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Stabilization of Heavy Metals in Municipal Solid Waste Incineration Fly Ash in Circulating Fluidized Bed by Microwave-Assisted Hydrothermal Treatment with Additives

Qili Qiu, Xuguang Jiang,* Guojun Lv, Shengyong Lu, and Mingjiang Ni

State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, Zhejiang, China

ABSTRACT: In this work, a microwave-assisted hydrothermal treatment was investigated to solidify the heavy metals of municipal solid waste incineration fly ash in a circulating fluidized bed. The influences of additive dosage, temperature, liquid/solid (L/S) ratio, and reaction time with addition of NaH_2PO_4 were investigated. The chemical components, hydrothermal product, and the leaching concentration of fly ash were determined by X-ray fluorescence, X-ray diffraction, and inductively coupled plasma atomic emission spectroscopy. Also, pH tests were conducted to assess the environmental adaptability of the treated fly ash. In terms of the solidification effect of heavy metals, the effectiveness of additives was in the order Na_2HPO_4, NaH_2PO_4, H_3PO_4, and $FeSO_4$. Experimental results revealed that heavy metals in fly ash were solidified by a microwave-assisted hydrothermal process, under the optimized conditions of 1.5 mol/kg NaH_2PO_4, 2 mL/g L/S ratio, 10 min reaction time, and 200 °C, and the heavy metal contents met the standard limitation in GB 16889-2008. In pH tests, it was found that the safety range of the treated fly ash was widened from 7.5−11 to 5−13, which indicated that the properties of environmental stability and acid- and alkali-resistance of fly ash were enhanced. Therefore, hydrothermal treatment with microwave heating is a feasible approach for the solidification of heavy metals in fly ash in just 10 min. The treated fly ash is suitable for safe disposal or even for recovery and reutilization.

1. INTRODUCTION

As of 2013, there were 166 municipal solid waste incineration (MSWI) plants operated in China, which helped to decrease about 30% of the total municipal solid waste (MSW).[1] Therefore, incineration has been accepted as an indispensable method for managing solid wastes. Fly ash, the product of solid waste incineration, has components such as heavy metals, dioxins, and furans which are harmful to human beings and the environment.[2−5] Thus, MSWI fly ash is regarded as a kind of hazardous waste and needs to be treated before being transported to sanitary landfills.

Cement solidification[3,6] and chemical stabilization[7−9] are the main methods of fly ash disposal technology. However, these methods require a large amount of cement, increase the volume and the weight of the products, and even cause secondary pollution.[10−12] Moreover, thermal treatment is a very costly method to dispose of fly ash for developing countries. As a promising technology, hydrothermal treatment has attracted much attention, especially in academic studies, with the considerable merits of economic, technical, and environmental effectiveness.[13,14]

Recent studies have shown that additives can be used to improve the hydrothermal process. Alkali metals are popular additives in the hydrothermal process, as reported by Jin et al.,[15] Chen et al.,[16] and Hu et al.[17] Hu et al.[18] found that the leaching of Cu, Pb, and Cr from fly ash was controlled during the hydrothermal process with ferric/ferrous salt with acid washing pretreatment. Li et al.[19] indicated the leaching of toxic heavy metals could be effectively reduced with silica fume additions, because of the formation of C−S−H. Also, with alkaline compounds (Na_2CO_3) at 375 °C, the extracted concentrations of As, Mn, Pb, Sr, and Zn were reduced by about 66.18%, 86.11%, 58.33%, 83.87%, and 81.91%, respectively.[20] Phosphate also has been applied to hydrothermal processes, and its dosage could be reduced compared to chemical solidification at room temperature.[21]

To lower the energy consumption, microwave heating was introduced to the hydrothermal treatment. Microwave synthesis has been used for preparing several zeolites, such as nano-NaX zeolite,[22] analcime, hydroxysodalite, tobermorite, phillipsite, etc.[23−26] In our previous work, it was found that microwave-assisted hydrothermal treatment for just 20 min at 125 °C with alkaline additive resulted in solidification of about 80% of heavy metals. However, the leaching concentration of Cd did not satisfy the standard limit, while concentrations of the other heavy metals met the specified standards.[27] Because PO_4^{3+} is known to decrease the Cd leaching concentration and result in a long-term stabilization,[21,28] in this paper, phosphate instead of NaOH was used as the additive to solidify the heavy metals of MSWI fly ash by hydrothermal treatment with microwave heating.

2. MATERIALS AND METHODS

2.1. Materials. The raw materials were collected from the circulating fluidized bed (CFB) of an incinerator plant located in Zhejiang province, with an 800 ton daily capacity of MSW combustion; the plant is equipped with an air pollution control (APC) system. The system included selective noncatalytic reduction (SNCR) denitration, a semidry scrubber, activated carbon injection, and fabric filter. The fly ash sample used in this study was dried at 105 °C in an oven for 24 h. Various properties of the fly ash were analyzed

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before and after hydrothermal treatment, including determination of major elements, mineralogical analysis, and leaching test. The instruments used for analysis were an X-ray fluorescence (XRF) spectrometer (Thermo Fisher, Intelli Power 4200) and an X-ray diffractometer (XRD, Rigaku Rotaflex).

The chemical reagents, phosphoric acid (H_3PO_4), disodium hydrogen phosphate (Na_2HPO_4), sodium dihydrogen phosphate (NaH_2PO_4), ferrous sulfate ($FeSO_4$), acetic acid (CH_3COOH), nitric acid (HNO_3), hydrochloric acid (HCl), hydrofluoric acid (HF), and sodium hydroxide (NaOH), used in this study were all of reagent grade. Deionized water was used to dilute and prepare the solutions for analysis.

