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Utilization of MSWI fly ash for stabilization/solidification of industrial waste sludge

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Abstract

This work investigated the potential for utilization of MSWI incineration fly ash as solidification binder to treat heavy metals-bearing industrial waste sludge. In the study, Municipal Solid Waste Incineration (MSWI) fly ash was used along with ordinary Portland cement to immobilize three different types of industrial sludge while MSWI incineration fly ash was stabilized at the same time. The results showed that the matrixes with heavy metals-bearing sludge and MSWI fly ash have a strong fixing capacity for heavy metals: Zn, Pb, Cu, Ni and Mn. Specimens with only 5–15% cement content was observed to be sufficient to achieve the target compressive strength of 0.3 MPa required for landfill disposal. An optimum mix comprising 45% fly ash, 5% cement and 50% of the industrial sludge could provide the required solidification and stabilization. Addition of MSWI can improve the strength of matrix. Meanwhile, the main hydration products of new S/S matrix are ettringite AFt, Friedel's salt and C–S–H. These hydration products play an important role in the fixing of heavy metals. The co-disposal of MSWI fly ash with heavy metals-bearing sludge can minimize the enlargement of the landfill volume and stabilize the heavy metals effectively.

Keywords: MSWI fly ash; Heavy metals; Sludge; Stabilization/solidification; Co-disposal

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1. Introduction

As the quantity of hazardous industrial wastes increases significantly owing to rapid industrialization, its appropriate management is required to reduce the negative impacts on humans and ecosystems. Hazardous wastes include organic and inorganic wastes. Inorganic hazardous wastes, commonly found in aqueous solution or suspension, often require pretreatment before landfill. The metal-bearing waste is one of the inorganic wastes needed for pretreatment. One inorganic waste stream which requires treatment before disposal is metal plating waste. The metal-bearing wastes usually exist in the form of filter cake or sludge and it contains a large of toxic heavy metals. The solidification/stabilization (S/S) processes are viable for most metallic waste streams [1].

Several binder systems are currently available and widely used for S/S [2]. Portland cement is one of the most ordinary binders used for S/S matrix. This stabilization process relies on the formation of calcium silicate hydrate ($CaO{\cdot}SiO_2{\cdot}nH_2O$, briefed as C–S–H), ettringite hydrate ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$, abbreviated as AFt) and monosulphate ($3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}12H_2O$, abbreviated as AFm) in the matrix, due to the hydration reaction of Portland cement, and thus the heavy metals both chemically fixed in the lattice of hydration production and physically encapsulated in the matrix [3].

Coal fly ash is one type of binding supplement materials in waste stabilization formulation, which mainly used in two kinds of mixtures: Portland cement plus coal fly ash or lime plus coal fly ash. A fly ash/lime mixture also contains reactive CaO, SiO_2 and Al_2O_3. These sources of reactive oxide can react with each other in the hydration process to generate C–S–H and AFt. Hence, when these matrixes added with coal fly ash, the binding stabilizing properties are due to the formation of both C–S–H and AFt. At present, a number of studies have been focused on the solidification/stabilization of heavy metal sludge and other hazardous wastes using cement, lime, and coal plant fly ash [4–8].

Municipal Solid Waste Incineration (MSWI) fly ash contains easily leachable heavy metals and potentially toxic dioxin, so it

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is regarded as hazardous and must be landfilled after solidification/stabilization [9]. In Shanghai, 20,000 tonnes of MSWI fly ash per year is produced and it has to be placed into a safe landfill. This landfill amounts will rapidly increase in several years due to municipal solid waste incineration. It has been noticed that whatever heavy metals-bearing sludge or MSWI fly ash is in the S/S process of pretreatment, Portland cement or other binder materials have to be mixed together with these hazardous wastes in order to get heavy metal effectively fixed. It is evident that these useful resources such as cement or other binder materials will be squandered with less value in the S/S process. Inevitably, the net volume for hazardous waste filled in the landfill site will reduce due to co-filling of other binder materials.

