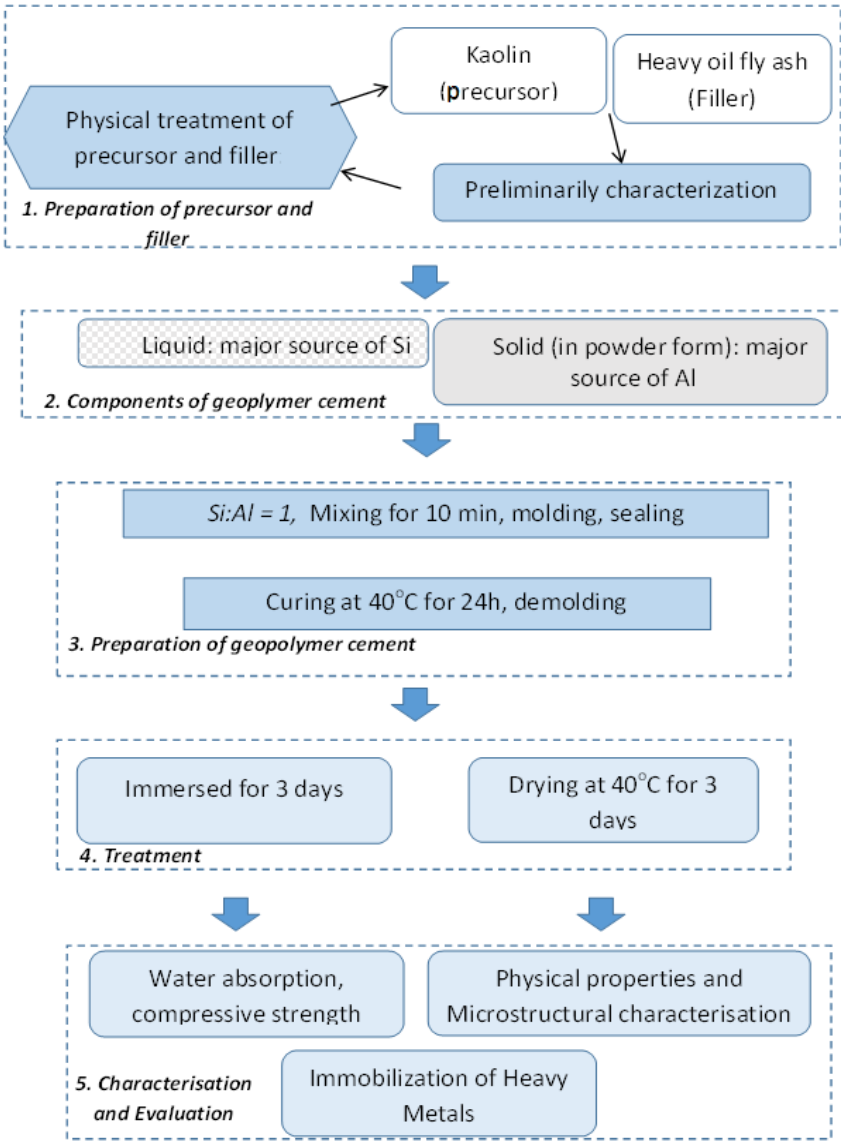

Figure 1. Schematic diagram of the experimental procedure

Testing methods

X-ray Diffraction Studies

X-ray Diffraction (XRD) was carried out on HFO sample and on powdered samples of kaolin geopolymer (SK) and heave oil fly ash cement (GA) to analyse microstructural of HFO. It was applied to identify major crystalline of HFO and potentially newly formed phases after geopolymerization process. A Shimadzu diffractometer-6000 (Japan) with a Co tube and a scanning range from 5º to 80º 2θ at a scan rate of 2°/min was used. Qualitative analysis was carried out using the crystalline phases, identified by detecting and analyzing the positions of the peaks using the software package supplied with the instrument.

Scanning Electron Microscopy and Energy-dispersive X-ray spectroscopy (SEM/EDX)

The Scanning Electron Microscope combined with Energy-dispersive S-ray spectrometry (SEM–EDX) was used to study elemental analysis, chemical characterization and morphology of HFO particles and stabilized HFO particles, after geopolymerization process.

It was conducted with an Inspect F50 scanning electron microscope (SEM) (The Netherlands). Samples were mounted in epoxy resin and the surfaces were ground flat by 600 grit abrasive paper. The samples were then polished to achieve a smooth surface. The polished samples were placed into a vacuum and etched into argon gas for 20 minutes. The microstructures of the samples were examined with SEM and photographs were taken to be analyzed. Finally, the energy

dispersive spectroscopy (EDX) was used to determine the elemental composition of manually chosen areas in the HFO before and after stabilization process.

