Heavy metals removal/stabilization from municipal solid waste incineration fly ash: a review and recent trends

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Abstract
Waste treatment using thermal technologies, such as incineration, leads to the production of pollutants and wastes, including fly ash (FA). Fly ash contains heavy metals (HMs) and other contaminants and can potentially pose high risks to the environment and negatively impact health and safety. Consequently, stabilizing fly ash prior to either use or landfilling is crucial. The toxicity of fly ash through heavy metal leaching can be assessed using leaching tests. The leaching rates of heavy metals primarily depend on the surrounding conditions as well as fly ash properties and metal speciation. Physical separation, leaching or extraction, thermal treatment and solidification/chemical stabilization are proposed as suitable approaches for fly ash treatment. Economic considerations, environmental concerns, energy consumption and processing times can define the efficiency and selection of the treatment approach. This review considers the latest findings and compares the advantages and shortcomings of different fly ash treatment methods with the aim of highlighting the recent advances in the field. The review concludes that the simultaneous implementation of various methods can lead to highly efficient heavy metals removal/stabilization while simultaneously taking economic and environmental considerations into account.

Keywords Municipal solid waste · Incineration · Fly ash · Heavy metals removal · Stabilization · Metal extraction

Introduction
The global population boom, which is expected to reach 9.7 billion by 2050, in conjunction with excessive industrial activities, has seen solid waste production volumes significantly increase and is predicted to reach 2.2 billion tonnes per year by 2025 [1]. Currently, the conventional methods to dispose of wastes are landfilling and incineration. However, due to the noticeable carbon footprint and other environmental repercussions, including groundwater contamination, soil erosion and land occupation, landfilling is the least favored waste management method. Compared to landfilling, incineration reduces the volume and mass of wastes by 90% and 75%, respectively [2], as well as leads to the production of a considerable amount of energy in the forms of heat and electricity [3–8].

Despite its noteworthy advantages, certain shortcomings and limitations have diminished the efficiency of the incineration process. This waste thermal treatment method inevitably leads to the generation of by-products, namely bottom ash (BA) (around 80% by wt.) and fly ash (20% by wt.) [9], containing heavy metals (e.g., Zn, Pb, Cu, Cd, Cr and Ni), chlorides, and organic compounds (dioxins, furans, PCBs, VOCs and PAHs) [3, 10]. Generally, bottom ash is not considered to be as hazardous and problematic as fly ash and can be employed as a constructional material. As heavy metals cause severe health problems, their emission is considered to be a great concern [11]. The presence and concentration of various heavy metals in fly ash residue can be defined by feedstock traits, operating conditions and flue gas treatment facilities [11, 12].

It is suggested that fly ash can be and is currently used as a constructional material [13], a thermochemical energy...
storage (TCES) material [8], a H₂S removal agent [14], a low-cost adsorbent for gas and water treatment [15] and in some instances it can be converted to a zeolite-based catalyst [16]. As heavy metals pose a threat to the environment, the release of fly ash heavy metals should be controlled and minimized prior to its reutilization or disposal.

Figure 1 depicts the proposed fly ash treatment methods as reported in the literature. Generally, leaching or extraction, thermal treatment and solidification/chemical stabilization are considered as common approaches for fly ash treatment [2, 17, 18]. In the extraction method, the harmful species can be extracted with the help of electrodialytic or a leachate, which can be water or an acid [2, 19, 20]. Washing fly ash using water is considered to be the simplest separation method which leads to the removal of soluble salts [11]. Acid washing is a practical technique for heavy metals removal, but it considerably changes the pH and material characteristics [21]. However, this method leads to the production of wastewater and is not economically feasible [3, 20].

Solidification/stabilization is the most common fly ash neutralization-stabilization technique [11]. The heavy metal release rate can be efficiently controlled using cement or a polymeric binder [22]. This method hinders heavy metal emissions with the contribution of physical and chemical interactions leading to the encapsulation, fixation or adsorption of pollutants [3, 11].

Thermal treatment methods, which can be divided into vitrification, melting/ fusing and sintering [6], are more efficient fly ash stabilization techniques, compared to their counterparts. It is reported that the leachability of heavy metals, as well as fly ash weight and volume, reduce significantly after thermal treatments [2, 6, 10]. The exposure of fly ash to high temperature atmosphere leads to decomposition of the hazardous pollutants. Also, under such conditions, a substantial proportion of heavy metals are evaporated or encapsulated in the remaining vitrified residue [22, 23]. It is worth noting that the stabilization of fly ash after thermal treatment is principally due to the physical and chemical alterations, such as mineral phase transformation, particle adhesion, conglomeration, and formation of SiO₂-Al₂O₃-CaO chemical bonds in the ash [6, 10]. The release of volatile heavy metals in the atmosphere, and substantial energy consumption along with significant operational expenses and initial investment, are the biggest drawbacks of thermal treatment methods [2, 20].

Potential contamination and heavy metals release from the fly ash are typically evaluated through leaching tests to determine the leachability of the contaminants from the fly ash. The most common leaching tests are USEPA’s Toxicity Characteristic Leaching Procedure (TCLP) and the European standard test (EN12457/1-4) [12, 24]. While in the EN 12457/1-4 test the extraction medium is distilled water (L/S ratio of 10 for 24 h), in the USEPA TCLP method the granular material is continually stirred, commonly in an acetic solution with an L/S ratio of 20 for 18 h [25]. Inductively coupled plasma emission spectrometry (ICP-OES) and atomic fluorescence spectrometry (AFS) are two standard methods for analyzing heavy metals in fly ash [26]. The most considerable shortcoming of the leaching tests is the time required for the measurements. Adoption of rapid and fast response analysis, such as laser induced breakdown spectroscopy (LIBS) technology, is of great interest as a result [26, 27].
Metal mobility can determine its leachability. The sequential extraction procedure can provide an insight into fly ash heavy metal speciation and mobility [28, 29]. As defined by this method, the heavy metals are classified into five categories, namely, exchangeable, carbonated, Fe–Mn oxides, organic matter and residual form [28]. The exchangeable and carbonate fractions are the most unstable forms leading to high leachability of heavy metals. In contrast, high proportions of Fe–Mn oxides, organic matter, and residual fractions bring about a more stable fly ash with lower probability of heavy metal extraction [2]. It should be noted that close to half of the heavy metals are in residual fractions entrapped in crystal lattices and are not likely to pose a threat to the environment [24].

Fly ash characteristics

Fly ash consists of fine particles from the flue gas trapped by filters or electrostatic precipitators. Fly ash is a mixture of empty pass ashes (EA), boiler ashes (BOA) and the electrostatic precipitator ashes (ESPA). It is found that 70–75% of FA is made up of ESPA [30]. It is mainly composed of several toxic substances, such as metal salts, and its composition varies depending on the composition of the waste [20]. The main fly ash elements are generally Si, Ca, K, Na, Al, Cl, Fe, which are not environmentally hazardous. However, Pb, Cr, Cd, Zn, Hg, Cu, Ni and As, present in trace amounts that accumulate in fly ash particles through the volatilization and condensation processes, are toxic and can cause a significant environmental threat [31]. The concentrations of fly ash heavy metals from different sources are compared in Table 1.

Generally, the contents of the major fly ash constituents decrease in order \( \text{Zn} > \text{Pb} > \text{Cu} > \text{Cr} > \text{Ni} > \text{Cd} > \text{As} > \text{Hg} \) [38, 41]. It should be noted that Zn, Cd, Pb, Hg and As show higher volatility, while Ni is less volatile [41]. Due to their considerable volatility, Pb and Zn can be transformed into \( \text{PbCl}_2 \) and \( \text{ZnCl}_2 \) through the incineration process and then vaporize. However, as the formation of \( \text{ZnCl}_2 \) is restricted, Zn is mostly encapsulated in the stable mineral species or can be found as \( \text{Zn}_2\text{SiO}_4 \) or \( \text{ZnAl}_2\text{O}_4 \) in fly ash. This is the main reason for the high Zn content in fly ash [42].

Figure 2 provides the XRD spectra of a raw fly ash material, showing \( \text{CaCO}_3 \), \( \text{CaSO}_4 \), \( \text{Fe}_2\text{O}_3 \), \( \text{SiO}_2 \), NaCl and...
KCl are the main fly ash crystalline components [13, 31, 41, 43, 44]. It is reported that waste composition and moisture level, incinerator type and operating conditions, specifically temperature, can define the fly ash composition and metals distribution to a large extent [38, 42, 43]. For instance, it is reported that close to 45% of Cd, Cr, Hg and As originates from food waste, and 37% of Pb comes from plastic and rubber streams, while 10–15% of the total heavy metals are produced from paper and cellulosic wastes [38]. Taking the type of incinerator into consideration, it is reported that under identical operating conditions the employment of a fluidizing bed incinerator leads to the production of higher amount of fly ash (two to three times larger) in comparison to other incinerator types [41]. Moreover, in a study carried out by Zhang et al. [45], the thermal behaviour of MSWI fly ash from a grate furnace (GF) and a circulating fluidized bed (CFB) were compared. They reported that the fusion temperature of the CFB fly ash was 150 °C lower than the GF fly ash. The difference in temperature was attributed to the higher content of SiO2 in CFB fly ash which reacts with other components to form low-melting temperature compounds.

