Solidification/stabilization of simulated cadmium-contaminated wastes with magnesium potassium phosphate cement

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ABSTRACT
Magnesium potassium phosphate cement (MKPC) is an effective agent for solidification/stabilization (S/S) technology. To further explore the mechanism of the S/S by MKPC, two kinds of Cd including Cd(NO3)2 solution (L-Cd) and municipal solid waste incineration fly ash (MSWI FA) adsorbed Cd (S-Cd), were used to compare the effects of the form of heavy metal on S/S. The results showed that all the MKPC pastes had a high unconfined compressive strength (UCS) above 11 MPa. For L-Cd pastes, Cd leaching concentration increased with the increase of Cd content, and decreased with the increase of curing time. With the percentage of MSWI FA below 20%, S-Cd pastes exhibited similar Cd leaching concentrations as those of L-Cd pastes, while when the content of MSWI FA come up to 30%, the Cd leaching concentration increased significantly. To meet the standard GB5085.3-2007, the highest addition of S-Cd was 30% MSWI FA (6% Cd contained), with the Cd leaching concentration of 0.817 mg/L. The S/S of L-Cd is mainly due to chemical fixation, and the hydration compound of Cd was NaCdPO4, while the S/S of S-Cd is due to physical encapsulation, which is dependent on the pore/crack size and porosity of the MKPC pastes.

Keywords: Cd, Magnesium potassium phosphate cement (MKPC), Municipal solid waste incineration fly ash (MSWI FA), Solidification/Stabilization (S/S)

1. Introduction
The solidification/stabilization (S/S) technology is the common and effective method for treating a variety of wastes, particularly heavy metal pollutants [1-3]. The US Environmental Protection Agency (EPA) has reported S/S technology was selected in 13% of ex situ source treatment technologies in decision documents in Superfund Remedy [4].

Cement-based and pozzolan-based materials are mainly agents in S/S technology [5-8]. Recently, more researches have been made on the S/S of waste by magnesium potassium phosphate cement (MKPC). MKPC, a ceramic matrix of magnesium potassium phosphate hydrate, has excellent densification and mechanical properties, such as reduced leach ability, higher propensity for binding with waste inclusion, higher resistance to sulphate attack, lower permeability, higher early age and long-term strengths and higher durability, adapting wider pH value environment, etc. [9-11]. In 1997, different phosphate ceramics were firstly used to solidify/stabilize the surrogate mixed-wastes (ash, cement sludge, and salts), and the application of the phosphate ceramics on S/S was potential and effective [12]. Then, more experiments demonstrated the satisfactory effects of chemically bind phosphate ceramic on S/S, including simulated pollutants containing Hg and HgCl2 [13], fly ash and soil, which contained heavy metals such as Cd, Cr, Pb, Ni and Hg [14], contaminated debris and irradiated lead bricks [15], and different heavy metal nitrate solutions [16-18]. Therefore, MKPC is an effective agent in S/S of heavy metals [13, 15, 16, 18] and even radioactive waste [19-22].

Although MKPC has shown positive effects on S/S, few researches was done on the mechanism of the S/S of heavy metals by MKPC. Singh et al. [12] proposed that the reason for the immobilization of chemically bonded phosphate ceramics is chemical stabilization, the reaction between contaminant metal salts and the phosphate solution, followed by physical encapsulation within the dense phosphate matrix. Rao et al. [14] found that the fly ash particles was encapsulated in the binder matrix. For the hydra-

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tion products of heavy metal, Jeong et al. [23] found PbO can form the PbHPO4 in magnesium phosphate cements. In the research of Buj et al. [24], only Ni(OH)2 was detected. And Zhen et al. [25] thought the hydration product of Cu2+ was CuKPO4・6H2O. However, probably because heavy metal concentration was below the detection limit of the XRD method, hydration products of heavy metal phosphate usually were not found in the solid pastes [12, 17, 24]. From above, the hydration products of heavy metal phosphate is not clearly, and this is usually related to the kinds and forms of heavy metals, such as ion form in the leachate and compound form in the solid wastes. Therefore, the mechanism of S/S by MKPC need to be further identified.