Therefore, how to solidify/stabilize hazardous wastes without enlargement of solidification volume is meaningful. The co-disposal of hazardous wastes in the landfill may be a potential solution. In view of chemical compositions, MSWI fly ash belongs to $CaO–SiO_2–Al_2O_3–SO_3–Cl$ system, which is rich in CaO, Cl, and SO_3, short of SiO_2 and Al_2O_3, compared with the mixture of coal fly ash/lime [10]. To form C–S–H and ettringite hydrate matrix with well fixing capacity for heavy metals, the addition of other wastes with richer Al_2O_3 is propitious in the S/S matrix of MSWI fly ash. Pollmann reported [11] that the new hydrate Friedel's salt ($3CaO \cdot Al_2O_3 \cdot 3CaCl_2 \cdot 12H_2O$) will be preferentially formed besides AFt hydrate phase as alumina-rich cement was added into MSWI fly ash mixture and they were hydrated. The positive fixing role of Friedel's salt on Cd had been observed [12].

As described above, both MSWI fly ash and metals plating sludge are hazardous waste with various heavy metals and they all need solidified/stabilized before landfill. Simultaneously, most metals plating sludge contain more Al_2O_3 and SO_3 in chemical composition [13]. Therefore, if MSWI fly ash and metals plating sludge are mixed and co-disposed, the formation of Friedel's salt, ettringite hydrate in the S/S matrix will be expected, and with the result that better fixing effectiveness on heavy metals can be achieved. If so, the saving of not only cement materials but also the landfill space will be available.

The objective of this study is to use MSWI fly ash as a useful binding raw material for co-disposing heavy metals-bearing sludge. The co-disposal effectiveness will be evaluated by the analysis of physical properties, leach properties and hydrates in the matrix.

2. Experimental

2.1. Materials

The MSWI fly ash used in this experiment was collected from the Senoko Incineration Plant. The chemical composition and the leachates of heavy metals from MSWI fly ash are shown in Tables 1 and 2, respectively. The leachate components of MSWI fly ash were determined by TCLP method as proposed in Section 2.3.

The three industrial waste sludges (labeled as A–C) were collected from different chemical and electronics plants in Singapore. Some heavy metals such as copper, lead, manganese, nickel and zinc of these three kinds of sludge are selected as target heavy metals according to the concentration of heavy metals in the raw sludge and allowed leaching out from landfill materials. Based on leach concentrations of heavy metals from raw sludge, shown in Table 5, three different sludge samples can be classified as Cu and Pb-based for sludge A, Zn- and Mn-based for sludge B, and Ni-based for sludge C. During the experiment, efforts were made to ensure the homogeneity of fly ash and sludge. The sludge was first dried in an oven at 103 °C and subsequently grounded to less than 9.5 mm in size to aid workability of the sludge-ash-cement matrix during casting.

Three sets of sludge based mixtures were designed. Each of three type sludge was mixed with different proportions of cement and MSWI fly ash according to Table 3. They were series A–C. The mixes were prepared at water to solid ratio of 0.3.

The sludge–cement–fly ash matrix was cast in 50 mm cubes and left to air-cured. Wet curing was initially selected but samples with a high proportion of fly ash disintegrated in the curing water. This is due to the high lime content in the fly ash, which reacts with water. The released heat caused thermal cracking in the cubes and weakened the sludge matrix. Air curing was subsequently adopted for all the samples. Only mix proportions 3–8 were cast for the three sludge samples, as mix proportions

Table 1
Chemical composition of MSWI incineration ash (wt.%)

Formula	
Na_2O	4.82
MgO	1.83
Al_2O_3	3.10
SiO_2	5.44
P_2O_5	1.62
SO_3	12.73
Cl	20.11
K_2O	4.31
CaO	42.55
TiO_2	0.92
Fe_2O_3	1.69
CuO	0.13
ZnO	1.17
Br	0.39
SnO_2	0.33
Sb_2O_3	0.15
BaO	0.15
PbO	0.42

Table 2
Leachate components of MSWI fly ash by TCLP method

Element	Concentration (mg/L)
Ag	0
Cd	0.0069
Cr	0.2479
Cu	0
Fe	0.0086
Mn	0.0036
Ni	0
Pb	25.27
Zn	3.589

Table 3
Different mix proportions (wt.%)

Mix	OPC (%)	MSWI FA (%)	Sludge (%)
1	0	0	100
2	0	50	50
3	5	0	95
4	5	45	50
5	10	0	90
6	10	45	45
7	15	0	85
8	15	40	45

1 and 2, which were without OPC, were deemed to be too weak for compressive strength tests.