The availability of fly ash trace metals and their environmental risks, is predominantly defined by metal speciation. Metal speciation is classified as the acid-soluble and exchangeable fraction (F1), the reducible fraction (F2), the oxidizable fraction (F3), and the residual fraction (F4) based on the Community Bureau of Reference (BCR) sequential extraction process considerations [46]. The environmental risk of these four categories decreases in the order of F1 > F2 > F3 > F4, where F4 is the most chemically stable fraction and cannot easily be released [2, 46]. Figure 3 depicts the BCR results from a fly ash sample [43], where Mn can mostly be found in the F4 fraction, Cd in the F1 and F3 fractions, Cu is distributed across all fractions, more than 50% of Zn resides in F1 and F2 fractions and 35% in F4, and 53% of Pb is retained in the F4 fraction [43]. Based on the BCR analysis, the release of Cu, Pb and Cd is more probable and their control measures should be prioritized.

It is worth noting that the heavy metals release rate is significantly affected by environmental conditions, especially pH [13]. Figure 4 provides information on the leachability variations for Cu, Pb and Zn as a function of pH. As can be seen from Fig. 4, in a high acidity environment can significantly enhance the leachability of heavy metals. Further, their release rate can be minimized, providing the pH is kept within the range of 5–12. It should be noted that the changes in heavy metals leachability under different acid–base conditions are due to alterations in the chemical species of the heavy metals [13]. The formation of crystal lattices by Si and Al can also favour HMs stability in FA [24].

It is also reported that heavy metals leachability of fly ash can be extensively determined by the CaO content, soluble chloride (S–Cl) content and pH of the fly ash [24, 27]. A higher CaO content implies there is a higher acid neutralizing capacity of the fly ash and as a result less leaching of heavy metals is expected. In contrast, a higher soluble chloride content enhances the probability of HMs release. It is reported that when the content of CaO exceeds 14%, the fly ash pH is over 11.8, and when soluble chloride is below

![Fly ash (sampled from a CFB MSW incinerator in Wuhan, China) metal speciation based on BCR sequential extraction analysis [43]](image)

![The leachability of Cu, Pb and Zn as a function of pH from fly ash of municipal solid waste incinerator (MSWI) in the Jinshan (Shanghai) [13]](image)
0.025 mol/L the leaching concentrations of HMs are almost below the standard’s limit [27]. In a study conducted by Liu et al. [24], the Φ index, defined as Eq. 1, was proposed as a practical parameter for determining the leaching risk of HMs by combining the three abovementioned variables. It is declared that when Φ is below 12.5, the leaching of HMs likely exceeds the standards’ limits.

\[
\Phi = -\log \left( \frac{c(H^+)}{c(f - CaO)} \right) \times \frac{c(Cl^-)}{c(Cl^-)}
\]  

where \(c(H^+)\), \(c(Cl^-)\), and \(c(f - CaO)\) are the molar concentration (mol/L) of hydrogen ion, chloride ion, and free CaO, respectively.

MSWI fly ash comprises crystalline and non-crystalline phases. Fly ash particles are found to be heterogenous within their bulk and also at an inter-particle level [47, 48]. In study conducted by Kitamura et al.[49], they found that a FA particle comprises a Si-based core that is insoluble, Al/Ca/Si-based semi-soluble matrices and a KCl/NaCl-based soluble layer on the surface. It is reported that most fly ash particles have a size in the range of 1 to 100 µm, with 50% of the particles possessing a diameter less than 15.7 µm [13]. Due to the porous structure of fly ash, finer particles provide higher surface area inevitably so that the vaporized heavy metals in the incinerator can be condensed and aggregated effectively on surface of the smaller particles in the flue gas cooling system leading to their higher concentration of heavy metals compared to larger particles, which increases their health and environmental impacts [43, 50].

HMs removal methods

Solidification/stabilization

Solidification/stabilization (S/S) is one of the most commonly employed heavy metals immobilization strategies prior to landfilling or fly ash reutilization. In this method, the leachability of heavy metals is reduced considerably with the help of an additive or a binder [51]. Table2 compares the heavy metals leachability of MSWI FA from different sources solidified/stabilized with different agents under the specific leaching condition.

Considering the effectiveness of the adopted binder, solidification with cement and polymeric binders can diminish leachability and toxicity of the fly ash. Due to the immobilization efficiency, low treatment expenses and easy processibility, cement solidification is by far the most used technique for fly ash treatment. However, this method increases the waste volume considerably and the HMs release rate changes over the course of time [51, 52]. A positive correlation between HMs leaching content and time has been reported with most HMs in a cement-modified fly ash released at an early stage. In this instance, 97% of the total leaching quantities detected occurred during the first week after solidification [52]. Figure 5 shows the changes in HMs release rate of a cement-solidified sample as a function of time. In the chemical stabilization technique, the employment of a chemical agent, that can be organic or inorganic, leads to physical and chemical alterations to the fly ash properties, which can thus decrease the HMs bio-availability. Gypsum, phosphate, bleach, sulfides (sodium thiosulfate, sodium sulfide) and polymer organic stabilizers are commonly adopted as a stabilizer for this purpose [51]. The use of ethylene diamine tetracetic acid (EDTA) and thiodiglycolic acid (TGA) as organic stabilizers has received great attention due to economic considerations, promising efficiency, easy processibility, and lower dosage requirement compared to the inorganic agents [19]. In a study conducted by Assi et al. [33], bottom ash of municipal solid waste incinerator was used as a fly ash HMs stabilizer. It was reported that due to the presence of calcium ions, amorphous silica and alumina in the bottom ash, the resulting cementitious properties and pozzolanic reactions in the FA/BA mixture were promoted. There was a considerable reduction in HMs leachability, especially for Pb and Zn, with at least two orders of magnitude leaching reduction compared to the non-modified fly ash. Moreover, this technique showed a satisfactory HMs stabilization efficiency over the course of time. In a study conducted by Fan et al. [39], the solidification of MSWI fly ash using Portland cement and coal fly ash-based geopolymer was investigated. Based on the leaching test results, under geopolymer treatment, the immobilization rates of Pb, Zn, and Cd were more than 99%. The geopolymer was a more effective stabilizer compared to cement due to the presence of active aluminosilicate in the MSWI fly ash contributing to the geopolymerization reaction leading to the encapsulation of heavy metals and chloride ions.

