Compound stabilization/solidification of MSWI fly ash with trimercapto-s-triazine and cement
Qiang Xue, Jiangshan Li and Zhuyun Hu

ABSTRACT
A new treatment technology of municipal solid waste incineration (MSWI) fly ash is presented in this paper. Feasibility of solidification/stabilization treatment of MSWI by successively adding trimercapto-s-triazine and cement, and the effect of addition, fly ash size and curing time were studied by batch tests. The results showed that MSWI posed a huge environmental risk, the particulate distribution showed normal distribution approximately. Treatment of fly ash with trimercapto-s-triazine and cement showed a good effect, the leaching toxicity of treated fly ash solidified blocks with 2% trimercapto-s-triazine and 20% cement could meet the standard for pollution control on the landfill site of MSW in China after curing for 7 days, and the flexural strength of solidified blocks could reach 2.4 MPa. Ground fly ash had a positive effect on both leaching toxicity and strength.

Key words | grind, MSWI fly ash, solidification/stabilization, trimercapto-s-triazine

INTRODUCTION
Municipal solid waste incineration (MSWI) is a mature technology used for a long time and is one of the thermochromy disposal technologies that accords to the principles of reducing quantity, harmless and reclamation for waste treatment (Han et al. 2000). With the MSW output heavily rising, incineration is becoming the main treatment method. According to reported statistics, the incineration ratio of MSW is expected to reach to 24%. But fly ash produced by incineration probably contains heavy metals with higher leaching concentrations, such as Pb, Cr, Cd and so on. It also contains massive dioxin-like materials (Li et al. 2004). Thus, MSWI fly ash is a hazardous waste with the harmful characteristics of heavy metals and persistent organic pollutants, which does harm to human health and the environment (Vogg et al. 1986; Yao & Liu 2007), and needs treatment before final disposal.

At present, treatment techniques of fly ash include melting/vitrification, cement solidification, chemical stabilization and acid or other solvent elution and so on (Mangialardi 2003). Solidification/stabilization technology is applied universally owing to its advantages of simple operation, good treatment effect and low cost (Fuoco et al. 2005; Song et al. 2008). Many scholars have studied the solidification/stabilization technology of fly ash. Ubbiaco & Calabrese (1998) studied the compressive strength and leaching characteristics of mixtures formed by fly ash and cement in different ratios. Jiang et al. (2003) applied the self-developed polyamines and polyethyleneimine heavy metal chelating agent to treat fly ash, and tests proved that the treatment effect was obviously better than that of Na2S and lime. The study results of Wang (2007) showed that fly ash chemically stabilized with copper and then solidified by cement had a good effect. But, many research results cannot meet the standards of pollution control on the landfill site of MSW in China and the compatibilization of solidified blocks is evident or the chemicals used for treatment are expensive. Solidification/stabilization technology of fly ash with the characteristics of good treatment effect and low cost has always been the focus for scholars.

Trimercapto-s-triazine had been used as a wastewater treatment chelating agent, it reacts with most of the metals in solution and generates condensate flocculent complex, which is deposited quickly, the decontamination process could be completed by removing the deposit. But it has never been used to treat fly ash (Tang et al. 2009). This paper took the MSWI fly ash from the Likeng incineration plant in Guangzhou as the research object, solidification/stabilization treatment of it was studied by successively adding trimercapto-s-triazine and cement, the feasibility of trimercapto-s-triazine in treating MSWI was studied by...
batch tests and the effect of fly ash size was studied. The study results will supply a new method for the safe disposal of fly ash.

**MATERIALS AND METHODS**

**Materials**

**MSWI fly ash and its chemical components**

The fly ash used in this study was from Likeng waste incineration power plant in Guangzhou city. A mechanical grate incinerator is used in this plant, and the processes of limestone semi-dry and bag filter dedusting are used in the flue gas purification system. Fly ash was trapped down from the dust collector under stable operation for incinerator at full load.

Incineration fly ash is a heterogeneous material formed under high temperature, the main components of which are compounds of Ca, Si, Al and Fe that were measured with a Siemens SRS303 X-ray fluorescence and the results are presented in Table 1.

**Trimercapto-s-triazine**

Trimercapto-s-triazine (C₃S₃N₃Na₃) is an organic sulfide that can react with various heavy metal ions (e.g. Hg, Pb, Cu) to produce insoluble and chemical stable chelates. It is mainly used in treating wet desulfurization wastewater in coal-fired power plants. The trimercapto-s-triazine used in this study was obtained from Changsha Greenstar Environmental Protection Technology Co. Ltd in China.

