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Article

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Abstract: Ball milling is investigated as a method of reducing the leaching concentration (often termed stabilization) of heavy metals in municipal solid waste incineration (MSWI) fly ash. Three heavy metals (Cu, Cr, Pb) lose much of their solubility in leachate by treating fly ash in a planetary ball mill, in which collisions between balls and fly ash drive various physical processes, as well as chemical reactions. The efficiency of stabilization is evaluated by analysing heavy metals in the leachable fraction from treated fly ash. Ball milling reduces the leaching concentration of Cu, Cr, and Pb, and water washing effectively promotes stabilization efficiency by removing soluble salts. Size distribution and morphology of particles were analysed by laser particle diameter analysis and scanning electron microscopy. X-ray diffraction analysis reveals significant reduction of the crystallinity of fly ash by milling. Fly ash particles can be activated through this ball milling, leading to a significant decrease in particle size, a rise in its BET-surface, and turning basic crystals therein into amorphous structures. The dissolution rate of acid buffering materials present in activated particles is enhanced, resulting in a rising pH value of the leachate, reducing the leaching out of some heavy metals.

Keywords: ball milling; MSWI fly ash; heavy metals; stabilization; water washing

1. Introduction

Municipal solid waste incineration (MSWI) fly ash has been classified as hazardous waste because of the presence of contaminants such as heavy metals and dioxins. Currently, treatment of fly ash has become an urgent environmental issue in China. The most common method of fly ash elimination is landfill disposal, after cement-based solidification of heavy metals. However, cement addition does not degrade polychlorinated dibenzo-*p*-dioxins (PCDD) and -furans (PCDF). Besides, the volume of fly ash significantly increases after treatment, which rapidly reduces existing landfill capacity. New landfill sites are often opposed to by local residents. So it is important to develop novel methods to render MSWI fly ash harmless and—if possible—recyclable.

Mechanochemical (MC) treatment changes the structure and physicochemical properties of fly ash through different mechanical forces such as compression, collision, friction and shear, accompanied by slight heating (ca. 50 °C). MC treatment has been successfully used in the destruction of persistent organic pollutants (POPs) such as hexabromobenzene [1], chlorophenol [2,3], perfluorooctane sulfonates [4] (PFOS), polychlorinated biphenyls [5,6] (PCBs) and also of polymers such as polyvinyl chloride [7] (PVC). Besides such chlorinated, brominated and fluorinated organic compounds, also dioxins and furans [8,9] in MSWI fly ash can be almost completely degraded with MC treatment. Mitoma et al. [10] milled fly ash together with calcium-based reagents in a planetary ball mill and

attained a degradation of near 100%. Yan et al. [11] milled fly ash without any additive, yet achieved good degradation efficiency of PCDD/Fs. The result indicates that both metal oxides and quartz contained in fly ash may play the role of abrasive or reductive reagents. Fly ash contains metal oxides such as CaO, Al₂O₃, Fe₂O₃, MgO and quartz.

Except for the degradation of POPs, MC can also be adopted to induce reaction between mineral materials or metals [12,13], and to modify the mineral materials by mechanical activation [14–17]. For instance, El-Eskandarany et al. [18] synthesized alloy powders of Nb₅₀Zr₁₀Al₁₀Ni₁₀Cu₂₀ by milling elemental Nb, Zr, Al, Ni, and Cu powders. In addition, they also reduced the haematite with magnesium to metallic Fe by MC treatment [13]. Hamzaoui et al. [17,19] modified fly ash using MC treatment, promoting the mechanical performance of substituted cement paste, moreover transforming proclay kaolinite to amorphous kaolinite which is similar to metakaolinite.

Recently, MC treatment has been introduced to stabilise heavy metals in both contaminated soil and fly ash. For example, Montinaro et al. [20] used dry ball milling to remedy sandy, bentonitic and kaolinitic soils, contaminated by heavy metals Cd²⁺, Pb²⁺, and Zn²⁺, reducing the leachable fraction of heavy metals to levels below the USEPA regulatory thresholds.

So far only lead was effectively solidified by MC treatment. Nomura et al. [21,22] stabilised Pb in fly ash by milling it with CaO in a dry planetary ball mill; the concentration of Pb in leachate was reduced by 93%. Li et al. [23,24] stabilised lead in fly ash by wet ball milling. Pb elution was reduced by about 96% compared to untreated fly ash: Pb was sealed inside the milled fly ash during the fragmentation and subsequent agglomeration of particles. Stabilisation may be explained by the creation of fresh surfaces during ball milling, trailed by the formation of insoluble compounds, as caused by the high surface energy of freshly ground particles. Heavy metals are also possibly entrapped into aggregates: the crystalline structure acts like a net; this net shows some defects in which heavy metals are entrapped [20].

Dioxins and heavy metals are the two chief contaminants in MSWI fly ash, yet MC treatment is a simple, low cost, ecologically safe, and effective method for detoxification of MSWI fly ash, i.e., both degradation of dioxins and stabilization of heavy metals. MC treatment requires no heating, so that no hazardous gases are produced or sophisticated Air Pollution Control Devices needed. Furthermore, local residents could easily accept a fly ash MC treatment plant. However, the stabilization mechanism of heavy metals in MSWI fly ash was studied only recently. In the present work, we analyse the efficiency of MC treatment of heavy metals (Cu, Cr, Pb, Cd, Ni, and Zn) in MSWI fly ash without additives and also investigate the mechanism of heavy metals stabilization.

2. Materials and Methods

2.1. Sampling and Pretreatment

Fly ash was taken from the bag filter of a circulating fluidized bed (CFB) MSWI plant located in Hangzhou, Zhejiang Province, China. The incinerator has a capacity of 800 tons per day and operates at approximately 850 °C–950 °C. The flue gas treatment involves spray neutralisation with a hydrated lime suspension and activated carbon injection. Part of the fly ash was washed with water to remove soluble salts, such as sodium chloride, potassium chloride and calcium chloride. A two-stage process with a water/solids ratio of 5 was adopted. At each stage, the solution was vibrated for 30 min on a horizontal water bath oscillator at 25 °C. Both the fly ash (FA) and the washed fly ash (WFA) were placed in an oven at 105 °C onto plates for 24 h, to be dried.