Chen et al. [3] conducted a study to understand the feasibility of fly ash stabilization using supplementary cementitious materials (SCMs) and green stabilizers. It was concluded that use of SMCs, such as fumed silica, improved the formation of the C–S–H (calcium silicate hydrate) structure leading to significant metal encapsulation and immobilization. The adoption of fumed silica in the binder was considered as a novel, efficient and low-carbon method for hazardous fly ash treatment. Further, it was found that the incorporation of phosphate-based and sulphate-based additives, such as potassium dihydrogen phosphate (KDP), incinerated sewage sludge ash (ISSA), and phosphorus gypsum (PG) could enhance HMs immobilization to a large extent. Fan et al. [62] undertook a study to assess the effectiveness of a novel solidification binder obtained by blending MgO and silica fume. They
| FA type          | FA source            | Average particle size | Leaching condition                   | Leachability of raw FA (mg/L) | S/S agent                     | Leachability of treated FA (mg/L) | References |
|------------------|----------------------|-----------------------|--------------------------------------|-------------------------------|--------------------------------|-----------------------------------|------------|
| MSWI fly ash     | Shanghai, China      | 11 μm                 | Distilled water L/S = 10 at 25 °C, for 3 days | Zn = 56.11 Pb = 26.47 Cu = 8.17 Cd = 1.62 Cr = 2.47 | Portland cement | Zn = 0.085 Pb = 0.068 Cu = 0.039 Cd = 0.005 Cr = 0.012 | [52]        |
| MSWI fly ash     | Thailand             | 75 μm                 | Not reported                         | Pb = 6.82 Cd < 0.005 Cr = 0.095                                     | Portland cement | Pb < 0.005 Cd < 0.005 Cr = 0.309 | [9]         |
| MSWI fly ash     | China                | Not reported          | Acetic acid L/S = 20 for 18 h         | Zn = 4.43 Pb = 1.467 Cu = 0.01                                      | 10% cement + 2% NaH₂PO₄ | Pb = 0.04 | [53]        |
| MSWI fly ash     | Chongqing, China     | 48 μm                 | Acetic acid L/S = 20 for 20 h         | Zn = 52.88 Pb = 10.92 Cu = 5.43 Cd = 5.73 Cr = 0.24                   | 30% waste glass + cement | Zn = 0.42 Pb = 0.65 Cu = 0.55 Cd = 0.82 Cr = 0.03 | [54]        |
| MSWI fly ash     | Guangzhou, China     | Not reported          | Sulphuric acid and Nitric acid L/S = 10 for 18 h | Zn = 3.657 Pb = 28.26 Cu = 0.076 Cr = 10.86            | 4% ferrous Sulphate + 15% Portland cement | Pb = 0.0059 Cr = 0.5052 | [55]        |
| MSWI fly ash     | Anhui, China         | < 9.5 mm              | Acetic acid L/S = 20 for 18 h         | Pb = 15                                    | 1.5% Gelatinized sticky rice (SR) + 10% cement | Pb = 8 | [56]        |
| MSWI fly ash     | Brescia, Italy       | Not reported          | Distilled water L/S = 10 at 25 °C, for 2 h | Zn = 4.98 Pb = 80 Cu = 1.41 Cr = 0.22                                      | MSWI bottom ash | Zn = 0.28 Pb = not detected Cr = 0.25 | [33]        |
| MSWI fly ash     | Dalian, China        | 9.5 mm                | Acetic acid L/S = 20 for 4 h          | Zn = 129 Pb = 40 Cu = 15.4 Cd = 5.36 Cr = 1.1                             | Coal fly ash-based geopolymer | Zn = 0.3 Pb = 0.035 Cd = 0.015 | [39]        |
| MSWI fly ash     | Chongqing, China     | Not reported          | Acetic acid L/S = 20 for 18 h         | Zn = 133.11 Pb = 12.48 Cu = 17.02 Cd = 9.29                          | Alkali-activated slag (AAS) cement | Zn = 40 Pb = 4.2 Cd = 1 | [57]        |
| MSWI fly ash     | Yue Yang, China      | 75 μm                 | Acetic acid L/S = 20 for 18 h         | Zn = 126 Pb = 1.48 Cu = 78.5 Cr = 17.37                             | Shell coal gasification fly ash (SFA)-based geopolymer | Zn = 5.04 Pb = 0.015 Cr < 0.01 | [58]        |
| MSWI fly ash     | Wuhan, China         | Not reported          | Acetic acid L/S = 20 for 18 h         | Zn = 52.15 Pb = 2.11 Cu = 11.00 Cr = 0.56                              | 50% Red mud-based geopolymer | Zn = 6.45 Pb = 0.02 Cu = 0.28 Cr = 2.08 | [59]        |
| MSWI fly ash     | Chongqing, China     | 75 μm                 | Acetic acid L/S = 20 for 18 h         | Zn = 135 Pb = 0.08 Cd = 1.01 Cr = 35.1                               | Red mud (RM) and coal gangue (CG) bend with a ratio of 8:2 | Zn = 5 Pb < 0.01 Cd = 0.15 Cr = 0.5 | [60]        |
| MSWI fly ash     | Yancheng, China      | Not reported          | Sulphuric acid and Nitric acid L/S = 10 for 18 h | Pb = 1.591 Cd = 1.403                                               | Magnesium potassium phosphate cement (MKPC) | Pb = 0.8 Cd = 0.4 | [61]        |
| MSWI fly ash     | Shenzhen, China      | 50 μm                 | Not reported                         | Zn = 2.4 Pb = 9 Cu = 0.5 Cr = 0.22                                      | Silica fume | Zn = 0.05 Pb = 0.15 Cr = 0.05 | [3]         |
found that MgO–SiO$_2$–H$_2$O (M–S–H) binders reduced the HMs release rate by physical encapsulation and chemical bonding. The immobilization ratios of Pb, Zn and Cd were found to be 99.5%, 98.7% and 96.9%, respectively. The effectiveness of sodium carbonate solution as a fly ash stabilizing agent was investigated by Atanes et al. [11]. They reported that the Na$_2$CO$_3$ treatment lowered the leaching of HMs, with the Pb, Zn, Cu and Cd contents in the leachate reduced by 67.1, 77.4, 60.7 and 86.4%, respectively, following FA stabilization. The leaching test results for the raw and treated fly ash are compared in Table 3. The immobilization of HMs in this process was attributed to the formation of insoluble, non-leachable salts as metal carbonates, which can efficiently stabilize heavy metals. In a study conducted by Huang et al. [63] on MSWI fly ash HMs immobilization, the effect of integrating closed-loop electrokinetics (EK) with alkali compounds (sodium hydroxide flakes and sodium silicate) on

| FA type | FA source | Average particle size | Leaching condition | Leachability of raw FA (mg/L) | S/S agent | Leachability of treated FA (mg/L) | References |
|---------|-----------|----------------------|-------------------|-------------------------------|-----------|-------------------------------|------------|
| MSWI fly ash | Dalian, China | 28 μm | Acetic acid L/S = 20 at 23 ± 2 °C for 18 ± 2 h | Zn = 129 Pb = 40.3 Cu = 15.4 Cd = 5.36 Cr = 1.1 | MgO and silica fume mixture | Zn = 0.82 Pb = 0.045 Cd = 0.08 | [62] |
| MSWI fly ash | Mataró, Spain | 45 μm | Distilled water L/S = 10 for 24 h | Zn = 28.3 Pb = 24 Cu = 2.2 Cd = 0.056 | Sodium carbonate solution | Zn = 6.4 Pb = 7.9 Cu = 0.3 Cd = 0.022 | [11] |
| MSWI fly ash | Chongqing, China | 75 μm | Acetic acid L/S = 20 at 23 ± 2 °C for 18 ± 2 h | Zn = 9.74 Pb = 0.21 Cu = 0.75 | Sodium hydroxide and sodium silicate blend | Zn = 4.1 Pb = 0.0041 Cd = 0.62 | [63] |
| MSWI fly ash | France | 4 mm | Distilled water L/S = 10 for 24 h | Zn = 1 Pb = 34.2 Cu = 0.01 Cd = 0.01 Cr = 0.41 | Phosphoric acid | Zn < 0.03 Pb < 0.02 Cu < 0.01 Cd < 0.01 Cr < 0.9 | [12] |
| MSWI fly ash | Zhejiang, China | Not reported | Acetic acid L/S = 20 for 18 h | Zn = 44 Pb = 0.9 Cu = 9.5 Cd = 0.65 Cr = 1 | Ca$_3$(PO$_4$)$_2$ | Zn = 5 Pb = 0.05 Cu = 1 Cd = 0.2 Cr = 0.01 | [64] |
| MSWI fly ash | Shanghai, China | Not reported | Acetic acid (L:kg) of 20:1 at 23 ± 2 °C for 18 h | Zn = 5.41 Pb = 9.98 Cu = 13.87 Cd = 0.10 Cr = 0.12 | Dithiocarboxylate functionalized polymer (TEM_CSSNa) | Pb = 0.015 | [2] |
| MSWI fly ash | Shenzhen, China | 2 mm | Acetic acid L/S = 20 at 23 ± 2 °C for 18 | Zn = 120.41 Pb = 6.5 Cu = 17.71 Cd = 3.21 Cr = 0.05 | Sixthio guanidine acid (SGA) | Zn = 26.546 Pb = 1.284 Cu = 0.848 Cd = 0.608 Cr = 0.008 | [19] |
| MSWI fly ash | Hangzhou, China | Not reported | Acetic acid L/S = 20 for 18 h | Zn = 49.35 Pb = 1.37 Cu = 12.10 Cd = 1.82 Cr = 1.68 | 3% triethylamine (TEA) | Zn = 10.84 Pb = 0.225 Cu = 2.785 Cd = 0.305 Cr = 0.205 | [65] |
| MSWI fly ash | Italy | 4 mm | Distilled water L/S = 10 for 2 h | Zn = 14.3 Pb = 60.5 | Rice husk ash | Zn = 0.75 Pb = 8 | [66] |
| MSWI fly ash | Japan | Not reported | Distilled water L/S = 10 for 6 h | Zn = 8.23 Pb = 30.50 Cu = 0.15 Cr = 0.14 | Waste natural fishbone | Zn = 8 Pb = 3 | [1] |
activating solidification/stabilization was investigated. They reported that the leachability of Zn, Pb, and Cu was reduced by 57.84%, 80.19%, and 17.58%, respectively. The reduction in the release rates of HMs was attributed mainly to physical encapsulation and partly to geo-polymerization in the curing matrices. Chen et al. [67] conducted a study to pinpoint the effect of the integration of water wet extraction and accelerated carbonation by CO₂ mineralization on MSWI fly ash stabilization using a high gravity process, and investigated its use as a supplementary cementitious material (SCM) in cement mortar. Based on the TCLP results, the integrated stabilization process was useful for MSWI fly ash stabilization.