**Cement**

Ordinary 32.5 levels of Portland cement from Huaxin Cement Co., LTD in China was used in this study, the leaching concentration of Pb, Cu and Zn from cement was 0.11, 0.38 and 5.72 mg/l, respectively, other heavy metals could not be detected.

**Test method**

**Size analysis**

The samples (approximately 1 kg accurately weighed) of fly ash were passed through standard test sieves with different mesh sizes. The particle size of fly ash from Likeng was less than 300 μm, so the fly ash was screened out to six gradational granularities: <30, 30~38.5, 38.5~54, 54~74, 74~154 and >154 μm. Then, the weight of fly ash of different diameters was weighed and size distribution and cumulative distribution were calculated.

**Heavy metal concentration of raw fly ash**

Putting the samples (approximately 0.2 g accurately weighed) of fly ash on crucible, optimized method recommended by Zhao et al. (2003), was used to digest and inductively coupled plasma atomic emission spectroscopy was used to determine the heavy metal content in the digestion solution.

**Sample preparation**

Weighing 1,000 g fly ash, the trimercapto-s-triazine was dissolved into water first then mixed with the fly ash, so the water:fly ash ratio was 25%. The mixture was stirred for 3 min in mortar mixer. Afterwards, the weighed cement was added to it and stirred for another 3 min, the ratios of trimercapto-s-triazine-fly ash and cement-fly ash were determined according to the test requirements. Then, the mixtures were cast into 4 × 4 × 16 cm prisms and vibrated for 2 min. Those samples were demolded after 24 h and cured in a fog room at 20 ± 2°C for different times. Three parallel samples were made in each treatment.

**Leaching toxicity**

The leaching test was conducted according to the Chinese environmental standard – Solid Waste-Extraction procedure for leaching toxicity-acetic acid buffer solution method (HJ/T300-2007). Glacial acetic acid solution (diluting 17.25 ml superior grade pure glacial acetic acid to 11 deionized

<table>
<thead>
<tr>
<th>Chemical components (%)</th>
<th>CaO</th>
<th>Cl</th>
<th>SO₃</th>
<th>SiO₂</th>
<th>Na₂O</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>CO₂</th>
<th>K₂O</th>
<th>Fe₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂O</td>
<td>44.31</td>
<td>20.74</td>
<td>8.25</td>
<td>8.00</td>
<td>4.77</td>
<td>3.44</td>
<td>1.62</td>
<td>2.89</td>
<td>4.13</td>
<td>2.37</td>
</tr>
</tbody>
</table>
water) was used as leaching solution, the liquid-to-solid ratio (L/S) was 20. Close contact between the solid residue particles and the leaching solution in a 2 l PVC plastic bottle was ensured by a flip-type oscillator with frequency of $30 \pm 2 \, \text{r/min}$. After being swung for 18 h, the mixture was filtered through a φ0.45 mm membrane filter. WFX-110 type atomic absorption spectrophotometry was used to measure the concentration of Cd, Pb, Cr, Cu, As, Zn and Ni in the leachate.

Flexural strength

DKZ-5000 type electric anti-flexural meter from Nanjing Soil Instrument Factory Co., Ltd, in China was used to measure the flexural strength of fly ash solidified blocks.

RESULTS AND DISCUSSION

Size distribution

The result of size analysis is presented in Figure 1. The particle size distribution showed normal distribution approximately, the $d_{50}$ and average particle size was 62 and 85.31 $\mu$m respectively. The fly ash with particle size between 54 and 154 $\mu$m accounted for 64%, however, $>154$ and $<30 \mu$m were relatively little, accounting for 8.8 and 14.7% respectively. Fly ash with particle size $<74 \mu$m accounted for 66.8% from the size cumulative distribution curve.

Table 2 showed the heavy metal content and leaching toxicity of raw fly ash, the species of metals were numerous and content was large, concentration of Pb and Cd far exceeded the limits of identification standards for hazardous waste in China and may pose a huge environmental risk.

Leaching toxicity of fly ash solidified blocks

To study the effect of trimercapto-s-triazine addition on stabilization of heavy metals in fly ash, the addition was taken for 0.5, 1, 2, 5 and 10%, respectively, cement addition was taken for 20%. Leaching concentration of metals in treated fly ash solidified blocks after 7 days are shown in Table 3.

