WM&R

Potential industrial utilization of pre-treated municipal solid waste incineration fly ash

Yahaya Yakubu[1,2] ⓘD, Jun Zhou[3], Zhu Shu[3], Yigen Tan[3], Zhengliang Zhao[3] and Yassin Mbululo[1,4]

Abstract

This study sought to establish the effectiveness of water washing pre-treatment on the quality of municipal solid waste incineration (MSWI) fly ash (FA) for reuse and solidification or stabilization (S/S). Initial analysis of the FA sample shows that it did not meet the USEPA-1311 toxicity characteristic leaching procedure (TCLP) regulatory limits of 2011. As a result, a two-stage water washing process was carried out an attempt to improve the quality of the MSWI FA. After the washing pre-treatment, the heavy metals in the FA sample met the regulatory limits, thereby making it non-toxic for reuse or safe disposal. The leachate from the washing process also passed regulatory standards of China (GB 8978 – 1996) and the 2011 USEPA-1311. The washing process successfully removed more than 98% of each heavy metal under study. The process was excellent at removing cadmium (99.99%) and very good at removing the rest of the heavy metals. The 28-day compressive strength increased as the quantity of FA decreased. Also, all the heavy metals in the samples prepared with the pre-treated FA met the USEPA-1311 TCLP regulatory limit for reuse and safe disposal. The heavy metals leachability and compressive strength tests showed that the effect of cement-based S/S was largely influenced by its quantity in the samples. The highest compressive strength was attained by using 55% of the FA as replacement for cement. However, FA replacements of up 70% also yielded good results that met the 1989 USEPA standard of 0.34 MPa (50 psi).

Introduction

Washing pre-treatment of municipal solid waste incineration (MSWI) fly ash (FA) with water is an appropriate process for increasing its quantity in cementitious mixtures. However, it is associated with extra costs related with construction, operation, and management of the washing plant and waste-water treatment units. Waste-water generated during the washing process is a type of hydro-saline solution, usually containing high concentrations of heavy metals, alkali chlorides and sulphates which cause serious pollution problems. However, these salts can be recycled as resources instead of been discharged (Boghetich et al., 2005; Tang et al., 2014; Wu and Ting, 2006). Chen et al. (2016) suggest the reuse of discharged waste-water through concentration by evaporation if the technology is applied to industrialized mass production. Some of the metals in MSWI FA and leachate produced from washing treatment are valuable and should be recovered (Alorro et al., 2008, 2009; Ferreira et al., 2005). Tang et al. (2018) compared the efficacy of Cyanex 572 with Cyanex 923 and Cyanex 272 in a study to compare the use of a novel commercial extractant in the selective separation of zinc (Zn) from other metals in ash, and concluded that Cyanex 572 can be an economically and environmentally suitable extractant for the recovery of Zn and other metals from MSWI FA.

Disposal of sludge resulting from washing pre-treatment requires an initial treatment to lower the pH and ionic concentrations of cadmium, aluminium, zinc, and lead. Reduction in sulphate concentration is also necessary when waste-water is to be discharged into surface water. When sulphate reduction is not required, waste-water can be successfully treated by decreasing its pH to 7.6, which will cause the formation of aluminium hydroxide $(Al(OH)_3)$ flocs capable of reducing heavy metals concentration below the recommended limit values through adsorption (Mangialardi 2003).

Solidification or stabilization (S/S) is widely used for management of harmful wastes; especially those contaminated with

[1]School of Environmental Studies, China University of Geosciences (Wuhan), P. R. China
[2]Zoomlion Ghana Limited, Ghana
[3]Engineering Research Center of Nano-Geomaterials of Ministry of Education, China University of Geosciences, P. R. China
[4]Solomon Mahlangu College of Science and Education, Sokoine University of Agriculture, Tanzania

Corresponding author:
Yahaya Yakubu, School of Environmental Studies, China University of Geosciences (Wuhan), 388 Lumo Road, Wuhan, 430074, P. R. China.
Email: yinny76@hotmail.com

substances categorized as hazardous. The treatment process comprises mixing a binding reagent into the contaminated material (Malviya and Chaudhary, 2006; Wilk, 2004, 2007). This process protects public health and the environment by immobilizing contaminants within the treated material. Solidification or stabilization is an effective treatment method for a wide variety of organic and inorganic contaminants present in contaminated sludge, sediment and soil (Singh and Pant, 2006). The ability to successfully treat a wide range of contaminants within the same media is a key reason why this method is commonly used (Quina et al., 2008). Adding to its versatility is the fact that contaminated material can be treated on/off-site as already separated waste or dugout material (Wilk, 2002, 2004). The effectiveness and wider application of S/S treatment for hazardous waste and in remediation makes it significant that practitioners comprehend the chemical, physical, and regulatory aspects of the technology as well as how it is applied (USEPA, 2011).

Even though the terms solidification and stabilization appear similar, they refer to different effects that the binding materials produce to immobilize hazardous constituents. Solidification refers to changes in the physical properties of the waste or media (Chang et al., 2009). The desired changes of this process include a decrease of permeability, increase of the compressive strength, and encapsulation of hazardous components. On the other hand, chemical changes of the hazardous constituents in the waste are referred to as stabilization (Chang et al., 2009; Saeed, 2012; Singh and Pant, 2006). Desired changes in stabilization include converting the components into insoluble, immobile, or non-toxic form. Materials commonly used for binding include limestone, lime, cement kiln dust, lime kiln dust, Portland cement, fly ash, gypsum, slag, and phosphate mixtures, and a variety of proprietary reagents. Because of the great difference of waste components and media, a blend design should be carried out on each type of waste. Most mix designs are a blend of the aforementioned binding reagents. Organic binding reagents have also been tried, and they include thermoplastic, urea formaldehyde, and asphalt. Due to high cost they are rarely used in commercial scale compared to inorganic binders (Weitzman and Conner, 1989; Zhou et al., 2017).

Application of ordinary Portland cement for S/S purposes is practiced in many countries. This process without washing pretreatment is however not suitable for the treatment of soluble salts, because it can pose environmental problems in the long term (Quina et al., 2010). Since the process involves the use of additives, more space will be required when using this method. However, it is suitable for the treatment of toxic waste (Qian et al., 2008).

Portland cement is a generic material, apart from been the principal material used in concrete for construction, it is also a versatile S/S binding reagent with the ability to both solidify and stabilize a wide range of wastes. Mixtures of cement are popular for S/S treatments and have been used for a greater variety of wastes than any other binding reagent. It is often selected for the following reasons: (a) its ability to facilitate reduction of the toxicity of some contaminants, (b) its ability to chemically bind free liquids, (c) its capability of encapsulating waste particles surrounding them with an impermeable coating, (d) its potential to chemically fix hazardous constituents by reducing their solubility, and (e) its capacity to reduce the permeability of the waste form. These are made possible by physical changes in the waste and chemical changes to the hazardous constituents themselves (Chang et al., 2009; Chen et al., 2009; Saeed, 2012; Singh and Pant, 2006; Sun et al., 2016).