The phosphate stabilization technique, with two industrialized processes, namely, the Neutrec and VKI processes, is an interesting approach for fly ash treatment [12]. Sun et al. [68] studied the impacts of fly ash phosphate pre-treatment on HMs leachability. Figure 6 compares the leachability of raw and phosphate-treated fly ash at different temperatures. The TCLP results indicated that the leachability of

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**Table 3** Leaching test results for raw and treated fly ash (L/S = 10 L/kg, leaching time 24 h) (data obtained from [11])

| Parameter                   | Raw fly ash | Concentration (mg/kg) | Classification  | Treated fly ash | Concentration (mg/kg) | Classification |
|-----------------------------|-------------|-----------------------|-----------------|----------------|-----------------------|----------------|
| Total dissolved solids      | 263,333     | Hazardous             | 30,000          | Non-hazardous  |
| Cl⁻                         | 134,000     | Hazardous             | 2000            | Non-hazardous  |
| Zn                          | 28.3        | Non-hazardous         | 6.4             | Non-hazardous  |
| Cd                          | 5.6 x 10⁻²  | Non-hazardous         | 2.2 x 10⁻²      | Unreactive     |
| Pb                          | 24          | Hazardous             | 7.9             | Non-hazardous  |
| Cu                          | 2.2         | Non-hazardous         | 0.3             | Unreactive      |
| pH of leachate              | 12.05       |                       | 12.36           |                |
| Leachate conductivity (µS/cm)| 40          |                       | 9.24            |                |
HMs was reduced significantly following the phosphate stabilization process. This was attributed to the formation of pyromorphite and hydroxyapatite, which can hinder the mobilization and volatilization of heavy metals. Based on the BCR results, this stabilization technique changed metal speciation fractions and enhanced the fraction of more stable phases through dissolution and reprecipitation processes. It implies that the newly formed crystal lattices encapsulate heavy metals leading to their stability and reduced leachability. A study conducted by Vavva et al. [12] found that the phosphoric acid pretreatment of fly ash with an acid/ash ratio of 7% w/w followed by water washing was promising for HMs stabilization, specifically Pb. It was also concluded that washing the fly ash with water prior to phosphoric acid treatment could reduce the efficiency of the method.

Li et al. [2] investigated the effectiveness of a novel sulfur-based polymer stabilizer, dithiocarboxylate functionalized polymer (TEM_CSSNa), for HMs stabilization and compared its efficiency with two prevailing chemical stabilizers, sodium sulfide (Na$_2$S) and thiourea (Tu). They found that, compared to Na$_2$S and Tu, the use of a much lower amount of TEM_CSSNa invoked the same leaching result. Further, the polymer-based stabilizer was able to retain its stabilizing efficiency over a broad pH range. When using the same amount of stabilizer, TEM_CSSNa stabilization led to a lower leachate heavy metals content in comparison to Na$_2$S and Tu. The distributions of metal speciation before and after TEM_CSSNa stabilization are compared in Fig. 7.

As shown, stabilization reduced the acid-soluble fraction, although it enhanced the oxidizable and residual fractions of fly ash. This stabilization method reduced the leachability of HMs by formation of stable network structures and diminishing the metal mobility.

Wang et al. [19] investigated the stabilization efficiency of two tailor-made stabilization agents, namely, six thio guanidine acid (SGA) and tetra thio bicarbamic acid (TBA). Compared to traditional sulfur-based stabilizers, such as sodium dimethyl di thio carbamate (SDD) and Na$_2$S, the agents with multiple hydrosulfide chelating groups showed greater performance and could stabilize heavy metals more efficiently. The leachability results from this study are presented in Table 4. Based on the results, the heavy metals were not removed in this process with the stabilization technique merely changing the heavy metals speciation fractions by reducing the acid-soluble fraction and increasing the residual fraction. The findings imply that using a stabilizer with a higher functional group can enhance the probability of physical and chemical interactions among chelating agents and metal ions which can minimize their mobility and enhance their stability.

Table 4 Leachability (mg/L) of raw fly ash against treated fly ash using 0.1 mol/kg of various sulfur-based stabilizers (data obtained from [19]) (fly ash collected from a MSWI plant in Shenzhen, China)

| Element | Non-treatment | TBA | SGA | SDD | Na$_2$S |
|---------|---------------|-----|-----|-----|--------|
| Cd      | 3.21          | –   | 0.608 | 1.162 | 0.896 |
| Cr      | 0.05          | 0.02 | 0.008 | 0.018 | 0.014 |
| Cu      | 17.71         | 0.84 | 0.848 | 1.736 | 3.194 |
| Ni      | 6.45          | 0.526 | 1.144 | 0.924 | 1.514 |
| Pb      | 6.5           | 1.18 | 1.284 | 2.6   | 1.406 |
| Zn      | 120.41        | 30.812 | 25.546 | 48    | 22.886 |
The stabilization of fly ash via the incorporation of a locally available and non-toxic wastes materials, regarded as green agents, has received great attention in recent years. In a study conducted by Benassi et al. [66], the possibility of fly ash stabilization with rice husk ash (RHA), an agricultural waste which contains large amount of amorphous silica, was investigated. They found that this stabilization method led to a close to one order of magnitude reduction in Pb and Zn leachability. The stabilization efficiency of RHA was found to originate from the encapsulation of heavy metals by amorphous silica, as well as the carbonation reaction. It was also reported that the annealing of RHA, especially at higher temperatures which promotes the silica content, could augment its stabilization effectiveness. Li et al. [57] investigated the HM immobilization efficiency of alkali-activated slag (AAS) cement for the stabilization of MSWI fly ash. They reported that the AAS was an effective stabilization agent and could achieve an immobilization rate of 70% providing that the fly ash was pretreated with water. The feasibility of heavy metals stabilization with waste fishbone, which contains hydroxyapatite (HAP), was assessed by Mu et al. [1]. They reported that the L/S ratio in the leaching test and the settling period were key factors which defined the fishbone stabilization effectiveness. Under a solid-like condition (L/S < 1.5 mL/g), 66.35% of the Pb could be stabilized at a L/S of 1 mL/g for 24 h of settling when the fishbone content of the solid phase was 50% (w/w). The fishbone also exhibited a promising efficiency for Zn stabilization. In another study conducted by the same authors [69], the ignition of fishbone at 430 °C was found to enhance its metal stabilization efficiency. This was due to the removal of the non-HAP fraction as well as an increase in HAP crystallinity at an elevated temperature. Figure 8 compares the Pb stabilization efficiency under various conditions using natural and ignited fishbone.

Leaching extraction

Chemical extraction

Leaching/extraction with the contribution of a chemical agent is considered as a practical technique to improve the stability of fly ash by removing the chloride, salts, alkali and heavy metals. The main approaches include water washing, acid extraction, alkali extraction, energy extraction and biological extraction or any possible combination of these techniques [51]. It should be noted that the type of leachate, pH, liquid/solid ratio, process time and temperature, particle size, presence of impurities, and the fly ash characteristics can define the efficiency of the process [51, 70, 71]. While the leaching of Cd and Cr are independent of extraction time, Pb leaching decreases with an increase in process time. Temperature changes impose insignificant impacts on Pb leachability, although the dependency of Zn, Al and Ni on temperature has been repeatedly reported [72–74]. Liquid/solid ratio can affect the extraction of Pb, Zn and Cd, but not Cr or Cu [29]. It should be noted that all heavy metals can be leached from fly ash under strong acidic conditions (pH < 4), and under alkaline conditions (pH > 11) where some metals (such as Cu, Pb, Zn and Cr) are soluble, although not as soluble as in acidic media [25]. Table 5 gives information about the heavy metals extraction rate from the chemically treated MSWI fly ash with water, different acidic, alkaline, and chelating agents.

Water washing pretreatment Water is the most commonly employed leachate due to its environmental and economic qualities. However, water washing can only remove compositional chloride (except insoluble chloride) and surface metals [9, 70]. The order B > Mo > Se > Li > Sr > Cr > As > Ba > Cd > V > Sn > Rb > Zn > Cu > Ni > Pb > U > Co > Mn, indicates the leaching rate of soluble metals by water washing [70]. Water washing cannot lead to the efficient removal of toxic metals and it has been reported that almost no reduction in Fe, Al, Zn, Pb, Cu and Cd concentrations can be obtained from water washing [71]. Consequently, the water washing approach should be implemented as a contributing and supplementary method along with acid/base extraction approaches for better HMs removal.