The object of this paper is to further explore the mechanism of the S/S of Cd by MKPC. Cd in different media were used to identify the effects of the form of heavy metal on S/S, and high loads of Cd were used to improve to identify the hydration products. The performances of each MKPC pastes were compared by heavy metals leaching concentrations, unconfined compressive strength (UCS), XRD, scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS) analysis.

2. Materials and Methods

2.1. Experimental Materials

The main ingredients of MKPC were Dead-burned MgO (M), KH2PO4 (K), a new retarder A, which composed of Na2HPO4・12H2O, and Na2B4O7・10H2O, etc. The component proportion of MKPC was the mass ratio of M/K=3:1, A/M=12%, which was based on our previous studies[26, 27]. Simulated waste water containing cadmium (L-Cd) was a certain concentration of Cd(NO3)2 solutions. Simulated waste solid containing Cd (S-Cd) was fabricated by dissolving a certain amount of Cd(NO3)2 in distilled water, and then mixing with MSWI FA (Referred to as FA), which was from the Yancheng garbage incineration power plant, then drying at 30˚C. The chemical composition of heavy metal was in Table 1), which was measured according to the standard of Methods for Chemical Analysis of Cement (GBT176-2008). Because the Cd contents in the FA is low (21mg/kg), as shown in Table 2, we did not calculated Cd in the original FA.

2.2. Preparation of MKPC Pastes

The MKPC pastes were made according to the JGJ/T70-2009. A certain amount of K, retarder A and water were mixed and stirred slowly for 1 min using a static slurry blender (NJ-160A), after which M and/or FA were added and the mixture was stirred for another 2 min quickly. The samples were then placed in a 30 × 30 × 30 mm3 mold and vibrated on a vibrating table, after which the pastes were placed under natural conditions (15˚C-25˚C, 50-70% relative humidity) to cure. The water-to-solid ratios (W/S) were varied in the pastes to keep the same fluidity of about 100 mm. For L-Cd pastes, the W/S changed little with the Cd(NO3)2 addition, while for S-Cd pastes, the W/S increased with the addition of FA, from 0.125-0.173. The pastes were cured 7 and 28 d under standard conditions. The pastes of L-Cd were named as L, the pastes of 10%, 20% and 30% S-Cd (the percentage was calculated according to the weight of MgO) were named as S10, S20, S30, respectively, and the pastes of 0, 2, 4, 6 and 8% Cd(NO3)2 (the percentage was calculated according to the weight of MKPC), were named as 1, 2, 3, 4, and 5, respectively. Three parallel samples were fabricated for each plot. Some samples of the pastes were showed in Fig. 1.

2.3. Analysis Methods

The UCSs of the MKPC pastes were tested by WED-100 electronic universal material testing machine. The loading rate was controlled within the range of 0.5~1 MPa/min. The MKPC pastes were ground into small powders and sieved through a 1 mm mesh to test the leaching concentration. The heavy metal leaching concentrations were measured by AAS 3000 atomic absorption spectrophotometer according to Chinese solid waste-extraction procedures HJ/T299-2007 "Solid Waste-Extraction Procedure for Leaching Toxicity - Sulphuric Acid & Nitric Acid Method". DX-2700 X-Ray Diffraction meter (XRD) was used to determine the mineralogical composition of the MKPC pastes (parameter setting: tube voltage 40 kV, tube current 100 mA, slit DS=SS=1°, RS=0.3 mm, step length 0.05/step, scanning speed 10/min).