2.2. *Compressive strength tests*

Compression strength of the specimens was tested using the unconfined compression machine with a maximum load of 5 kN. The cubes were tested for their 3- and 7-day compression strength at a loading rate of 1.52 mm/min. Three samples for each mix series were tested. While efforts were made to provide three samples for each test series, some samples were damaged during the de-molding process due to their very low strength. As a result, only mix A2 and mixes 3–8 of the three sledges were cast and tested.

2.3. *Leaching test*

The USEPA TCLP method [14] is commonly used to determine if a waste is hazardous or otherwise. Previous studies showed that the Senoko fly ash meets all leaching test requirements for landfill disposal, except for lead Pb leaching. In this study, TCLP was mainly used to determine the effectiveness of the solidification/stabilization of heavy metals in the sludge. The TCLP tests carried out in this study were in accordance with the standard procedures prescribed by USEPA.

TCLP specimens for mixes 3–8 and mix A2 were prepared using the crushed 3-day cube samples. Mixes 1 and 2 (except A2) were prepared using raw undried sludge, together with the fly ash, to evaluate their leaching properties in the raw form without stabilization. Due to the greasy nature of sludge B, the TCLP samples (mixes 1 and 2) were not able to achieve lower than 9.5 mm in size. The leachate was tested using ICP Emission Spectrometry. The main purpose of the TCLP was to evaluate the effectiveness of the fly ash and cement in stabilizing the sludges. TCLP results were also compared with the concentration limits allowed for landfill given by the Singapore Ministry of the Environment (ENV).

2.4. *Characters of reaction products*

2.4.1. *X-ray diffraction (XRD) analysis*

The mineral phases in the samples were identified by X-ray diffraction (XRD) measurements in Dmax/RB diffractometer from Rigaku Co. with Cu Kα radiation 34 kV, 20 mA. Once the diffraction patterns were obtained, both manual matching of the peak positions and a computer-aided search for the compounds were performed. The results were presented in intensity -2θ format.

2.4.2. *DTG analysis*

DTG curves were obtained on a Model TGA51 Thermogravimetric Analyzer (Shimadzu) in the temperature range 30–900 °C with a heating rate of 10 °C min^{-1}, under dynamic nitrogen (50 ml min^{-1}) atmosphere and samples weighing ∼5 mg in Pt crucible.

2.4.3. *FTIR-spectrophotometer*

The spectra were recorded using a Perkin-Elmer 1725X IR Fourier transform spectrophotometer. For diffused reflectance spectra, the samples were prepared by dispersing 55 mg of the air-dried sample in 295 mg of KBr. The spectral measurement in the 400–4000 cm^{-1} region was made at 4 cm^{-1} resolution with the use of 120 scans.

3. Results and discussion

3.1. *Compressive strength of fly ash–cement matrix*

There are a number of recommended minimums compressive strength required for solid waste disposal at landfills [15]. One of which is Resource Conservation & Recovery Act's (RCRA) recommendation of 0.3 MPa [16]. The actual compressive strength of the disposed waste is dependently if there is any compaction at the landfill site. In some countries, however, cost considerations might restrict this option in favor of direct dumping. In this study, the RCRA's recommended value of 0.3 MPa was adopted as the target compressive strength of the solidified matrix. The compressive strengths of 3 and 7 days for the various sludge–cement–fly ash matrices are given in Table 4.

From Table 4, the strength of A1 is very low and cannot be detected. As 5–10% of Portland cement mixed together with sludge, 0.2 MPa of strength or less is gotten at 7 days. Only sludge A with 15% of cement, the strength of matrix can be over the threshold. The 7 days strength of other two kinds sludge still cannot get 0.3 MPa.

As MSWI fly ash is mixed with sludge, significant improvement of strength can be observed. Sample A2 with the addition of 50% incineration fly ash represented 7 days compressive strength of 0.36 MPa, satisfying the landfill threshold of 0.3 MPa without any cement addition. When cement was also added into mixture with sludge, further improvement of strength can be gotten and it increases with the addition of cement in the matrix. For Sample A4 with 5% cement, the strength even at 3 days had been 0.36 MPa. This result reiterated the usefulness of fly ash as a cementations binder. It also implies that the fine fly ash plays an important chemical binding role in addition to filling up the tiny gaps within the "waste Crete" mix itself. Serious C exhibited a similar result in the strength improvement of MSWI fly ash on sludge mixtures.