2.3. Microwave-Assisted Hydrothermal Process. For each trial, fly ash was mixed with additives and deionized water in different liquid/solid (L/S) ratios. Then the samples were heated by the microwave apparatus (Sineo MDS-6) for a certain time. After this microwave-assisted hydrothermal process, the reactant was cooled to room temperature and centrifuged to separate the solid and liquid. The solid (treated fly ash) was collected and dried at 105 °C for 24 h. Orthogonal experiments were conducted to get the optimum amount of additive, and single-factor experiments were conducted to get the optimum experimental conditions.

2.4. Leaching Test. The leaching test is used to assess whether the fly ash can be used for landfilling.[6] The standard procedure for solid waste extraction and measuring leaching toxicity using acetic acid buffer solution method (HJ/T300-2007) was employed in this study. According to this Chinese standard, an extraction buffer of acetic acid and sodium hydroxide (pH 2.64 ± 0.05) was chosen as the leaching fluid, with a liquid/solid ratio of 20 mL/g. The mixed samples were then shaken for 18 ± 2 h. Afterward, the suspension was filtered using a 0.6−0.8 μm borosilicate glass fiber filter.[29] Then the filtrate was analyzed using inductively coupled plasma mass spectrometry (ICP-AES, Thermo Scientific XII).

2.5. Leaching Test in Different pH. The pH test procedure was very similar to the leaching test. The only difference was that the leaching solution was replaced by a series of solutions of different pH values, prepared using HNO_3 and NaOH. The pH range was about 1−13. The filtrate was analyzed by both a pH meter (Mettler Toledo) and ICP-AES to obtain the pH value and the leaching concentration of heavy metals. This experiment was very important in order to determine the effect of the microwave-assisted hydrothermal treatment on heavy metals.

3. RESULTS AND DISCUSSION

3.1. Characteristics of Raw Fly Ash. The heavy metal characteristics of the raw fly ash sample are shown in Table 1. The presence of heavy metals in fly ash provides the potential to contaminate landfill environments. Because of the loose structure of fly ash, heavy metals can readily leach into the surrounding environment.[30] Our analysis showed that the contents of heavy metals in raw fly ash were quite high, especially Zn (7126 mg/kg), Cu (2794 mg/kg), Ba (1640 mg/kg), and Pb (1180 mg/kg). However, Hg could not be detected in the raw fly ash because it exists in the vapor phase during combustion. The leaching concentrations of Cd (1.948 mg/L), Cu (64.787 mg/L), Ni (1.521 mg/L), Pb (7.851 mg/L), Se (0.255 mg/L), and Zn (124.498 mg/L) were above the permissible regulatory limits, as per the Chinese national standard GB16889-2008. When these results are compared with those of with other studies,[3,6,18,31] the leaching concentrations of the toxic elements in the sample were much higher. Particularly, the concentrations of Pb and Cd were more than 31 and 13 times the respective limits (0.25 and 0.15 ppm), respectively, and this is a cause for concern because both these heavy metals have high toxicity.

Table 1. Heavy Metal Characteristics of Raw Fly Ash

heavy metal	content (mg/kg)	leaching concentration (mg/L)	limitation (mg/L)[27]	detection limits (mg/L)
As	10.35 ± 0.12	0.179 ± 0.01	0.3	0.001
Ba	1640 ± 4.60	0.5765 ± 0.03	25	0.0064
Be	1.02 ± 0.03	<DL	0.02	0.0088
Cd	44.14 ± 0.06	1.948 ± 0.08	0.15	0.001
Cr	570.8 ± 1.40	2.213 (total) ± 0.04	1.5/4.5	0.014
Cu	2794 ± 8.10	64.787 ± 0.08	40	0.001
Hg	<DL	<DL	0.25	0.0071
Ni	203.4 ± 0.61	1.521 ± 0.03	0.5	0.020
Pb	1180 ± 2.40	7.851 ± 0.10	0.25	0.0008
Se	64.24 ± 0.16	0.255 ± 0.01	0.1	0.0026
Zn	7126 ± 12.23	124.498 ± 0.12	100	0.0037

3.2. Orthogonal Experiment. In this study, a set of orthogonal experiments were designed (as shown in Table 2) to determine the feasibility of the procedure and the optimum dosage of additive and to assess the relation between additive dosage and solidification effect. The experiments were carried out with the fixed L/S ratio of 3 mL/g, and the additives evaluated were Na_2HPO_4, NaH_2PO_4, H_3PO_4, and $FeSO_4$. The results of these orthogonal experiments provided the basis for determining the range of variables in the single-factor experiments. The ratio of leaching concentration difference (between raw and treated fly ash) to the leaching concentration of raw fly ash was defined as "the curing rate". The total curing rates of the four different influencing factors were termed I, II, III, and IV. The difference between the maximum and minimum of these curing rates was termed as the "range", and it indicates the solidification effect of different influencing factors. The larger the range, the greater its role in the hydrothermal process.

Table 2. Design of Orthogonal Experiments

factor	reagent	dosage (mol/kg)	temperature (°C)
level 1	Na_2HPO_4	0.1	125
level 2	NaH_2PO_4	0.2	150
level 3	H_3PO_4	0.3	175
level 4	$FeSO_4$	0.4	200

Based on the solidification of heavy metals, the effectiveness of additives was found to be in the order Na_2HPO_4, NaH_2PO_4, H_3PO_4, and $FeSO_4$. In terms of the Cd stabilization, Na_2HPO_4 again performed the best, while its cost is only one-third that of NaH_2PO_4. Previous studies have also shown that phosphate had an effect on stabilizing Cd.[21,28] With the increase in additive dosage and temperature, the solidification and stabilizing effect also showed an increasing trend. However, the performance of $FeSO_4$ was independent of dosage, not only on the total curing rate but also on single heavy metal curing rate. Also, in this dosage range, the leaching concentration of Cd did not decrease to a level below its permissible limit, so it is necessary to increase the dosage. The complete experimental results are shown in Table 3. In conclusion, Na_2HPO_4 was selected as the optimum additive for the subsequent experiments.

