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Toxicity mitigation and solidification of municipal solid waste incinerator fly ash using alkaline activated coal ash

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ABSTRACT

Municipal solid waste (MSW) incineration is a common and effective practice to reduce the volume of solid waste in urban areas. However, the byproduct of this process is a fly ash (IFA), which contains large quantities of toxic contaminants. The purpose of this research study was to analyze the chemical, physical and mechanical behaviors resulting from the gradual introduction of IFA to an alkaline activated coal fly ash (CFA) matrix, as a mean of stabilizing the incinerator ash for use in industrial construction applications, where human exposure potential is limited. IFA and CFA were analyzed via X-ray fluorescence (XRF), X-ray diffraction (XRD) and Inductive coupled plasma (ICP) to obtain a full chemical analysis of the samples, its crystallographic characteristics and a detailed count of the eight heavy metals contemplated in US Title 40 of the Code of Federal Regulations (40 CFR). The particle size distribution of IFA and CFA was also recorded. EPA's Toxicity Characteristic Leaching Procedure (TCLP) was followed to monitor the leachability of the contaminants before and after the activation. Also images obtained via Scanning Electron Microscopy (SEM), before and after the activation, are presented. Concrete made from IFA, CFA and IFA-CFA mixes was subjected to a full mechanical characterization; tests include compressive strength, flexural strength, elastic modulus, Poisson's ratio and setting time. The leachable heavy metal contents (except for Se) were below the maximum allowable limits and in many cases even below the reporting limit. The leachable Chromium was reduced from 0.153 down to 0.0045 mg/L, Arsenic from 0.256 down to 0.132 mg/L, Selenium from 1.05 down to 0.29 mg/L, Silver from 0.011 down to .001 mg/L, Barium from 2.06 down to 0.314 mg/L and Mercury from 0.007 down to 0.001 mg/L. Although the leachable Cd exhibited an increase from 0.49 up to 0.805 mg/L and Pd from 0.002 up to 0.029 mg/L, these were well below the maximum limits of 1.00 and 5.00 mg/L, respectively.

1. Introduction

According to the EPA the US produced around 243 million tons of MSW in 2009. Of the 243 million tons, 82 million were recycled (including composting), and 29 million were incinerated to produce electricity, through a process known as Waste-to-Energy (WTE) (EPA, 2009). Although, MSW management has changed significantly over the past four decades, with the replacement of open dumps and polluting incinerators for well-designed landfills and highly efficient WTE facilities, some challenges remain. In WTE processes the heat released by the incineration is recovered to produce electricity, while reducing the volume of the MSW by up to 95% by volume (Siddique, 2008). Although the volume of MSW is greatly reduced, several volatile metals and organic compounds (such as dioxins and furans) are concentrated in the ash that results from the incineration, generating a much smaller but toxic waste stream. Toxicity can be associated the presence of heavy metals (Pb, Cd, Cr, Mn, Hg) and organic pollutants (dioxins and furans) in coal fly ash produced by MSW incinerators (Lancellotti et al., 2010). The toxicity levels in IFA, which is the part of waste stream that is captured from the flue gases by pollution control devices, is typically more toxic than the bottom ash, which is collected at the bottom of the combustion chamber. IFA may contain high levels of heavy metals and other compounds that can easily be leached into the ground or released into the atmosphere, posing a potential danger to humans and the environment, thus this material is typically classified as a hazardous waste (Siddique, 2008; Lancellotti et al., 2010; Ferreira et al., 2003). In addition, IFA is a cause of concern because of limited sites for its disposal.

The Soilroc process is one of the most widely used techniques to reduce the toxicity of IFA. The process starts with the production of monosilicic acid by adding silica reagent to an acidic liquid waste, the IFA is then introduced to the monosilicic acid. Subsequently

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alkalis are added to raise the PH from 1.5 to 11 which causes the metal silicates to precipitate and the monosilicic acid to polymerize and form insoluble bulk mass. The resulting material may be filtered or solidified with OPC (Ezell and Suppa, 1989). Although the IFA is effectively treated, it does not represent the best stabilization solution, as it generate other waste, needs a great amount of energy and the final product typically cannot be used due to its toxicity. Therefore, there is a need for an alternative solution that neutralizes the heavy metals in the fly ash, enabling it to be utilized in selected industrial construction applications (e.g., acid sewers, cradles for concrete pipes, waste storage facilities). On the other hand researchers have reported that many coal-derived fly ashes, obtained from power generating stations, have chemical characteristics that allow them to be activated using highly alkaline solution to create a binder that could potentially immobilize the heavy metals contained in IFA (Davidovits, 2008; Zheng et al., 2010; Minarikova and Skvara, 2005; van Jaarsveld et al., 1997). This binder is commonly referred to as geopolymer.