All samples from sludge B, however, registered extremely low compressive strength and experienced extreme deformation during the tests. The failure of the stabilization process was due

Table 4
Compressive strength of different mix proportions

Sludge mix	3-Day compressive strength (MPa)	7-Day compressive strength (MPa)
A2	0.12	0.36
A3	0.16	0.22
A4	0.61	0.99
A5	0.17	0.15
A6	1.31	2.05
A7	0.90	1.31
A8	1.94	2.05
B3	0.03	0.03
B4	0.06	0.07
B5	0.05	0.04
B6	0.03	0.03
B7	0.05	0.04
B8	0.03	0.03
C3	[a]	[a]
C4	0.29	0.67
C5	[a]	[a]
C6	0.18	0.52
C7	0.1	0.14
C8	1.11	1.76

[a] Samples disintegrated upon demoulding from cast (due to very low strengths).

to its greasy nature, which inhibited the mixing and hydration of the fly ash and cement. This phenomenon had been reported previously by Minocha et al. who have noted that phenol, grease and oil had detrimental effects on the compressive strength of solidified sludge samples [5]. Hence, sludge B could not be solidified by fly ash and cement under the studied proportion.

3.2. Heavy metals leachability

The leachate of heavy metals from raw fly ash is present in Table 2. The leachate of Pb was 25.27 mg/L, five times higher than the landfill limit by Singapore ENV. Table 5 lists the leachate of main heavy metals from three raw sludges A–C. As three sludge samples came from different metal electroplating process, they presented different targeted heavy metals with high concentrations of leaching. Sludge A was Cu and Pb-based, its leach concentration was 60 mg/L for Cu and 5.1 mg/L for Pb. Sludge B was Zn and Mn-based, its leach was 3790 mg/L for Zn and 37.5 mg/L for Mn. Sludge C was Ni-based and its leach was 22 mg/L. Among these targeted heavy metals, the leach concentrations for Pb, Zn and Ni far exceed the limits allowed for landfill given by ENV, Singapore. As listed in Table 5, the leaching values of other heavy metals besides above targeted heavy metals from three raw sludge samples were far below the limit.

To effectively stabilize/solidify these targeted heavy metals, cement and MSWI fly ash were used as a binder of stabilization matrix. Figs. 1–3 give the TCLP leach results of targeted heavy metals from different S/S matrixes. Addition of cement into sludge constituting a sludge–cement matrix played a positive role in fixing of heavy metals. However, addition of 5% cement only had a less effectiveness on the fixing of heavy metals. As shown in Fig. 1, the leaches from matrix A3 were 13.9 mg/L for Cu and 3.2 mg/L for Pb. This result was verified by Fig. 2 for matrix B and Fig. 3 for matrix C. There out, targeted heavy metals Zn and Ni were still over the limit allowed for landfill after immobilized with 5% cement. It was also noticed that the fixing capacity for heavy metals was significantly improved when the additions of cement were beyond 10%. The leachates of heavy metals Cu, Pb, Ni from the matrixes is below 1.0 mg/L or less.

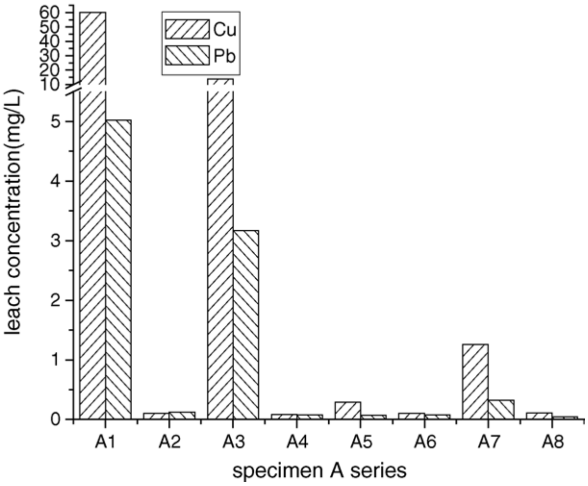

Fig. 1. Results of leaching test of specimen A.