3.3. Single-Factor Experiments. *3.3.1. Effect of Dosage of Na_2HPO_4.* The leaching results after the hydrothermal treatment with different Na_2HPO_4 dosages (additive to fly ash: 0.4−1.6 mol/kg) are shown in Figure 1. Experiments were

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Table 3. Results of Orthogonal Experiments

				curing rate of leaching concentration						
trial	additive	concentration	temperature	Cd	Cr	Cu	Ni	Pb	Zn	total
1	1	1	1	0.32	0.31	0.35	0.58	0.84	0.58	3.00
2	1	2	2	0.42	0.60	0.42	0.60	0.93	0.61	3.58
3	1	3	3	0.52	0.82	0.58	0.62	0.97	0.65	4.16
4	1	4	4	0.59	0.86	0.66	0.62	0.95	0.68	4.37
5	2	1	2	0.64	0.85	0.73	0.60	0.98	0.66	4.46
6	2	2	1	0.43	0.61	0.50	0.59	0.93	0.60	3.66
7	2	3	4	0.61	0.79	0.63	0.66	0.97	0.67	4.34
8	2	4	3	0.65	0.78	0.76	0.65	0.98	0.68	4.50
9	3	1	3	0.43	0.49	0.50	0.62	0.85	0.66	3.55
10	3	2	4	0.57	0.74	0.66	0.67	0.95	0.66	4.24
11	3	3	1	0.55	0.79	0.69	0.56	0.97	0.63	4.20
12	3	4	2	0.41	0.55	0.54	0.62	0.88	0.64	3.64
13	4	1	4	0.59	0.43	0.51	0.65	0.87	0.66	3.71
14	4	2	3	0.61	0.37	0.55	0.59	0.92	0.63	3.66
15	4	3	2	0.62	0.41	0.57	0.56	0.89	0.61	3.68
16	4	4	1	0.63	0.46	0.60	0.53	0.91	0.59	3.72
I	15.11	14.71	14.57	I, II, III, IV: total curing rates of influence factors at the corresponding levels I + II + III + IV = 62.44						
II	16.95	15.14	15.35							
III	15.63	16.37	15.87							
IV	14.76	16.22	16.66							
range	2.19	1.66	2.09							

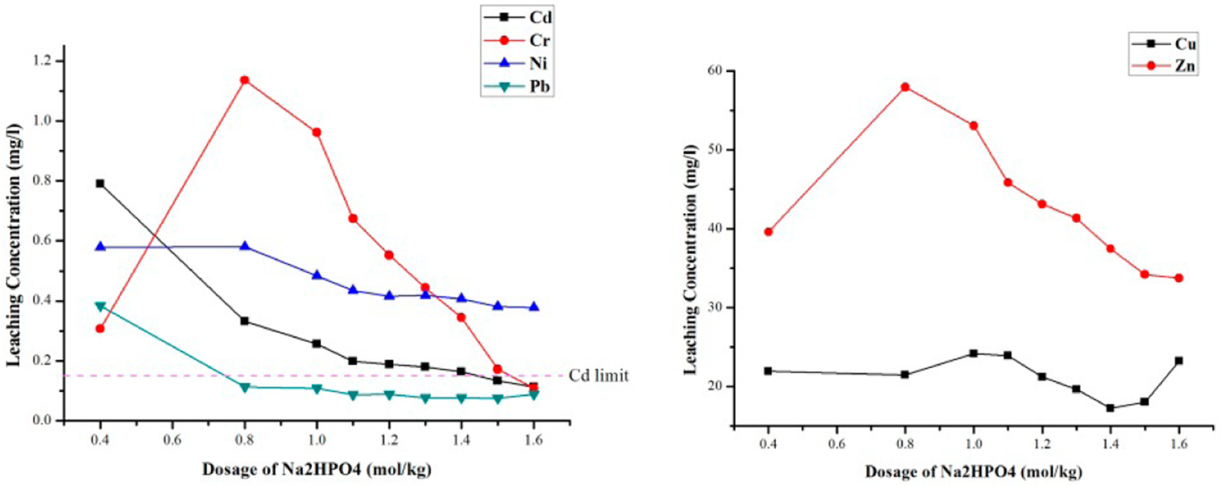

Figure 1. Leaching concentrations of heavy metals after treatment with different dosages of additive. As the dosage of Na_2HPO_4 increased, the leaching concentrations of Cd, Ni, and Pb decreased. When the dosage reached 1.5 mol/kg, the leaching concentrations dropped below the limits specified by GB16889-2008, including Cd concentration. Under these conditions, leaching concentrations of Cd, Cr, and Pb were decreased by 93.1%, 92.2% and 90.4%, respectively, while Ni, Zn, and Cu were reduced by 75.0%, 72.5%, and 72.2%, respectively. However, the Pb concentration remained almost unchanged after reaching a certain value, when the dosage was above 0.8 mol/kg. This indicates that Pb had been solidified to the maximum level. On the other hand, Cr and Zn presented an early increasing and later decreasing trend with increase in the dosage, which might be due to the pH of the leaching solution. Also, Cr and Zn showed a decreasing trend when the dosage was increased to a certain value. Considering the curing percent, it was concluded that Na_2HPO_4 had a better effect on Cd, Cr, and Pb than on Ni, Zn, and Cu.

carried out with a L/S ratio of 3 mL/g at 200 °C for 20 min of microwave heating.