Cement-based S/S has been used to treat wastes that have only inorganic or a mixture of hazardous constituents. Mix designs are usually made up of additives or by-products in addition to Portland cement. FA is also usually applied in order to capitalize on its pozzolanic effect when mixed with hydrating Portland cement (ASTM D5370-14, 2014). Slag and cement kiln dust possess minor cementitious properties and are sometimes applied for economic reasons. Lime and kiln dust can also be used for the adjustment of pH or to remove water, by utilizing their high heat of hydration. It is feasible to apply limestone too for pH adjustment and bulking (Luna Galiano et al., 2011; Tang et al., 2016). The most common use of S/S is in the management of wastes with inorganic hazardous constituents. This is because the danger is associated with the heavy metals content in inorganic-contaminated wastes. Since these wastes have failed the toxicity characteristic leaching procedure (TCLP) test, they are classified as hazardous waste. Solidification or stabilization treatment is therefore frequently used to decrease the leaching potential of the hazardous component from the waste. After pre-treatment, the waste usually does not exhibit the hazardous characteristic and can be allowed in the landfill as non-hazardous waste.

Most hazardous wastes require treatment to a maximum extent to reduce their potential risks after disposal. Solidification or stabilization treatment is often used on wastes to comply with this requirement, as it is the only practically available technology used to treat large volumes of heavy metals-contaminated soil, sludge, or sediment resulting from remediation projects. Wilk (2004, 2007) suggests cement to be exclusively suitable for application as a S/S reagent for metal contaminants, because it reduces the mobility of inorganic compounds by, (a) formation of insoluble hydroxides, silicates, or carbonates; (b) physical encapsulation; and (c) substitution of the metal into a mineral structure. It can also reduce the toxicity of some heavy metals by inducing changes in their valence state.

Fly ash from MSWI is regarded as hazardous waste material for which landfilling is often the most suitable treatment. Solidification or stabilization with cement as a binder is the most often applied pre-landfill treatment method for MSWI FA globally (Chen et al., 2009; Polettini et al., 2001; Quina et al., 2008). It does not only involve the conversion of the ash into a granular or monolithic material which guarantees easy handling and transportation to landfill sites, but also immobilizes toxic pollutants through chemical incorporation, adsorption and/or physical encapsulation (Chang et al., 2009; Glasser, 1997). Fly ash from MSWI is similar to cement clinker because it contains a high

concentration of Ca, Si and Al. Additionally, when it is exposed to temperatures higher than 850°C in a post-combustion chamber, the reactions that occur are also similar to those in a cement kiln, resulting in FA and boiler ash with cementitious properties. A large fraction of most MSWI FA is made up of unreacted hydrated lime, which is a known binding agent. As the majority of MSWI FA possess cementitious properties, it is very likely that S/S of these materials can also be attained by only adding water, thus considerably decreasing the environmental impact of the treatment (Dermatas and Meng, 2003).

Portland cement based S/S technology is an attractive alternative for the management of heavy-metal-contaminated waste before disposal, and decreases the discharge of contaminants into the environment. The effectiveness of cement-based S/S can be improved by varying the water/solid ratios, particle size, cement phase compositions, controlling temperature, and other parameters that influence strength development, setting, and long-term durability of solidified wastes. Heavy metals in MSWI FA may undesirably affect the cementing medium; hence, pre-treatment to render it harmless by the addition of an adsorbent is necessary in some instances. In addition to precipitation and sorption, heavy metals may enter the hydrates lattice. Phases related with heavy metals in cement-based S/S systems are often amorphous or poorly crystalline mixtures of varying compositions in nanoscale, thereby making their characterization very difficult (Chen et al., 2009).

The main aim of this paper is to evaluate the effects of water washing as an effective pre-treatment process for removing/reducing heavy metals and chlorides in MSWI FA for wider application in the cement and concrete industry or for safe disposal. As a result, the FA sample used in this study was pre-treated through washing with distilled water and used with cement for the production of bricks at a laboratory scale.

Materials and methods

The FA sample used in this study was obtained from the Xinghuo waste incineration power plant in Wuhan City, Hubei Province, P.R. China. This facility is designed to handle 1000 tons of household waste per day, which accounts for about 25% of the total production of domestic waste. The total installed capacity of this power plant is 24 megawatts. It uses the grate furnace process technology of incineration. Incineration of municipal solid waste (MSW) discharges lots of dust and harmful acidic smoke which need to be purified. Gas purification technology of the incineration plant is done by an initial injection of hydrated lime ($Ca(OH)_2$) to neutralize harmful acid gas, and after which the gas is channelled through bag filters to intercept dust, acid gas neutralization products, residual hydrated lime, and so forth. The gas purification process produces a large amount of FA, which has harmful effects on humans and the environment, due to presence of heavy metal pollutants and others. Thus, treatment of the FA before reuse or disposal is quite significant.

Pre-treatment of the FA was carried out under room conditions by subjecting it to a two-stage washing process with distilled water, using a liquid-to-solid (L/S) ratio of 10 for 15 minutes, and stirring speed of about 30 revolutions per minute (rpm). After the washing process it was filtered and dried at 105°C for 24 hours, before laboratory tests were conducted.

Chemical and mineralogical analyses

The chemical composition of the FA samples (raw and washed) was determined by X-ray fluorescence (XRF, AXIOSmAX, PANalytical B. V.), while their mineral phases were determined by X-ray powder diffraction (XRD, D8-FOCUS, Bruker AXS).

Concentration of heavy metals

In order to establish the concentration of heavy metals in the FA samples, the TCLP test was conducted according to the USEPA-1311 method. To achieve this, the pre-treated samples were all sieved before the leaching test. The extraction liquid, with a pH value of 2.88 was prepared by dissolving 5.7 mL of glacial acetic acid in 1 L of deionized water. After that, a given amount of the extraction liquid was added to a polyethylene (PE) bottle containing the FA sample, with an L/S ratio of 20:1, followed by a rolling-over process at 30 rpm for 20 hours on an oscillator. Thereafter, the leachates from the samples (raw and washed fly ashes, and the prepared brick samples) were filtered using syringes and filters with effective pore size of 220 nm and analysed by ICP-MS (Elan DRC-e, PerkinElmer).

Sample preparation

The pre-treated MSWI FA sample was dried at 105 °C for 24 hours and sieved with a 0.45 mm sieve. After that, cement was added using various FA-to-cement percentages, thus: 100 (FAC100), 75:25 (FAC75), 70:30 (FAC70), 65:35 (FAC65), 60:40 (FAC60), and 55:45 (FAC55). Using the Indian standard (IS 516-1959) as a guide, the FA and cement were mechanically mixed with a Cole-Parmer ultra-compact mixer at room temperature before water was added and cast into cubic moulds (3.2 cm × 3.2 cm × 3.2 cm). The quantity of water used the samples was determined by gradual addition in order to obtain a paste that can be cast into the moulds, starting with the sample containing only FA (FAC100). After that, the quantity of water used for the rest of the samples was obtained by adding 4% to each preceding sample. So, every 5% increase in the quantity of cement corresponded with 4% increase in the level of water used.