Table 1. Chemical Composition Percentage of FA (%)

<table>
<thead>
<tr>
<th>Components</th>
<th>SiO2</th>
<th>Al2O3</th>
<th>CaO</th>
<th>SO3</th>
<th>Fe2O3</th>
<th>MgO</th>
<th>Na2O</th>
<th>K2O</th>
<th>Cl</th>
<th>Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>w/ (%)</td>
<td>39.89</td>
<td>19.43</td>
<td>13.50</td>
<td>5.33</td>
<td>4.61</td>
<td>2.28</td>
<td>1.80</td>
<td>1.40</td>
<td>1.28</td>
<td>10.48</td>
</tr>
</tbody>
</table>

Table 2. Heavy Metals Content of FA (mg/kg)

<table>
<thead>
<tr>
<th>Metals</th>
<th>Fe</th>
<th>Zn</th>
<th>Ni</th>
<th>Cu</th>
<th>Pb</th>
<th>Cr</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg/kg</td>
<td>39094</td>
<td>13441</td>
<td>406</td>
<td>63</td>
<td>49</td>
<td>46</td>
<td>21</td>
</tr>
</tbody>
</table>
QUANTA200 SEM with EDS were used to analyze the morphology and structure characteristics, and the elements of the hydration products.

3. Results and Discussion

3.1. UCS of MKPC Pastes

Fig. 2 presented the UCSs of the MKPC pastes with different L-Cd or S-Cd (28 d). All the MKPC pastes showed a high UCSs much higher than the requirement of land filled by America (0.35 MPa) [28], and by Canada (3.45 MPa) [29]. UCSs of MKPC pastes decreased with the increase of Cd and/or FA. That is to say, Cd and/or FA may inhibit to the increase of strength of paste. When the addition amount of FA was higher than 20%, the UCS decreased mostly. The strength of compressive pastes of S30-5, which is 30% FA (contained 8% Cd) was the lowest, 11 MPa.

3.2. Cd Leaching Concentration of MKPC Pastes

Fig. 3 presented the Cd leaching concentration of different MKPC pastes cured for 7 and 28 d. The Cd leaching concentration of all the pastes decreased with the increase of curing time. Under the identical curing condition, for each kind of MKPC pastes, the Cd leaching concentration increased with the increase of Cd content added in the MKPC pastes, and decreased with the increase of curing time. Under a curing time of 28 days, the highest Cd addition percentage and leaching concentration of L-Cd pastes were 8% and 0.383 mg/L, respectively. This leaching concentration is much lower than 1 mg/L in the “Identification Standards for Hazardous Wastes - Identification for Extraction Toxicity” (GB5085.3-2007). With the percentage of FA below 20%, S-Cd pastes exhibited similar Cd leaching concentration as that of L-Cd pastes, with the continuing increase of FA percentage, the Cd leaching concentration increased significantly, and the paste of highest waste added, which met the leaching standard was 30% FA (6% Cd contained), with the Cd leaching concentration of 0.817 mg/L.

3.3. XRD Analysis

Fig. 4 showed the XRD patterns of eight different MKPC pastes. In Fig. 4, the peaks of paste L-1 were unhydrated MgO, hydration products of MgKPO₄·6H₂O and a small amount of Mg₃(PO₄)₂. Compared to the paste L-1, paste L-4 had one more peak of NaCdPO₄, which indicated that PO₄³⁻ reacted with Cd²⁺ and Na⁺ (from Na₂HPO₄·12H₂O) produced NaCdPO₄. All pastes containing FA (S10-1, S20-1, S30-1, S10-4, S20-4 and S30-4) still had SiO₂ peak, which showed most of the SiO₂ was still in the crystalline form, and did not participate in the hydration reaction to form new crystal. This is similar to the results of Lin [30]. For the paste S10-4, S20-4 and S30-4, with the increase of FA, the peaks of the NaCdPO₄ decreased. In paste S30-4, NaCdPO₄ crystals were almost undetectable, indicating that FA inhibited the reaction among PO₄³⁻, Cd²⁺ and Na⁺, which was probably due to some of Cd was adsorbed by FA, and not in an iron form.
3.4. SEM Analysis