This result is very promising in comparison with the hydrothermal treatment using NaOH as the additive for this fly ash sample. In our previous experiments, NaOH could not decrease Cd concentration to satisfy the regulatory limit. Therefore, Na_2HPO_4 is a better additive in the hydrothermal process for good solidification of Cd. NaOH and Na_2HPO_4 are both alkaline substances, and the major difference is the phosphate group. In the hydrothermal process, OH^- makes a great contribution to the dissolution of Si^{4+} and Al^{3+} ions, while Na^+ in alkaline solution promotes the crystallization rate of zeolites.[32] In general, the solidification mechanism in this study was very similar to traditional hydrothermal methods, which were effective for treating heavy metals by adsorbing or entrapping them into the aluminosilicate minerals.[33] Moreover, the heavy metals were converted to a stable form, which led to the lower leaching concentration. Therefore, the improved solidification with Na_2HPO_4 is likely due to the fact that the PO_4^{3-} anion benefits the solidification of Cd in a direct or indirect way. Dissolved phosphate has been successfully used for solidifying heavy metals as a chelating agent;[34,35] therefore,

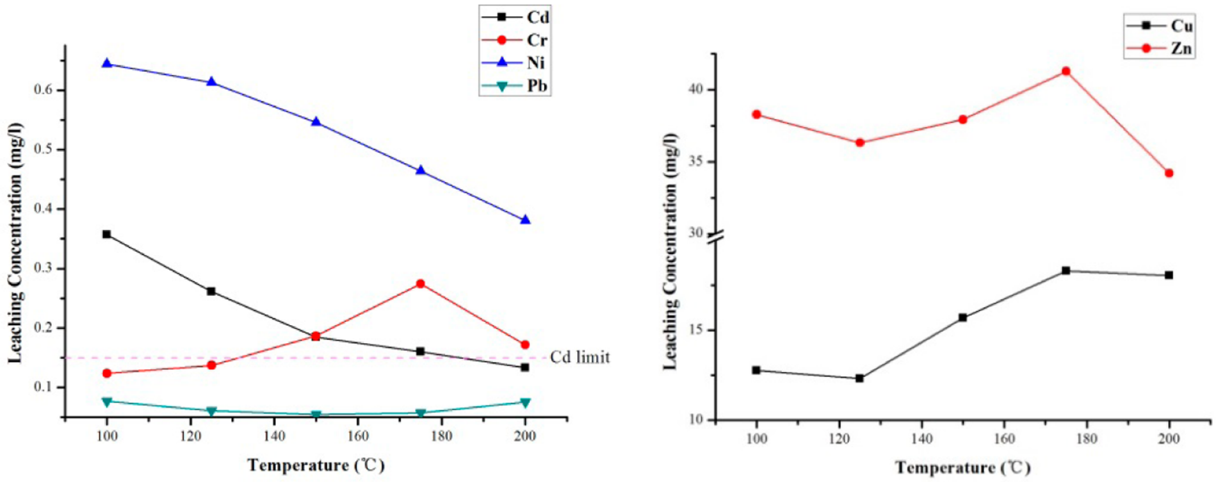

Figure 2. Leaching concentrations of heavy metals after treatment with different reaction temperatures.

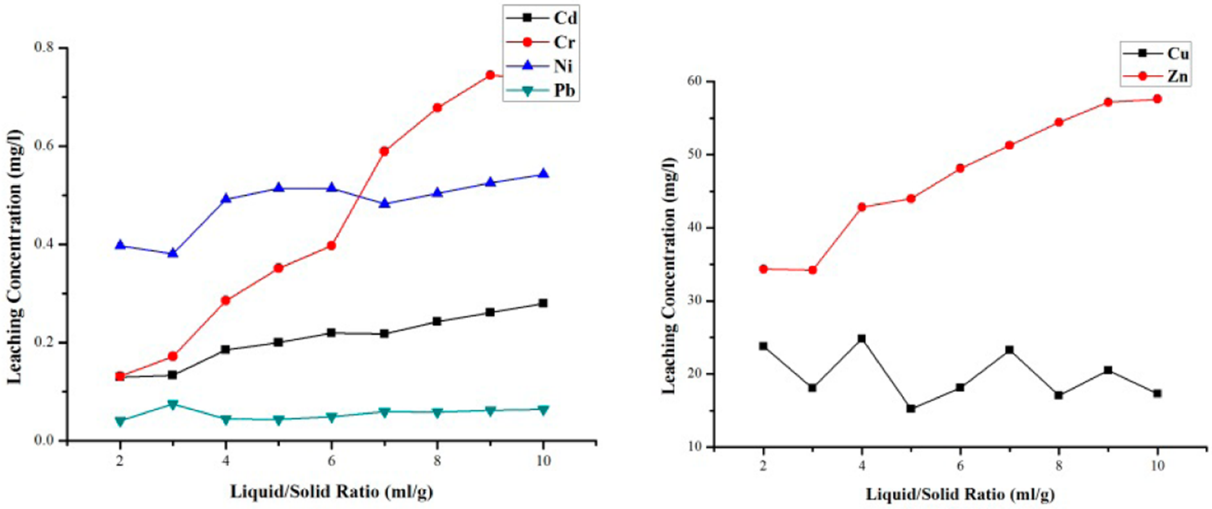

Figure 3. Leaching concentrations of heavy metals after treatment with different liquid/solid ratios.

PO_4^{3-} has its unique chelating effect to assist treating heavy metals.