It can be seen from Table 3 that if we only used the cement solidification method to treat fly ash, the leaching toxicity could not meet the standard of pollution control on the landfill site of MSW in China although it might have some effect. With the increase of trimercapto-s-triazine addition, the leaching toxicity of heavy metals in fly ash solidified blocks decreased. When trimercapto-s-triazine addition increased to 2%, the leaching toxicity of all heavy metals could meet the standard of pollution control on the landfill site of municipal solid waste in China, such a small addition certainly reduced the cost of processing greatly. The treatment effect of trimercapto-s-triazine on Pb, Ni, Cu, Zn and Hg was excellent, but that on As and Cr was general. The long-term stability of the treated fly ash was also studied. Results showed that the leaching potential of metals from treated fly ash decreased with time in the following 20 days and then kept stable, this must be ascribed to the increasing function of cement. Taking divalent heavy metal ion M, for example, as can be seen from Figure 2, the reaction between trimercapto-s-triazine and heavy metal ions in fly ash produced the stable chelate $M_3(C_3S_3N_3)$ (Matlock et al. 2002).

Table 2 | Basic properties of fly ash from Likeng

<table>
<thead>
<tr>
<th>Metals</th>
<th>Pb (mg/kg)</th>
<th>Cd (mg/kg)</th>
<th>As (mg/kg)</th>
<th>Ni (mg/kg)</th>
<th>Cu (mg/kg)</th>
<th>Hg (mg/kg)</th>
<th>Zn (mg/kg)</th>
<th>Cr (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heavy metal content (mg/kg)</td>
<td>858</td>
<td>365</td>
<td>1,102</td>
<td>150</td>
<td>619</td>
<td>23</td>
<td>3,982</td>
<td>3,012</td>
</tr>
<tr>
<td>Leaching concentration (mg/l)</td>
<td>14.56</td>
<td>5.57</td>
<td>2.48</td>
<td>0.31</td>
<td>5.67</td>
<td>0.34</td>
<td>98.95</td>
<td>6.89</td>
</tr>
<tr>
<td>China standard (mg/l)</td>
<td>5</td>
<td>1</td>
<td>5</td>
<td>5</td>
<td>100</td>
<td>5</td>
<td>100</td>
<td>5</td>
</tr>
</tbody>
</table>

Figure 1 | Particle size distribution of fly ash from Likeng.
Heavy metals and their compounds were immobilized within fly ash solidified blocks through physical fixation, substitution, deposition or adsorption (He et al. 2006). Cement addition could affect fly ash stabilization by changing the amount of hydration products. Solidification/stabilization treatment of fly ash was done with 2% trimercapto-s-triazine and different qualities of cement. Leaching concentration of heavy metals is shown in Figure 3 after curing for 7 days. With the increase of cement addition, leaching concentration of the three heavy metals decreased in different degrees. But when cement addition was 20%, leaching concentration of the three heavy metals could meet the standard of pollution control on the landfill site of MSW in China. If cement addition was increased continuously, although leaching concentration of heavy metals decreased rapidly, the matter went against final disposal owing to the obvious compatibilization of solidified blocks.

**Table 3 | Leachability of the fly ash (mg/l)**

<table>
<thead>
<tr>
<th>Metals</th>
<th>Concentrations in the leach solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Pb</td>
<td>3.521</td>
</tr>
<tr>
<td>Cd</td>
<td>0.964</td>
</tr>
<tr>
<td>As</td>
<td>2.419</td>
</tr>
<tr>
<td>Ni</td>
<td>0.190</td>
</tr>
<tr>
<td>Cu</td>
<td>0.672</td>
</tr>
<tr>
<td>Hg</td>
<td>0.428</td>
</tr>
<tr>
<td>Zn</td>
<td>28.300</td>
</tr>
<tr>
<td>Cr</td>
<td>1.847</td>
</tr>
</tbody>
</table>

– : not detected.

![Figure 2](https://i.imgur.com/2.png)  
*Figure 2 | Reactive principle sketch of trimercapto-s-triazine and two-valent heavy metal M.*

![Figure 3](https://i.imgur.com/3.png)  
*Figure 3 | Effect of cement addition on leaching toxicity.*