Physical characterization of HFO

Bulk density and total porosity of HFO have been determined using helium pycnometry (Helium AccuPyc 1330, Micromeritics, USA). Helium–air pycnometry is a nondestructive, quick and reliable tool that measures the volume of solid objects of irregular or regular shape whether powdered or in one piece; therefore, helium–air pycnometry is a well-suited technique to be used for HFO analysis [1]. The pycnometer determines skeletal volumes by observing the reduction of gas capacity in the sample chamber caused by the presence of the given sample. Helium, as well as other suitable gases, penetrates the smallest pores and surface irregularities common in CCB samples, allowing the volunme obtained to be used for the computation of the ultimate theoretical density of the solid comprising the sample.

Leaching test

To study the effectiveness of geopolymerization on immobilization of HFO heavy metals in the geopolymer matrix, the leaching test results from the HFO-geopolymer cement were compared with the leaching test results from the HFO powder. The toxicity of the chemical elements are classified according to the International Union of Pure and Applied Chemistry (IUPAC).

For fly ash leaching analysis, 1g of fly ash (HFO) was heated at 95ºC for two hours with 10ml of 70% HNO_3 and 3ml of 60% $HClO_4$, according to German standard (DIN 38414). The solution was cooled down and diluted with 10ml HCl 1:1 (density 1.18gml^{-1}). The diluted solution was then filtered and diluted with distilled water up to 50ml [32].

For the leaching test of the 50 g of powdered GA sample with grain size <100 µm were placed in 500 ml deionized water. After agitating the sample at room temperature for 24 hours, it was filtered and analyzed by means of Inductively Coupled Plasma–Optical Emission Spectrometry (ICP-OES) (GBC-Quantima sequential, Australia). The leaching tests were done at a constant pH solution of 7.

Geopolymer cements characterization

Physical characteristics of fabricated specimens have been studied by bulk density and water absorption of fabricated specimens; these tests were developed according to Standard Methods ASTM C97 / C97M – 15 Standard Test Methods for Absorption and Bulk Specific Gravity of Dimension Stone.

Flexural strength and compression strength were used to mechanical characterization of the fabricated specimens for each series. These tests were performed according to ASTM C78 / C78M – 16 (Standard Test Method for Flexural Strength of Concrete, Using Simple Beam with Third-Point Loading) and ASTM C116-90 (Test Method for Compressive Strength of Concrete Using Portions of Beams Broken in Flexure), respectively. Both tests have been developed at room temperature and with a universal testing machine. The bending specimen's dimensions were: height=15 mm, width=30 mm and length=160 mm; the distance between the supports was 120 mm and the speed of the machine head during testing was 0.1 mm/minute. Compression tests were performed on the failed bending specimens, placed on their side with a loading area=40×15 mm^2 and height=30 mm. The speed of the machine head during testing was 2 mm/minute.

RESULTS AND DISCUSSION

Microstructural characteristics

Metakaolin and HFO particles were transformed into solid and hard matrix through the geopolymerization process. The XRD patterns (Figure 2) of the resulting materials —SK, and GA, cements— show high humps between 15º to 35º. The hump with a few peaks indicates that the main phases of the resultant products are largely amorphous [33-37]. The XRD peaks correspond to the mineral anatase (TiO_2), which already existed in the precursor (kaolin) as previously reported [29]. In general, no significant change in the mineral composition is observed with adding HFO (GA cement). This is indication that HFO could be used as functional filler, with limited contribution in setting reactions.

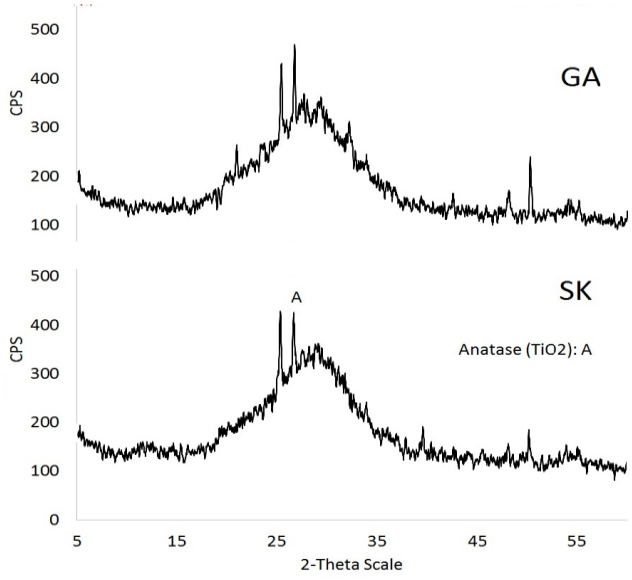

Figure 2, Qualitative XRD patterns of the cements

The heavy oil fly ash studied is made up mostly of porous particles with a bulk density of 0.34g/cm^3, and total porosity of 82% as reported by the helium pycnometer measurements, and this is in good agreement with previous studies [1]. The SEM micrograph of HFO seen in Figure 3A shows that the surface of the HFO particle is not smooth; it is characterized by the presence of hollow voids several microns in diameter. These hollow voids were formed by the eruption of gas during

combustion. In consequence these particles would be weak and easily disintegrate in liquids, and therefore release toxic heavy metals such as Pb, Ni, Cr, and Cu. The SEM analysis has been also applied to HFO stabilized particle in GA sample (Figure 3B, point 1); it shows that HFO particles are fully surrounded and bonded by geopolymer gel (point 2).;The higher magnification SEM images of the stabilized HFO particle better display the macropores as reported in Figure 3C showing that these pores are filled with geopolymer gel filling during the reactions (Figure 3C, point 3). In consequence we could conclude this geopolymer matrix could stabilize the HFO particles, preventing their disintegration and therefore the release of toxic heavy metals [25].