The prepared brick samples were left to dry under room conditions for 7 days, after which they were removed from the moulds and allowed to further cure under room conditions for 21 days. This was then followed by the determination of their physical and chemical properties (compressive strength, heavy metal leachability, density, and mineral phases). Table 1 presents the various quantities of FA, cement, and water used for each sample.

Test methods for samples

Leaching test. The TCLP test was conducted according to the USEPA-1311 method, by using the crushed, ground, and sieved brick samples. The extraction liquid, with a pH value of 2.88 was prepared by dissolving 5.7 mL of glacial acetic acid in 1 L of deionized water. A given amount of the extraction liquid was added to a PE bottle containing the crushed, ground and sieved samples, with an L/S ratio of 20:1, followed by a rolling-over process at 30 rpm for 20 hours on oscillators. The leachate from the samples was filtered by using syringes and filters with effective pore size of 220 nm and analysed by ICP-MS (Elan DRC-e, PerkinElmer).

Property characterization. The 28-day compressive strength of the samples was measured according to the Chinese Standard (GB/T 17671-1999) on a WE-50 universal testing machine (Shandong Jinan Testing Machine Factory, China), by averaging from three cube samples for each composition. The mineral phases of the samples were determined by XRD (D-FOCUS, Bruker AXS), with step scanning in the 2θ range from 5° to 70° at a rate of 4°/min using Cu Kα radiation and Ni filter at a generator voltage of 40 kV and a current of 40 mA.

Results and discussion

Characterization of fly ash

The pH of the leachate after washing was 11.9 and 12.4 for the first and second washing, respectively, while that of the washed FA after drying was 12.3. Also, the moisture content of the raw FA (5.31%) was determined by subtracting its final weight from the initial weight after drying a certain quantity in an oven at 105 °C for 24 hours. The loss on ignition (LOI) for the raw FA was 16.67%, whiles that of the washed FA was 15.33%.

Table 1. Materials used for fly-ash cement (FAC) samples.

Sample code	Weight (g)		
	FA	Cement	Water
FAC100	46.5	–	38.4
FAC75	40	10	40
FAC70	40	12	41.6
FAC65	40	14	43.2
FAC60	40	16	44.8
FAC55	40	18	46.4

Chemical and mineralogical composition of raw FA

The chemical composition of the untreated FA expressed as metal oxides or in their elemental state is presented in Table 2.

With reference to Table 2 the chemical composition of the untreated FA expressed as metal oxides or in their elemental state have been presented. Silicon oxide (SiO_2) formed the major chemical component of the FA (64.72%), followed by aluminium oxide (Al_2O_3) (14.83%). The rest constituted less than 5% each. From the chemical composition presented in Table 2, the presence of high level of silicon, aluminium, and calcium oxides, and the absence chloride and sulphate contents in the raw FA makes it very suitable for use in the cement and concrete industries (Gao et al., 2008; Faming et al., 2014) (Table 2). However, due to the presence of certain heavy metal oxides (manganese oxide (MnO), tin oxide (TiO_2), barium oxide (BaO), strontium (Sr), and zirconium (Zr)), the ash must be subjected to preliminary treatment before reuse and/or landfilling. Also, there is the need to carry out other analyses to further confirm the presence/absence of chloride salts and sulphate. Regarding the heavy metal oxides, Fe_2O_3 is the most concentrated heavy metal oxide (5.33%), followed by manganese oxide (MnO) (1.92%). The rest constituted less than 1.00% each (Table 2).

The mineralogical composition of the FA sample is complex (Table 2). Lower peak intensities in the X-ray diffractogram (Figure 1) of the raw FA show that most of the compounds are mainly in the amorphous form. Higher concentration of chlorides in the FA is observed through the higher peaks of the crystalline forms of silicon chloride ($SiCl_4$) and calcium chloride hydroxide (CaCl(OH)). The peak of halite (NaCl) confirms the presence of relatively small quantities of Na.

Chemical and mineralogical composition of washed FA

With regards to the chemical composition of the washed FA (Table 3), carbon dioxide constituted the highest (37.67%), followed by calcium oxide (32.30%). These were followed by silicon oxide (13.20%), aluminium oxide (5.66%), magnesium oxide (2.97%), sodium oxide (1.77%), with the rest accounting for less 1% each. With reference to the heavy metal oxides, iron oxide is the most concentrated heavy metal oxide (2.32%), followed by zinc (0.76%), and lead (Pb) (0.19%). The rest constituted less than 0.10% each.

Table 2. Chemical composition of raw fly ash (FA).

Composition	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	MnO
Content (%)	64.72	14.83	5.33	1.92	2.27	1.70	2.78	0.001
Composition	TiO_2	P_2O_5	CO_2	Ba	Sr	Zr	Others	
Content (%)	0.78	0.001	4.88	0.06	0.02	0.02	0.67	

Chemical composition of the pre-treated FA sample is also complex (Table 3). Lower peak intensities in the X-ray diffractogram (Figure 2) for the washed FA show that most of the compounds in the ash are mainly in the amorphous form. The high number of $CaCO_3$ peaks in the X-ray diffractogram of this FA indicate high level of calcite in the ash. Higher concentrations of portlandite, quartz (SiO_2) and anhydrite ($CaSO_4$) are also observed in the ash through their high peaks. The peak of calcium silicate hydroxide ($Ca_7Si_{16}O_{38}(OH)_2$) confirms its presence in a relatively small quantity.