The SEM photographs of the former pastes were showed in Fig. 5. In Fig. 5, paste L-1 showed a high degree of hydration and crystallization. Compared with paste L-1, paste L-4 had more amorphous composition, mainly due to $\text{PO}_4^{3-}$ preferred to react with $\text{Cd}^{2+}$ and $\text{Na}^+$ to produce $\text{NaCdPO}_4$ and inhibited the generation of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ crystal, which is consist with the XRD analysis. Paste S10-1, S20-1 and S30-1 mainly showed amorphous phase, and with the increase of FA, the cracks in the paste increased, indicating that FA weakened the crystallization in MKPC. In paste S10-4, S20-4 and S30-4, amorphous phase were also the main forms. Compared to FA, FA containing Cd generated not crakes, but more pores in the pastes, which is similar to the studies of Lai et al. [22]. The main reason is that the FA surface area is larger than the dead burned MgO powder, when using it to partial substitute MgO, MKPC need to more water to keep the same fluidity, the excess water more than the hydration reaction needed (W/S...
from 0.125 to 0.173) may increase the pore/crake size and pore/crake porosity in the MKPC paste [24, 31]. Additional, the replacement of MgO with a certain amount of FA, reduced the amount of gel generated by hydration reaction, which may also lead to larger porosity probably.

3.5. EDS Analysis

Fig. 6 showed the EDS spectrum of point (A)-(H) in the SEM photographs. And the corresponding molar percent of elements were put in the Table 3. From Fig. 6 and Table 3, it can be seen

![EDS spectra](image)

Table 3. Molar Percentage of Elements for EDS

<table>
<thead>
<tr>
<th>Point</th>
<th>O K</th>
<th>Mg K</th>
<th>Na K</th>
<th>P K</th>
<th>K K</th>
<th>Al K</th>
<th>Si K</th>
<th>Ca K</th>
<th>Cd L</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>64.68</td>
<td>12.95</td>
<td>0.05</td>
<td>11.37</td>
<td>10.95</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>64.28</td>
<td>22.13</td>
<td>2.57</td>
<td>5.2</td>
<td>4.73</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.09</td>
</tr>
<tr>
<td>C</td>
<td>65.58</td>
<td>23.95</td>
<td>-</td>
<td>5.36</td>
<td>4.97</td>
<td>-</td>
<td>0.13</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>D</td>
<td>66.64</td>
<td>15.03</td>
<td>-</td>
<td>7.2</td>
<td>9.89</td>
<td>-</td>
<td>1.24</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>E</td>
<td>70.83</td>
<td>19.1</td>
<td>0.45</td>
<td>0.23</td>
<td>6.24</td>
<td>0.17</td>
<td>2.98</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>F</td>
<td>65.85</td>
<td>6.08</td>
<td>0.57</td>
<td>4.12</td>
<td>19.98</td>
<td>0.23</td>
<td>1.21</td>
<td>1.1</td>
<td>0.86</td>
</tr>
<tr>
<td>G</td>
<td>61.49</td>
<td>16.55</td>
<td>0.66</td>
<td>8.55</td>
<td>11.39</td>
<td>-</td>
<td>0.42</td>
<td>0.49</td>
<td>0.46</td>
</tr>
<tr>
<td>H</td>
<td>72.52</td>
<td>8.04</td>
<td>-</td>
<td>3.99</td>
<td>5.86</td>
<td>4.02</td>
<td>3.16</td>
<td>0.15</td>
<td>2.26</td>
</tr>
</tbody>
</table>
that for paste L-4 (point B), Cd was well solidified/stabilized in the pastes, which is consistent with the XRD analysis. For S-Cd pastes, the points contained Si element that always also contained a certain amount of Cd element, showing that part of Cd still adsorbed around the SiO2 in FA, which probably existed in the forms of hydrogen cadmium or cadmium nitrate, because of a chemical reaction cannot occur between Cd and SiO2.