2.2. Ball Milling Experiments

A new type of planetary ball mill with a commercial name of all-dimensional planetary ball mill (QXQM-2, Changsha Tencan Powder Technology Co., Ltd., Changsha, Hunan, China) was used for the MC treatment (Figure 1). Compared with the planetary ball mill, this unit adds a dimension of rotation. The whole object consisting of disk and all pots slowly rotates (1 rpm) around a main

spindle to avoid sedimentation of materials caused by gravity, making powders to be ground more completely. The milling pots, with volume of 500 mL, and balls with either 8 (2.1 g) or 12 (7.1 g) mm diameter are made of stainless steel. About 40 g fly ash and 40 g WFA were charged into each pot, together with 10 big balls and 43 small balls under atmospheric conditions, with a ball to powder ratio of 4 wt./wt. The mill was operated for 20 h, with a 30-min driving belt cooling interval every 30 min [25]. The rotation speed of the disk and pots were respectively set as 300 rpm and 600 rpm, and the rotational direction changed automatically every 30 min. After MC treatment, both milled fly ash (MFA) and washed and milled WFA (MWFA) were collected for heavy metals leaching tests and analysis.

Stabilization efficiency was calculated based on the following formula:

$$\frac{HM_{original} - HM_t}{HM_{original}} \times 100\% \quad (1)$$

where $HM_{original}$ —the leaching concentration of heavy metals before milling and HM_t —the leaching concentration of heavy metals after a period of milling.

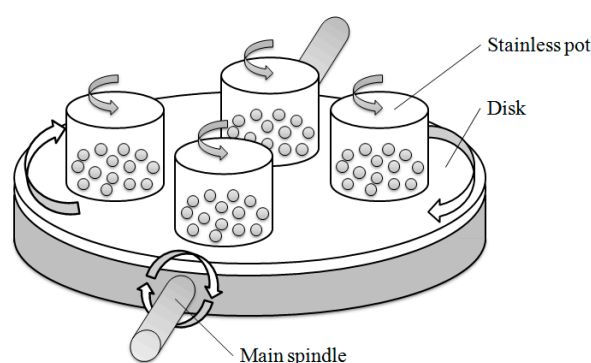


Figure 1. Schematic representation of an all-dimensional planetary ball mill.

2.3. Analytical Methods

The leaching of heavy metals from the MC treatment residue was investigated by means of a test based on method HJ/T300-2007 from the Ministry of Environmental Protection of the People's Republic of China and followed by the determination of the heavy metal concentrations by coupled plasma atomic emission spectrometry (ICP-AES, iCAP6300). The HJ/T300-2007 method is a leaching test similar to TCLP (USEPA method 1311). Table 1 shows the results from a comparison of these two methods. In the pH related leaching test, different volumes of glacial acetic acid (including 0, 1, 3, 6, 9, 12, 13, 14, 15, 16, 17, 22, 27 and 34 mL) were respectively diluted with deionised water to 1 L to prepare different extraction reagents. Moreover, the operating conditions including liquid (milliliter)/solid (gram) (abbreviated as L/S) ratio, shaking frequency (r/min), time (hour), and temperature were the same as method HJ/T300-2007.

Table 1. A comparison of HJ/T300-2007 and TCLP.

Methods	Preparation of Extracting Reagent	pH (Extracting Reagent)	L/S	Shaking Conditions
HJ/T300-2007	Dilute 17.25 mL glacial acetic acid with deionised water to 1 L	2.64 ± 0.05	20:1	Rotary shaking at 30 ± 2 r/min for 18 ± 2 h, at room temperature
TCLP	Dilute 5.7 mL glacial acetic acid with deionised water to 1 L	2.88 ± 0.05	20:1	Rotary shaking at 30 ± 2 r/min for 18 ± 2 h, at room temperature

The pH value of leachate was measured using a pH meter (S470 SevenExcellence™, Mettler Toledo, Shanghai, China). The chemical composition of fly ash was analysed by X-ray fluorescence (XRF). The crystalline structure of the fly ash particles was identified by X-ray diffraction analysis (XRD, X'Pert PRO PANalytical B.V., Almelo, The Netherlands). The specific surface area was determined by an Autosorb-1-C surface area analyser. The diameter of fly ash particles was analysed using a laser particle diameter analyser (LS-230 Coulter). Scanning electron microscopy (SEM) was used to observe the morphology of the fly ash particles before and after grinding.

3. Results and Discussion

3.1. Characteristics of Milled and Washed Fly Ash—Heavy Metals Leaching Tests

The main cations, anions, and heavy metals of raw fly ash, MFA and WFA were analysed by XRF. Except for oxygen, calcium cations showed the highest concentration, followed by Si and Al (Table 2). As expected, the concentration of the four main heavy metals (Zn, Cu, Pb and Cr) barely changed after 10 h of milling: MC treatment cannot eliminate heavy metals, but it might amend their speciation. Water washing dissolves soluble salts (mainly composed of Cl^- , Na^+ and K^+), with a weight loss of about 11%.

Crystalline compounds were analysed by XRD. Figure 2 shows that water-soluble compounds (NaCl and KCl) were efficiently removed during water washing, as evidenced by the disappearance of their XRD patterns in the washed fly ash (Figure 2b). The wave shapes of Figure 2a,c–e are quite similar, except for the decrease of some peak heights, indicating that no new visible crystals generated during mechanical treatment. Compared with raw fly ash (Figure 2a), the peak intensity of NaCl, KCl, CaCO_3 and CaSO_4 obviously weakened during the milling of fly ash, while that of SiO_2 and Fe_2O_3 had visible expansions indicating the formation of some nanostructured materials (Figure 2c–e).