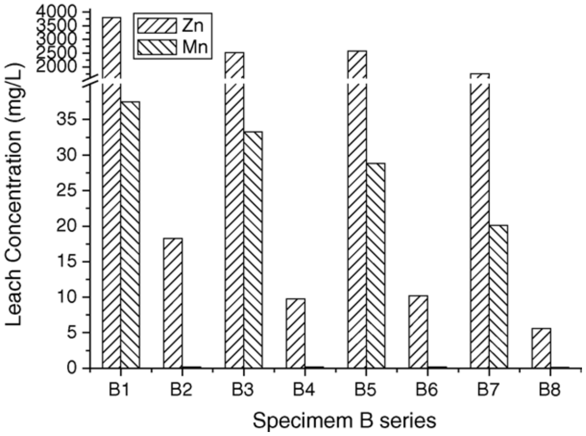

Fig. 2. Results of leaching test of specimen B.

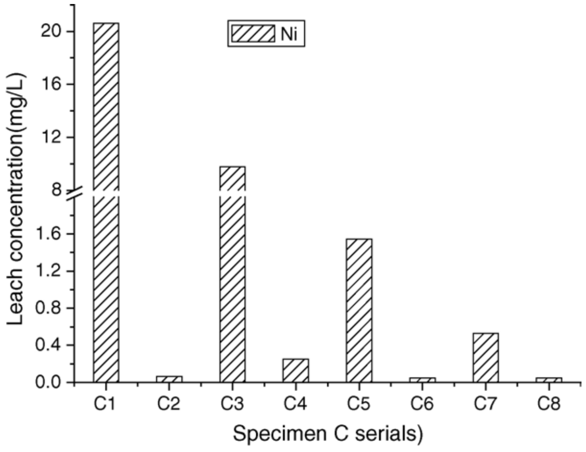

Fig. 3. Results of leaching test of specimen C.

Table 5
TCLP results of the different sludge samples

Element	ENV standard	TCLP concentrations of mix samples (mg/L)							
		A1	A2	A3	A4	A5	A6	A7	A8
As	5	<0.030	0.038	<0.030	<0.030	<0.030	<0.030	<0.030	<0.030
Cr	5	0.057	0.151	0.02	0.095	0.048	0.134	0.03	0.104
Cu	100	60.2	0.099	1.254	0.084	0.292	0.104	13.88	0.107
Fe	100	0.184	0.051	0.062	0.041	0.031	0.033	0.063	0.036
Pb	5	5.022	0.12	0.322	0.071	0.067	0.078	3.17	0.044
Mn	50	0.144	0.221	0.225	0.06	0.124	0.045	0.816	0.067
Ni	5	0.591	<0.002	0.17	0.015	0.043	0.017	0.742	0.005
Zn	100	1.077	0.104	0.092	0.039	0.022	0.064	0.413	0.018
Element	ENV standard	TCLP concentrations of mix samples (mg/L)							
		B1	B2	B3	B4	B5	B6	B7	B8
As	5	<0.030	<0.030	<0.030	<0.030	<0.030	<0.030	<0.030	<0.030
Cr	5	0.295	0.018	0.009	0.378	<0.001	0.708	<0.001	0.539
Cu	100	2.055	0.158	5.463	0.976	4.515	0.905	2.376	0.58
Fe	100	2169	5.239	1.72	0.678	0.499	0.386	0.237	0.12
Pb	5	0.527	2.693	0.14	<0.001	0.053	<0.001	<0.001	<0.001
Mn	50	33.3	0.172	37.5	0.143	28.8	0.147	20	0.092
Ni	5	3.23	0.065	4.184	0.02	2.981	<0.002	1.95	<0.002
Zn	100	2522	18.27	3799	9.746	2577.5	10.18	1747	5.57
Element	ENV standard	TCLP concentrations of mix samples (mg/L)							
		C1	C2	C3	C4	C5	C6	C7	C8
As	5	<0.030	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Cr	5	<0.001	<0.001	<0.001	0.125	0.028	0.162	0.085	0.148
Cu	100	0.333	0.012	0.116	0.286	0.22	0.242	0.243	0.266
Fe	100	0.045	0.067	0.021	<0.001	0.01	<0.001	<0.001	<0.001
Pb	5	1.198	9.404	0.185	0.092	0.076	0.057	0.053	0.016
Mn	50	0.093	0.009	0.077	0.078	0.026	0.025	0.012	0.024
Ni	5	20.6	0.067	9.787	0.25	1.544	0.046	0.531	0.048
Zn	100	0.268	1.602	0.019	<0.003	<0.003	<0.003	<0.003	0.01