3.6. Effects of L-Cd and S-Cd on MKPC

UCSs of MKPC pastes decreased with the increase of Cd and/or FA (Fig. 1). The reasons may be different for Cd and FA. For heavy metal Cd, Ma et al. [18] and buj et al. [24] also found that the UCS generally was inversely proportional to heavy metal concentrations when W/S was relatively high. And buj et al. [24] thought this was mainly due to heavy metal generated defects at the crystalline matrices and weaken them. In XRD pattern (Fig. 4), L-Cd generates new crystal of NaCdPO4. This new crystal probably influences the initial crystalline matrices of pure MKPC, so the UCS decreased. For the addition of FA, the decrease of UCS is similar to the results of many other studies [22, 32-34]. In Fig. 5 (c-e) and Fig. 5 (f-h), the pore/crake size and pore/crake porosity (the volumes of permeable voids) was increased with the addition of FA. Thus, these increased permeable voids may decrease the mechanical strength of the pastes according to the Griffith Crack Theory.

The Cd leaching concentration decreased with the increase of curing time (Fig. 3). From the research of Hongyan et al. [31], longer material age (curing time) makes the porosity lower and the pore structure finer. With the low porosity and the fine pore structure, the permeability of the paste is low and the leaching of Cd is decreased. On the other hand, with increase of the curing time, the continued hydration reaction between heavy metal and PO43- further improved the S/S of Cd [23].

Cd leaching did not increase with the low FA addition (below 20%) may be due to the filling effect of FA. Similarly, Liu et al. [35] found that appropriate amount of ground granulated blast furnace slag (GGBFS) added would be beneficial for both leaching performance and UCSs of the pastes and postulated that GGBFS played the role of filling the voids of the matrix. Ribeiro et al. [36] also proved magnesium phosphate cement matrix was highly effective in encapsulating grinding dust, especially for a content of 10%. And when the FA increased to 30%, the pore/crake size and pore/crake porosity in the pastes increased. The adsorbed Cd in FA is the main reason that more Cd leaching out from the paste (S30-4).

3.7. S/S Mechanism Analysis

Form all above results, we postulated that when S/S of Cd in wastewater, the main mechanism [14] is the phosphate reacting with Cd ions and generating low solubility phosphate. Cd is directly fixed by a chemical bond in the MKPC, which is similar to that in apatite cement [37, 38]. When S/S of Cd in FA, some Cd desorbed from FA is chemically fixed just like in the wastewater, while most of Cd adsorbed in the pores inside or among FA could not directly react with phosphate in MKPC, and mainly were encapsulated into the MKPC matrix. That is to say, pore/crack size and porosity of the MKPC paste determined its performance of encapsulation on Cd. Furthermore, if the pore/crack size and porosity is low enough, the performances of the MKPC on S/S of L-Cd and S-Cd are similarly, regardless of chemical fixation or physical encapsulation.

4. Conclusions

UCSs of all MKPC pastes decreased with the increase of Cd and/or FA. The UCS of paste S30-5 (30% FA contained 8% Cd) was the lowest, 11 MPa. This value was much higher than the strength requirement for waste landfill.

For L-Cd pastes, Cd leaching concentration increased with the increase of Cd content, and decreased with the increase of curing time. With the percentage of MSWI FA below 20%, S-Cd pastes exhibited similar Cd leaching concentrations as those of L-Cd pastes, while when the content of MSWI FA come up to 30%, the Cd leaching concentration increased significantly.

The S/S of L-Cd is mainly due to chemical fixation, and the hydration compound of Cd was NaCdPO4, while the S/S of S-Cd is due to physical encapsulation. The pore/crake size and porosity in MKPC pastes determined the performance of encapsulation of MKPC. If the pore/crake size and porosity is low enough, the performances of the MKPC on S/S of L-Cd and S-Cd are similarly, regardless of chemical fixation or physical encapsulation. Thus we proposed that the performance of S/S of waste will be improved by reducing the pore or filling particles in the MKPC.

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