Table 2. The main cations, anions, and heavy metals in the fly ash.

Cations, Anions, and Heavy Metals	Raw Fly Ash	Milled Fly Ash (10 h of Milling)	Washed Fly Ash
O ^a	34.71 ± 0.3	35.69 ± 0.3	37.97 ± 0.3
Ca ^a	16.98 ± 0.15	15.95 ± 0.15	17.88 ± 0.15
Si ^a	11.18 ± 0.10	13.26 ± 0.11	13.18 ± 0.11
Al ^a	5.80 ± 0.08	5.84 ± 0.08	6.39 ± 0.09
Cl ^a	7.43 ± 0.13	6.12 ± 0.12	1.37 ± 0.06
C ^a	7.50 ± 0.13	7.61 ± 0.13	7.96 ± 0.13
Mg ^a	3.41 ± 0.07	3.02 ± 0.07	3.92 ± 0.07
Fe ^a	2.86 ± 0.07	2.98 ± 0.07	3.48 ± 0.08
P ^a	1.46 ± 0.04	1.24 ± 0.04	1.87 ± 0.04
S ^a	1.28 ± 0.04	1.06 ± 0.04	1.61 ± 0.04
Na ^a	4.44 ± 0.09	4.25 ± 0.09	1.91 ± 0.06
K ^a	1.68 ± 0.06	1.67 ± 0.06	0.897 ± 0.043
Ti ^a	0.554 ± 0.03	0.55 ± 0.03	0.634 ± 0.031
Zn ^b	4160 ± 210	4110 ± 210	5060 ± 250
Cu ^b	996 ± 50	980 ± 50	1170 ± 60
Mn ^b	770 ± 39	780 ± 39	931 ± 47
Pb ^b	677 ± 34	685 ± 34	815 ± 41
Cr ^b	408 ± 20	453 ± 24	484 ± 24
Ni ^b	77 ± 4	83 ± 4	94 ± 5
Cd ^b	26 ± 6	32 ± 6	20 ± 9

Notes: ^a Unit: % (w/w); ^b Unit: mg/kg.

Different sensitivity of these crystalline phases to ball milling is due to their hardness. The decrease in intensity is presumably due to partial amorphisation of phases, a typical effect induced by ball milling [12,26], and the extent of amorphisation kept enhancing with the increase of milling time. It is

known that high energy ball mill can cause the transformation of crystalline material into amorphous state, increasing the amorphous content and enhancing its activity [14–17].

