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Cement mortars hybridized with zeolite and zeolite-like materials made of lignite bottom ash for heavy metal encapsulation

Kedsarin Pimraksa [a,b,*], Prinya Chindaprasirt [c], Tanwalak Huanjit [a], Clarence Tang [d], Tsugio Sato [e]

[a] Department of Industrial Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand
[b] Materials Science Research Center, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand
[c] Sustainable Infrastructure Research and Development Center, Department of Civil Engineering, Faculty of Engineering, Khon Kaen University, 40002, Thailand
[d] Siam Research and Innovation Co., Ltd., Saraburee 18260, Thailand
[e] Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 980-8577, Japan

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Bottom ash (BA) from Mae Moh lignite power plant was used to synthesize zeolite and zeolite-like materials. Low temperature synthesis (100–110 °C) was completed using SiO_2 to Al_2O_3 with molar ratios of 2.94 and 2.92, respectively. Factors investigated that affect synthesis include particle size distribution, pretreatment of BA, concentration of alkali solution and liquid to solid ratio. The synthesized product qualities were characterized by mineralogical composition, morphology, specific surface area, pore size, pore volume and cation exchange capacity. Natrolite-K zeolite (NAT-K) was obtained with a solution of BA and 7 M KOH. Zeolite-like material (potassium aluminosilicate hydrate: KASH) was obtained using very fine BA and 9 M KOH solution. The NAT-K, KASH and BA powders were used to replace type I Portland cement at 0, 5, 10, 20 and 30% by weight to produce composite materials for heavy metal encapsulation. The compressive strength and bulk density of the NAT-K- or KASH-hybridized cement mortars were tested at 1, 7 and 28 days. The heavy metal encapsulation capacity was also tested using the 28-day cement mortar containing either 5 wt% NAT-K or KASH adsorbed with Cr, Ni and Cd ions. The results showed that 5 wt% of NAT-K could improve early strength of cement mortar and the 28-day specimens with 5–10 wt% of NAT-K replacement had compressive strength similar to that of the normal cement mortar. The NAT-K and KASH encapsulate Cr, Ni and Cd ions in the structures of cement mortar matrices more than 97%.

1. Introduction

Worldwide, the coal industry annually produces several million metric tons of by-products such as fly ash (FA), bottom ash, boiler slag and flue gas desulfurization material (Ríos and Williams, 2008). The yearly output of lignite bottom ash (BA) produced at the Mae Moh power plant in Thailand is approximately 0.8 MT, and it is discarded in landfills as solid wastes. The BA needs proper grinding to obtain a reasonably fine particle size for use as pozzolan (Sathonsaowaphak et al., 2009). The BA from the coal industry contains heavy metals and is harmful to the environment. It is often used as a low-cost replacement for more expensive sand in the production of concrete blocks. In many countries, it is used as a base course in road construction (Cheriaf et al., 1999). Synthesis of zeolites from BA is one of the promising ways to create a more environmentally friendly use of the unused solid waste. One of the good examples is synthesis of zeolite A from BA obtained from coal-fired boilers within the paper industries in Thailand (Chareonpanich et al., 2011). The BA obtained from the paper industry contains more crystalline silica content than that obtained from steam boilers at Mae Moh power plant. Moreover, due to the different coal source, their chemical and mineralogical compositions are not similar. In this study, low temperature zeolite synthesis from lignite BA obtained from Mae Moh power plant is investigated.

Zeolite has a crystalline aluminosilicate structure with a SiO_4 tetrahedra framework. Parts of the structure are substituted with AlO_4 tetrahedra which require charge-compensating cations. These tetrahedral units are connected with each other as repeating units forming 3-D porous framework structures in a molecular size (Kadono et al., 2008). The advantage of zeolites over resins, apart

* Corresponding author. Department of Industrial Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand. Tel.: +66 819506645; fax: +66 53892262.
E-mail addresses: kpimrak.p@cmu.ac.th, kedsarin.p@cmu.ac.th (K. Pimraksa).

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from their much lower cost, is their ion selectivity. Because of the characteristics of zeolite structures and their adsorbent properties, they have been applied as chemical sieve, water softener and adsorbents (Hui et al., 2005). Various types of zeolites can be synthesized from different source materials and under different conditions. BA, like fly ash, is considered as a starting material because of its promising chemical and mineralogical compositions and abundant availability. Although coming from the same source, mineralogical compositions of BA are totally different from FA due to their combustion temperature. For example, FA contains inert material such a mullite which is not easy to be dissolved (Chindaprasirt and Pimraksa, 2008). However, BA has been utilized less because its particle size is large and grinding is required to reduce the particle size and to increase its reactivity.

In previous work, we found that the optimum refluxing conditions for zeolite synthesis from Mae Moh BA with $d_{[4,3]}$ of 23 micron and Si/Al molar ratio of 1.5 or SiO_2/Al_2O_3 ratio of 3.06 were 5 M KOH solution, liquid to BA ratio (L/S ratio) of 8 and reaction time of 24 h (Pimraksa et al., 2010). This resulted in the formation of a zeolite-like material in the form of potassium aluminum silicate hydrate (KASH) ($KAlSiO_4.15H_2O$) as a main composition and phillipsite-K ($K_2[Al_2Si_{2.2}O_{6.4}].2H_2O$) as a minor phase. When 3 M NaOH solutions were used, there was no zeolite formation. This research, therefore, aims to study further the synthesis of zeolite phases from Mae Moh BA to discover more potential uses of BA for heavy metal encapsulation. Various factors affecting this synthesis, including KOH concentration, liquid to solid ratio, iron content and particle size distribution of BA were investigated. The quality of the synthesized zeolite is characterized in terms of mineralogical composition, microstructure, pore size, pore volume and CEC.