The sludge–cement matrix B was an exception. The leach of Zn from matrix B7 was still as much as 1747 mg/L, even if with 15% addition of cement.

It is important that the fixing capacities of matrixes for heavy metals were reasonably strong as MSWI fly ash was co-disposed with metals-bearing sludge without addition of cement. As shown in Figs. 1 and 2, the leaches of heavy metals Cu, Pb, Ni from matrix A2 and B2 were less than 1.0 mg/L, better than the sludge–cement matrixes with 15% cement. Even for matrix B2, the leach of Zn was down from 3790 mg/L for raw sludge to 18.3 mg/L. Evidently, Zn can be effectively fixed in the sludge-MSWI fly ash matrix although matrix B7 with 15% cement still had little role in fixing high concentration of heavy metals Zn from sludge B. When cement was added into sludge-MSWI fly ash as the third constituent, further improvement of fixing capacities can be made. Especially for sludge B series, the leachate of Zn from matrix B8 with 15% cement was as low as 5.6 mg/L.

The final pH values of the different leaching samples were ranged between 9 and 11. It is well known that the pH value has a significant influence on the speciation of heavy metals in aqueous medium with high alkalinity. The amphoteric behaviors of Pb and Zn have been extensively reported. They are either deposited as a metal hydroxide plumbite or re-dissolved in a basic medium as zincate, dependent of pH [17]. As shown in Fig. 2, Zn concentration leached from the matrix with MSWI fly ash was much lower than that from the matrix with cement although cement had a more significant role in enhancing pH of matrixes than MSWI fly ash. The zinc leaching from B7 was 1747 mg/L while the leaching from B8 was just 5.57 mg/L. Similarly, there were similar results in other matrixes. Therefore, it can be concluded that the matrix with the MSWI fly ash has a strong fixing capacity for heavy metals.

In terms of immobilization effectiveness, addition of cement as the third constituent was unnecessary as the matrixes with sludge and MSWI fly ash have sufficient strong fixing capacities to prevent the leaching of heavy metals. However, small amount of cement was also needed for effectively enhancing the compressive strength of matrixes so as to satisfy landfill limits.

3.3. *Characterization of reaction products in S/S matrix*

According to the compressive strength analysis, the specimens with only 5–15% cement content were sufficient to achieve the target compressive strength of 0.3 MPa required for landfill disposal. From the leaching result, it is evident that MSWI fly ash was a good material in effectively stabilizing the heavy metal sludge. To understand what were responsible for the stabilization of heavy metals in the sludge-MSWI fly ash–cement matrixes,

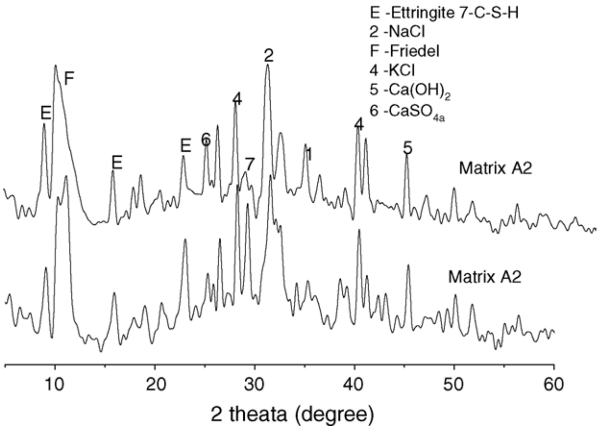

Fig. 4. XRD patterns of matrixes after 7 days of hydration.

the reactive products for two matrix specimens were identified by XRD, DTA and FTIR.