The complete elimination of the chloride phase after washing proves the effectiveness of water washing pre-treatment. From the results of Figure 1 and Figure 2, it can be seen that all the chlorides phases (sylvite, silicon chloride, and halite) were removed after the washing process, which is consistent with the study by Wang et al. (2016) on the effects of water washing on cement-based stabilization of MWSI FA. Also, from the studies of Faming et al. (2014) on mechanical properties of concrete after chlorine salt extraction in freeze–thaw environment and Gao et al. (2008) on utilization of washed MSWI FA as partial cement substitute with the addition of dithiocarbamic chelate, it was concluded that the presence of chloride and sulphate affect the potential utilization of ashes in cement and concrete industries. This therefore means that washing serves as a promising process of improving the quality of raw FA for application in the aforementioned sectors, since it is able to reduce the chloride content appreciably.
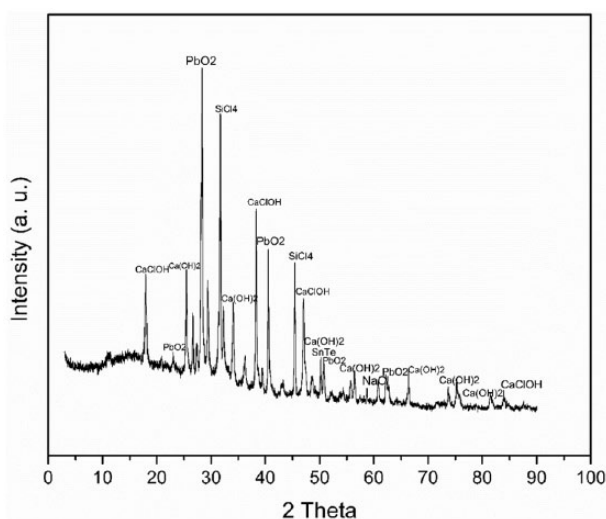

Figure 1. X-ray diffractogram of raw FA. SnTe – tin telluride, SiCl₄ – silicon chloride, NaCl – halite, CaClOH – calcium chloride hydroxide, PbO₂ – lead oxide, Ca(OH)₂ – portlandite.

Chemical composition of leachate from pre-treatment

Table 4 presents a comparison of the heavy metals composition of the leachate from the washing process, the USEPA TCLP-1311 and the China (GB 5085.3-2007) regulatory limits. It can be seen from the results that the leachate complies with both regulatory limits and can be discharged without further treatment under both circumstances.

From Table 5 Ni and Cu are far less than their respective GB 5085.3-2008 limit by more than 96 times and 5000 times, respectively, whilst Zn was almost one thousand hundred times less. Also, using the USEPA limits, Cu was almost 167 times less, Zn was more than 54 times less, and Cr was more than 45 times less (Table 5).

Chemical composition of cement

The chemical composition of the cement sample was also analysed by XRF in order to get a fair idea on its composition (Table 5). From Table 5, the cement sample also has a quite complex composition.

In the cement sample, calcium oxide was the dominant oxide (58.56%), followed by silicon oxide (22.96%). They were followed by aluminium oxide (9.87%), sulphur oxide (SO_3) (2.84%), magnesium oxide (1.43%), with the rest occupying less than 1% each. Also, the most predominant heavy metal was iron oxide (2.43%). This was followed by titanium oxide (0.49%), and manganese oxide (0.16%), with the rest constituting less than 0.10% each. The cement sample also contained a smaller amount of chlorine (0.04%).

Pre-treated MSWI FA

Table 6 presents the comparison of heavy metals identified in the raw and washed FA samples using inductively coupled plasma mass spectrometry (ICP-MS), and the USEPA-1311 TCLP regulatory limes.

From Table 6, all the heavy metals in the raw FA sample exceeded the USEPA-1311 TCLP regulatory limits. Chromium (Cr) exceeded the limit by almost three times, cadmium (Cd) exceeded the limit by more than seventeen times, while copper (Cu) was almost two times higher. This makes the sample toxic under the USEPA-1311 TCLP classification, thereby requiring pre-treatment and proper handling.

However, after the washing pre-treatment the concentration of all the heavy metals reduced drastically (Table 6), thereby making the ash compliant with the regulatory requirements. It is

Table 3. Chemical composition of washed fly ash (FA).

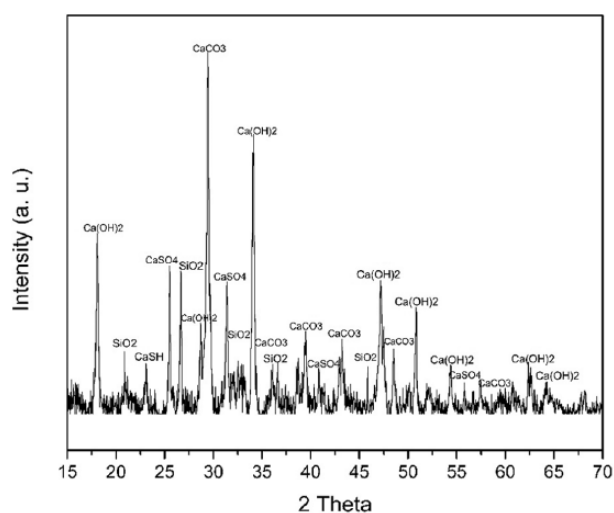| Composition	SiO₂	Al₂O₃	Fe₂O₃	MgO	CaO	Na₂O	K₂O	MnO	P₂O₅
Content (%)	13.2	5.66	2.32	2.97	32.3	1.77	0.69	0.08	0.54
Composition	CO₂	Cr	Ni	Cu	Zn	Pb	Others		
Content (%)	37.67	0.02	4e⁻³	0.07	0.76	0.19	1.79		

Figure 2. X-ray diffractogram of washed FA. $CaSO_4$ – anhydrite, $CaCO_3$ – calcite, CaSH – calcium silicate hydroxide $(Ca_7Si_{16}O_{38}(OH)_2)$, SiO_2 – quartz, $Ca(OH)_2$ – portlandite.

Table 4. Comparison of heavy metals in leachate and regulatory limits.

Heavy metal	Leachate (mg/L)	USEPA regulatory limit (mg/L)	China (GB 5085.3-2007) (mg/L)
Cr	0.044	2	–
Co	0.003	–	–
Ni	0.052	–	5
Cu	0.018	3	100
Zn	0.091	5	100

'–' means not available at the time of this study.

worth mentioning that the washing process almost removed all the contents of the heavy metals identified in the raw ash. More than 98% of each heavy metal was successfully removed (Table 6). From the ICP-MS results of the raw and washed FA samples (Table 6) the washing process was excellent in removing Cd (99.99%) and very good at removing the rest. About 99.96% of cobalt (Co) was eliminated, 99.95% of Cu, 99.95% of Zn, 98.61% of Cr, and 98.12% of nickel (Ni) (Table 6).

Potential reuse and S/S through cement addition

Evaluation of the chemical and mineralogical characteristics. Table 7 presents the concentration of the heavy metals in samples prepared using the washed MSWI FA and cement (FAC samples). The pH of the mixture of crushed samples (< 1 mm size) and extraction solution was determined in order to find out its effect(s) on the leachability of the heavy metals in the samples. From the results in Table 7, it appears the heavy metals leachability decreased as pH increased, even though some of the sample pH values are so close to each other. This is corroborated by Yahaya et al. (2018), who concluded from their study on the effects of pH dynamics on S/S of MSWI FA, and recommended a pH range of

5 to 11 for the management of MSWI FA. The FAC samples have been so effective in the S/S of all the heavy metals because the pH values are within the recommended range (5 to 11) that is why the FAC samples have been so effective in the S/S of all the heavy metals.