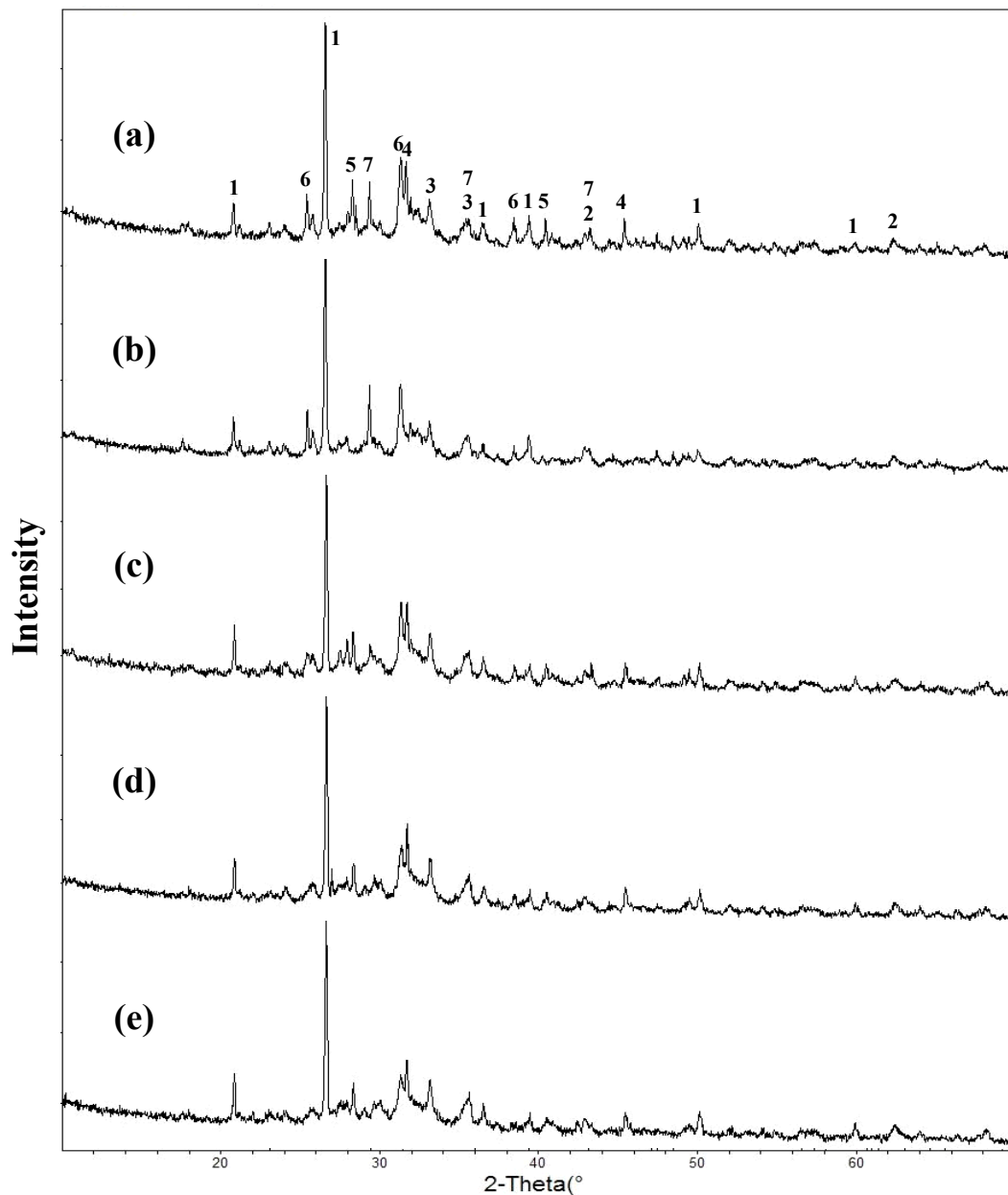


Figure 2. XRD patterns of (a) raw fly ash; (b) washed fly ash; (c–e) milled fly ash after (c) 1 h; (d) 4 h; (e) 10 h of milling. 1: SiO₂, 2: MgO, 3: Fe₂O₃, 4: NaCl, 5: KCl, 6: CaSO₄, 7: CaCO₃.

Both MFA and MWFA were leached according to method HJ/T300-2007 (Table 1). The results of the leaching test on fly ash after 10 h of milling are shown in Table 3. For FA, the leaching concentration of Cu, Cr, and Pb decreases from 15.48 mg/L, 1.113 mg/L, and 1.215 mg/L to 10.69 mg/L, 0.444 mg/L, and 0.662 mg/L after 10 h of milling, respectively. For WFA, the leachate concentration decreases from 13.29 mg/L, 0.848 mg/L, and 1.006 mg/L to 3.55 mg/L, 0.016 mg/L, and 0.141 mg/L after 10 h of milling, respectively for Cu, Cr, and Pb. MC treatment shows the strongest stabilization effect for Cr, with 60.1% for FA and 98.1% for WFA, respectively. The values for Cu and Pb were 30.9% and 45.5% for FA, against 73.3% and 86.1% for WFA. After a period of milling the leaching of Cu, Cr, and Pb was efficiently suppressed; hence, washing out the soluble salts strongly promotes stabilization.

However, for Zn, Cd, and Ni MC treatment has little effect on the stabilization. Particularly, the leaching concentration of Ni obviously increased after ball milling. In addition, the pH value of leachate kept rising as milling time increasing.

Table 3. Leaching test results after milling.

Heavy Metals	Milling Time	Cu	Pb	Cr	Ni	Cd	Zn	pH
FA	0 h ^a	15.48	1.21	1.11	0.39	0.69	48.00	5.50
	2 h	12.86	0.83	0.71	0.49	0.67	46.79	5.59
	6 h	11.73	0.74	0.57	0.56	0.66	46.05	5.66
	10 h	10.69	0.66	0.44	0.618	0.663	45.45	5.71
WFA	0 h ^a	13.29	1.006	0.85	0.356	0.705	47.40	5.69
	2 h	7.01	0.53	0.30	0.58	0.65	43.15	6.00
	6 h	5.21	0.31	0.14	0.71	0.62	40.96	6.11
	10 h	3.55	0.14	0.016	0.80	0.59	39.11	6.29

Notes: Unit: mg/L. ^a: Not milled.

3.2. Variation in the Particle Size of Milled Fly Ash

The mean particle size and the specific surface area (BET) both evolve as function of milling time (Figure 3). Before milling the average particle size of fly ash was 56.8 μm ; it rapidly decreased to 7.8 μm during the first hour of milling and then slightly reduced further reaching 4.3 μm after 10 h of milling. Before milling the BET specific surface of fly ash only attained 1.2 m^2/g ; yet it quickly augmented to 3.1 m^2/g after 2 h of milling. After that, the BET of fly ash only slightly changed as milling goes on. Thus, the increase of BET surface accompanies the reduction of mean particle size.

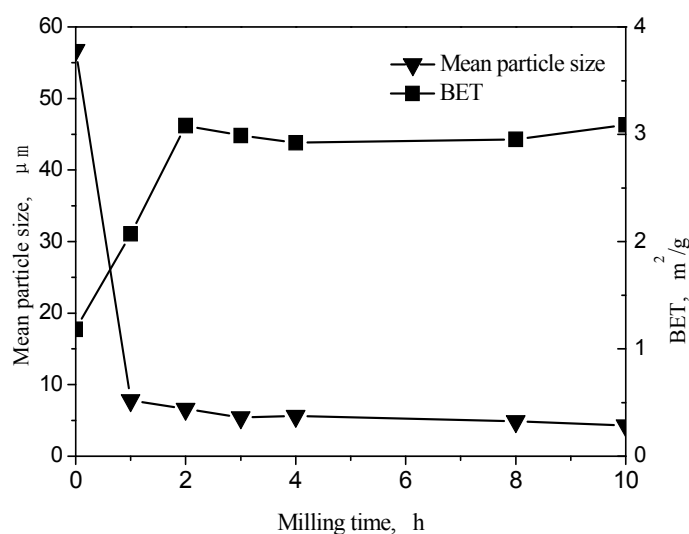


Figure 3. The evolution of the mean particle size and the BET specific surface vs. milling time.

The evolution of particle size distribution during milling is shown in Figure 4. Each distribution curve exhibits a poly-modal size distribution (Figure 4a). After only 1 h the initial curve obviously strongly shifts to the left (finer particles); later evolution becomes much slower. A peak with a mean size of ca. 1–2 μm emerges during grinding, and its peak height keeps slowly growing with rising milling time. The cumulative sketch in Figure 4b demonstrates a shift towards small size classes for all milling time (<10 h), indicating that the fragmentation of particles play a main role compared with agglomeration during milling process.

