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Characterization and utilization of fly ash of heavy fuel oil generated in power stations

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ABSTRACT

Unlike coal fly ash, fly ash of heavy fuel oil has received much less attention in the literature. In this work, detailed physicochemical characterization of heavy fuel oil fly ash (FA) is provided. The ash has a carbonaceous matrix and contains V, Ni, Zn, Cr, Cu, and Pb with variable amounts. V was the most abundant heavy metal with enrichment factor of 277 in the FA. The presence of V in the FA is attributed to the formation of $Mg_3V_2O_8$ oxides at high combustion temperature as confirmed by XRD. Particle size distribution showed that the mean particle diameter of the FA was 70.5 μm. Extraction recovery up to 85% of metals was achieved using 1.0 M HNO_3 and at room temperature. Standard metal-leaching tests confirmed that the elution of the toxic metals and the level of eluted Zn were much higher than the regulated value for the solid residues. Five stable geopolymers GPs containing 41.7 wt.% FA were prepared. All GPs showed high compressive strength and low water absorption which support their application as lightweight construction composites. Most importantly, adding FA to GP had significantly reduced metal migration into the environment as confirmed by the synthetic precipitation leaching procedure.

1. Introduction

In many countries, coal is the most employed fuel for thermal power generation [1]. However, heavy fuel oil, diesel and natural gas are also used for power generation [2]. Currently, all Jordanian power stations are powered by heavy fuel oil, diesel, and/or natural gas [3]. Upon burning coal or heavy fuel oil, fly and bottom ash are generated [4]. Fly ashes of variable particle diameters are emitted leaving the bottom ash in the combustor [4]. Fly ash (FA) is often physically trapped using electrostatic precipitator [1]. About 20% of FA is used in concrete production and in other construction areas, whereas, large amount of FA is directly discharged as landfills and ash ponds [5–8].

The chemical composition of FA is dependent upon the nature of the feeding fuel, either coal or petroleum material. FA of coal origin is characterized by the high content of Si and Al which make it a suitable ingredient for normal Portland cement [5] and an excellent starting material for geopolymers [9]. Besides Al, Si, Fe and Ca, FAs of coal origin are also rich in metals like As, Be, B, Cd, Cr, Co, Mg, Mo Pb, Se and V. According to ASTM C618, FAs are categorized into Class F or Class C based on the content of Si, Al, and Ca [10]. Building brick containing 50% class C FA showed a comparable stability to normal clay brick [10]. Physicochemical properties, industrial applications, and safe disposal of coal FA have been discussed in many research papers. The most important applications of FAs are concrete production, road basement material, waste stabilization/solidification, cement clinkers, amendments of soft soil, and more recently in geopolymers [1,4,5,11–14].

Fly ash of heavy fuel oil has received less attention, and the published studies are mainly limited to surface characterization [2,15–17]. Heavy oil FA is characterized by a high C content and low Si/Al content [16]. Limited studies have addressed characterization and utilization of heavy oil FA [15–17]. In a previous study, selective extraction and separation of V/Ni from heavy fuel FA, collected from Al-Hussein power station/Jordan, was reported [15]. In Jordan, there are eight thermal power stations all powered by heavy fuel, diesel and/or natural gas [3]. The largest stations are Al-Aqaba and Al-Hussein stations with a total power capacity of 4870 GWh in 2010 [3]. The generated FA in the stations was estimated to be 418.5 tons in 2009 [15], however, an increase in the FA amount is expected due to the growth rate of energy demand. Public agencies have addressed the potential risk of the FA generated in the local power stations. The main conclusion was that FA is a toxic material and should not directly discharge into the environment [15]. Although the generated amounts of the FA seemed to be not too high, the chemical analysis indicated a high level of toxic metals; hence their extraction is highly recommended [15].

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In the current work, detailed characterization studies of heavy fuel oil FA produced in the Al-Aqaba power station are carried out. The studies included determination of toxic metals in the FA, particle size distribution, and practical application of the FA. Metals leachability by different solvents was carefully studied to assess the impact of the FA on the environment. Based on the characterization studies, the best utilization of the FA will be outlined.

2. Experimental procedures

2.1. Sampling of fly ash from Al-Aqaba power station

The examined FA was collected from the Al-Aqaba thermal power station (400 km south of Amman, Jordan). This station is the largest one in the country with a power capacity of 4090 GMh [3]. The FA samples were collected from the mechanical hoppers in the station. The collected samples were mixed and homogenized using suitable coning and quartering procedures. Finally, the sample was sieved to particle diameter less than 100 μm and stored in glass bottles. The station consumes 500 tons heavy oil per hour [3].

2.2. Characterization of the fly ash

The surface of the FA was characterized using scanning electron microscopy and energy dispersive X-ray spectrometry SEM/EDX (FEI-INSPECT-F50-SEM/EDX, The Netherlands). A laser diffractometer was used to measure particle size distribution of FA particles (Microtrac Zetatrac, Microtrac, Particle Size Analyzer, USA). Crystalline phases were detected using X-ray powder diffraction XRD (Shimadzu X-Ray Diffractometer XRD-6000, Japan). Phase identification was carried out using PC-Identity and ICDD database. Chemical composition of the FA was measured by X-ray fluorescence measurements (Shimadzu XRF-1800 Sequential X-Ray Fluorescence Spectrometer, Japan). Carbon content in the heavy fuel and the FA was determined using CHN analyzer (ELTRA CW multiphase-determinator, Germany).

