate that the natural zeolite (clinoptilolite) can be used as a cement replacement not only for its pozzolanic properties, but also as an effective adsorbent of heavy metals. This work presents applicability of natural zeolite to a mixture with OPC in order to immobilize heavy metals from a mixing water. In the work, tests of natural