3.3.2. Effect of Temperature. The results of leaching concentrations of heavy metals after treatment at different hydrothermal temperatures are presented in Figure 2. In this series of experiments, the selected conditions were L/S ratio of 3 mL/g, 1.5 mol/kg dosage of additive, and 20 min reaction time. It was found that Cr, Pb, Cu, and Zn were solidified within the limits at 100 °C, while Cd and Ni had not been reduced to reach their specified limits. With increase in the temperature from 100 to 200 °C, the leaching concentrations of Cd and Ni were decreased from 0.3569 and 0.6441 ppm to 0.1335 and 0.3807 ppm, respectively, which satisfied the regulatory limits. As can be seen from the temperature curve, leaching concentrations of Cd and Ni reduced steadily with the increasing temperature. It is clear that a higher temperature is needed to make a positive effect on the solidification of Cd and Ni. However, this trend could not be observed for the other heavy metals. The leaching concentrations showed a slight drop as the temperature changed. This means that temperature is not the key factor for treating the Cr, Pb, Cu, and Zn heavy metals, but only for Cd and Ni. In particular, the Pb concentration was about 0.6 ppm, which remained almost the same as the temperature varied. Also, in the reaction solution, only 9% Pb of total leaching content was detected, that is, an overwhelming majority of Pb was solidified by the microwave-assisted hydrothermal process. Moreover, Cd, Cr, and Ni almost could not be detected in the reaction solution, while the contents of Cu and Zn were very small. It has been reported that the microwave process causes the activation time and crystallization to be reduced from several hours to a few minutes. The microwave process reduced the activation time and crystallization from hours to a few minutes when Si and Al dissolved completely. Moreover, the dissolution of Si and Al, as well as the crystallization process of the product, were enhanced with the increase in temperature.[36] These benefits are crucial for the rapid synthesis of zeolites. Only if the synthesis of zeolite is effective will the stabilization of heavy metals be better.

Studies have shown that high Na^+ content[37] and high temperature[38] were conducive to the formation of materials (zeolites) with high cation exchange capacity. These reports are consistent with the results in this study showing that higher temperature leads to the higher solidification ratio of the total heavy metals.

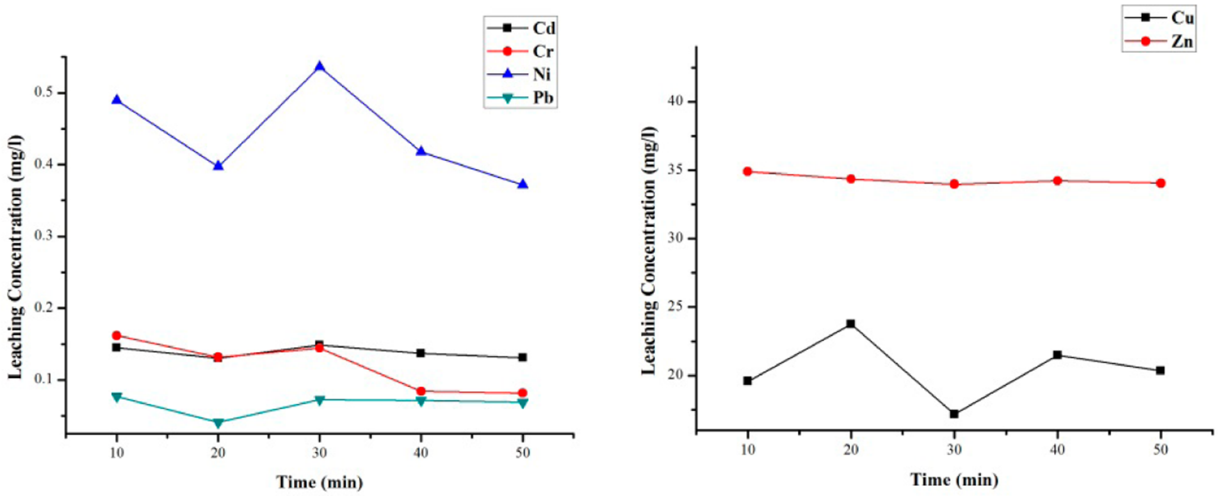

Figure 4. Leaching concentrations of heavy metals after treatment with different reaction times.