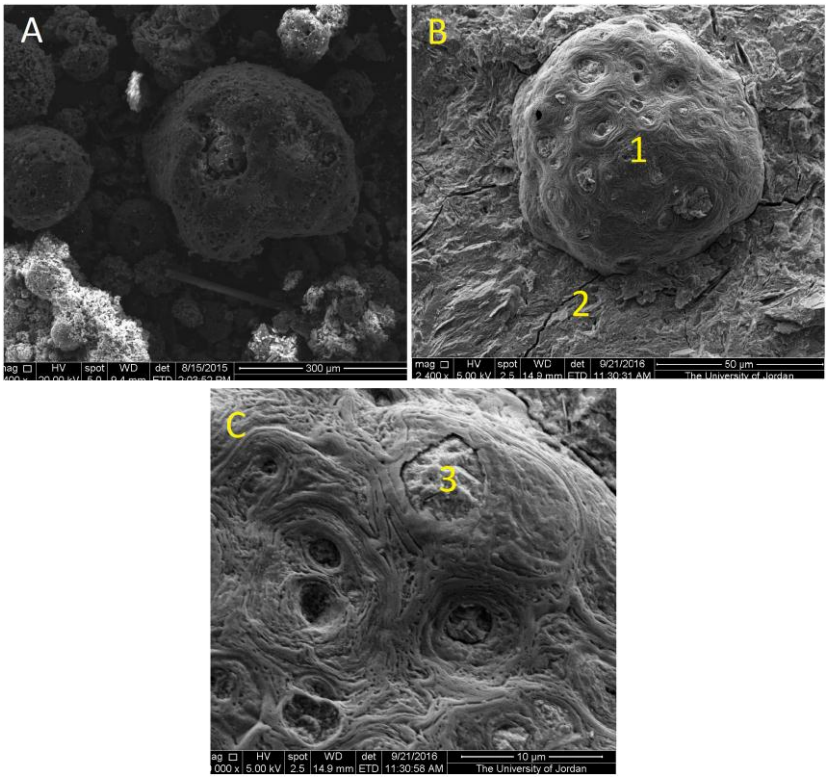

Figure 3. SEM image of A) HFO particle, B) typical HFO stabilized particle (GA), and C) Higher magnification SEM image of the HFO particle

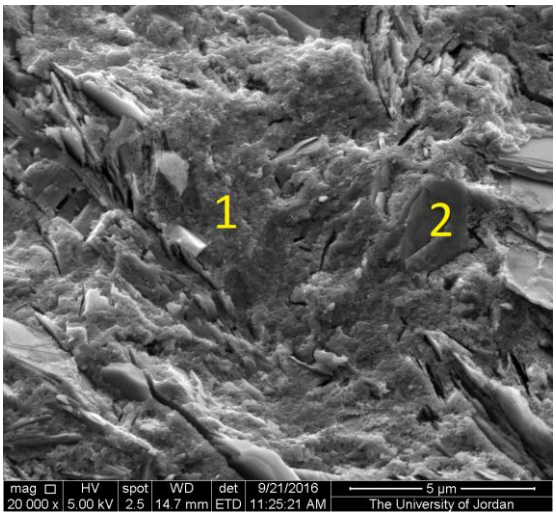

Figure 4. SEM image of geopolymer gel, and partially reacted metakaolin

Metakaolinite, as a precursor in this study, was attacked by the alkaline solution during geopolymerization as seen in Figure 4. Microstructural observations through SEM analyses reveal phase heterogeneities; geopolymer gel (point 1), and partially reacted metakaolin (point 2). The chemical analyses by EDX involved scanning three different areas of the HFO particles and the geopolymer gel (GA and SK), as displayed in Figure 5. The HFO particle comprises 72% carbon, in addition to Na, Si, Al, and S. The low percentages of Si (2%) and Al (3%) oxides of the HFO contents point to the limited contribution of these particles to the composition of the geopolymer gel. Thus, they are stable even after the hardening of the material, as shown in Figure 3B.