Acidic leaching Acidic extraction results in the removal of HMs by weakening the crystal matrix structure of the fly ash in which heavy metals are encapsulated. Acid extraction can remove insoluble chloride, sulfate and heavy metals more so than water washing and alkali extraction where stronger acids with lower pH values exhibit higher efficiency [9,
| Fly ash type   | FA source | Average particle size | HMs content in FA (mg/kg) | Extraction agent and condition | Extraction level (%) | References |
|---------------|-----------|-----------------------|---------------------------|-------------------------------|----------------------|------------|
| MSWI fly ash  | Finland   | Not reported          | Zn = 11.128 Pb = 7610 Cu = 558 Cr = 316 | Water at 33 °C for 24 h | Zn = 11% Pb = 0.1% Cu = 4% | [75]       |
| MSWI fly ash  | Sweden    | Not reported          | Zn = 5780 Pb = 5730 Cu = 5400 | Water L/S = 50 for 24 h | Zn = 13% Pb = 0.1% Cu = 4% | [76]       |
| MSWI fly ash  | Italy     | 40 μm                 | Zn = 14.400 Pb = 5076 Cu = 881 | 4 M H₂SO₄ for 6 h at pH = 1 | Zn = 90% Pb = 25.3% Cu = 94.5% | [5]        |
| MSWI fly ash  | Finland   | Not reported          | Zn = 11.128 Pb = 7610 Cu = 558 Cr = 316 | 3 M H₂SO₄ at 33 °C for 24 h | Zn = 75% Pb = 5% Cu = 100% | [75]       |
| MSWI fly ash  | Finland   | Not reported          | Zn = 11.128 Pb = 7610 Cu = 558 Cr = 316 | 3 M HCl at 33 °C for 24 h | Zn = 67% Pb = 100% Cu = 96% |           |
| MSWI fly ash  | Sweden    | Not reported          | Zn = 5780 Pb = 5730 Cu = 5400 Cd = 90 Cr = 190 | 1.5 M H₂SO₄ L/S = 10 for 24 h | Zn = 100% Pb = 5% Cu = 100% | [76]       |
| MSWI fly ash  | China     | <500 μm               | Zn = 5416.32 Pb = 3204.83 Cu = 3113.91 Cd = 109.40 Cr = 517.22 | 1 M HCl for 1 h, L/S = 7, and pH < 2 | Zn = 68.5% Pb = 74.5% Cu = 31.2% | [29]       |
| MSWI fly ash  | Japan     | Not reported          | Not reported            | 0.1 M citric acid for 1 h, L/S = 40 | Zn = 100% Pb = 96.9% Cu = 100% |           |
| MSWI fly ash  | Japan     | 20 μm                 | Not reported            | 20% Acetic acid for 1 h, L/S = 7 | Zn = 60% Pb = 95% |           |
| MSWI fly ash  | Japan     | Not reported          | Zn = 5500 Pb = 1900 Cu = 410 Cd = 76 | Ca (OH)₂ L/S = 100 pH = 12.3 | Zn = 91% Pb = 79% | [78]       |
| MSWI fly ash  | Sweden    | Not reported          | Zn = 5780 Pb = 5730 Cu = 5400 Cd = 90 | 0.1 M ethylenediaminetetraacetate (EDTA) L/S = 5 for 24 h | Zn = 40% Pb = 94% Cu = 100% | [76]       |
| MSWI fly ash  | Japan     | <0.59 mm              | Not reported            | 3% EDTA for 24 h, L/S = 40 | Zn = 50% Pb = 90% Cu = 55% | [79]       |

References: [75, 76, 5, 75, 76, 29, 77, 72, 78, 76, 79]
However, due to the alkaline nature of fly ash (CaCO$_3$ and CaO invoke the highly alkaline nature of fly ash) and the presence of Cl and mineral salts (Na, Ca, K), the pH of the extraction environment is elevated, which results in an inadequate HMs removal. The main rationale behind fly ash pretreatment using water washing is the removal of soluble salts which can enhance the efficiency of HMs removal by acid extraction, where it is reported that water washing can remove Cl, K and Na by up to 80% [5]. It should be noted that, aside from the acid type, the concentration of the used acid plays a key role in acid extraction. For instance Zn and Cd leachability can be governed mainly by acid concentration and not the acid type [72]. Figure 9 illustrates the impact of HCl concentration on the efficiency of heavy metals removal after 60 min at a L/S of 25.

The leaching agents used for HMs removal can be categorized as organic and inorganic acids [29]. Sulfuric (H$_2$SO$_4$), hydrochloric (HCl), nitric acids (HNO$_3$) are the most commonly employed inorganic acids for HMs extractions. It is reported that metal solubility in inorganic acids decreases in the order aqua regia > HCl > HNO$_3$ > H$_2$SO$_4$ [81]. The feasibility of HMs extraction using different acid solutions is compared in Table 6 [29]. As seen in Table 6, HCl shows a better efficiency for HMs removal compared to the other agents. Despite its low cost, H$_2$SO$_4$ is not considered as a highly efficient leachate for metals extraction, especially Pb and Hg, and its use leads to the formation of insoluble sulphates [81, 82].

Table 5 (continued)

| Fly ash type     | FA source | Average particle size | HMs content in FA (mg/kg) | Extraction agent and condition | Extraction level (%) | References |
|------------------|-----------|-----------------------|--------------------------|--------------------------------|----------------------|-----------|
| MSWI fly ash     | China     | Not reported          | Zn = 700 Pb = 300 Cu = 180 | 3% dithiocarboxylate-functionalized poly-aminoamide dendrimer (PAMAM-0G-DTC), leaching with acetic acid L/S = 20 for 18 h, pH = 4 | Zn = 57.1% Pb = 100% Cu = 89% | [40]      |
|                  |           |                       |                          | 3% sodium dimethyl dithiocarbamate (SDD), leaching with acetic acid L/S = 20 for 18 h, pH = 4 | Zn = 14.3% Pb = 6.7% Cu = 27.8% |
|                  |           |                       |                          | 3% dithiocarboxylate-functionalized tetraethylenepentamine (TEPA-DTC), leaching with acetic acid L/S = 20 for 18 h, pH = 4 | Zn = 28.6% Pb = 33.3% Cu = 44.5% |
|                  |           |                       | Zn = 3487.23 Pb = 2369.31 | 3% Sodium sulfide (Na$_2$S), leaching with acetic acid L/S = 20 for 18 h, pH = 4 | Pb = 78.9% | [80]      |
|                  |           |                       | Cu = 603.34 Cd = 62.33 Cr = 132.91 | 3% Sodium phosphate (Na$_3$PO$_4$), leaching with acetic acid L/S = 20 for 18 h, pH = 4 | Pb = 72.5% |
|                  |           |                       |                          | 3% thiourea (H$_2$NCSNH$_2$), leaching with acetic acid L/S = 20 for 18 h, pH = 4 | Pb = 74.6% |
|                  |           |                       |                          | 3% mercapto functionalized dendrimer (TEPA-SNa), leaching with acetic acid L/S = 20 for 18 h, pH = 4 | Pb = 100% |

Fig. 9 The effects of HCl acid concentration on the leachability of heavy metals from MSWI fly ash (collected from a MSWI plant on the south China mainland) after 60 min at a L/S of 25 [29].

It has been reported that acid extraction by H$_2$SO$_4$ under elevated temperature and pressurized conditions can enhance its effectiveness [73, 83]. Further, the concurrent use of H$_2$SO$_4$ and HNO$_3$ has been introduced as a practical method for enhancing the efficiency of H$_2$SO$_4$ extraction [70]. Acid extraction using organic acids can be performed with acetic (AA), lactic (LA), citric (CA), oxalic (OA) and gluconic acids (GA) [70] As shown in Table 7, the metal removal
efficiency decreases in the order CA > AA ~ LA > OA [77]. Weibel et al. [71] studied the acidic treatment of fly ash and reported that Zn, Cd, Pb, Cu contents were decreased by 40%, 53%, 8%, and 6%, respectively, following acidic extraction. The extraction of Pb and Cu was attributed to cementation process and the formation of a PbCu-alloy-phase and secondary precipitation (PbCl2). Also, it was found that under the same conditions, incorporating hydrogen peroxide into the acidic treatment process could increase the extraction level of Pb, Cu, and Cd to 57%, 30%, and 92%, respectively.

Alkali leaching
Alkali leaching is an alternative to acid leaching for removing heavy metals from fly ash. The process can be performed using NaOH, NH3 or Na2CO3 solutions. Similar to acid extraction, the concentration of the alkaline leachate as well as the leachate type play a vital role in the metal removal efficiency of the process. The leachability of various heavy metals in an alkaline environment can be defined largely by their availability and speciation in the fly ash [78]. It is reported that during the alkaline extraction process, metals with an amphoteric nature, such as Pb and Zn, form Pb(OH)3− and Zn(OH)3− compounds, inducing a high extraction rate [78, 84, 85]. In cases where the oxide form of Pb is not available, poor Pb extractability should be expected under an alkali condition [72]. In a study conducted by Dontriros et al. [9], the results of acidic and alkali stabilization of fly ash with nitric acid and sodium carbonate were compared. As shown in Fig. 10, it was found that Zn, Pb and Cd were removed by HNO3 solution to a greater degree than for Na2CO3 solution treatment.

