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Immobilization of Heavy Metals for Building Materials in the Construction Industry – an Overview

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Abstract

Coal bottom ash (CBA) is a one of coal combustion by-products from the production of electricity in coal fired power plants. Although it is classified as hazardous waste and the usage of this material is very limited, it is also an alternative material that benefits the construction industry in replacing cement or fine aggregate at certain percentage. CBA contains heavy metals. The possibility of heavy metals fluxes from the concrete is of great concern as it may cause highly potential adverse environmental impacts especially if the concentration is at beyond regulated standards. This will stop the reuse of CBA in the construction industry and may lead to deficit to entities like power plants due to the high cost of CBA disposal. Thus, this paper presents an overview on the studies of heavy metals immobilization for building materials in the construction industry. Techniques applied for heavy metals immobilization during solidification and stabilization (S/S) process using alkali activation, hydration, thermal treatment and synthesis of dicalcium silicate (β-Ca_2SiO_4) were briefly described.

Selection and peer-review under responsibility of the scientific committee of the 6th International Conference on Recent Advances in Materials, Minerals & Environment (RAMM) 2018.

Keywords: immobilization; heavy metal; coal bottom ash; power plants; construction industry

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1. Introduction

Coal bottom ash (CBA) is coarse, granular, incombustible by-products that are collected from the furnaces bottom for generation and electric power at coal-fired power plants. CBA contains heavy metals and classified as hazardous substances [1]-[2]. CBA and coal fly ash (CFA) produced by the same electrical power plant have similar chemical composition. It is noted that, CBA has a lower loss on ignition compared to coal fly ash due to unburned coal particles [2].

Heavy metals are metallic elements that have a relatively atomic numbers and weight with high density of at least 5 times greater than water [3]. At certain level of concentration and period of exposure, heavy metals can be toxic because they are not metabolized by the body and tend to accumulate in the soft tissues. Heavy metals toxicity can result in deterioration of mental and central nervous system, poison of blood composition and corrosion of other vital organs. Minamata and Itai-itai diseases are caused by prolong exposure on heavy metals contamination [4]-[6].

Tenaga Nasional Berhad is a national electric utility industry in Malaysia subjected to mass production of CBA [7]. The practice of CBA reuse as building material is an elegant engineering solution for waste management [8]-[10] following the European Waste Framework Directive 2008/98/EC [11]. The legislated regulation requires waste to be managed without threatening human health and the environment (eg. water, air, soil, plants or animals, noise or odours). Apparently, the reuse of CBA will provide a sustainable electrical power generation in Malaysia.

However, possibilities of heavy metals fluxes from concrete may cause highly potential adverse environmental impacts. This will stop the reuse of CBA in the construction industries and may lead to deficit to entities like coal-fired power plants due to the high cost of CBA disposal. Thus, immobilization of heavy metal is vital. This paper presents an overview on heavy metals immobilization during solidification and stabilization (S/S) process using various techniques such as alkali activation, hydration, application of natural zeolite and thermal treatment for synthesis of dicalcium silicate (β-Ca_2SiO_4).

2. Heavy Metals Immobilization Techniques

This part presents descriptions of heavy metals immobilization during solidification and stabilization (S/S) process using techniques like alkali activation, hydration, application of natural zeolite and thermal treatment for synthesis of dicalcium silicate (β-Ca_2SiO_4).

2.1. Solidification and stabilization (S/S)

Solidification and stabilization (S/S) of heavy metals contaminated material (eg. sludge, industrial wastes) is required to reduce its toxicity, ease the handling preparation and transportation to landfill sites [12]-[13]. S/S has been recognized as the best demonstrated available techniques for 57 regulated hazardous wastes by the US EPA [14].

Solidification process involves in mixing wastes (liquid, semi-solid sludge or a powder form) with solidifying agents to provide physical binding of waste into monolithic form or granular material [15]-[16]. In this phase, chemical interaction between components is not necessarily happening [16].