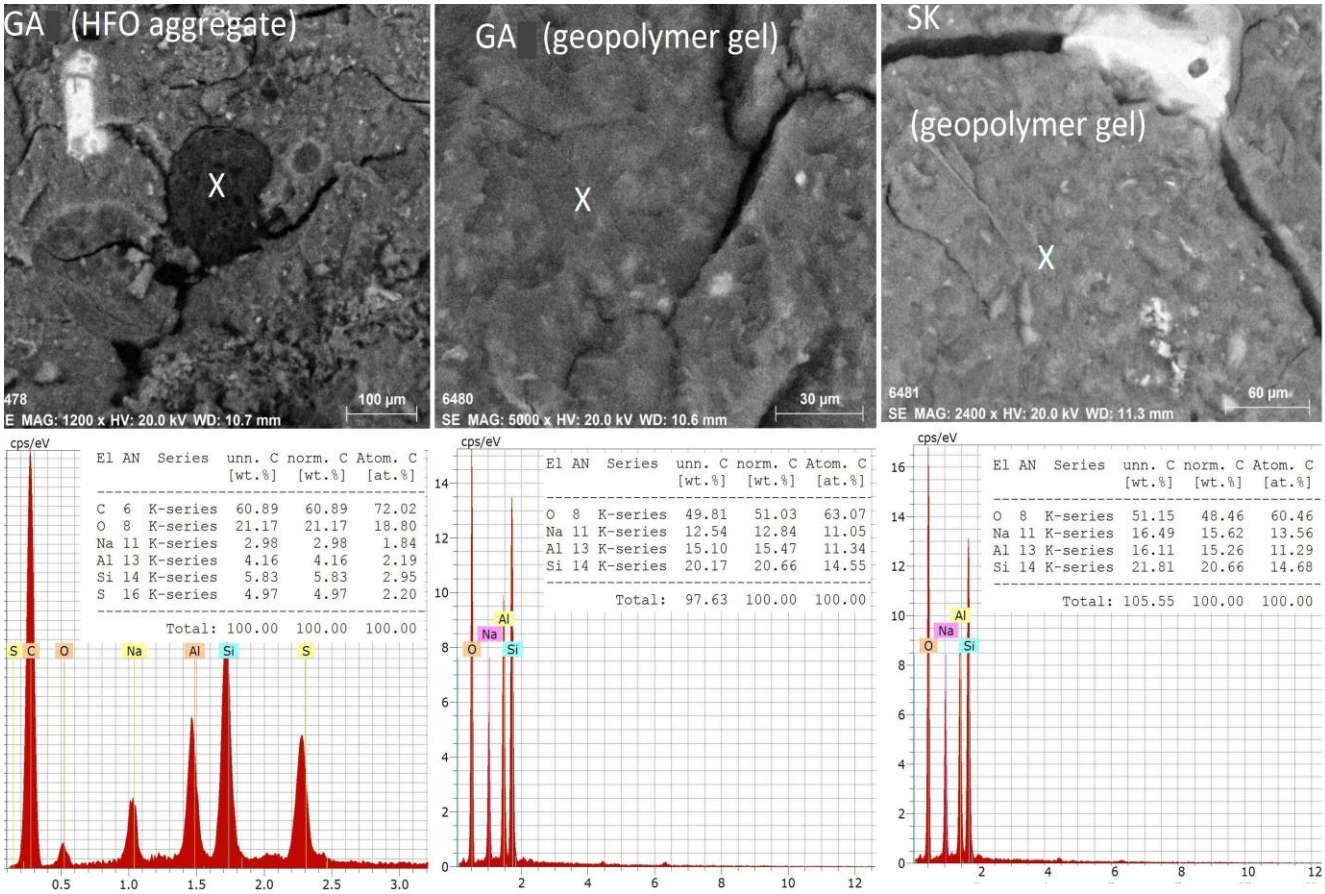

Figure 5. EDX analysis of different phases; HFO particle, and geopolymer gel of GA and SK

The chemical EDX analysis, reflected in Table 1, gives the complete set of compositional data expressed as mean molar percentage of the HFO, GA, and SK. The geopolymer gels of GA and SK cements are composed of the same elements. Carbon and sulfur, constituents of HFO, are not involved in the geopolymerization process and the resultant geopolymer gel. The Si/Al and Al/Na molar ratios of the precursors are 1. The Si/Al molar ratio changed to 1.3 in the reference geopolymer cement (SK). This indicates that the Al oxide decreased in the resultant gel, due to the partial reaction of metakaolin (source of Al in the geopolymerization reactions). When compared with reference geopolymer (SK), a slight decrease in Na oxide is observed in the geopolymer gel of GA. This reduction in the molar percentage of Na in GA could be the result of adsorption of this element by the porous HFO particles. However, the molar percentages of Al, Na, and Si of the geopolymer gel in SK and GA cements are still within an acceptable range, in view of previous studies [36, 38]. We may therefore conclude that the HFO particles preserve their physical structure after geopolymerization, with no significant involvement in the chemical composition of the resultant geopolymer gel.

Table 1. EDX analysis of different phases

Elements	HFO particle	GA	SK
C	72.0	0.0	0.0
O	18.8	63.1	60.5
Na	1.8	11.1	13.6
Al	2.2	11.3	11.3
Si	3.0	14.6	14.7
S	2.2	0.0	0.0
Molar ratio	HFO	GA	SK
Si/Al	1.3	1.3	1.3
Al/Na	1.2	1.0	0.8
Si/Na	1.6	1.3	1.1

Geopolymer cements properties

It may well be that HFO particles have no significant chemical effect on the geopolymer cement as stated in the previous section; however they could bear an influence on the physical and mechanical properties because of their low density and high porosity [1]. In consequence both properties have been analyzed below.