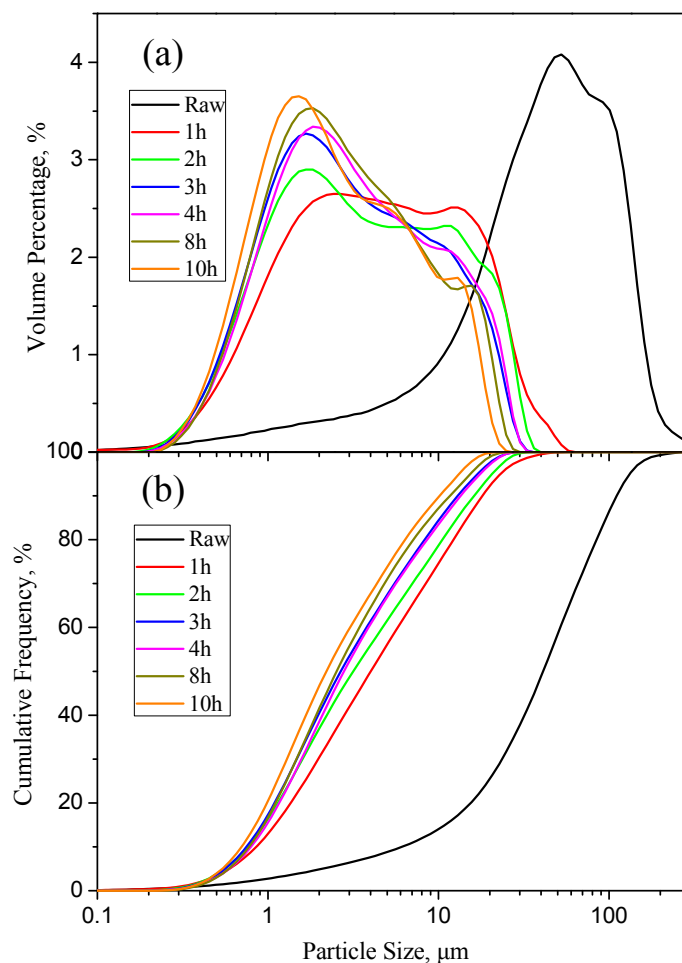


Figure 4. Evolution in the particle size distribution during milling: (a) 0–3 h; (b) 3–10 h.

The surface of particles was observed by SEM. Figure 5a,b shows the raw fly ash before milling: it consists of many large particles. After 2 h of milling these were reduced to smaller sizes (Figure 5c,d), further milling (Figure 5e,f) kept bringing changes in size, which coincided with the evolution of particle size.

For the heavy metals stabilization in soil, Montinaro et al. [20] found that Pb, Cd and Zn complexes diffuse within the solid matrix following the accumulation of crystalline defects. Therefore, the heavy metals are irreversibly adsorbed into crystalline reticulum to prevent their leaching. However, in the present work, MC treatment has no effect on stabilization for Cd, Zn, and Ni. The elements Ni, Cu, and Zn have the adjacent position in the periodic table of elements, and they also have similar chemical characteristics such as electrovalence and ionic radius. If Cu can be solidified by irreversible chemical adsorption, Ni and Zn are supposed to give similar results (contradicting the results in Table 3). Therefore, this kind of mechanism is not suitable for the explanation of the stabilization of Cu, Cr, and Pb in MSWI fly ash.

Li et al. [23] reported that—to achieve stabilization—Pb in fly ash was sealed into the milled fly ash during wet milling. Nevertheless, the size of fly ash decreased significantly after milling as in Figures 3–5, and the BET of fly ash increased as in Figure 3. These phenomena are in conflict with the sealing of heavy metals. Besides, such purely physical inclusion should bring the same effect to all heavy metals, including Cd, Zn and Ni. In another word, also Cd, Zn and Ni ought to be solidified, which conflicts with the results in Table 3. Consequently, the stabilization mechanism in the present work (dry milling) mightn't be the sealing of heavy metals.