The highest amount of Cr leached in FAC100 (21.00 mg/L), which had a mixture pH of 9.3, whiles the least leached at pH 7.5 of FAC75 (3.88 mg/L) (Table 7). FAC70 and FAC55 had the same level of Cr leachability (4.46 mg/L) at pH of 7.6 and 10.9, respectively, which is the third highest (Table 7). FAC60 had the second highest leachability (4.5 mg/L) at pH 9.3, and at pH of 7.5, FAC65 leached 4.26 mg/L of Cr, making it the fourth highest (Table 7). From Table 7 it is evident that the amount of FA has a significant effect on the immobilization of the heavy metals. This is more pronounced across FAC60 and FAC55, which appear to generally reduce the heavy metal leachability. The highest amount of Zn leached in FAC75 (66.2 mg/L), followed by FAC70 (52.8 mg/L). These were followed by FAC65 (40.0 mg/L), FAC100 (22.2 mg/L), FAC60 (16.6 mg/L), and FAC55 (1.0 mg/L). Nevertheless, all the heavy metals in the FAC samples met their USEPA-1311 TCLP regulatory limits (Cu = 250 mg/L, Pb = 50 mg/L, Cd = 10 mg/L, Cr = 50 mg/L and As = 50 mg/L). A look at the X-ray diffractograms (Figs. 3 to 8), show that almost all the heavy metals identified by the ICP-MS results are missing, with the exception of Zn, which appeared in FAC75 diffractogram as hydrozyncite $(Zn_5(CO_3)_2(OH)_6)$ (Figure 4).

The X-ray diffractogram of FAC100 (Figure 3) contains a number of carbonates and chloride peaks, with calcium silicate chloride representing the predominant peak. It was followed by calcite, and calcite and magnesia. FAC100 is the only sample in which a chloride phase has been identified. The presence of chlorides (calcium silicate chloride) among the phases identified in Figure 3 can be attributed to the presence of its free form (reactive) after the washing pre-treatment, even though it could not be detected in earlier analysis. It is therefore possible that this chloride reacted with calcium silicate hydroxide to form calcium silicate chloride by substituting the hydroxyl (OH^-) group.

Among the phases identified in the FAC75 X-ray diffractogram (Figure 4) calcium oxide has been identified as an oxide that favours cementitious properties. Also, sodium silicate possesses good binding properties when available in cementitious material. The rest of the phases identified are lithium bismuth tungsten oxide $(LiBiW_2O_8)$, hydrozyncite $(Zn_5(CO_3)_2(OH)_6)$, and sodium silicate hydrate $(Na_6Si_2O_7 \cdot 11H_2O)$ (Figure 4). The presence of lithium and tungsten in lithium bismuth tungsten oxide might affect the physical properties of the samples (e. g. compressive strength).

Among the phases identified in Figure 4, lithium bismuth tungsten oxide constituted the highest phase, followed by calcium oxide, sodium silicate hydrate, and hydrozyncite. The formation of sodium silicate hydrate might be attributed to the presence of zinc in hydrozyncite, which is known to delay hydration in cementitious matrices. Also, as the content of FA increases in the sample, so does the phases of heavy metals (Figures 4 and 5). The results

Table 5. Chemical composition of cement.

Composition	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	MnO	TiO_2	P_2O_5
Content (%)	22.96	9.87	2.43	1.43	58.56	0.17	0.69	0.16	0.49	0.15
Composition	Ba	Sr	Zr	Cr	Cu	Zn	Pb	SO_3	Cl	Others
Content (%)	0.02	0.09	0.03	0.03	0.01	0.01	0.01	2.84	0.04	0.01

Table 6. Comparison of fly ash (FA) heavy metals content and toxicity characteristic leaching procedure (TCLP) regulatory limits.

Heavy metal	Raw FA (mg/L)	Washed FA (mg/L)	% Reduction	USEPA-1311 -TCLP regulatory limit (mg/L)
Cr	136.74	1.90	99.15	50
Co	99.81	0.04	99.96	–
Ni	45.79	0.86	98.12	–
Cd	172.08	0.01	99.99	10
Cu	499.90	0.18	99.95	250
Zn	6430.31	3.30	99.95	–

'-' not available at the time of this study.
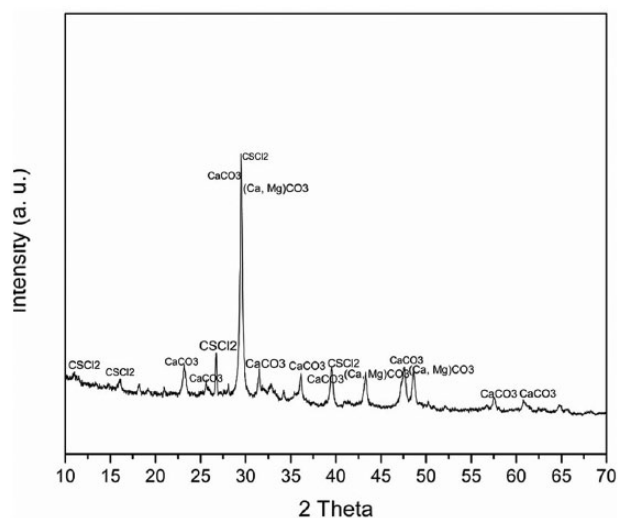
Figure 3. X-ray diffractogram of FAC100. CSCl2 – calcium silicate chloride (Ca_2SiO_3Cl), $CaCO_3$ – calcite, (Ca, Mg)CO_3 – calcite, magnesia.
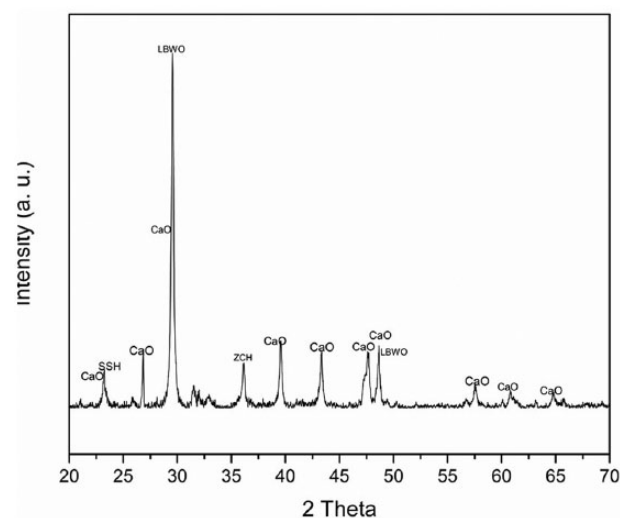
Figure 4. X-ray diffractogram of FAC75. ZCH – hydrozyncite ($Zn_5(CO_3)_2(OH)_6$), CaO – calcium oxide, LBWO – lithium bismuth tungsten oxide ($LiBiW_2O_8$), SSH – sodium silicate hydrate ($Na_6Si_2O_7.11H_2O$).

of FAC70 X-ray diffractogram (Figure 5) is a bit complex due to the number of new phases identified. Lithium bismuth oxide peaked higher, followed by aluminium boron hydride (AlB_3H_{12}). They were followed by calcite, potassium barium phosphate ($KBaPO_4$), and sodium silicate (Na_4SiO_4) (Figure 5).