Physical properties

On the one hand, the bulk density and water absorption of the geopolymer cements are given in Figure 6. The bulk density of the geopolymer without HFO (SK) is 1.41 g/cm^3 - comparable with other reports [34-39]. Adding low density HFO particles with weight ratio of 20% as compared with the metakaolin used would decrease the bulk density to 1.34 g/cm^3. This limited decrease in bulk density could result from geopolymer gel filling HFO macropores during the reactions. On the other hand, the water absorption decreased by adding 20% of HFO particles (GA), from 21% to 18%, as seen in Figure 6.

Results of bulk density and water absorption indicate that the pore system of the HFO was blocked or filled by geopolymer gel after geopolymerization, as we have concluded before.

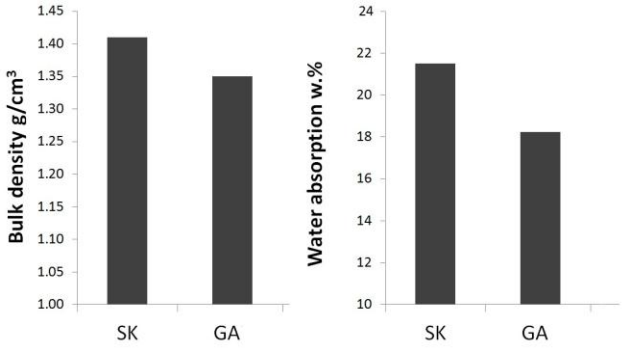

Figure 6. Bulk density and water absorption of the produced geopolymer cements

Mechanical properties

Figure 7 displays the maximum compressive strengths of HFO-based geopolymer (GA), 31MPa and 28MPa, respectively under dry and immersed conditions. These values are approximately 9 and 29% lower than SK geopolymer. In the case of immersed sample compressive strength of GA is lower than 30 MPa, the value established by EH-08.

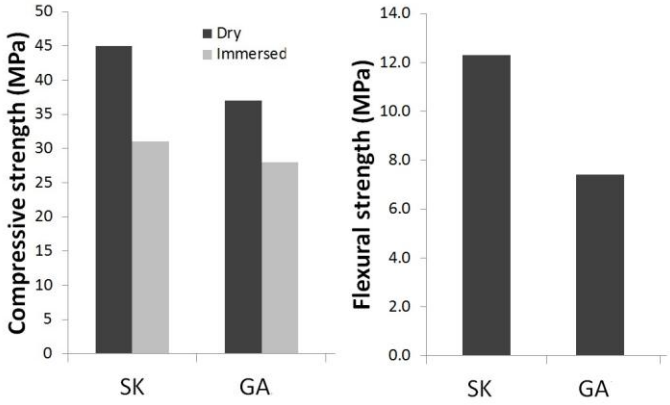

Figure 7. Mechanical properties of the produced geopolymer cements

In the case of the flexural strength for dry conditions, HFO-based geopolymer has resulted 7.5MPa (Figure 7), 39% lower than SK geopolymer. These results have shown that using calcinated natural kaolinitic soil as the precursor material and HFO as a filler in the starting mixture affects the microstructure and strength of the produced geopolymers to a certain degree. Although the mechanical properties of HFO-based geopolymers have been lower than SK geopolymers, values are comparable with those of ordinary concrete with values around [40]. Hence, the HFO-based geopolymers studied here satisfy the criteria for use in housing and general construction applications.

Leaching behavior

A preliminary study was carried out to analyze the HFO leachate from heavy metals, and the effectiveness of immobilization of these heavy metals in the geopolymer matrix. Table 2 shows the concentration of different metals leached from the HFO powder and the HFO-based geopolymer matrix (GA) after immersion in a solution of pH=7 for one day. The toxicity of the chemical elements are classified according to the International Union of Pure and Applied Chemistry (IUPAC) [38].

The HFO powder exhibits high leachability for Na, Zn, Al, Ni, Fe, Pb, Mn, Cu and trace elements Ca, Mg and Co in neutral conditions. The first toxic element is Ni, which causes allergy for many years; often it will remain for the rest of life [41]; Co inhalation can lead to 'hard metal disease', respiratory sensitization, pneumonia, wheezing, and asthma [42]; Exposure to Pb can be toxic to humans and wildlife [43]; Excessive Cu absorption can occur through the skin, by inhalation or by ingestion [44]. Finally, The toxic action of Cr is confined to the hexavalent compound (Cr VI), which is a highly toxic carcinogen and may cause death to humans and animals if ingested in large doses [45].