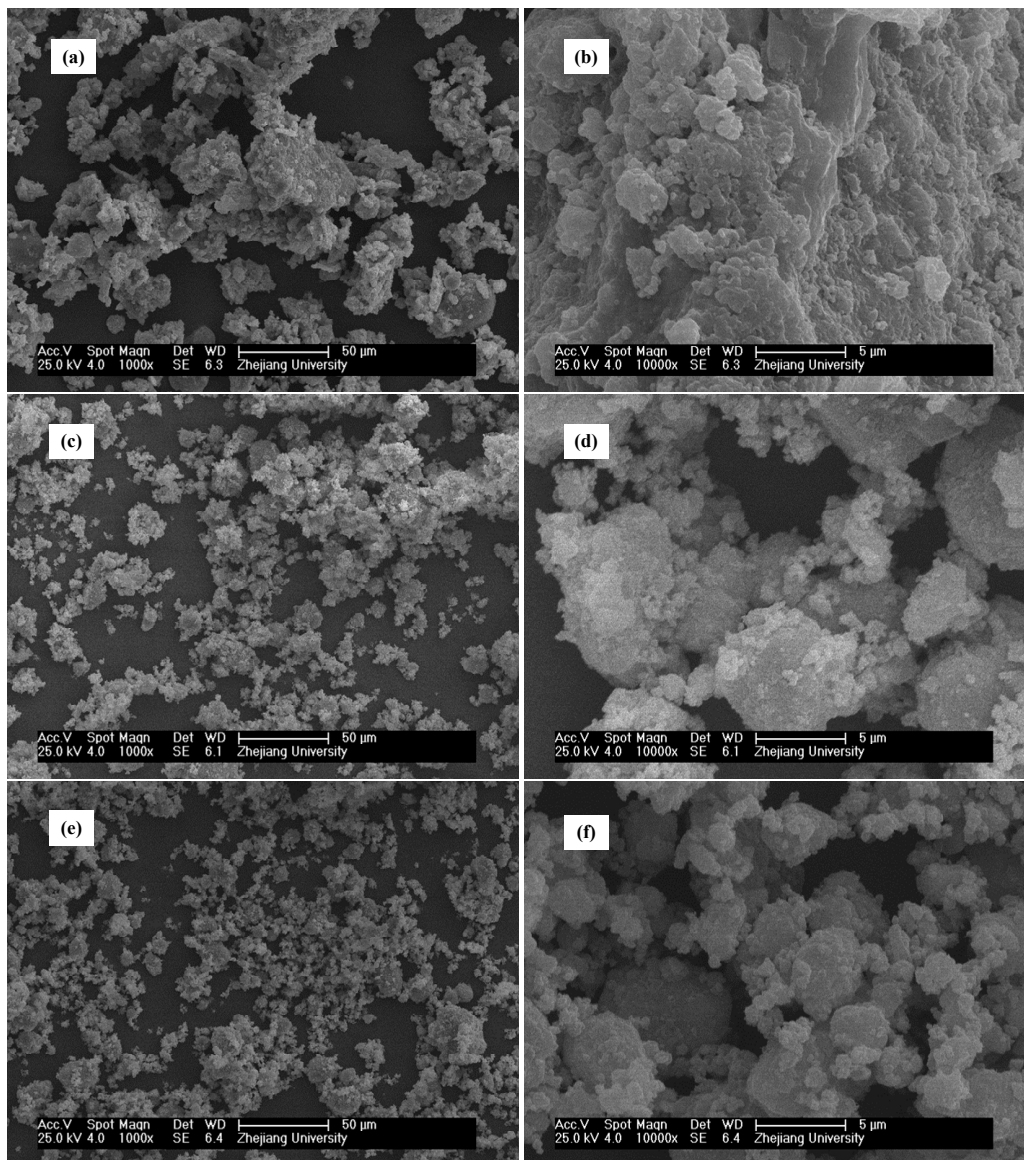


Figure 5. SEM micrographs for (a) raw fly ash magnified at $\times 1000$ (1k); (b) raw fly ash at $\times 10k$; (c) 2 h MFA at $\times 1k$; (d) 2 h MFA at $\times 10k$; (e) 10 h MFA at $\times 1k$; (f) 10 h MFA at $\times 10k$.

The MC treatment of powdered particles comprehends repeated flattening, cold-welding, fracturing and re-welding [12]. As a result, the particle size greatly decreased, accompanying with rising BET (Figure 3). Particles are repeatedly fragmented and again aggregated, forming many fresh surfaces and significantly increasing surface energy, accumulating crystalline deformation and vacancies and leading to amorphisation of crystals [16,27] as shown in Figure 2. Thus, the particles are activated by high energy ball milling, which is defined as mechanical activation, and the diffusivity of various compounds is largely enhanced [12,28]. It is known that the dissolution rate of organic and inorganic materials can be enhanced by mechanical activation [29–36]. Fly ash contains metallic oxides, such as CaO, MgO, Fe₂O₃, Al₂O₃, and carbonates CaCO₃ etc. (Table 2 and Figure 2), exerting strong acid buffering activity. With the activation of fly ash particles, the solubility of these basic compounds will increase, resulting in a rising pH value of leachate (Table 3). Washing pretreatment removed lots of soluble salts, which had no effect on acid buffering. Therefore, the washed fly ash showed a slight rise in the pH value of leachate, compared with raw fly ash.

3.3. Leaching Test Results Related to pH and the Assessment of Stabilization

Different acetic acid buffer solutions were prepared to operate a leaching test for raw fly ash, with the aim to obtaining information on the influence of the pH value of leachate on the concentration of the heavy metals leached. The test results were shown in Table 4, and Figure 6 was also made based on it. Figure 6 reveals that this concentration augmented as the pH value of leachate diminishes, within a pH range of 4.5–11. This is a typical leaching property of heavy metals of MSWI fly ash. Especially, in a pH range of 5.5–6.5 (Figure 7), the leaching concentration of Cu, Cr, and Pb changed significantly, while that of Cd, Zn, and Ni varied little.

Table 4. Leaching concentration of heavy metals related to pH.

pH	Cr	Pb	Cd	Ni	Cu	Zn
10.98	0.044	0.0069	ND	ND	0.016	0.075
10.76	0.26	0.0052	ND	ND	0.037	0.010
10.57	0.50	0.0031	ND	ND	0.050	0.0045
9.63	1.06	0.0020	ND	0.0003	0.077	0.0009
8.30	1.36	0.0019	0.015	0.031	0.10	0.0087
7.49	1.25	0.05	0.45	0.16	0.93	20.16
6.92	0.009	0.11	0.46	0.22	1.98	36.20
6.75	0.013	0.18	0.52	0.27	3.49	45.98
6.16	0.079	0.39	0.54	0.31	6.59	54.67
5.74	0.26	0.70	0.60	0.40	9.54	61.44
5.42	0.75	1.08	0.66	0.41	12.31	63.18
4.91	1.82	2.86	0.75	0.56	11.92	68.56
4.69	2.31	4.40	0.76	0.62	15.52	72.96
4.47	2.61	5.75	0.77	0.63	18.69	74.26

Notes: Unit: mg/L; ND: The concentration was lower than the detection limit of the ICP (<0.0001 mg/L).