However, the X-ray diffractogram for FAC65 (Figure 6) contains only three phases. Calcite and magnesia ((Ca, Mg)CO_3) formed the major phase, followed by calcium sulphate hydrate ($CaSO_4.0.15H_2O$), and antimony tungsten oxide (Sb_2WO_6).

The presence of calcite and magnesia, and calcium sulphate hydrate in FAC65 is very favourable for cementitious property development (Figure 6).

FAC60 had only calcite representing all of its peaks. All the heavy metals are completely missing from the X-ray diffractogram (Figure 7). The presence of only calcite peaks is further

confirmed by Rémond et al. (2002), who put forward that the addition of FA into cement pastes results in an increase in quartz and calcite that are already present in the ash, after their study on the effects of incorporating MSWI FA in cement pastes and mortars.

Lithium bismuth tungsten oxide peaked very high, followed by calcite in the X-ray diffractogram for FAC55 (Figure 8). These were followed by silicon sulphide (SiS_2), and relatively small levels of calcium aluminium boron oxide hydroxide hydrate ($Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$), and ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}$). Ettringite is well known for its fixing capacity for heavy metals as stated in a study on pH effects on S/S of MSWI FA by Yahaya et al. (2018). This is further corroborated by Rémond et al. (2002), who studied the effects of
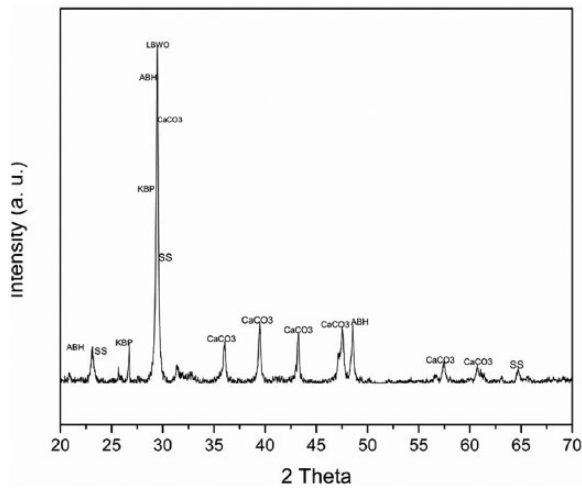
Figure 5. X-ray diffractogram of FAC70. $CaCO_3$ – calcite, LBWO – lithium bismuth tungsten oxide ($LiBiW_2O_8$), ABH – aluminium boron hydride (AlB_3H_{12}), KBP – potassium barium phosphate ($KBaPO_4$), SS – sodium silicate (Na_4SiO_4).
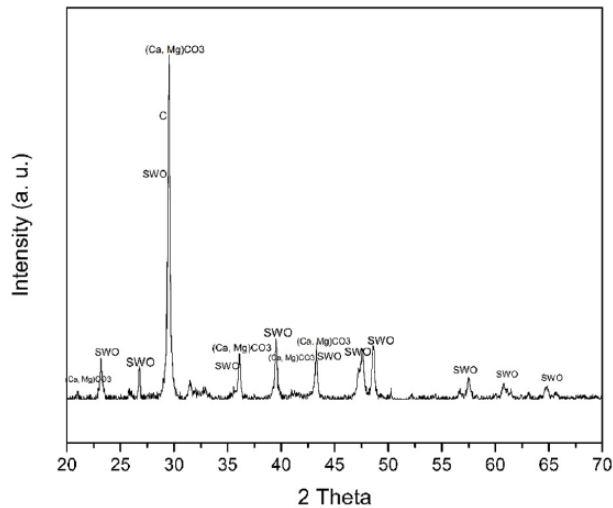

Figure 7. X-ray diffractogram of FAC60. $CaCO_3$ – calcite.

Figure 6. X-ray diffractogram of FAC65. C – calcium sulphate hydrate ($CaSO_4.0.15H_2O$), (Ca, Mg)CO_3 – calcite, magnesia, SWO – antimony tungsten oxide (Sb_2WO_6).

Figure 8. X-ray diffractogram of FAC55. $CaCO_3$ – calcite, CABHH – calcium aluminium boron oxide hydroxide hydrate ($Ca_6Al_2(SO4)_3(OH)_{12}.26H_2O$), CSHH – ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}$), SiS$_2$ – silicon sulphide, LBWO – lithium bismuth tungsten oxide ($LiBiW_2O_8$), SWO – antimony tungsten oxide (Sb_2WO_6).

incorporating MSWI FA in cement pastes and mortars and concluded that the main crystalline hydrates formed due to the addition of MSWI ash to cement pastes are ettringite, Friedel's salt and thenardite. Though more the X-ray diffractogram for FAC55 is relatively complex, it was very effective in S/S of all the heavy metals (Figure 8 and Table 7).

Evaluation of the physical characteristics of FAC samples. The 1989 USEPA commonly applied physical tests in routine project performance standards which comprised of the unconfined compressive strength (0.34 MPa/> 50 psi), hydraulic conductivity, and paint filter test. As a result, the compressive strength results of this research are compared with the recommended values of the USEPA (1989) and checked as 'passed' or 'failed' (Table 8). The densities and compressive
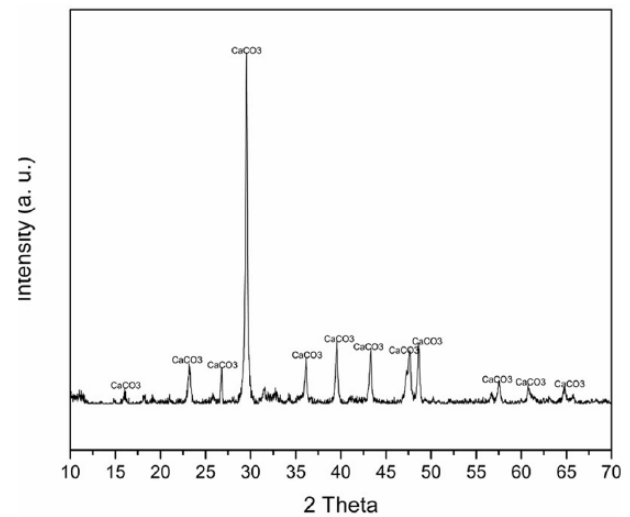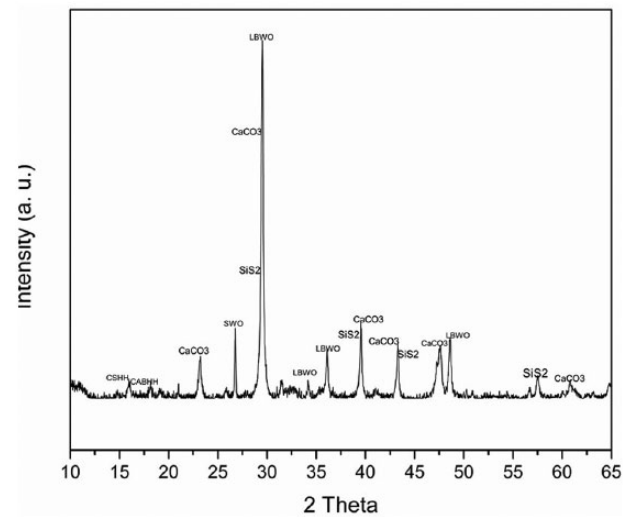
strengths of the samples (FAC75 to FAC55) increased as the quantity of FA decreased and cement increased. From the results in Table 8, there exist a strong correlation between density and compressive strength ($r^2 = 0.899$). Substituting 25% of FA by cement did not produce a good compressive strength. However, most samples yielded an appreciable level of compressive strength, which means that substitutions of cement by FA of up to 70% are effective in strength development. This is also confirmed by Wang et al. (2016) who utilized 33% of cement, cured for 7 days and achieved appreciable results.