Meanwhile, stabilization is a process of converting a toxic waste to a physically and chemically more stable form. This process alters hazardous waste chemically to produce less toxic or less mobile form [17]-[18]. It involves chemical interactions between waste and the binding agent.

Binding agents (mineral admixtures or chemical additive for stabilization methods) used in the S/S process are Ordinary Portland Cement (OPC), coal combustion products (eg. coal fly ash, coal bottom ash and boiler slag), pozzolanic material (eg. metakaoline and silica fume), natural pozzolan (zeolites), lime (calcium carbonate; $CaCO_3$), burnt lime (calcium oxide; CaO), cement kiln dust, calcium silicate hydrate (C-S-H) and gypsum (calcium sulfate dehydrate; $CaSO_4 \cdot 2H_2O$) [1].

Binding agents like metakaoline [19], natural zeolites [20], calcium silicate hydrate (C-S-H) [21] and dicalcium silicate (β-Ca_2SiO_4) [22] have been reported by other scholars for its good capacity of immobilization system for heavy metals.

Moreover, application of lime (calcium carbonate; $CaCO_3$) is not recommended because carbonation almost has no isolation effect on heavy metals [23]. Although Habib [4] claims that immobilization of heavy metals was found high with the usage of cementitious material (clay and lime) which was almost 99% (metal ions in the aqueous system), the heavy metals immobilization occurred were likely due to physicochemical properties of clay.

2.2. Alkali activation

Alkali activation is generic term used for reaction of a solid aluminosilicate under highly concentrated alkaline environment, to produce a hardened geopolymer binder [24]-[25]. The hardened geopolymer binder is based on a combination of hydrous alkali-aluminosilicate and / or alkali-alkali earth-aluminosilicate phases [24]. This definition may also apply to high-volume blends of pozzolans (siliceous and aluminous materials) or blast furnace slag with smaller quantities of Portland cement. This cementitious material is an amorphous or semi-crystalline in nature [26]. By principal, if the Portland cement is the main source of alkalinity, such cements are excluded from the definition of alkali-activation [24]. Geopolymer binder can provide comparable strength performance to traditional binders in practical applications due to its low permeability, long term durability to acid attack and has good immobilization system for heavy metals [27].

Pesonen [28] introduced recovered bio-fuel fly ash (REF-biofuel FA) using alkali activation technique. REF-biofuel FA contained of 50% REF (plastic (not polyvinyl chloride), carton, paper and wood collected from industrial and premises) and 50% biofuel (wood bark) from Finnish heat and electricity power plant, which uses a bubbling fluidized bed boiler to combust REF. According to Pesonen [28], the application of REF-biofuel FA was at the worst performance because the FESEM images showed that the mortar contained only Portland cement was less dense and had more loose material than the other mortars. This mortar could weather easily over time exposing the bioavailability of heavy metals. Simultaneous use of Portland cement and alkali activation would be the preferred S/S technique for immobilization of Barium (Ba), Copper (Cu), Lead (Pb) and Zinc (Zn) but not suitable for oxy-anionic elements like Chromium (Cr) [28].

Guo [23] addressed the behavior of Pb compound species depends on its chemical properties. Pb compound species that is soluble in alkaline solution will be converted to amorphous form and will be chemically bonded into the geopolymer gel. Meanwhile, the Pb compound species that inert to sodium hydroxide solution will be segregated from the binder and trapped by physical encapsulation [23].

Liu [29] reported that, municipal solid waste incineration bottom ash (IBA) contains metallic aluminum that will generate gas when in contact with cement paste. Alkali activation removes the metallic aluminum in IBA and minimizes aeration in IBA blended cement mortars. This treatment enhances pozzolanic properties of IBA and the resulting alkali-treated IBA possessed pozzolanic reactivity similar to coal fly ash. The research suggested that the alkali-treated IBA can potentially be used as supplementary cementitious materials for concrete production [29].