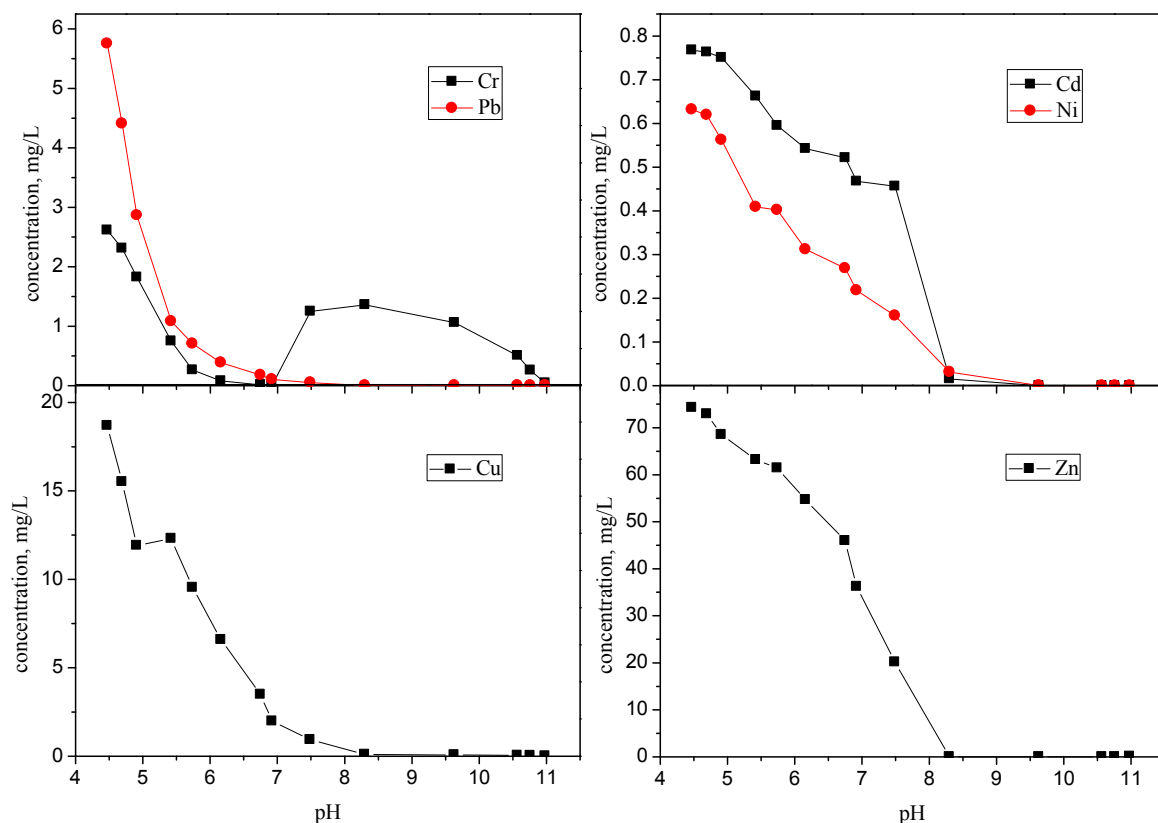


Figure 6. Evolution of leaching concentration of heavy metals vs. pH for raw fly ash.

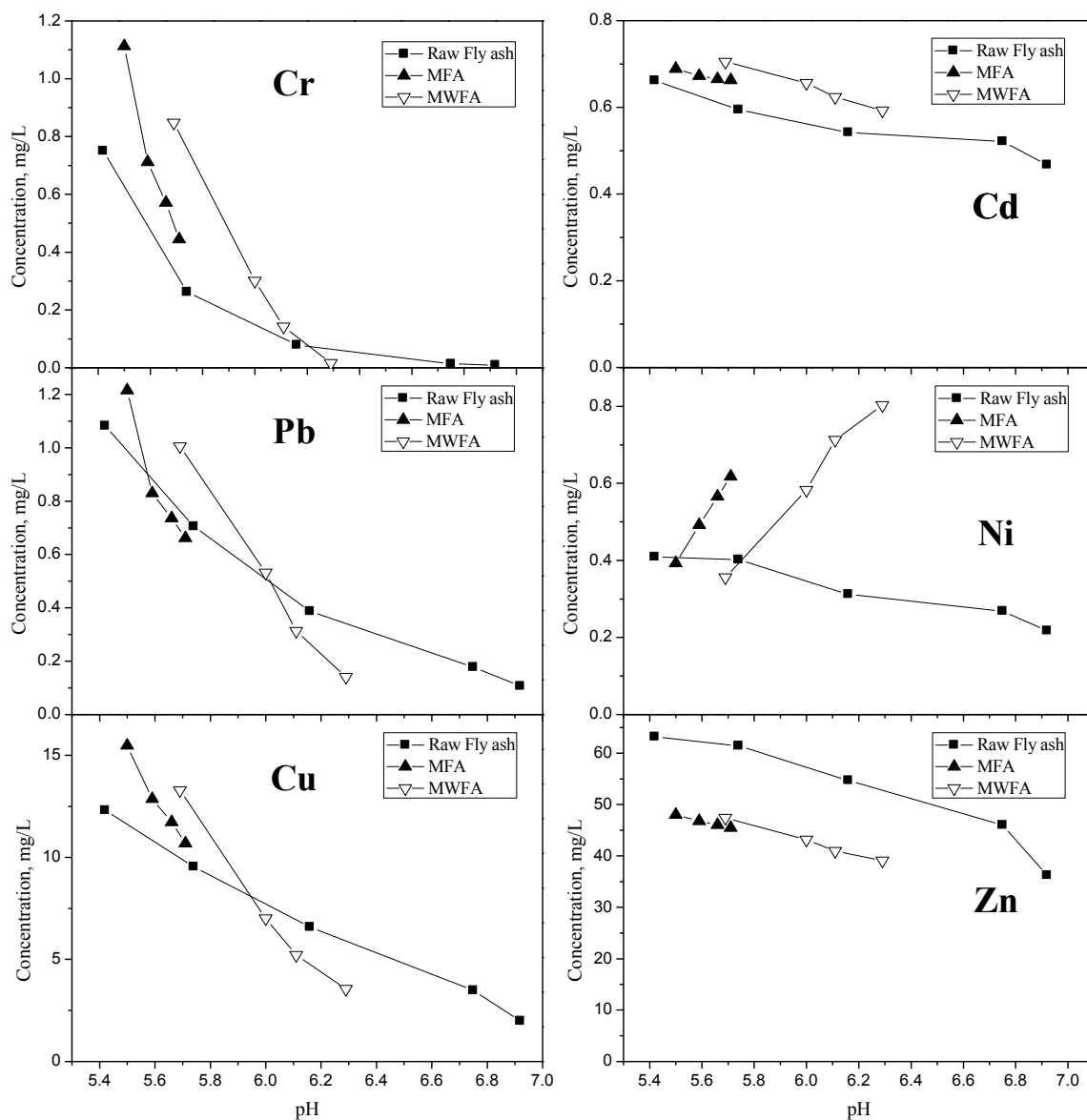


Figure 7. Evolution of leaching concentration vs. pH for raw fly ash, MFA, and MWFA.