From the results in Table 8 only FAC75 'failed' (0.25 MPa) the USEPA 1989 standard (0.34 MPa), the rest passed. The highest compressive strength was achieved by FAC55 (0.93 MPa), followed by FAC100 (0.91 MPa). These were followed by

Table 7. Inductively coupled plasma mass spectrometry results of fly-ash cement (FAC) samples.

Sample	pH	Cr	Mn	Co	Ni	Cu	Zn	Cd	Pb
		mg/L							
FAC100	9.3	21.00	1.33	0.32	2.02	1.83	22.20	1.79	0.20
FAC75	7.5	3.88	2.44	0.33	2.52	2.62	66.20	3.20	0.24
FAC70	7.6	4.46	3.08	0.29	2.26	2.26	52.80	2.62	0.15
FAC65	7.5	4.26	2.32	0.29	2.24	1.99	40.00	2.36	0.20
FAC60	9.3	4.50	2.08	0.20	1.89	1.18	16.60	1.45	0.16
FAC55	10.9	4.46	0.74	0.13	1.57	0.77	1.02	0.30	0.05

Table 8. Physical characteristics of fly-ash cement (FAC) samples.

Sample	Density (g/cm^3)		Compressive strength (MPa)		Compared with the USEPA standards MPa/ psi (0.34/>50)
	Mean	SD	Mean	SD	
FAC100	1.18	0.07	0.91	0.03	Passed
FAC75	1.05	0.15	0.25	0.04	Failed
FAC70	1.09	0.04	0.37	0.02	Passed
FAC65	1.13	0.05	0.45	0.03	Passed
FAC60	1.2	0.05	0.84	0.03	Passed
FAC55	1.25	0.04	0.93	0.02	Passed

FAC60 (0.84), FAC65 (0.45 MPa) and FAC70 (0.37 MPa). It is further evident from the results that a decrease in the quantity of MSWI FA corresponded with an increase in the compressive strength. But quite strikingly, the compressive strength of FAC100 is the second highest, which might indicate that the FA alone has very high cementitious properties. This is corroborated by Dermatas and Meng (2003) in their study on the utilization of FA for S/S of heavy metal contaminated soils. Also, Mangialardi et al. (1999) proved the feasibility of washing pre-treatment as a means of maximizing the incorporation of MSWI FA in cementitious matrixes of up to 90% by weight of total solid. Based on the results in Table 8, it is possible to extend this value to 100% (i.e. by using only the FA). The X-ray diffractogram of FAC100 (Figure 3) has high level of calcite and silicates as evidenced by their respective peaks, which might be a contributing factor for the high strength development of this sample. It is important to state that the plastic moulds used in this experiment did not produce bricks of the exact mould dimensions (3.2 cm × 3.2 cm × 3.2 cm), so the density of the bricks might differ due to the differences in their final size. However, since the compressive strength depends on each brick's dimensions, the weak compressive strength of the FAC75 sample may be linked to the formation of the hydrozyncite phase, the high presence of heavy metals and chlorine in the cement sample. Therefore substituting 25% of the pre-treated FA with cement was not enough to produce a good compressive strength. Other reasons might be attributed to the plastic moulds used, the smaller amount of calcium oxide, and a hydrated form of sodium silicate (Figure 4). Also, the higher amount of lithium bismuth tungsten oxide does not facilitate strength development.

Conclusion

Water washing pre-treatment was carried out on a MSWI FA sample which did not comply with the USEPA-1311 TCLP regulatory limits of 2011. But after the washing pre-treatment, it met the regulatory requirements, thereby making it safe for reuse or disposal. Moreover, the leachate from the washing process met the China (GB 8978 – 1996) and USEPA-1311 regulatory discharge limits. The water washing pre-treatment immobilized/ removed almost all the contents of the heavy metals identified in the raw FA. More than 98% of each heavy metal was successfully immobilized/removed. The process was very excellent in immobilizing/removing Cd and very good at removing the rest of the heavy metals (Cu, Co, Zn, Cr, and Ni).

The concentration of heavy metals generally decreased with the FA content, even though the observed pattern was quite complex. However, the density and compressive strength generally increased as the quantity of FA decreased. Also, almost all the heavy metals identified by the ICP-MS analysis were not present in the X-ray diffractograms, except Zn, which appeared in the FAC75 diffractogram as hydrozyncite ($Zn_5(CO_3)_2(OH)_6$). The presence of chlorides (calcium silicate chloride) among some of the phases identified in the samples (except FAC100) can be attributed to its presence in the cement. The heavy metals leachability and compressive strength tests showed that the effect of cement-based S/S was influenced by its percentage addition. Among the mix proportions tested in this study, the highest compressive strength was attained by FAC55, which incorporates 55% of FA as a replacement for cement. However, replacements of up 70% still produced results that met the USEPA-1311 recommended limits.

Declaration of conflicting interests

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ORCID iD

Yahaya Yakubu https://orcid.org/0000-0001-6219-1242

References

Alorro RD, et al. (2008) Recovery of heavy metals from MSW molten fly ash by carrier-in-pulp method: Fe powder as carrier. *Minerals Engineering* 21: 1094–1101. Available at: http://dx.doi.org/10.1016/j.mineng.2008.02.005.

Alorro RD, et al. (2009) Recovery of heavy metals from MSW molten fly ash by CIP method. *Hydrometallurgy* 97: 8–14. Available at: http://dx.doi.org/10.1016/j.hydromet.2008.12.007.