3.3.1. XRD analysis

From XRD patterns in Fig. 4, there are three new reaction products in addition to remained phases from raw MSWI fly ash, such as KCl, NaCl, $CaSO_4$ and $Ca(OH)_2$. For A2 matrix with 50% sludge and 50%MSWI fly ash, ettringite phase AFt and Friedel's salt phase were formed after 7 days hydration. The main peaks for AFt were at 9.73, 5.61 and 3.88 Å, and that for Friedel's salt phase were at 7.86, 2.86 and 3.86 Å. Compared with A2 matrix, A8 matrix, with 45% sludge, 40% MSWI fly ash and 15% cement, had C–S–H phase formed besides AFt and Friedel's salt. This C–S–H phase peaks at 2.97 and 1.84 Å. C–S–H phase is an important phase responsible for development of strength of cement-based materials. Addition of cement was responsible for the formation of C–S–H phase in A8 matrix, which made the compressive strength of A8 matrix better than that of A2 matrix.

3.3.2. DTG analysis

The characters of reaction products for A2 matrix at different curing time were also scanned by derivate thermo-gravimetric analysis (DTG). As shown in Fig. 5, there are two endothermic peaks at 1 day hydration: the peak at 51 °C is due to removal of absorb water, the peak at 159 °C corresponds to removal of structural water in Friedel's salt and ettringite phases giving products reduced crystallinity [18]. The endothermic peaks of reaction products at 7 days of hydration are similar to that at 1 day. This result suggests that both Friedel's salt and ettringite phases can be rapidly formed at early period.

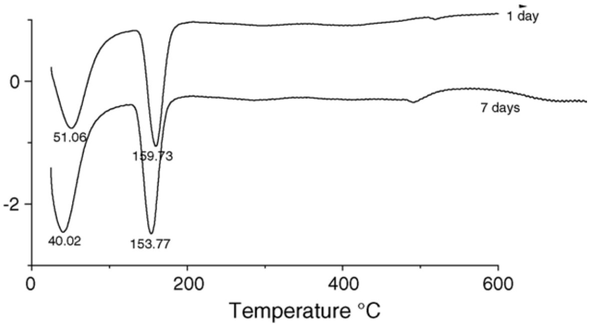

Fig. 5. DTG patterns of A2 matrixes at different curing time.

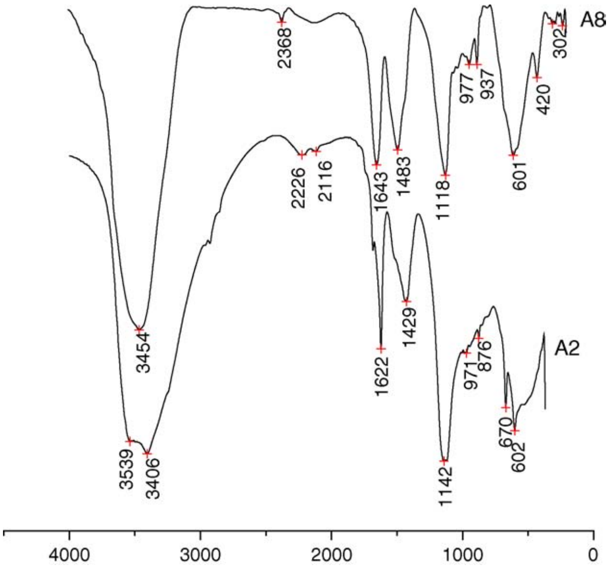

Fig. 6. FTIR patterns of matrixes A2 and A8 after hydration for 7 days.

3.3.3. FTIR analysis

The micro-surrounding of structure for reaction products can be characterized by Fourier transform infrared (FTIR) spectrum. As seen in Fig. 6, there are two bands at 601 and 876 cm^{-1}, related with symmetric and asymmetric vibrations of Al–OH bands in the $Al(OH)_6$ octahedra structure of ettringite and Friedel's salt [19]. The band at 1622 cm^{-1} is an H–O–H vibration (ν_2H_2O) of interlayer water for Friedel's salt phase, whereas the broad band at 3406 and 3539 $cm^{-1}$is due to vibration of OH ions, (νOH) in structural water. Chloride does not absorb in the range 400–4000 cm^{-1}. Glasser attributed this to the ionic nature of the chloride bonding [20]. The peaks located at 1142 and 1118 cm^{-1}, which is attributed to ν_3SO_4, supporting the presence of ettringite. The band at 937 cm^{-1} for matrix A8, due to Si–O stretching band [21], is a sound proof of C–S–H phase presence.

