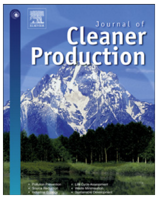
Journal of Cleaner Production 192 (2018) 782–789

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro



Characterization of calcium-containing phases in alkali-activated municipal solid waste incineration bottom ash binder through chemical extraction and deconvoluted Fourier transform infrared spectra

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ARTICLE INFO

Article history:
Received 27 October 2017
Received in revised form
12 March 2018
Accepted 5 May 2018
Available online 7 May 2018

Keywords:
Alkali activation
Municipal solid waste incineration bottom ash
Calcium silicate hydrate
Fourier transform infrared spectroscopy
Spectral subtraction
Deconvolution

ABSTRACT

It has been reported that municipal solid waste incineration bottom ash (IBA) can be a potential precursor for alkali-activated materials (AAM). This study investigates chemical composition and structure of calcium-containing phases in an alkali-activated IBA (AA-IBA) binder by a novel combination of selective chemical extraction and Fourier transform infrared (FTIR) spectral subtraction and deconvolution. Salicylic acid/methanol extraction is used to isolate the calcium-containing phases from the AA-IBA binder. X-ray powder diffraction and FTIR spectroscopy are used for sample characterization. Spectral subtraction is carried out to assign FTIR peaks of calcium-containing phases and deconvolution is used to discover various individual Si-O peaks hidden in the single broad FTIR peak. Results show that the AA-IBA consists of about 20 wt.% calcium silicate hydrate (C-S-H) and pirssonite ($Na_2Ca(CO_3)_2 \cdot 2H_2O$). Chemical structure of the C-S-H in AA-IBA is found to be broadly similar to that in aged Portland cement paste, with possibly a higher degree of polymerization of the silicate chains. The methodology established in this study is significant and can greatly benefit the development of sustainable construction materials because many industry by-products and solid wastes are Si and/or Al rich, which could be potential AAM precursor.

1. Introduction

Incineration has been widely adopted in waste management as an effective means to reduce the mass and the volume of municipal solid waste. This strategy is used especially in land scarce countries such as Japan and Singapore, as incineration greatly reduces the demand for landfill space. Furthermore, green energy can be generated through waste-to-energy facilities. It was reported that in 2005, 4.8% of the electricity and 13.7% of domestic heat in Denmark were produced from waste combustion (Bosmans et al., 2013). Two types of ash residues are generated after waste incineration, i.e. incineration fly ash (IFA) and incineration bottom ash (IBA). IBA accounts for 80–90% of the total ash by weight and is much less toxic than IFA (Chimenos et al., 1999; Li et al., 2012). Therefore, IBA has greater potential for further utilization. It has been reported that IBA may be used as filler for road construction (Hjelmar et al., 2007), as raw material for cement production (Krammart and Tangtermsirikul, 2004) and zeolites and tobermorite synthesis (Jing et al., 2007; Penilla et al., 2003), as substitute for aggregates in concrete production (Kuo et al., 2013), and as adsorbent for heavy metal removal (Zhang et al., 2011). The focus of this paper is on a new and different IBA utilization as an engineering material.

Alkali-activated materials (AAMs) refer to reaction products of aluminosilicate powder with alkaline solution, i.e. binders produced by the reaction of an alkaline solution with a solid silicate powder rich in calcium silicate or aluminum silicate (Duxson et al., 2007a; Provis, 2014). AAMs show comparable mechanical strength and durability to Portland cement and may be considered as an alternative binder for manufacturing concrete. Their environmental

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https://doi.org/10.1016/j.jclepro.2018.05.049
0959-6526/

impact is much reduced compared to Portland cement concrete (Shi et al., 2011) as many industrial by-products such as coal fly ash and blast furnace slag can be used as AAM precursors (Duxson et al., 2007a).

Qiao et al. (2008) used lime to activate a thermally treated IBA and found a mixed carbonate-AFm phase as the reaction product. In other studies, NaOH and sodium silicate solution were used to activate metakaolin-IBA blends (Lancellotti et al., 2013, 2014), with metakaolin used to adjust the Si/Al ratio for geopolymer formation. IBA was also blended with slag or fly ash for cleaner AAM production (Gao et al., 2017; Wongsa et al., 2017). In the work of Lancellotti et al. (2015), pre-treated IBA (3-month-aging followed by metal removal through magnetic and eddy current separation) was activated by concentrated NaOH and sodium silicate solutions to develop a geopolymer. In another study, Chen et al. (2016) demonstrated a novel approach of using untreated IBA as a gas-foaming agent and AAM precursor for the synthesis of an aerated AAM binder. In that study, untreated IBA was activated by a mixture of sodium hydroxide and sodium silicate solutions to produce lightweight binders with density as low as 600 kg/m^3, although without clearly defining their chemical structures.

The reaction product of AAM could be calcium silicate-based hydrates, e.g. C-(A)-S-H, for precursors rich in calcium or zeolite-like polymers, e.g. geopolymer (N-A-S-H), for precursors lacking calcium (Li et al., 2010; Provis, 2014). These two types of gels can co-exist in an AAM (Bernal et al., 2010; Puligilla and Mondal, 2015). Presence of different gel in AAM binder greatly alter the performance including carbonation, acid resistance and fire resistance (Duxson et al., 2007b; Shi et al., 2011). It has been reported that a mixture of the two gels with proper proportions resulted in improved durability as compared to binders with a single gel (Bernal et al., 2010; Zhuang et al., 2016). Thus, understanding gel composition of an AAM is of great importance and interest.