Table 2. Concentration (ppm) of leached metals from HFO powder and GA after immersion in pH = 7 for 1 day

Element	Toxicity (IUPAC) [38]	HFO (ppm)	GA (ppm)
Na	X	21.6	179.2
Ca	X	0.6	1.6
Zn	X	164.0	0.0
Mg	X	0.1	0.6
Fe	X	3.3	0.1
Mn	X	1.0	0.0
Al	X	189.0	39.2
Ni	Toxic	32.0	0.0
Co	Toxic	0.1	0.0
Pb	Toxic	1.6	0.0
Cu	Toxic	1.2	0.0
Cr	Toxic	4.1	0.0

Interestingly, Ni, Cr, Cu, Mn, Zn and Pb do not show considerable leaching in GA despite their presence in the HFO powder. For the GA specimens, however, these heavy metals are effectively immobilized and exhibit concentrations significantly lower than those of HFO powder. The GA matrix exhibits high leaching of Na, and Al. The sources of these two elements are the residual precursors of the geopolymer: sodium silicate solution (Na), and metakaolin (Al). As evident in Table 2, adding HFO to the geopolymers significantly reduced leaching of the toxic heavy metals. Stabilization of HFO heavy metals can occur chemically through incorporation into the geopolymeric structure as a charge balancing cation and/or physically through encapsulation within the geopolymer gel [25, 38]. In this process, chemical stabilization dominates the physical encapsulation because the structural breakdown of the geopolymer gel does not lead to substantial release of the heavy metals.

CONCLUSIONS

In this study, HFO particles were stabilized using a geopolymerization technique. One important finding resides in the possibility of using HFO for mass production of geopolymer cement with high mechanical performance and acceptable physical properties, a sound alternative to Portland cement.

Metakaolin and HFO particles were transformed into solid and hard matrix through the geopolymerization process. The resultant phases are largely amorphous. The HFO is serving in the resultant cement as functional filler, with limited contribution in setting reactions. The HFO particles preserve their physical structure after geopolymerization, with no significant involvement in the chemical composition of the resultant geopolymer gel. The geopolymer matrix stabilizes the HFO particles, preventing their disintegration and therefore the release of toxic heavy metals. The HFO pores are filled with geopolymer gel filling during the reactions.

HFO particles bear an influence on the physical and mechanical properties because of their low density and high porosity. The mechanical properties of HFO-based geopolymers are comparable with those of ordinary concrete. Hence, the HFO-based geopolymers studied here satisfy the criteria for use in housing and general construction applications.

This study shows that HFO powder exhibits high leachability for Na, Zn, Al, Ni, Fe, Pb, Mn, Cu and trace elements Ca, Mg and Co in neutral conditions. Interestingly, Ni, Cr, Cu, Cd, Mn, Zn and Pb do not show considerable leaching after stabilizing in the geopolymer matrix. Stabilization of HFO heavy metals can occur chemically through incorporation into the geopolymeric structure as a charge balancing cation and/or physically through encapsulation within the geopolymer gel.

Our research group has developed a preliminary study to use a metakaolin-based geopolymer matrix that could provide a satisfactory binder for the immobilization of a number of toxic heavy metals, given its low permeability, resistance to acid and chloride attack, and durability [28-29]. It is worth mentioning that the leachability of contaminants from stabilized metal geopolymer wastes is lower than that from hardened Portland cement stabilized wastes [30,31].

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REFERENCES

[1] Al-Malack, M.H., Bukhari, A.A., Al-Amoudi, O.S., Al-Muhanna, H.H., Zaidi, T.H., 2013, "Characteristics of Fly Ash Produced at Power and Water Desalination Plants Furing Fuel Oil," Int. J. Environ. Res., 7(2), pp. 455-466.

[2] Kwon, W., Kim, D., Kim, Y., 2005, "Characterization of Heavy Oil Fly Ash Generated from a Power Plant," The AZo Journal of Materials Online (Azojomo), DOI : 10.2240/azojomo0135

[3] Bulewicz, E.M., Evans, D.G., Padley, P.J., 1974 " Effect of Metallic Additives on Soot Formation Processes in Flames," Proceedings of the 15th International Symposium on Combustion, The Combustion Institute, Pittsburgh, PA, 1461-1470.

[4] Feldman, N., 1982, "Control of Residual Fuel Oil Particulate Emissions by Additives", Proceedings of the 19th International Symposium on Combustion, The Combustion Institute, Pittsburgh, PA, 1387-1393.

[5] Blinova, I., Bityukova, L., Kasemets, K., Ivask, A., Käkinen, A., Kurvet, I., Bondarenko, O., Kanarbik, L., Sihtmäe, M., Aruoja, V., Schvede, H., Kahru, A., 2012, " Environmental Hazard of Oil Shale Combustion Fly Ash", J. Hazard. Mat., 229–230, 192-200.

[6] Velts O., Hautaniemi M., Kallas J., Kuosa M., Kuusik R., 2010, "Modeling calciumdis-solution from oil shale ash: part 2. Continuous washing of the ash layer," Fuel Process. Technol., 91(5), pp. 491–495.

[7] Xiao, Y., Jalkanen, H., Yang, Y., Mambote, C., Boom, R., 2010, "Ferrovanadium Production from Petroleum Fly Ash and BOF Flue Dust", Minerals Engineering, 23 (14), 1155-1157.