ASTM D5370-14 (2014) *Standard Specification for Pozzolanic Blended Materials in Construction Applications*, ASTM International, West Conshohocken, PA, www.astm.org

Boghetich G, et al. (2005) Chloride extraction for quality improvement of municipal solid waste incinerator ash for the concrete industry. *Waste Management & Research : The journal of the International Solid Wastes and Public Cleansing Association, ISWA*, 23, pp.57–61.

Chang CY, et al. (2009) Characteristics of elements in waste ashes from a solid waste incinerator in Taiwan. *Journal of Hazardous Materials* 165: 766–773.

Chen QY, et al. (2009) Immobilisation of heavy metal in cement-based solidification/stabilisation: A review. *Waste Management* 29: 390–403. Available at: http://dx.doi.org/10.1016/j.wasman.2008.01.019.

Chen X., et al. (2016) Chlorides removal and control through water-washing process on MSWI Fly Ash. *Procedia Environmental Sciences* 31: 560–566. Available at: http://linkinghub.elsevier.com/retrieve/pii/S1878029616000876.

Dermatas D and Meng X (2003) Utilization of fly ash for stabilization/solidification of heavy metal contaminated soils. *Engineering Geology* 70: 377–394.

Faming L, Shujin Y. and Jie M (2014) Mechanical properties of concrete after chlorine salt extraction in freeze-thaw environment, pp.360–367.

Ferreira C, et al. (2005) Removal of selected heavy metals from MSW fly ash by the electrodialytic process. *Engineering Geology* 77: 339–347.

Gao X, et al. (2008) Utilization of washed MSWI fly ash as partial cement substitute with the addition of dithiocarbamic chelate. *Journal of Environmental Management* 88: 293–299.

Glasser FP (1997) Fundamental aspects of cement solidification and stabilization. *Journal of Hazardous Materials* 52: 1997.

Luna Galiano Y, Fernández Pereira C, et al. (2011) Stabilization/solidification of a municipal solid waste incineration residue using fly ash-based geopolymers. *Journal of Hazardous Materials*, 185: 373–381. Available at: http://dx.doi.org/10.1016/j.jhazmat.2010.08.127.

Malviya R and Chaudhary R (2006) Factors affecting hazardous waste solidification/stabilization: A review. *Journal of Hazardous Materials* 137: 267–276.

Mangialardi T (2003) Disposal of MSWI fly ash through a combined washing-immobilisation process. *Journal of Hazardous Materials* 98: 225–240.

Mangialardi T, et al. (1999) Optimization of the solidification/stabilization process of MSW fly ash in cementitious matrices. *Journal of Hazardous Materials* 70: 53–70.

Polettini A, et al. (2001) Properties of Portland cement – stabilised MSWI fly ashes. *Journal of Hazardous Materials* 88: 123–138.

Qian GR, et al. (2008) Properties of MSW fly ash-calcium sulfoaluminate cement matrix and stabilization/solidification on heavy metals. *Journal of Hazardous Materials* 152: 196–203.

Quina MJ, Bordado JC and Quinta-Ferreira RM (2008) Treatment and use of air pollution control residues from MSW incineration: An overview. *Waste Management* 28: 2097–2121.

Quina MJ, Bordado JCM and Quinta-Ferreira RM (2010) Chemical stabilization of air pollution control residues from municipal solid waste incineration. *Journal of Hazardous Materials* 179: 382–392.

Rémond S, Pimienta P and Bentz D (2002) Effects of the incorporation of municipal solid waste incineration fly ash in cement pastes and mortars II: Modeling experimental study. *Cement and Concrete Research* 32: 303–311. Available at: http://linkinghub.elsevier.com/retrieve/pii/S0008884601006743.

Saeed KA (2012) Interferences of cement based – solidification/stabilization and heavy metals : a review. (January), pp.2555–2565.

Singh TS and Pant KK (2006) Solidification/stabilization of arsenic containing solid wastes using portland cement, fly ash and polymeric materials. *Journal of Hazardous Materials* 131: 29–36.

Sun X, et al. (2016) A review on the management of municipal solid waste fly ash in American. *Procedia Environmental Sciences* 31: 535–540. Available at: http://linkinghub.elsevier.com/retrieve/pii/S1878029616000803.

Tang H, Erzat A and Liu Y (2014) Recovery of soluble chloride salts from the wastewater generated during the washing process of municipal solid wastes incineration fly ash. *Environmental Technology (United Kingdom)* 35: 2863–2869. Available at: http://dx.doi.org/10.1080/09593330.2014.924568.

Tang J, et al. (2018) Comparative study of the application of traditional and novel extractants for the separation of metals from MSWI fly ash leachates. *Journal of Cleaner Production* 172: 143–154. Available at: http://linkinghub.elsevier.com/retrieve/pii/S0959652617324599.

Tang Q, et al. (2016) Solidification/stabilization of fly ash from a municipal solid waste incineration facility using portland cement. *Advances in Materials Science and Engineering*, 2016.

USEPA (2011) *Exposure Factors Handbook: 2011 Edition*. Available at: c:%5CDocumentsandSettings%5Cturner_j%5CDesktop%5CJT_Biblioscape_8_111003%5CJT_Bib8_111003%5Cattachments%5Cefh-complete.pdf.

Wang X, Li A and Zhang Z (2016) The effects of water washing on cement-based stabilization of MWSI fly ash. *Procedia Environmental Sciences* 31: 440–446. Available at: http://linkinghub.elsevier.com/retrieve/pii/S1878029616000967.

Weitzman L and Conner JR (1989) Descriptions of Solidification/Stabilization Technologies, Immobilization Technology Seminar–Speaker Slide Copies and Supporting Information, U.S. EPA, CERI-89-222.

Wilk CM and DeLisio R (2002) *Solidification/stabilization treatment of arsenic- and creosote- impacted soil at a former wood-treating site*. SR997, Skokie, IL: Portland Cement Association.

Wilk CM (2004) Solidification/Stabilization treatment and examples of use at port facilities. *Ports 2004*, pp.1–10. Available at: http://ascelibrary.org/doi/abs/10.1061/40727(2004)92.

Wilk CM (2007) Principles and use of solidification/stabilization treatment for organic hazardous constituents in soil, sediment, and waste. *WM'07 Conference* (2): 10.

Wu HY and Ting YP (2006) Metal extraction from municipal solid waste (MSW) incinerator fly ash - Chemical leaching and fungal bioleaching. *Enzyme and Microbial Technology* 38: 839–847.

Yahaya Y, et al. (2018) Effects of pH dynamics on solidification/stabilization of municipal solid waste incineration fly ash. *Journal of Environmental Management* 207: 243–248. Available at: http://linkinghub.elsevier.com/retrieve/pii/S0301479717311179.

Zhou X, et al. (2017) Reductive solidification/stabilization of chromate in municipal solid waste incineration fly ash by ascorbic acid and blast furnace slag. *Chemosphere* 182: 76–84. Available at: http://dx.doi.org/10.1016/j.chemosphere.2017.04.072.