2.3. Extraction of metals from the FA

Different solvents, prepared from HNO_3, NaOH, EDTA, NaCl and $CH_3CH_2CO_2Na$, were tested for metal extraction. The earlier reagents had efficient performance for metal extraction from the solid residues [18]. All extractions were carried out using 1.0 M solution and the "liquid to solid" "L/S" ratio was maintained at 50.0 cm^3/g. The samples were mechanically agitated for 2.0 h at 25 °C (±2 °C). The FA was removed by centrifugation (5000 rpm) and the clean supernatant was analyzed for metals using inductively coupled plasma-mass spectrometry (ICP-MS) (Shimadzu ICPS-7510 Sequential Plasma Spectrometer, Japan).

2.4. Preparation and testing of geopolymers

Five geopolymers (GPs) were prepared containing variable amounts of the FA. The main ingredient of the GP was natural clay (60% kaolinite, particle size 45–63 μm, and plasticity limit 22%) which was collected from El-Hiswa deposit, 300 km south of Amman, Jordan). Geopolymerization was carried out by gradually adding 11.4 M NaOH to 100.0 g clay with gentle stirring. The ratios of ingredients (clay, NaOH, H_2O, and the FA) were selected to end up with a high stable composite as will be discussed later. The pastes of the GPs were homogenized using a controlled speed mixer at 200 rpm for 10 min to avoid agglomeration of the mixtures [19]. The samples were molded immediately in special stainless steel cylinders and subjected to an external pressure of 15 MPa to speed up the geopolymerization process [19]. The samples were removed and cured at 80 °C for 28 days to achieve the maximum hardness of the composite. Density, compressive strength, water absorption, and conductivity were measured as outlined in the literature [19]. Synthetic precipitation leaching procedure (SPLP) was adopted for measuring metal leachability from the GPs [20]. For conductivity and SPLP tests, particle diameter of 1.0 mm was used and L/S ratio was fixed at 50 cm^3/g. Conductivity was measured using Jenway instruments (Jenway, UK).

3. Results and discussions

For better FA utilization, detailed physicochemical analyses were carried out beforehand. Depending on the results, the following procedures are possible: a) chemical washing [21], b) stabilization/solidification [22,23], d) incineration [23], d) extraction [24], c) immobilization with construction materials like normal Portland cement [5,25] and e) ingredient for geopolymers [12,13,19–23,26]. The last two options seemed to be attractive as a large volume of the FA would be trapped within a solid matrix [19]. Particle size distribution and content of heavy metals can determine the best utilization of the FA.

3.1. Physicochemical properties of the FA

3.1.1. Particle size distribution

Measuring particle size distribution of the FA is essential to assess its industrial application [4,5]. Particle size distribution was recorded using a laser-based technology and the result is given in Fig. 1.

As shown in Fig. 1, a normal distribution curve of the FA is shown, covering the size range 21.2–91.5 μm. In fact, fine particles 0.2–90 μm are often produced in the case of effective fuel combustion [4,5]. Larger particles (90–300 μm) containing char, partially-combusted carbon matter are often produced in poor combustion [27,28]. The following parameters were estimated: $dp_{<10\ \mu m}$, $dp_{<50\ \mu m}$, $dp_{<90\ \mu m}$, D_{10}, D_{50}, and D_{90} [4]. The estimated values of the earlier parameters are: 0%, 8.5%, 99.5%, 47.4 μm, 72.3 μm, and 92.4 μm, respectively. $dp_{<10\ \mu m}$ gives the undersized% by volume of particles of diameter less than 10 μm and the same is true for $dp_{<50\ \mu m}$ and $dp_{<90\ \mu m}$. In this case D_{10} is 47.4 μm and this indicates that 10% of the FA particles have a diameter less than 47.5 μm. In general, the FA particles are fine with D_{90} value 92.4 μm (i.e., 90% of particles have a diameter less than 92.4 μm). Arithmetic mean diameter (AMD), which is estimated from D values, is 70.5 μm [4]. The FA of dp < 10 μm is recommended in normal concrete to replace fine cement particles, however, coarser particles ≤45 μm are more suitable as fillers in other construction materials or as adsorbents [4,5]. Accordingly, the examined FA would be used as filler/ingredient in construction materials or in geopolymers.

3.1.2. Chemical analyses

Detailed chemical characterization of the FA was carried out by measuring the total metal content and by recording the X-diffraction pattern. To have a better explanation for the chemical results, the chemical content of the feeding fuel was determined and the results indicated

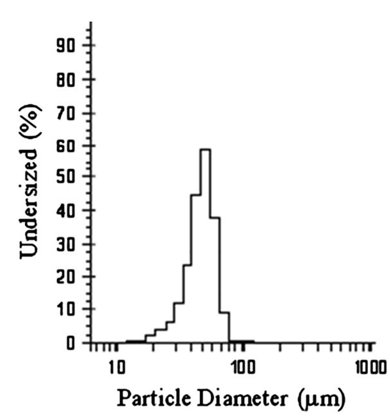

Fig. 1. Particle size distribution profile of FA.