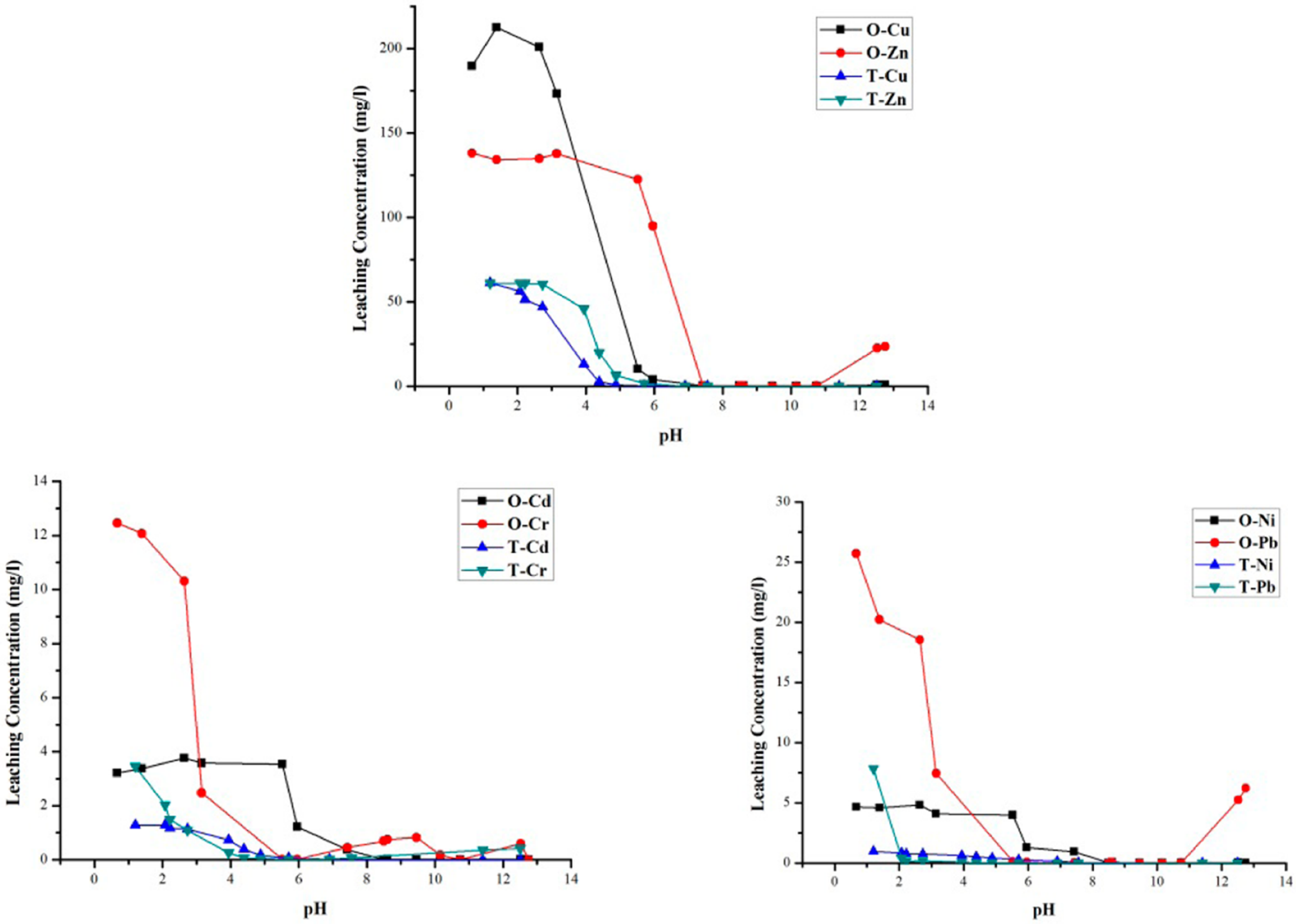

Figure 5. Leaching concentrations of heavy metals in original and treated fly ash with leachates of different pH values.

3.3.3. Effect of Liquid/Solid Ratio and Reaction Time. The heavy metal concentrations in the leaching liquid are presented in Figure 3. The experimental conditions were 1.5 mol/kg additive, 20 min, 200 °C, and a L/S ratio varying from 2 to 10 mL/g. The results showed that the greater the L/S ratio, the better the effect. This result, that the higher concentration of additive led to a better effect on curing the heavy metals, was very acceptable. As seen in Figure 3, the leaching concentrations of Cd, Cr, Ni, and Zn rose from 0.1300, 0.1317, 0.3973, and 34.35 ppm to 0.2799, 0.7359, 0.5428, and 57.61 ppm, respectively. The Cu concentration showed some unstable fluctuations, while the Pb concentration remained almost unchanged. Water used in the treatment diluted the concentration of additives. Therefore, when these results are combined with those of section 3.3.1, it can be concluded that the amount of water added should be kept as small as possible.

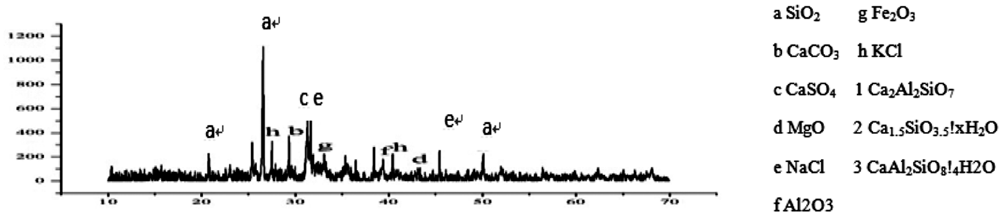

Figure 6. XRD patterns of the raw fly ash.

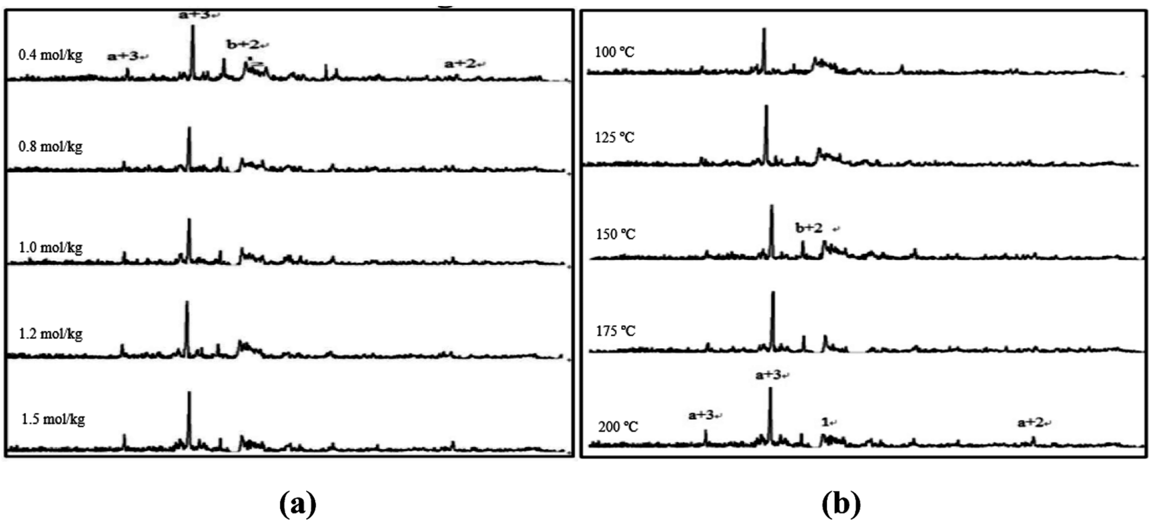

Figure 7. XRD patterns of treated fly ash with (a) different dosages of additive and (b) different temperatures.