Chelating agents
Despite its higher processing costs, leaching with chelating agents can be a great choice for metal extraction as this method is independent of the system pH [79]. Ethylenediaminetetraacetic acid (EDTA) is the most prevalent chelating agent and its use leads to the efficient removal of most metals [70]. It is reported that the extraction of metals by EDTA in the pH range of 3–9 leads to the promising extraction of Pb (60–100%), Zn (50–100%), Cu (60–95%), and Cr (20–50%) [79]. Zhang et al. [40] investigated the efficiency of three chelating agents, dithiocarbamate-functionalized polyaminoamide dendrimer (PAMAM-0G-DTC), sodium dimethyl dithiocarbamate (SDD), and dithiocarbamate-functionalized tetraethylene pentamine (TEPA-DTC), for HM stabilization. They found the PAMAM-0G-DTC agent exhibited the best stabilization efficiency at a lower dosage and a wider pH range compared to the other agents. The better performance was attributed to the formation, and subsequent embedment of the HMs, in the three-dimensional network structure.

Table 6
The extraction efficiency (%) of heavy metals from fly ash (collected from a MSWI plant on the south China mainland) by various inorganic acidic leachates [29]

| Extracting acid (1 molar, L/S = 25) | Zn | Pb | Cu | Cd | Cr |
|-----------------------------------|----|----|----|----|----|
| HAc                              | 59.5 | 60.32 | 19.59 | 72.66 | 17.53 |
| HCl                              | 68.44 | 74.53 | 31.17 | 72.18 | 20.15 |
| HNO3                             | 73.5 | 65.11 | 30.50 | 69.88 | 21.92 |
| H2SO4                            | 81.71 | 5.16 | 32.01 | 70.83 | 24.58 |

Table 7
The extraction efficiency (%) of heavy metals from fly ash (obtained from Taiheiyo Cement Corp., Japan) by various organic acids (L/S = 40, acid concentration = 0.1 M, T = 25 °C, leaching time = 60 min) (data obtained from [77])

| Extracting acid | Final pH | Al | Ca | Fe | Cu | Zn | Pb |
|----------------|----------|----|----|----|----|----|----|
| Citric acid    | 3.13     | 100 | 93.1 | 67 | 100 | 100 | 96.9 |
| Acetic acid    | 3.02     | 88.4 | 100 | 23.2 | 100 | 100 | 70.1 |
| Lactic acid    | 3.06     | 92.2 | 100 | 40.7 | 100 | 100 | 62 |
| Oxalic acid    | 3.09     | 43.3 | 0.41 | 46.5 | 45.8 | 44.9 | 2.7 |

Fig. 10
The extraction factor of fly ash (obtained from a MSW incineration plant in southern Thailand) heavy metals after 60 min using: 0.01 M HNO3 (A), 0.1 M HNO3 (B), 0.1 M Na2CO3 (C), 0.25 M Na2CO3 (D) [9]
Electrodyalytic separation

Electrodyalytic separation (EDS) is technology introduced for heavy metals removal from fly ash. A scheme depicting the EDS approach is presented in Fig. 11. In this method, the water is initially acidified by electrolysis as within an acidic environment the HMs extraction is more straightforward. When the HMs are dissolved, the metal ions are separated with the help of electrodes and an applied electric field [10, 86]. When the electric field is applied, the metal ions undergo electromigration towards the cathode facilitating their separation [87].

The pH of the medium, current density, process time, L/S ratio and the type of assisting agent have been reported as the key factors determining the effectiveness of this electro-chemical process [21, 88, 89]. Figure 12 illustrates the changes in leachate HM concentration in relation to the L/S, pH and processing time for electrodialytic separation. The change in pH of the fly ash suspension during the process can increase mobility of the heavy metals such that the adsorbed and precipitated HMs can be removed more efficiently [87]. An assisting agent can also be introduced as a practical technique for improving HMs release [70]. A solution comprising 0.25 M ammonium citrate and 1.25% NH₃ was found to be the best choice for improving the concurrent removal of all metals [70, 87]. Pedersen et al. [87] studied the electrodyalytic removal of fly ash heavy metals using ammonium citrate as an assisting agent. They found that the removal rates of Cd, Pb, Zn, Cu, and Cr were 86%, 20%, 62%, 81% and 44%, respectively, after 70 days of remediation. It was also reported by Chen et al. [10] that a combination of water washing and EDS could significantly reduce the leachability of the heavy metals, whereby Cd, Cu, Pb and Zn predominantly accumulated in residual phases in the ash after the washing and EDS treatment. The EDS method also provided the advantage of less energy consumption and the less toxic chlorine gas (Cl₂) production. Tao et al. [18] linked the EDS setup to a bio-electrochemical systems (BES) for fly ash heavy metals removal. They found that this combination could effectively remove fly ash heavy metals where the removal rates of Cu, Zn and Pb were 98.5%, 95.4% and 98.1%, respectively. Zhang et al. [86] reported that using three-dimensional electrodes instead of two-dimensional electrodes can substantially improve the HMs removal efficiency.

Thermal treatment

Thermal treatment approaches

Despite the high operational costs, thermal treatment is one of the most preferred stabilization methods due to several advantages. These advantages include simultaneous solidification of heavy metals and destruction of waste organic compounds at elevated temperature conditions, leading to less severe environmental issues caused by dioxins and HMs. After thermal treatment, the reduction in fly ash volume is expected to be around 60% or more [51, 90]. The thermal treatment methods for fly ash can be divided into three categories, namely, sintering, fusion and vitrification, performed across temperature ranges of 900–1100 °C, 1100–1450 °C, and 1250–1500 °C, respectively [91]. The thermal treatment of fly ash can be performed in different reactor configurations, such as a rotary reactor or a muffle oven, with higher temperature and treatment time [22]. Thermal treatment of MSWI FA generally comprises four stages: moisture evaporation, decomposition and absorption, main devolatilization, and continuous mineral decomposition [92]. Simple crystal forms in raw fly ash, such as halite and sylvite, are expectedly transformed to more complex crystals in thermally treated samples, such as chlorellestadite, polyhalite and enstatite [93]. Following thermal treatment, the remaining HMs are encapsulated by a glassy network which can efficiently inhibit their leachability. One of the main concerns associated with the thermal treatment of fly ash is the release of secondary air pollutants which comprise volatile metals, such as Pb and Zn [10]. The evaporation rates of Pb, Cd, Cu and Zn are estimated to be in the range of 83–95%, 48–95%, 70–80%, and 20–40%, respectively, during the sintering process at 1000 °C [34]. It is reported that the chloride content of the ash can govern the evaporation rate of Cd, Pb and Zn to a larger extent, where a lower chloride provides better thermal stability of the volatile fractions [10]. Water washing pretreatment can be introduced as a practical technique for surpassing the evaporation of volatile metals during thermal treatment [34, 94]. In a study conducted by Chen et al. [10], the leaching of As, Cr, Pb and Zn from fly ash...
ash after thermal treatment without and in combination with water washing was compared. It was found that the thermal treatment of prewashed fly ash could minimize the leaching of all heavy metals to meet the standard values for landfilling. Chiang et al. [95] studied the impacts of water washing at various L/S ratios on the thermal stabilization of fly ash and found that this simple pre-treatment was able to extract most of the chlorides, leachable salts, and amphoteric heavy metals (Pb and Zn) from the fly ash. It was also found that the L/S ratio played a key role in this treatment method. Figure 13 illustrates the vitrification efficiency of HMs as a function of L/S ratio. As seen in Fig. 13, a higher L/S ratio favors a higher vitrification efficiency. Furthermore, water washing can enhance the vitrification of Cu and Pb more effectively than Zn and Cd. Wu et al. [96] compared water washing and phosphate stabilization pretreatments on the evaporation rates of HMs from fly ash. They observed that 45–55% and 60% of the heavy metals were removed from the fly ash by washing and phosphate pretreatments, respectively. The consequent HMs evaporation rate from the raw, water-washed and phosphate stabilized fly ash was 90%, 50%, and 25%, respectively. In a study conducted by Gu et al. [97], the effects of calcination and water washing as pretreatment methods on the medium temperature carbonation of the MSWI fly ash were examined. While the pretreatments were found to increase the leaching concentration of HMs in acid solution, carbonation of the pretreated samples at 400–450 °C was able to significantly decrease the leaching concentration.

Geng et al. [98] investigated the effects of adding red mud (RM) to MSWI fly ash in the thermal process. They reported that SiO₂ and Al₂O₃ in RM were able to enhance the HM stabilization with the optimal FA/RM ratio found to be 3/7. When compared to FA which had a melting temperature of 1400 °C, the melting temperature of the FA/RM mixture was found to be 1100–1300 °C. In this context, the leaching concentration of vitrified slag was much less than the standard limits. The same findings were reported by Lin et al. [99] who assessed the thermal cotreatment of MSWI fly ash and sewage sludge (SS), which contained high amounts of SiO₂ and Al₂O₃.