As for MFA and MWFA, the pH value of leachate respectively increased from 5.5 and 5.69 to 5.71 and 6.29 after milling (Table 3). Correspondingly, their leaching concentration kept decreasing as pH rising. The evolution of leaching concentration versus pH value for raw fly ash, MFA, and MWFA were demonstrated in Figure 7. For all heavy metals except for Ni, their curves had almost the similar declining tendency, and the value of concentration was close. Therefore, after MC treatment, the concentration of Cu, Cr, and Pb in leachate lessened greatly, while that of Cd and Zn showed less loss, explaining why MC treatment was more effective for Cu, Cr, and Pb than for Cd and Zn. The leaching concentration of Ni increased largely, because the activation of particles caused by milling might be the main factor in controlling the leaching of Ni compared with the change of pH. In conclusion, MC treatment will activate fly ash particles and escalate the solubility of basic crystals therein: as a result, the pH value of leachate rises, resulting in reducing leachate concentration of some heavy metals, which are sensitive to the change of pH (Cu, Cr, and Pb). Moreover, washing pretreatment gave a higher ratio of acid buffer materials in fly ash, and the MWFA was supposed to have more variation of pH of its leachate, presenting in the promotion of stabilization efficiency.

A sequential extraction test has been used to assess the MC treatment applied for heavy metals stabilization in fly ash. The fly ashes were successively extracted three times with the same extracting reagent used in method HJ/T300-2007, and the operating conditions (L/S, shaking frequency, time, and temperature) were the same as in Table 1.

The results are shown in Table 5: the reducing of leaching concentration of heavy metals was only effective at the first leaching step, mainly caused by the rise of pH. The leachate concentration of heavy metals in milled fly ash was even higher than that in raw fly ash at the second and third step, because acid buffer materials had been largely consumed at the first step. The sum of three times leaching concentration increased after milling for all elements in Table 5 except for Pb, indicating that MC treatment indeed helped enhancing dissolution as the conclusion in 3.2. Particularly, the leaching concentration of Pb decreased after milling at all steps, indicating that MC treatment had a real stabilization effect to Pb. The solubility of sulphate especially for CaSO_4 in fly ash increased after milling, because the crystal of CaSO_4 had obvious amorphisation during milling as in Figure 2. Thereafter, Pb could combine with SO_4^{2-} to form PbSO_4 , which is an insoluble compound both in water and acid, reducing the leaching of Pb in leachate.

Table 5. Sequential extraction test results.

Heavy Metals	Steps	Cu	Cr	Pb	Cd	Ni	Zn	Al	Fe	Mn
FA	1st	15.48	1.11	1.21	0.69	0.39	48.00	17.61	5.34	5.21
	2nd	5.48	1.17	1.61	0.096	0.28	22.92	292.90	57.19	3.55
	3rd	1.82	0.34	0.52	0.019	0.096	4.03	127.30	10.63	1.18
	Sum	22.79	2.62	3.34	0.80	0.77	74.95	437.81	73.17	9.95
MFA ^a	1st	10.69	0.44	0.66	0.66	0.62	45.45	23.27	6.35	7.38
	2nd	8.14	1.81	1.32	0.11	0.23	28.62	343.90	71.59	3.53
	3rd	2.83	0.58	0.41	0.023	0.047	4.91	159.80	33.23	1.18
	Sum	21.67	2.83	2.40	0.80	0.90	74.07	526.97	111.17	12.09
WFA	1st	13.29	0.85	1.006	0.70	0.35	47.40	35.06	4.15	4.76
	2nd	7.78	1.35	2.49	0.15	0.30	29.87	318.90	57.55	4.57
	3rd	2.25	0.39	0.80	0.030	0.11	7.48	150.10	14.33	1.36
	Sum	23.32	2.60	4.30	0.89	0.77	84.75	504.06	76.03	10.70
WMFA ^a	1st	3.55	0.016	0.14	0.59	0.80	39.11	2.19	0.12	9.15
	2nd	17.58	2.59	1.71	0.39	0.33	48.27	387.40	57.47	5.65
	3rd	4.95	0.97	0.48	0.056	0.077	9.26	204.60	25.68	1.90
	Sum	26.09	3.58	2.33	1.03	1.21	96.64	594.18	83.27	16.71

Notes: Unit: mg/L; ^a: 10 h of milling.

4. Conclusions

MC treatment reduces the leaching concentration of Cu, Cr, and Pb, and a preliminary water washing pretreatment effectively promotes the efficiency of stabilization by removing the soluble salts. Fly ash particles can be activated through high energy ball milling, resulting in a significant decrease of particle size, an increase of its BET-surface, and the amorphisation of basic crystals. The dissolution rate of acid buffering oxides and carbonates from activated particles is enhanced, resulting in a rising pH value of the leachate, reducing the leaching concentration of some heavy metals which are sensitive to the variation of pH value. The stabilization of Cu and Cr is more like slowing down their release, because more leaching concentration of them was observed at the second and third extraction step. However, the leaching concentration of Pb may truly be reduced through the formation of insoluble sulphate. This could be an illuminating direction for the real stabilization of other heavy metals in fly ash in future research.

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