At the same time, the water required for the disposal must be adequate. Therefore, 2 mL/g was selected in the follow-up experiments as the best L/S ratio. This low L/S ratio results in less water wastage.

The leaching concentrations of heavy metals after treatment with different reaction times under the optimum conditions are shown in Figure 4. It can be seen that reaction time had a slight impact on the leaching concentrations of heavy metals, varying from 10 to 50 min. Within just 10 min, all heavy metals were reduced to meet the regulatory requirements. The curing rates of Cd, Cr, Cu, Ni, Pb, and Zn were 92.6%, 92.7%, 69.8%, 67.8%, 99.0%, and 72.0%, respectively, under the conditions of 1.5 mol/kg Na_2HPO_4, 2 mL/g water, 200 °C, and 10 min. These results indicate that microwave heating had a high efficiency for solidifying heavy metals by hydrothermal treatment. This phenomenon of shortening the reaction time by microwaves has been reported in several studies.[23,26] The formation of zeolites can be enhanced with the microwave heating, and the reaction time is reduced to 2 h. Querol et al.[23] reported that the activation time for obtaining zeolites by using microwaves was sharply reduced from 24−48 h to 30 min. In this study, to solidify the heavy metals in fly ash, the reaction time was just 20 min (10 min heating time and 10 min hold time at 200 °C) for the reason that microwaves can be absorbed by water directly, resulting in improved efficiency.

3.4. Effect of pH on Leaching Concentrations of Raw and Treated Fly Ash. To simulate the leaching situation of treated fly ash in the environment, pH tests were performed on both the treated and raw fly ash samples, and the results are shown in Figure 5. "O-" refers to the heavy metal in original fly ash, and "T-" refers to the heavy metal in treated fly ash. Under the hydrothermal treatment, the concentration of heavy metal ions is obviously affected by the solution pH value. Heavy metals, especially Zn, Pb, Cr, and Cu, subside from the alkaline solution when the pH value is greater than 8.[39] If their precipitation is not stable enough, they will dissolve again in the low-pH solution.

It is widely known that the pH of leachate has a significant influence on the leaching process of fly ash. The leaching concentration of raw fly ash sharply decreased when the pH exceeded 7. The trends of leaching concentration of these two samples were very similar, but the safety range of treated fly ash was broader than that of the raw one. The leaching concentrations of heavy metals were higher at low pH range and sharply went down to zero at a certain pH. For Zn, Pb, and Cr in raw fly ash, the leaching concentration began to rise again when the pH was greater than 11, which was due to the properties of amphoteric metals.

Compared with the raw fly ash, the leaching concentrations of treated fly ash were much lower. For example, Zn concentration of treated fly ash was only 1.57 ppm, while it was more than 100 ppm in the raw sample at the pH of 5.7. Moreover, the leaching concentrations of Cd and Cr were close to zero, when the pH was only 2 after microwave-assisted hydrothermal treatment. Also, the Cr concentration in the treated fly ash did not show an increase at pH > 11. All these phenomena indicate that the treatment in this study was effective for curing heavy metals in fly ash and that the treated fly ash had high stability in the acidic and alkaline environments. The safety range of the treated fly ash was expanded from pH 7.5−11 to pH 5−13. Also, at pH 5, the leaching concentrations were close to zero and satisfied the limitation specified in GB16889-2008. That is, heavy metals were simply precipitated in this hydrothermal process, the irreversible precipitation−dissolution reaction, such as in physical package

Table 4. Hydrothermal Results with NaOH Added in Other Traditional Studies

dosage	temperature	time	result	source
0.5 M, 10 mL/g	180 °C	48 h	Leaching concentrations of Zn/Cd exceeded the standard.	13
2 M, 15% m/m	200 °C	12 h	The concentration of heavy metals in leachate was reduced.	43
0.5 M, 4 mL/g	150 °C	12 h	The stabilization rate of heavy metals exceeded 95%.	44
20% m/m	375 °C	5 h	The leaching concentrations of As, Pb, and Zn were decreased by about 51.08%, 58.33%, and 86.89%, respectively.	20
Na_2HPO_4, 1.5 mol/kg	200 °C	10 min	Leaching concentrations achieved the standard, and the solidification rate was above 80% in average.	this study

function of silicon aluminate jel and crystal, chemical adsorption, space geometry migration of heavy metals, etc.[40]

3.5. XRD Analysis and Results. XRD patterns of the raw fly ash are shown in Figure 6. The major components, such as SiO_2, $CaCO_3$, $CaSO_4$, MgO, NaCl, Al_2O_3, Fe_2O_3, and KCl, were detected, and the composition was basically identical to other fly ash samples. The XRD patterns of treated fly ash (under the optimum conditions with 0.4, 0.8, 1.0, 1.2, and 1.5 mol/kg additive and at the temperatures of 100, 125, 150, 175, and 200 °C) are presented in panels a and b of Figure 7, respectively. Because the XRD patterns in Figure 7a are taken at the temperature of 200 °C and XRD patterns in Figure 7b are under the condition of 1.5 mol/kg NaH_2PO_4, the lowest XRD curves of both panels are the same.