There are many kinds of zeolites suitable for use in encapsulation. Among those that perform best for ion exchange are the ones with a large number of negative charges in the framework. For ion adsorption capacity, zeolites with a large number of cavities and large surface areas in the framework works best (Alex and Dong-ke, 2003). Zeolite-like materials have also been considered for adsorption applications because of their high specific surface area (Gao et al., 2009). Waste encapsulation is now in high demand as huge amount of toxic industrial wastes have been disposed of in landfills. Therefore, it is very important to find a high potential waste encapsulation material. Zeolites possess some pozzolanic properties and they can be used as a pozzolanic material by blending with normal cement (Poona et al., 1999; Jana, 2007). They contribute to concrete strength mainly through the pozzolanic reaction, similar to other widely used pozzolans such as silica fume, metakaolin and fly ash. The zeolite is a meta-stable phase that readily undergoes dissolution under basic conditions with different manner from BA and one of the most reactive pozzolans such a metakaolin due to their molecular structures (Pelisser et al., 2012). The demand for such supplementary cementing materials has been markedly increasing in order to reduce cement production to cope with global warming (Yilmaz et al., 2007). In addition to the strength improvement, zeolites, when present in cement and concrete structures, also play an important role in the encapsulation of several types of heavy metals (Atkins et al., 1995; Olmo et al., 2003; Ok et al., 2007). Both the pozzolanic reactivity and waste encapsulation of zeolites are thus of much interest to cement chemists, concrete technologists and environmental scientists. Therefore, this study aims to use BA obtained from the Mae Moh power plant (Thailand) as a starting material for zeolite synthesis and to find the optimum condition for synthesis. The pozzolanic reactivity of the synthesized zeolite is then studied and compared with the ground BA. A comparison in pozzolanic reactivity of BA synthesized zeolites and BA was performed in this study for the first time. Not only pozzolanic reactivity, the heavy metal (chromium (III), nickel (II) and cadmium (II)) encapsulation ability of the zeolite materials and zeolite-like-hybridized cement mortars is also studied. It is commonly known, that Cr, Ni and Cd ions are typically found in electroplating wastes (Telukdarie et al., 2006). Moreover, Cr ion is one of the carcinogenic metals which can be very harmful to the ground and water, seriously concerned in many countries which run a leather industry as their main market. Active absorbers for those heavy metal removal are, therefore, very important for mitigation of the negative impact (Giannetti et al., 2004). The knowledge obtained from this study will no doubt lay a solid groundwork for the conversion of lignite BA into zeolite and zeolite-like materials, for waste encapsulation using zeolite-hybridized cement material as well as for the utilization of BA in a high potential way.

2. Experimental methods

2.1. Materials

Lignite BA used for zeolite synthesis was obtained from the Mae Moh power plant. The BA was ground by ball milling to obtain various particle size distributions. The BA volumetric mean diameter ($d_{[4,3]}$) after grinding for 12, 24 and 48 h were 13.3, 6.6 and 3.0 μm, respectively. The ground BA was treated to remove the iron compound using the looped magnetic separator until the iron content was lowered by 50%. The chemical composition of BA determined using X-ray fluorescence spectrometry (XRF) is shown in Table 1. BA was stirred in 5–9 M KOH solutions for 24 h in a 25 °C room to investigate the concentrations of reactive cations (Si^{4+} and Al^{3+}). The investigated condition, shown in Table 2, was determined to be the best condition based on the results of a previous study (Pimraksa et al., 2010). The reactive ions were measured using Atomic Absorption Spectroscopy (AAS). The total content of heavy metals contained in BA and type I Portland cement were determined using AAS and Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) carried out in accordance with ASTM D3688-78.

2.2. Zeolite synthesis

The as-received BA and the BA from which iron was removed BA, with SiO_2/Al_2O_3 molar ratios of 2.94 and 2.92, respectively, were used as starting materials. The conditions of zeolite synthesis are shown in Table 2. The effects of ground BA particle size, iron oxide removal from BA, KOH concentration and liquid to solid ratios on zeolite quality were studied. It was shown that the zeolite phase obtained from the refluxing method was better than that from the hydrothermal method (Pimraksa et al., 2010). Therefore, the refluxing method was selected for synthesis. The ground BA was stirred with the KOH solution for 30 min to allow the dissolution of silicate and aluminate ions. Refluxing was carried out at 100–110 °C for 24 h. The reaction time and temperature were taken from

Table 1
Chemical compositions of as-received BA and magnetically treated BA.

Compositions	As-received BA (%)	Magnetic treated BA (%)
SiO_2	38.69	41.19
Al_2O_3	22.25	24.19
Fe_2O_3	13.75	6.89
CaO	13.16	13.14
MgO	2.83	2.62
Na_2O	0.53	0.73
K_2O	1.97	2.25
TiO_2	0.39	0.38
SO_3	0.82	0.71
P_2O_5	0.16	0.16
LOI	5.19	3.50