**Key parameters during fly ash thermal treatment**

**Processing temperature and heating rate** The melting temperature of fly ash, governed predominantly by the CaO, SiO₂, Al₂O₃, MgO and Fe₂O₃ content, is considered to be an important parameter in the fly ash thermal treatment approach [91]. In a study conducted by Jakob et al. [23], the temperature and time dependency of Zn, Pb, Cd and Cu were investigated. They reported that evaporation was more effective when the process was conducted below the melting temperature of the fly ash. Higher temperatures diminished the efficiency which was attributed to the formation of more stable species at a higher temperature. At a higher temperature the formation of aluminosilicates, which can improve the encapsulation of HMs by the ash matrix, was promoted leading to a lower heavy metals leaching rate, even under an
acidic environment [100]. However, a higher HMs evaporation rate at a higher temperature has also been reported in the literature, as shown in Fig. 14 [96]. It should be noted that above $T = 1100 \, ^\circ\text{C}$, it is found that a rise in the temperature affects the leachability of HMs peripherally [101].

The heating rate also plays a significant role in HMs stabilization or evaporation. It is reported that the probability of stable compound formation is enhanced under slow heating conditions which can diminish the volatility of heavy, invoking more efficient stabilization [102]. Under rapid-heating/combustion conditions the release of heavy metals is promoted.

**Reactor atmosphere** The atmosphere applied to the thermal reactor can also determine the HMs distribution. Hu et al. [103] studied Cr behaviour during thermal treatment of fly ash in an electrically heated horizontal furnace across a temperature range of 1023–1323 K under air or N$_2$ atmospheres. They found that, under a N$_2$ atmosphere, the oxidation of Cr$_2$O$_3$, due to its reaction with CaO, led to a significant reduction in Cr leachability. Dong et al. [4] reported that a reducing atmosphere favoured Cd and Zn evaporation and lowered the volatility of Cu, Ni and Cr. Compared to oxidizing conditions, Lane et al. [32] found that the thermal treatment of fly ash under a reducing atmosphere enhanced Zn volatility, although it reduced the volatility of Pb and Cu. Figure 15 compares the volatility of Zn, Pb and Cu under both atmospheres. Zhu et al. [104] investigated the feasibility of vacuum-aided heat treatment (VAHT) of HMs and specified that the VAHT process at 900 °C, 10 Pa and over a 4 h time period led to elimination of 100% of the Cd, 93.1% of the Pb, and 81.0% of the Zn and the leachable fraction of fly ash decreased significantly.

**Fly ash composition** The evaporation of HMs during thermal treatment can be significantly influenced by fly ash composition. Fly ash composition mainly depends on the waste thermal recycling method, for instance, incineration, pyrolysis and gasification, as well as operating conditions. A comparison between biomass thermal recycling methods demonstrated that during the incineration process, Co, Zn, Mn, Cu, Ni and Cr were generally concentrated in the fly ash with Zn, Mn and Cu as the main elements. In contrast, when using the pyrolysis process, Cu, Zn, Fe, and As were primarily concentrated in the fly ash with 98.8% of the total Pb found in residual biochar [46]. Moreover, it was reported that an increase the pyrolysis temperature greatly reduced the bioavailability and leachability of HMs [46]. Hu et al. [100] found that, at an elevated temperature the reaction between Ca-compounds and Si/Al compounds was enhanced leading to the formation of aluminosilicates that are desirable for HMs stabilization. It was concluded that the CaO content can affect the thermal stabilization of fly ash to a great extent. In another study by the same authors, the sintering efficiency of CaO-rich FA was improved after the inclusion of Si/Al-rich MSWI bottom ash [105].

**Fly ash size distribution** The size distribution of fly ash particulates can considerably affect the thermal stabilization process, where it has been reported that the smaller size particles improve the thermal stabilization efficiency [34]. Further, it has been found that finer fly ash particles contain large amounts of heavy metals [16]. The lower ultimate degree of metal volatilization from larger particles is due to the delayed diffusion of near-to-center metallic compounds to the particle surface hindering their evaporation [106]. Milling, whether dry or wet, can be introduced as a practical
Chlorination

During the thermal treatment method, heavy metals can be evaporated or stabilized, which is predominantly regulated by the temperature of the processing unit [35]. Compared to metal oxides, metal chlorides have a lower boiling point such that they can evaporate more readily. While in many cases the fly ash is water prewashed to remove chlorides and sulfates to improve HMs stabilization, the inclusion of chlorinated additives within the thermal treatment process is considered as one way to increase HMs volatility for better separation from the fly ash [10, 110]. The incorporated chlorinating agent can conceivably react directly with the metal oxide or they can release Cl₂ following their reaction with oxygen or water [35, 36]. The most commonly employed chlorinating agents for this purpose are NaCl, MgCl₂, CaCl₂, FeCl₃ and AlCl₃. These agents hold advantages over gaseous Cl₂ through higher selectivity toward chlorination of hazardous elements and simpler handling [111]. Despite a low efficiency for removing Cr and Ni, HCl is also used as an effective Cl donor [111].

Liu et al. [35] undertook a study to assess the impacts of different chlorinating agents in the evaporation rate of heavy metals. Figure 16 compares the efficiency of the used Cl donors in removing Cu, Pb, Zn and Cd via a thermal treatment process at 1000 °C. Irrespective of the type of chlorinating agent, their addition enhanced the evaporation rates of all metals with the effectiveness of HMs removal decreasing in the order MgCl₂ > CaCl₂ > FeCl₃ > AlCl₃ > NaCl [35]. The presence of silicates and aluminates in fly ash can adversely affect the chlorination efficiency of Cl donors. They diminish the probability of volatile heavy metals formation, for instance, Cd(OH)₂, CdO, CrO₂Cl₂, (CuCl)₃, CuCl, NiCl₂, PbO, PbCl₂, ZnCl₂ compounds, and lead to higher HMs stabilization [111]. Generally, the effectiveness of the chlorinating agents on HMs removal follows the order Cu > Zn > Cd > Pb [112]. As the removal of Ni below 900 °C is essentially impossible in a thermal rector, the volatilization of Ni is especially influenced by chlorinating agents. For instance, CaCl₂ is very efficient for Ni removal [36]. Pb removal from ash is generally satisfactory where close to 90% of Pb can be removed at 800 °C without the contribution of any chlorinating agents. The addition of MgCl₂ can enhance the removal of Pb to 95% at the same temperature. At a higher temperature Pb removal becomes independent of the amount and type of the Cl donor. While the inclusion of chloride can affect the evaporation of Cu in a marginal way,
Zn removal is highly influenced by the type and amount of the chloride. It has also been reported that CaCl₂ and MgCl₂ can efficiently enhance Zn evaporation [36]. Nowak et al. [113] studied the thermal treatment of municipal solid waste fly ash mixed with CaCl₂. They found that at 1050 °C and after 45 min heating, Cd, Cu, Pb and Zn were removed by 95%, 60%, 98% and 80%, respectively.

The processing time, type, concentration and size of the chlorinating agent, and the applied atmosphere and temperature can be significant in determining the efficiency of heavy metals removal via the chlorination approach. With regards to the processing time, it was reported that longer dwelling times did not affect the evaporation of Cd and Pb, while it enhanced the removal rate of Cu and Zn [111]. It is worth noting that a higher surface area of the chlorinating agent can positively influence the efficiency of its heavy metal removal. For instance, a milled Cl donor can enhance the evaporation rate of HMs to a much greater extent than the flake forms [36]. Further, the higher the percentage of the included Cl donor, the better the heavy metals evaporation rate. Irrespective of the type of chlorinating agent and the process atmosphere (for example, oxidative, reductive or inert), the thermal treatment of fly ash in the presence of a Cl donor at a higher temperature increases the probability of metal chlorides formation. A higher evaporation rate of heavy metals is subsequently expected, as shown in Fig. 17. When the operating temperature is not sufficiently high, a low HMs evaporation rate should be expected. Xie et al. [110] proposed a molten salts (NaCl–CaCl₂) thermal treatment method to enhance the stabilization of heavy metals at relatively mild conditions (600/800 °C). Compared to the traditional thermal method, the molten salts approach better enhanced the chlorination of heavy metals. This was mainly attributed to the more straightforward indirect chlorination of metal oxides in the presence of Al₂O₃ and SiO₂. It was found that due to the good thermal stability of heavy metals in molten slats, less than 5% of heavy metals were volatilized, indicating the promising HMs stabilization of this method with a lower volume of secondary air pollution.