When the XRD patterns of the sample before and after treatment are compared, it can be seen that the peaks for NaCl and KCl were not found in Figure 7, suggesting that both of them dissolved in the reaction solution. A similar conclusion could be drawn from the XRF results, which showed that lower amounts of Na, K, and Cl elements were determined. In addition, $CaSO_4$ was also not detected in Figure 7a, but it showed a gradually decreasing trend in Figure 7b. This means that the amount of $CaSO_4$ in fly ash will decrease steadily at temperatures below 200 °C and completely disappear at 200 °C, as it transforms to poorly soluble calcium compounds. In Figure 7a, it can be seen that there are only slight changes due to the use of different additives. However, it is obvious that new materials were formed because the peaks of Al_2O_3 disappeared and the peaks of SiO_2 and $CaCO_3$ reduced compared to the original one in Figure 6, as well as Figure 7b. Moreover, the same substances occurred in all five curves of Figure 7a. In other words, the dosage of Na_2HPO_4 did not change the kinds of hydrothermal products but only changed the rate of production. As the dosage increased, the contents of $CaAl_2SiO_8{\cdot}4H_2O$ (the peaks marked "a+3") and $Ca_{1.5}SiO_{3.5}{\cdot}xH_2O$ (the peaks marked "a+2") increased, while $Ca_2Al_2SiO_7$ (the peak marked "1") changed only slightly. In Figure 7b, it was found that $Ca_{1.5}SiO_{3.5}{\cdot}xH_2O$ did not exist when the heating temperature was below 150 °C. This same observation was made in our previous work in Qiu et al.[45] Between 150 and 200 °C, the production of $Ca_2Al_2SiO_7$ was only slightly changed. Moreover, $CaAl_2SiO_8{\cdot}4H_2O$ and $Ca_{1.5}SiO_{3.5}{\cdot}xH_2O$ increased with the increasing temperature, which was similar to the trend observed from variation of dosages. In summary, the production of zeolites increased with the increase of temperature and dosage of Na_2HPO_4. These results are consistent with the leaching concentration of heavy metals. It is possible that the formation of zeolites was not complete, but the solidification of heavy metals in this CFB fly ash sample was perfectly sufficient in the leaching test. To obtain zeolite products using microwaves in future studies, more investigations will be required with a long reaction time.

It is revealed that the microwave process in this study facilitates the dissolution of Si and Al and the rapid generation of zeolites and then contributes to solidifying the heavy metals in fly ash.[41] On the basis of the solidifying effect and the XRD analysis, it was concluded that the higher temperature and the higher amount of additive helped to produce more zeolites and gave better solidification of the heavy metals. Considering the function of hydrothermal treatment in this study and the traditional hydrothermal process, there is not much difference. However, the efficiency is much higher in this study, as the process required just 10 min for heating to 200 °C. Moreover, all the heavy metals in the fly ash samples are solidified within the regulatory limits under the optimized conditions, so the treated fly ash can be disposed of as general waste. In the case of hydrothermal solidification, it was determined that the zeolite crystals settled on the surface of fly ash particles. Accordingly, heavy metal ions were absorbed instead of being released into the solution.[42] Therefore, the hydrothermal processing method provides a feasible approach for solidifying and reusing MSWI fly ash on a large scale.[36,43] Moreover, the less toxic fly ash can be reutilized easily in other fields, especially in construction.

4. ECONOMIC ANALYSIS

Compared to the traditional hydrothermal process, the reaction time for solidifying heavy metals in fly ash by using microwaves was only 10 min, which is a drastic reduction from several hours[20,43,44] or even 48 h.[13] The dosage (mass) of Na_2HPO_4 needed in this study was almost the same as that of NaOH in other studies, and moreover, the reagent cost is only about half that of NaOH. More importantly, all heavy metals were stabilized and solidified within the permissible limits, and the curing rates of Cd, Cr, and Pb were as high as 92.6%, 92.7%, and 99.0%. The maximum power output of the microwave apparatus in our study was about 1000 W, and the maximum handling capacity of the device in this paper was about 80 g. The limit of disposal capacity is related to the size of the equipment, so large-scale disposal can be achieved in industrial production when the device is large, which will lead to further energy savings. Because the equipment requirements are very low, only a microwave field and a sufficiently large sealed pressure vessel are needed. Therefore, it would be easy to scale up this process using large-scale equipment. The cost for large-scale treatment can be greatly reduced, which is very reasonable.[45] The hydrothermal treatment results with NaOH as the additive in other traditional studies are listed in Table 4. In summary, it is evident that the microwave-assisted process has tremendous economic advantages. Because of the merits of high efficiency, scalability, and low energy consumption, this microwave-assisted treatment is a promising way to dispose of MSWI fly ash or other hazardous wastes.

5. CONCLUSIONS

An efficient microwave-assisted hydrothermal treatment has been developed in this work for the solidification of heavy metals in MSWI fly ash. The effects of additive dosage, temperature, L/S ratio, pH, and reaction time were determined. The results are concluded as follows:

(1) Heavy metals in MSWI fly ash were solidified by a microwave-assisted hydrothermal process, and their contents were below the specified limits set by GB16889-2008. The optimized process conditions were 1.5 mol/kg Na_2HPO_4, 2 mL/g L/S ratio, 10 min reaction time, and 200 °C.

(2) Low L/S ratio, high temperature, and higher dosage of additive all contribute to the higher efficiency in solidifying the heavy metals.

(3) It is concluded that the treated fly ash has a higher environmental stability than the original fly ash. The pH safety range of treated fly ash widened from the original range of 7.5−11 to 5−13.

(4) Compared to the traditional hydrothermal treatment, the process reported in this paper is more energy-saving, time-saving, and economic. Therefore, the application potential of this method is very promising.

■ AUTHOR INFORMATION

Corresponding Author

*Tel: +86 571 87952775. Fax: +86 571 87952438. E-mail: jiangxg@zju.edu.cn.

Notes

The authors declare no competing financial interest.

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