[8] Sippula, O., Hokkinen, J., Puustinen, H., Yli-Pirilä, P., Jokiniemi, J., 2009, "Comparison of particle emissions from small heavy fuel oil and wood-fired boilers", Atmospheric Environment, 43 (32), pp. 4855-4864.

[9] Reddy, S.M., Shaik Basha, H.V., Joshi, B., 2005, "Evaluation of the Emission Characteristics of Trace Metals from Coal and Fuel Oil Fired Power Plants and their Fate during Combustion", J. Hazard. Mat., 123 (31), pp. 242-249.

[10] Lai, A., 2010, "Ferrovanadium Production from Heavy Fuel Oil Fly Ash and BOF Dust", Master thesis, Delft University of Technology, The Netherlands.

[11] Mohammed, H., Sadeek, S., Mahmoud, A., Zak D., 2016, "Comparison of AAS, EDXRF, ICP-MS and INAA performance for determination of selected heavy metals in HFO ashes", Microchemical Journal, 128, pp. 1-6.

[12] Mohammed, H., Sadeek, S., Mahmoud, A., 2016, "Accurate determination of uranium and thorium in Egyptian oil ashes", Microchem. J., 124, pp. 699–702.

[13] Di Pietro, A., Visalli, G., Munaò, F., Baluce, B., La Maestra, S., Primerano, P., Corigliano, F., De Flora, S., 2009, " Oxidative damage in human epithelial alveolar cells exposed in vitro to oil fly ash transition metals", Int. J. Hyg. Environ. Health, 212, pp. 196-208.

[14] Pattanaik, S., Huggins, F.E., Huffman, G.P., Linak, W.P., Miller, C.A., 2007, "XAFS studies of nickel and sulfur speciation in residual oil fly-ash particulate matters (ROFA PM)", Environ. Sci. Technol, 41, pp. 1104-1110, http://dx.doi.org/10.1021/es061635m.

[15] Kosson, D.S., van der Sloot, H.A., Sanchez, F., Garrabrants, A.C., 2002, "An integrated framework for evaluating leaching in waste management and utilization of secondary materials", Environ. Eng. Sci., 19, pp. 159–204.

[16] Mihucz, V.G., Szigeti, T., Dunster, C., Giannoni, M., De Kluizenaar, Y., Cattaneo, A., Mandin, C., Bartzis, J.G., Lucarelli, F., Kelly, F.J., Záray, G., 2015, "An integrated approach for the chemical characterization and oxidative potential assessment of indoor PM 2.5", Microchem. J., 119, pp. 22–29, http://dx.doi.org/10.1016/j.microc.2004.10.021.

[17] Huang, S.K., Zhang, Q., Qiu, Z., Chung, K.F., 2015, "Mechanistic impact of outdoor air pollution on asthma and allergic diseases", J. Thorac. Dis., 7, pp. 23-33, http://dx.doi.org/10. 3978/j.issn.2072-1439.2014.12.13

[18] Tata´r, E., Csiky, G. M., Mihucz, V. G., Za´ray, G., 2005, "Investigation of adverse health effects of residual oil fly ash emitted from a heavy-oil-fuelled Hungarian power plant", Microchemical Journal, 79, pp. 263-269.

[19] Camilleri, J., Anastasi, M., Torpiano, A., 2013, "The microstructure and physical properties of heavy oil fuel ash replaced Portland cement for use in flowable fill concrete and the production of concrete masonry units", Construction and Building Materials, 38, pp. 970-979.

[20] Shanmugam N., Ibnelwaleed, A., Hussein, I. A., Badghaish, A., Shuaib, A. N., Furquan, S. A., Al-Mehthel, M. H., 2015, "Evaluation of oil fly ash as a light stabilizer for epoxy composites: Accelerated weathering study", Polymer Degradation and Stability, 112, pp. 94-103.

[21] Azhar Uddin, M., Shinozaki, Y., Furusawa, N., Yamada, T., Yamaji, Y., Sasaoka, E., 2007, "Preparation of activated carbon from asphalt and heavy oil fly ash and coal fly ash by pyrolysis", J. Anal. Appl. Pyrolysis, 78, pp. 337-342.

[22] Shi, C., Fernandez-Jimenez, A., 2006, "Stabilization/solidification of hazardous and radioactive wastes with alkali-activated cement", J. Hazard. Mater., B137, pp. 1656-1663.

[23] Van Jaarsveld, J.G.S., van Deventer, J.S.J., Schwartzman, A., 1999, "The potential use of geopolymeric materials to immobilize toxic metals: Part II. Material and leaching characteristics", Miner. Eng., pp. 75–91.

[24] Lee, W.K.W., van Deventer, J.S.J., 2002, "The effects of inorganic salt contamination on the strength and durability of geopolymers. Colloids Surf. A Physicochem", Eng. Asp., 211, pp. 115-126.