This study proposed a methodology to characterize and to quantify the calcium-containing phases in a complex mixture, e.g. alkali-activated IBA (AA-IBA) in the current study. The calcium-containing phases in an AA-IBA binder were examined through a selective chemical extraction and FTIR spectral analysis. Salicylic acid/methanol (SAM) extraction was engaged to dissolve certain calcium-containing phases (e.g. calcium-(alumino)-silicate-hydrate, C-(A)-S-H) from the AA-IBA binder. X-ray powder diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy were used to characterize samples before and after SAM extraction. FTIR spectroscopy has been used to investigate the gel composition in AAMs (Bernal et al., 2010; Criado et al., 2007). Spectral subtraction was performed to assign FTIR peaks of calcium-containing phases dissolved by the SAM extraction. Deconvolution was used to identify the various individual Si-O stretching peaks that make up the single broad FTIR peak. The deconvoluted Si-O peaks were then assigned to silicate molecules with various nanostructural connectivities to yield insights into the chemical structures of silicate phases. Potential presence of non-calcium-containing phases (e.g. sodium-alumino-silicate-hydrate, N-A-S-H) in the AA-IBA is recognized. This will be probed by means of ^{29}Si and ^{27}Al nuclear magnetic resonance (NMR) spectroscopy and will be reported in a companion study.

2. Materials and methods

2.1. Synthesis of alkali-activated IBA binder

The IBA used in this study was collected from a local waste-to-energy incineration plant, which is a mass burn facility capable of treating 800 tons of solid waste and generating 22 MW of energy per day. An advanced grate burning system with a multi-stage grate furnace is used for waste incineration at a burning temperature of 800–1000 °C. After incineration, water is splashed on the bottom ash to prevent release of dust and ferrous metals are recovered through magnetic separation. No other post combustion recoveries are used in the facility. The resulting IBA has a granular size ranging from micrometers to decimeters.

The IBA was collected once every two weeks over a period of 5 months. After each collection, IBA was oven dried at 60 °C for 3 days to remove surface moisture. The IBA collected over 5 months was combined and ground in a ball mill for 30 min followed by sieving to ensure all particles were smaller than 150 μm. Fig. 1 shows the particle size distribution of the IBA powder and Table 1 summarizes the chemical composition of IBA determined by means of a wavelength-dispersive X-ray fluorescence (WDXRF, Bruker SRS 3400) with an accuracy of 0.3%. A sensitivity library, i.e. the relationship between the theoretical and measured intensity of an element, was used for the quantitative analysis. Loss on ignition (LOI) for IBA heated to 750 °C was determined following ASTM D7348 (2013). As can be seen, IBA used in this study contains high amount of silicon and calcium, similar to the blast furnace slag, suggesting IBA may be a potential AAM precursor. Other major elements include Fe and Al, and these oxides together with SiO_2 and CaO exceed 70% of the total weight of IBA. Trace elements such as Cu, Cr, and Mn were found in IBA. Leaching of heavy metals from AA-IBA was generally reduced by orders of magnitude as compared to that from IBA as reported by Chen et al. (2016).

The activating solution was prepared by mixing sodium hydroxide solution (8 M) and sodium silicate solution at a mass ratio of 1:2. The sodium silicate solution was a commercial product (industrial grade, supplied by International Scientific Pte Ltd) with 9.65% Na_2O and 29.16% SiO_2. The sodium hydroxide solution was prepared using NaOH pellets (analytical grade, supplied by Merck) and distilled water. To prepare the AA-IBA binder, IBA was mixed with the activating solution at a liquid-to-solid ratio of 1.0 by weight in a planetary mixer for 5 min. Fresh pastes were poured into 50 mm cubic molds, sealed in plastic bags, and cured in oven at 75 °C for 3 days before demolding.

2.2. Tests

Compressive tests in accordance with ASTM C109/C109M (2016) were conducted to determine the strength of AA-IBA binder at the age of 3 days and dry density of the cubic specimens were recorded before the compressive test. To evaluate the hydrolytic stability of the AA-IBA binder, the cubic specimen was placed into boiling water for 20 min to check its integrity (Davidovits, 2008).

The SAM extraction was used to dissolve phases such as calcium silicates, calcium silicate hydrates, calcium hydroxides and free

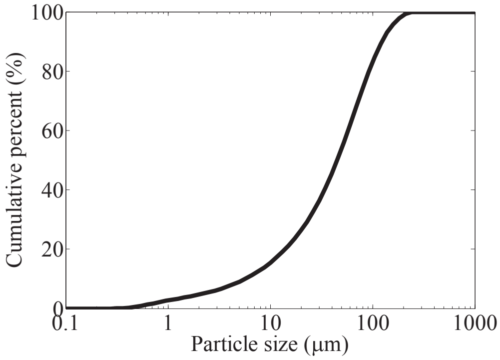

Fig. 1. Particle size distribution of ground IBA powder.