One low-cost approach to enhance the chlorination of heavy metals is the inclusion of alkali or alkaline metal chlorides which can release HCl and Cl₂ upon heating. Yu et al. [112] investigated the thermal treatment of a fly ash mixture from a fluidized bed incinerator (HK fly ash) and a fly ash mixture from a grate incinerator (HS fly ash) under various operating conditions. The HS fly ash contained a

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**Fig. 17** The volatilization rate of fly ash (from the waste-to-energy plant in Vienna, Austria) heavy metals against temperature in different atmosphere using various Cl donors [36]

high content of alkali or alkaline earth metals which could act as a Cl donor for enhancing HMs evaporation. It was noted that the addition of HS fly ash could increase the melting temperature of HK fly ash which had a direct impact on better evaporation of the HMs. Figure 18 provides details on the dependency of the heavy metals evaporation rate on the HS/HK ratio as well as processing time. It was found that HMs leaching decreased notably with an increase in HS/HK ratio. The vaporization rate of Zn, Pb and Cd was affected marginally after the addition of HS fly ash, while Cu evaporation was notably promoted due to the formation of copper chlorides. The low efficiency of Zn vaporization was attributed to the formation of Zn$_2$SiO$_4$, ZnFe$_2$O$_4$ and ZnAl$_2$O$_4$. Yu et al. [114] performed a study to identify the mechanism of heavy metals vaporization by MgCl$_2$.6H$_2$O. They found that MgCl$_2$.6H$_2$O could release HCl during thermal treatment under oxidative, inert and reducing atmospheres. The Cl donor was able to considerably enhance the evaporation of Zn and Cu under the oxidative environment, while the vaporization of Cu was suppressed in an inert atmosphere. A higher content of the chlorinating agent improved evaporation efficiency. Moreover, the differences between fast and slow heating conditions on vaporization of the studied HMs were insignificant. Following the treatment, the HMs leaching rate was lower than the regulatory limits.

**Hydrothermal process**

Compared to fly ash thermal treatment methods, which are costly and energy-consuming, hydrothermal treatment can be conducted under mild conditions. It has been reported that this approach can lead to efficient stabilization of HMs as well as the decomposition of polychlorinated dibenzo-dioxins (PCDDs) and polychlorinated dibenzo-furans (PCDFs) [7]. It has been reported that the inclusion of alkali metals, as well as the use of ferric/ferrous salt with acid washing pretreatment, can enhance the effectiveness of the hydrothermal method for HMs stabilization [37]. However, Hu et al. [7] reported that hydrothermal treatment with a mixture of ferric and ferrous sulfate was only beneficial for

![Image](https://example.com/image1.png)

**Fig. 18** The impacts of ash mixture (HK fly ash was sampled from a fluidized bed incinerator in Wuhan city, Hubei province, China, HS fly ash was sampled from a grate incinerator in Huangshi city, Hubei province, China) and process time on the vaporization of heavy metals (in N$_2$ atmosphere at 1000 °C) [112]
the stabilization of As and Ni, while it adversely affected the stabilization of Zn, Pb, Cd, Ba, Cr and Cu. Qiu et al. [115], reported that the significance of influential factors defining the efficiency of the hydrothermal process was in the order reagent > concentration ≈ temperature > time > L/S ratio. As the traditional hydrothermal method is time-consuming, the microwave-assisted process has received great attention in recent years as it can considerably shorten the required processing time [116]. Hydrothermal treatment with microwave heating for just 20 min at 125 °C with an alkaline additive was reported to promote the solidification of approximately 80% of heavy metals. The use of NaH₂PO₄ in a separate study resulted in the solidification of fly ash HMs in only 10 min via a microwave-assisted hydrothermal process [37].

Radiation-assisted techniques

Radiation-aided thermal treatment of fly ash has received substantial interest recently [117]. Microwave irradiation is considered to be an efficient heating technique where, generally, materials with a high dielectric constant can rapidly transform microwave energy to heat [118]. Microwave treatment is introduced as a practical method for dioxin control and the destruction of PCDD in fly ash [119]. Chou et al. [120] reported that microwave treatment led to the sintering of fly ash into glass–ceramics, which could considerably hinder the leachability of heavy metals. The higher processing time was found to favour more efficient fly ash stabilization. Gong et al. [6] investigated heavy metals stabilization using microwave-assisted thermal treatment of fly ash. Both traditional and microwave-assisted thermal treatments were found to decrease the leachability of Pb, Cu and Zn at the cost of higher Cr release. The microwave-assisted approach offered a higher efficiency for treating fly ash due to improved vaporization of Pb, Cu and Zn during the thermal process. Figure 19 compares the vaporization efficiency of traditional and microwave-assisted thermal treatments for Pb and Cr. A higher temperature and longer processing time had a positive impact on the fly ash stabilization by increasing Pb vaporization.

Nam et al. [117] employed an electron beam accelerator to investigate the impacts of irradiation on the leachability of fly ash heavy metals. It was found that electron beam irradiation considerably increased HMs leachability due to the destructive mechanism of the high energy electron beams. The higher the irradiation intensity, the higher the concentration of heavy metals, especially Pb and Zn, in the leachate. Cu leachability was almost independent of irradiation intensity. Microwave beams can facilitate HMs removal within the acidic extraction process over a shorter time frame [70, 121]. Xue et al. [29] compared traditional and microwave-assisted acid extraction for heavy metals recovery. Compared to acid extraction, the microwave-assisted process displayed a better performance in terms of Zn, Pb, Cu and Cr removal. Only Cd was removed to a greater extent during traditional acid leaching. An increase in L/S ratio for both approaches considerably enhanced the extraction efficiency.

Conclusion

The fly ash heavy metals content is primarily determined by waste composition, operating conditions and flue gas treatment facilities. The leachability of heavy metals is promoted significantly under highly acidic condition, and their release rate can be minimized provided that the pH is maintained within the range of 5–12. As well as the extrinsic conditions, fly ash properties such as CaO content, soluble chlorine (S–Cl) content and fly ash pH can considerably impact the leachability of HMs. Higher CaO and lower soluble chlorine

Fig. 19 The impacts of temperature and holding time on the vaporization rate of Pb and Cr after traditional and microwave-assisted thermal treatment of fly ash (collected from a MSW incineration plant in Chengdu, China) [6]

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content imply the leaching probability of fly ash will be reduced.

Various strategies, such as leaching, thermal treatment and stabilization, can be employed to reduce the leachability of fly ash heavy metals. All these methods lead to the stabilization of fly ash via physical and chemical interactions between metal ions and the matrix, as well as possible changes in metals speciation due to the treatment. The chemical stabilization of fly ash with EDTA, and phosphate and sulfur-based stabilizers can efficiently decrease the HMs bioavailability. Despite water washing that can merely remove surface metals, acid extraction, which depends on the type and concentration of the acid, can remove the encapsulated metals with a high efficiency with metal solubility in acids decreasing in the order of HCl > HNO3 > H2SO4. The separation of HMs through EDS process with the assistance of 0.25 M ammonium citrate solution and 1.25% NH3 as an assisting agent, is also of great interest. In the case of thermal treatment methods, the great proportion of heavy metals are evaporated or encapsulated in the residue, and a higher temperature promotes the encapsulation of HMs by the ash matrix due to the formation of aluminosilicates. Compared to traditional thermal process, the microwave-assisted method can stabilize Pb, Cu, and Zn more efficiently.

It should be noted that due to the pros and cons of each fly ash treatment approach, it is challenging to keep the leachability of heavy metals below the standards’ limits by simply employing a single treatment method. While water washing cannot lead to the efficient removal of toxic HMs, its combination with other methods can be a practical strategy for the fly ash stabilization. Fly ash pre washing can enhance the efficiency of HMs removal by acid extraction by reducing the alkaline nature of fly ash. Also, water washing after acid extraction can be promising for HMs stabilization, specifically Pb. Reducing the chloride content of fly ash, water washing pretreatment can minimize the evaporation rate of Cd, Pb, Cu and Zn, as volatile metals, during thermal treatment (Cu and Pb can be stabilized more effectively than Zn and Cd). However, when the recovery of HMs is prioritized, the inclusion of chlorinated additives within the thermal treatment process is considered as one way to increase HMs volatility for better separation from the fly ash, and HMs separation efficiency by this method follows the order Cu > Zn > Cd > Pb. The HMs removal efficiency of the chlorinating agents decreases in the order of MgCl2 > CaCl2 > FeCl3 > AlCl3 > NaCl. Water washing and using an assisting agent can enhance the leachability of fly ash heavy metals, especially Cd, Zn, Cu, during the electrodialytic method. Compared to traditional acid leaching and hydrothermal fly ash treatment methods, microwave-assisted processes can facilitate HMs removal, more notably in terms of Zn, Pb, Cu. Consequently, the combinations of water washing/solidification, water washing/acidic leaching, water washing/electrodialytic separation, water washing/thermal treatment, and water washing/chemical stabilization/thermal treatment are proposed as effective approaches for highly efficient HMs removal/stabilization in accordance with the economic and environmental considerations which need to be met. However, in future studies more combinations of methods, under various conditions, should be studied to find better and more efficient FA treatment approaches. Another point that should be addressed in future works would be to consider an in-depth economic analysis of different approaches for heavy metals removal/stabilization to assess and compare the financial feasibility of the discussed methods, particularly on an industrial scale.

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