[25] El-Eswed, B.I., Yousef, R.I., Alshaaer, M., Hamadneh, I., Al-Gharabli, S.I., Khalili, F, 2015, "Stabilization/solidification of heavy metals in kaolin/zeolite based geopolymers", International Journal of Mineral Processing, 137, pp. 34-42.

[26] Sun, T., Chen, J., Lei, X., Zhou, C., 2014, "Detoxification and immobilization of chromite ore processing residue with metakaolin-based geopolymer", J. Environ. Chem. Eng., 2, pp. 304-309.

[27] Al-Degs, Y. S., Ghrir, A., Khoury, H., Walker, G. M., Sunjuk, M., Al-Ghouti M. A., 2014, "Characterization and utilization of fly ash of heavy fuel oil generated in power stations", Fuel Processing Technology, 123, PP. 41-46.

[28] Yousef, R.I., El-Eswed, B., Alshaaer, M., Khalili, F., Khoury, H.,2009, " The influence of using Jordanian natural zeolite on the adsorption, physical, and mechanical properties of geopolymers products", Journal of Hazardous materials, 165 (1), PP. 379-387

[29] Alshaaer, M., Alkafawein, J., Al-Fayez, Y., Fahmy, T., Hamaideh, A., 2015, "Synthesis of Geopolymer Cement Using Natural Resources for Green Construction Materials", Recent Advances in Earth Sciences, Environment and Development. Proceedings of the 8th International Conference on Engineering Mechanics, Structures, Engineering Geology (EMESEG '15), Konya, Turkey.

[30] Zhang, J., Provis, J.L., Feng, D., van Deventer, J.S.J., 2008, "Geopolymers for stabilization of Cr^{6+}, Cd^{2+} and Pb^{2+}, J. Hazard. Mater., 157, PP. 587-598.

[31] S. Baxter, W. L., Fonseca, F., 2008, "Biomass fly ash in concrete: SEM EDX and ESEM analysis", Fuel, 87, pp. 372–379.

[32] Mohsen, Q., El-maghraby, A., 2010, "Characterization and assessment of Saudi clays raw material at different area", Arabian Journal of Chemistry, 3, pp. 271-277.

[33] Rankers R. H., Hohberg, I., 2008, Institut für Bauforschung, RWTH Aachen, Schinkelstr. 3, D-5100 Aachen, Germany.

[34] Alshaaer, M., Zaharaki, D., Komnitsas, K., 2014, "Microstructural characteristics and adsorption potential of a zeolitic tuff–metakaolin geopolymer", Desalination and Water Treatment, DOI:10.1080/19443994.2014.938306.

[35] Saidi, N., Samet, B., Baklouti, S., 2013, "Effect of Composition on Structure and Mechanical Properties of Metakaolin Based PSS-Geopolymer", International Journal of Material Science (IJMSCI), 3 (4), doi: 10.14355/ijmsci.2013.0304.03 145

[36] Kriven, W.M., Bell, J.L., Gordon, M., 2003, "Microstructure and microchemistry of fully-reacted geopolymers and geopolymer matrix composites", Ceram. Trans., 153(4), pp. 227-250.

[37] Lin, T., Jia, D. He, P., Wang, M., Liang, D., 2008, "Effects of fiber length on mechanical properties and fracture behavior of short carbon fiber reinforced geopolymer matrix composites", Mater. Sci. Eng., A, 497 (1-2), pp. 181-185.

[38] Ahmari S., Zhang, L., 2013, "Durability and leaching behavior of mine tailings-based geopolymer bricks", Construction and Building Materials, 44, pp. 743-750.

[39] The International Union of Pure and Applied Chemistry (IUPAC), https://iupac.org/

[40] Amudhavalli, N. K., Mathew, J., 2012, "Effect of silica fume on strength and durability parameters of concrete", Int. J. Eng. Sci. Emerg. Technol., 3 (1) (2012), pp. 28–35

[41] Grimsrud, T.K., Berge, S.R., Haldorsen, T., Andersen, A., 2002, "Exposure to different forms of nickel and risk of lung cancer", Am J Epidemiol, 156, pp. 1123–1132.

[42] Dahms, K., Sharkova, Y., Heitland, P., Pankuweit, S., Schaefer, J.R., 2014, "Cobalt intoxication diagnosed with the help of Dr House, Lancet, 383 (574).

[43] Dairam, A., Limson, J.L., Watkins, G.M., Antunes, E., Daya, S., 2007, "Curcuminoids, curcumin, and demethoxycurcumin reduce lead-induced memory deficits in male Wistar rats", J Agric Food Chem., 55, pp.1039–1044.

[44] [1] Xiao, Y., Vijver, M.G., Chen, G., Peijnenburg, W.J., 2015, "Toxicity and Accumulation of Cu and ZnO Nanoparticles in Daphnia magna", Environ. Sci. Technol., 2015, 49 (7), pp. 4657–4664.DOI: 10.1021/acs.est.5b00538

[45] Costa, M., Klein, C.B., 2006, "Toxicity and carcinogenicity of chromium compounds in humans", Crit Rev Toxicol., 36(2), pp.155-63.