**Flexural strength of fly ash solidified blocks**

Strength of solidified blocks was an important index to reflect solidification effect. Flexural strength reflected anti-disintegration performance of fly ash solidified blocks under complex conditions of transportation and landfill. Figure 4 shows that flexural strength of fly ash solidified blocks presented a nonlinear relation with curing time, it increased from 2.4 to 5.9 MPa and the increase mainly concentrated on 7–15 days, flexural strength changed little at later stages. Strength of solidified blocks was mainly produced by cement hydration. The chemical reaction between clinker mineral in cement and water added to fly ash occurred rapidly, which produced calcium silicate hydrate, calcium aluminate hydrate with a space-grid structure and also massive alkali-activator Ca(OH)₂. Alkali-activator could quickly stimulate activity of oxides (e.g. SiO₂, Al₂O₃, Fe₂O₃) in fly ash. The active SiO₂, Al₂O₃ and others had unsaturated bonds, so they could react with Ca²⁺ ionized from Ca(OH)₂ under water and the resultants were calcium silicate and calcium aluminate. The gelation of hydrate cemented heavy metal compounds in fly ash and encapsulated them inside, which could also enhance strength of solidified blocks.
Cement addition is a main factor affecting the flexural strength of fly ash solidified blocks. If the addition was too little, the flexural strength would be small and fly ash solidified blocks could easily disintegrate, which could lead to the leaching risk of heavy metals. If the addition was too much, compatibilization of solidified blocks would be obvious, which could increase disposal cost. Curve of flexural strength of fly ash solidified blocks after 7 days with cement addition is shown in Figure 5. When cement addition was taken for zero, strength of solidified blocks was only 0.8 MPa. When cement addition increased from 5 to 15%, flexural strength of solidified blocks increased linearly. When cement addition increased continuously, the increasing rate of the flexural strength of solidified blocks decreased. In view of economy, cement addition should be taken for 20% in actual engineering.

Effect of grinding

There was a linear correlation between specific surface area and activity of the MSWI fly ash (Lee et al. 2006). The improvement of fly ash activity was beneficial to the chemical reaction between trimercapto-s-triazine, cement and fly ash, which could improve the effect of solidification/stabilization treatment of fly ash. Prophase research showed that grinding could increase activity of fly ash, thus improving the strength of solidified blocks (Kiattikomol et al. 2001; Qian et al. 2001). But there has been no study on the effect of grinding on leaching toxicity of solidified blocks. Fly ash size was divided into 75, 48, 38 and 25 μm, respectively by ball milling. Average particle size of undisturbed fly ash was 85.1 μm. During the test, trimercapto-s-triazine addition was taken for 2%, cement addition was taken for 20%, and fly ash solidified blocks were cured for 7 days.

Figure 6 shows that ground fly ash could promote the effect of processing, with the decrease of fly ash size, leaching toxicity of ash fly solidified blocks decreased. Based on comprehensive consideration of treatment cost and solidification/stabilization effect, the optimal fly ash size should be set for about 48 μm. If fly ash was ground continually, the treatment cost increases greatly but the improvement of solidification/stabilization effect was not obvious. The ground fly ash was homogeneous and its specific surface area increased, thus trimercapto-s-triazine and cement could mix and react with it preferably. The effect of fine grinding could also destroy vitreous metal oxide in fly ash, which could make surface structure of fly ash disintegrate and increase the number of unsaturated bonds in fly ash, thus promoting pozzolanic reaction. Through observation, the ground fly ash solidified block had a compact structure,
and the phenomenon of volume expansion even cracking did not occur.

CONCLUSIONS

The following conclusions can be drawn from our study:

1. The heavy metal content and leaching toxicity of MSWI fly ash from Likeng in Guangzhou city was far beyond the standard of environmental protection in China, which posed a huge environmental risk. The grain diameter distribution of fly ash showed a normal distribution approximately, and the mean value was 85.31 μm, the amount of fly ash with grain diameter less than 74 μm accounted for 66.8%.

2. Trimercapto-s-triazine had a good stabilization effect on the metals in MWSI fly ash, and the treatment of fly ash with trimercapto-s-triazine and cement is an economic and efficient method.

3. The addition of trimercapto-s-triazine and cement, particle size of fly ash and the curing time had effects on the treatment effect, the leaching toxicity of fly ash solidified blocks decreased with increasing trimercapto-s-triazine addition. When the addition of trimercapto-s-triazine reached 2%, the leaching concentration of all metals met the standard. The effect of cement addition on flexural strength far exceeded that on leaching toxicity of fly ash solidified blocks. The increase of flexural strength mainly concentrated on days 7–15. Particularly, ground fly ash had positive promotion effects on treatment effect. Based on comprehensive consideration of cost and effect, the addition of trimercapto-s-triazine and cement should be better determined as 2 and 20%, respectively. Particle size of fly ash was not less than 48 μm. The treated fly ash solidified blocks may be landfill or utilized as resources after curing for more than 7 days.

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