Geopolymers do not require the presence of ordinary Portland cement to harden or gain strength. They are synthesized under slightly elevated temperature conditions (typically up to 100 °C) from materials of geological origin (e.g., metakaolin) or byproducts, such as CFA, that are rich in silica and alumina. These materials are typically referred to as source materials. Geopolymer binders result from a chemical reaction that takes place when silica and alumina molecules from the source material react under highly alkaline conditions, typically provided by a sodium (or potassium) hydroxide solution and an alkaline silicate (e.g., sodium or potassium silicate). The outcome of this reaction is an amorphous 3D network of Si and Al atoms linked by O atoms in a fourfold coordination similar to the one exhibited by zeolites. The positive ion (Na^+ or K^+), provided by the activator solution, serves to balance the negative charge generated by having Al^{3+} atoms in a fourfold coordination. While the reaction mechanism of geopolymeric chains is still debated, many authors agree that the reaction can be divided into three main stages: (1) dissolution of silicate and aluminate species from the source material; (2) transportation and coagulation/gelation; and, (3) condensation forming a three dimensional network of silico-aluminates (Davidovits, 2008; Provis and van Deventer, 2007a,b; De Silva et al., 2007). Many authors have reported that heavy metals may become encapsulated and immobilized within this geopolymer 3D network. While the mechanism(s) responsible for the immobilization of the heavy metals is not yet fully understood, it has been proposed that initially metal ions are taken into the geopolymer network, subsequently they are bound into the structure in balancing charges roles and finally, the remaining metal ions are physically encapsulated in the binder (Zheng et al., 2010; Minarikova and Skvara, 2005; van Jaarsveld et al., 1997).

Recently, some researchers have investigated the chemical stability of geopolymers containing IFA by substituting up to 20% of metakaolin with IFA showing very promising results (Lancellotti et al., 2010), while other authors have focused on analyzing the effects of the Si/Al ratio when attempting to stabilize IFA utilizing the alkaline activation process (Zheng et al., 2010). In contrast, the present manuscript attempts to analyze the chemical, physical and mechanical behavior resulting from the gradual introduction of IFA to a CFA-based geopolymeric matrix, providing a comprehensive mechanical characterization and leaching tests of the resulting concrete product. This technology could provide an efficient, cost-effective and environmentally friendly solution to IFA disposal by reducing its toxicity levels.

2. Materials and methods

The IFA used during this study was obtained from a Canadian-based WTE facility. The CFA, which is class F according to ASTM C 618, was obtained from Dolet Hills Power Generation Plant, located in northern Louisiana, USA. A total of six samples were tested, IFA, CFA and four mixes of these two. The control sample of IFA was designated as 100-00. Then 20% of IFA was substituted by CFA, this mix was labeled as 80-20. Subsequently, 60%, 40%, and 80% of IFA was substituted by CFA, these were labeled as mixtures 60-40, 40-60, and 20-80, respectively. Finally, the control sample of CFA was labeled 00-100. To denote paste samples (after the activation) the suffix GP was added (e.g., 20–80 GP) and to label concrete samples suffix GPC was added (e.g., 20–80 GPC). It is worth to mention that although IFA is expected to produce low levels (if any) of geopolymeric chains due to the lack of silica and alumina, its activated products will still be labeled as GP and GPC to simplify the nomenclature.

Particle size distribution (PSD), scanning electron microscopy (SEM), chemical and X-ray diffraction (XRD) analyses were performed on the fly ash samples and the mixes. Geopolymer paste was also analyzed by using XRD and SEM imaging. Additionally, leaching tests were performed for each fly ash and the four mixes, as well as their resulting geopolymer paste and concrete to determine the stability of heavy metals in the geopolymer matrix and the potential mobility of these contaminants. Concrete was manufactured from each fly ash (IFA & CFA) and the four mixes utilizing the alkaline activation process and following ASTM standard C 192 (ASTM, 2003a). Setting time measurements were taken of fresh geopolymer paste using a standard Vicat needle. Compressive strength, elastic modulus, Poisson's ratio and flexural strength tests were performed on the geopolymer concrete specimens.

Chemical analysis of the fly ash samples and mixes was performed via X-ray fluorescence (XRF) following ASTM standard D 4326 using a Thermo Scientific ARL Quant'x Energy-Dispersive XRF Spectrometer (ASTM, 2003e). PSD was performed on the samples using Microtrac S3500 laser-based equipment by suspension of the samples in Isopropyl alcohol, and after passing of the particles through the necessary cycles of reading and dispersing by ultrasound, to ensure accurate readings. XRD analysis was conducted on 10 g powdered samples and the data was obtained using a Bragg–Brentano geometry power diffractometer using a 40 kV copper anode. For the data collection the two theta angle selected was in the range of 10 and 80°, with 0.5° step size, over a count time of 5 s per step. The amounts of crystalline and amorphous components were also determined by using Rietveld phase quantification method. SEM micrographs of untreated and treated samples were taken using Hitachi S-4800 scanning electron microscope. SEM was performed to show the ash particles before and after a reaction with the activator solution.

Leaching tests were performed according with the US Environmental Protection Agency's toxicity leaching characteristic procedure (TCLP) to determine the mobility of Chromium, Selenium, Arsenic, Silver, Cadmium, Barium, Mercury and Lead. Each of the six samples was tested in its fly ash (FA), GP and GPC forms to monitor changes in leachability of the heavy metals before and after geopolymerization. A representative sample of up to 0.5 g is digested in 9 mL of concentrated nitric acid and 3 mL hydrofluoric acid for 15 min using microwave heating system. The sample and acid are placed in inert polymeric microwave vessels, sealed and heated in the microwave system. The temperature profile is specified to permit specific reactions and includes reaching 180 ± 5 °C in approximately 5.5 min and remaining at 180 ± 5 °C for 9.5 min for the completion of these reactions. After cooling, the vessel contents may be filtered, centrifuged, or allowed to settle and then decanted, diluted to volume, and analyzed by the appropriate SW-846 method. The method allows several additional alternative acid and reagent combinations including hydrochloric acid and hydrogen peroxide. The method measures ions produced by a radio-frequency inductively coupled plasma. Analytes originating