2.3. Hydration

Calcium silicate hydrate (C-S-H) [30] is the principal hydration product and primary binding phase in Portland cement [31]-[32]. C-S-H provides physical absorption and encapsulation due to micro-pores with low permeability that allows heavy metals immobilization mechanism within the matrix itself. C-S-H has a large number of structural sites available for cations and anions to bind. The C-S-H phase materials have ability to heavy metal ions immobilization. Immobilization mechanism for C-S-H includes sorption, phase mixing, substitution and precipitation of insoluble compounds. Żak and Deja [21] studied the C-S-H application for heavy metals immobilization and found that the degree of immobilization (Cadmium (Cd), Zinc (Zn), Lead (Pb) and Chromium (Cr) cations) was exceeded 99.96% [21].

2.4. Application of natural zeolite

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. Vyšvařil and Bayer [20] studied the 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 mixing water in an amount of 1% and 5% by weight of the binder. The results indicated that the flexural and compressive strengths of the pastes containing 20% (weight) of natural zeolite were higher than those with OPC alone. It was also found out that the effectiveness in reducing the leachability of Barium (Ba), Cadmium (Cd), Copper (Cu), Nickel (Ni) and Lead (Pb) was better for the natural zeolite-blended cement pastes. The concentration of Cu, Ni and Pb in these leachates was lower than the limit in classification of leachability (IIa) specified by the regulation of Ministry of the Environment of the Czech Republic (Cu < 5 mg/L, Ni < 4 mg/L, Pb < 10 mg/L). However, the natural zeolite-blended cement pastes are not suitable to immobilize Mercury (Hg^{2+}), Strontium (Sr^{2+}) and Zirconium (Zr^{2+}) ions [20].

2.5. Thermal treatment for synthesis of dicalcium silicate (β-Ca_2SiO_4)

Rice husk or rice hull is an agricultural waste containing organic (carbohydrates, cellulose) and inorganic components (10% of silica). Dicalcium silicate (β-Ca_2SiO_4) is the second most important component of commercial Portland cement. Dicalcium silicate exhibits five polymorphs, namely γ, β, α, α'_L and α'_H. The β phase has very good hydraulic properties that will help development of mechanical strength when comes into contact with water. Cement based material must have low permeability, high strength and chemical resistance to avoid leaching [33]. The utilization of β-Ca_2SiO_4 will give benefits to the environment, agricultural sectors, power plants, construction industry for its practicality to waste management for both biomaterial and hazardous wastes.

Romano and Rodrigues [22] described the synthesis of β-Ca_2SiO_4 from rice hull with an insertion of heavy metals (copper and cadmium) for heavy metals leaching analyses. Silica was obtained from burning rice hull at 600℃ [22]. The dehydration/dihydroxylation of the chemical reaction observed in the ranged of 420℃ to 540℃ and 680℃ to 820℃ [34]. The first thermal event is known responsible for the silicate synthesis [35]-[37]. Meanwhile, at the second thermal event were due to the insertion of the remaining atoms into the structure of the intermediate silicate (synthesis of calcium silicate). The silica structure can uphold copper (Cu) and cadmium (Cd) up to 10%. The synthesis was a combination of Sonochemical and solid-state chemical reactions and completed at 800℃ which means this geopolymer cement scores more compared to commercial cement that requires 1500℃. Based on energy dispersive X-ray spectroscopy, the chemical elements analyses of dicalcium silicates added with Cu (2%) and Cd (2%) showed comparable experimental results to theoretical values [22].

3. Conclusion

Alkali activation, hydration, application of natural zeolite and thermal treatment for synthesis of β-Ca_2SiO_4 are among the techniques published in solidification and stabilization (S/S) process for heavy metals immobilization. In general, the application of β-Ca_2SiO_4 seems to be promising as it employs agricultural waste and efficient at retaining heavy metals ion from leaching. In spite of that, the aforementioned techniques described in this overview are fairly recommended for further investigation on application of CBA in construction industry. The reuse of CBA will not only provide a sustainable coal-fired electricity power in the country but also can be implemented in hazardous waste management towards constructive approach.

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