The Al–OH bending vibration of pure Friedel's salt occurs at 780 and 601 cm^{-1} [20]. For sludge-fly ash matrixes, however, there was no trace of Al–OH bending vibration at 780 cm^{-1} besides the vibration of AlO_6 octahedron at 601 cm^{-1} from Fig. 6. Additionally, a new Al–OH bending vibration at 670 cm^{-1} was detected. According to Mollah's results [22], this shift of wave should be related with the replacement of bivalent heavy metals for cations in the structure of ettringite and Friedel's salt phases resulting in the changes of $Al(OH)_6$ octahedra surrounding.

3.4. Possible S/S mechanisms

The S/S mechanisms of heavy metals have many ways including macro-encapsulation, micro-encapsulation, ion exchange in the lattice, absorption and adsorption [23]. Whatever the S/S mechanisms is, the ideal solidification materials should minimize the enlargement of the volume and most effectively stabilize the heavy metals.

Based on above results, heavy metals Zn, Ni, Pb, Cu and Mn can be still effectively fixed in the S/S matrix while heavy metals-bearing sludge was co-disposed with MSWI fly ash even without cement addition. In terms of compressive strength, the values of co-disposal matrixes were so low, only several MPa or less, so that it can be imaginable that the physical encapsulations are impossibly responsible for the fixing of heavy metals. If the co-disposal of heavy metals-bearing sludge with MSWI fly ash can be applied in the landfill site, the enlargement of solidification volume can be negligible so that landfill space will be saved.

In the new matrixes with sludge and MSWI fly ash, new hydration products ettringite and Friedel's salt phases have been detected. Ettringite and monosulphate are two important phases for the stabilization of heavy metals in traditional cement matrix. In the lattice structure of column-like AFt and interlayer-like AFm, the strong fixing for heavy metals, not only cation Zn, Pb, Cu but also anions AsO_4^{3-}, CrO_4^{2-}, have been reported [24,25]. Friedel's salt phase and AFm are both members of the AFm family of structurally related phases, which have layered structure, the basic building unit of which has the constitution $[Ca_4Al_2(OH)_{12}]^{2+}$ [26]. The Cd-Friedel's salt and Cd-AFm phases have been synthesized by the replacing of Cd for Ca in main unit $[Ca_4Al_2(OH)_{12}]^{2+}$ [12]. The positive fixing role of AFm family on B, Cr, Se and other heavy metals have also been observed [27]. Therefore, it can be deduced that the stabilization of the new matrix on heavy metals had a relation with the formation of ettringite and Friedel's salt phase.

For the matrixes with sludge and MSWI fly ash, the micro-surrounding changes of Al–OH in the structure of AFt and Friedel's salt due to the presence of heavy metals have been characterized by FTIR patterns. Therefore, it may be assumed that chemical binding, played an important role in the stabilization of heavy metals rather than physical encapsulation. The major way of chemical binding is the fixing of heavy metals in the structure of AFt and Friedel's salt. Certainly, physical and chemical adsorption of heavy metals on the surface of particles or minerals should be considered too. Certainly, careful examinations on the fixing mechanisms of heavy metals in the new matrix are necessary.

4. Conclusions

MSWI fly ash is a good binder for stabilizing the heavy metal-bearing sludge. The matrixes with heavy metals-bearing sludge and MSWI fly ash have strong fixing capacities for heavy metals Zn, Pb, Cu, Ni and Mn. Specimens with only 5–15% cement was observed to be sufficient to achieve the target compressive strength of 0.3 MPa required for landfill disposal. An optimum mix comprising 45% fly ash, 5% cement and 50% of the industrial sludge could provide the required solidification and stabilization. Addition of MSWI can significantly improve the strength of matrix. The main hydration products of new S/S matrix are ettringite, Friedel's salt and C–S–H. These hydration products play an important role in the fixing of heavy metals.

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