Cadmium Stabilization by Sewage Sludge Incineration Ash

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Research

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Abstract

Cadmium (Cd), as a common ingredient in the production process of nickel cadmium batteries, can lead to functional disorder in kidneys, liver, lungs, cardiovascular, immune and reproductive systems. Previous studies have shown that cadmium can be stabilized in ceramic systems using clay as precursor, but the excessive exploitation of nonrenewable clay resources has caused great concerns. Hence, it is essential to find alternatives to substitute nonrenewable clay minerals. Sewage sludge incineration residues, with oxides of aluminum and silicon as major component, have attracted much attention because of the potential resource utilization. In this study, CdO and CdNO$_3$ was used to simulate cadmium-bearing industrial waste, and the stabilization of cadmium was achieved in ceramic matrix provided by the residues of sewage sludge incineration. Through a 2-hour sintering procedure at temperatures ranging from 800°C to 1000°C, cadmium was found to be incorporated into CdAl$_2$Si$_2$O$_8$. The leachability of cadmium significantly declined in sintered samples when extracted in acidic environment. Meanwhile, samples that were pressed into pellets showed better cadmium stabilization efficiency, compared with powder samples. Therefore, this study suggests a promising technique to stabilize cadmium by the utilization of sewage sludge incineration residues as ceramic precursors. The success implementation of current study will further reduce the environmental burden caused by the release of heavy metals from industrial waste. Moreover, the recycling of sewage sludge incineration residues can be realized, and a waste-to-resource strategy is expected.

1. Introduction

Heavy metals, which are toxicity for most creatures, have caused serious environmental problems due to their non-biodegradability and acceleration in food chain for decades. [1–3] Cadmium, which commonly presents in the environment, has been considered as one of general heavy metals exhausted in industrial wastewater, especially from nickel cadmium battery production process. Continuous exposure to Cd-rich sources may lead to functional disorder in human's kidneys, liver, lungs, cardiovascular, immune and reproductive systems. [4–6]

Sewage sludge is an inevitable by-product of sewage treatment plants, which contains pathogens, heavy metals and organic pollutants. With the development of industrialization and modernization, the annual output of sewage sludge in various countries is also increasing. Some schemes try to reuse sewage sludge incineration residues directly for building materials, but the concentration of heavy metals containing in the untreated sewage sludge incineration residues usually exceeds the relevant standards in leaching process. Before utilization, sewage sludge incineration residues require stabilization process to comply with the law related to final applications. [7–9] Chemical precipitation, coagulation–floculation, flotation, ion-exchange and membrane processes are technologies that have been widely used to remove cadmium from industry waste and reduce the biological hazards of cadmium. However, the removal processes also produce sludge which aggregates large amount of cadmium and causes serious secondary pollution. Landfilling is a traditional method to treat sewage sludge. However, landfilling is not anymore suitable for treatment of Cd-laden waste, because it takes up too much space, and the reduction
of available land for landfill has already become a critical issue. Besides, high concentrations of organic matter and heavy metals in leachates will contaminate the surrounding water and soil once released in long term environment erosion. Therefore, it is of great importance to develop an effective strategy to treat the cadmium bearing waste. 

In recent years, sewage sludge management methods based on thermal treatment are becoming more and more popular. The volume of sewage sludge will be reduced by 85%, thus saves a lot of space. At the same time, viruses, bacteria and organic matter will be removed after thermal treatment. As a matter of fact, ceramic sintering has become one of the most efficient way to stabilize poisonous heavy metals. Previous studies have reported the utilization of sewage sludge incineration residues as precursor for zinc stabilization at high temperature. Spinel phase with formula of $\text{ZnAl}_x\text{Fe}_{2-x}\text{O}_4$ was greatly enhanced during thermal treatment process at elevated temperatures, and the leachability of zinc substantially declined because of the formation of the spinel structure. In system for co-stabilization of Pb/Cu/Zn, heavy metals achieved coimmobilization through ceramic sintering together with sewage sludge incineration residues, which significantly reduced the leachability of Pb, Cu and Zn in acid environment. The formation of crystal compounds such as $\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_y\text{Al}_{2-y}\text{O}_4$, $\text{PbAl}_2\text{Si}_2\text{O}_8$, $\text{Pb}_3(\text{PO}_4)_3$, and $\text{CuFe}_2\text{O}_4$ contributes to the stabilization of Pb/Cu/Zn metals at high temperatures (1000°C-1600°C) by adding silicon-containing compound to sewage sludge containing heavy metals. Further leaching experiment proves long term stabilization of heavy metals in ceramic products, therefore their threats to the environment are eliminated. However, the clay minerals used in ceramic systems has attracted attention due to the excessive exploitation of resources and the consequent environment pollution, so it is essential to find alternatives to replace nonrenewable clay minerals.

Owing to the high content of aluminum and silicon, the residues from incineration of sewage sludge may be reused as ceramic raw materials in stabilizing cadmium-laden waste. The following achievements can be made. Firstly, cadmium was incorporated in ceramic system with matrix rich in aluminum and silicon to achieve stabilization. Secondly, it will reduce the storage of sewage sludge, and realize resource utilization. Thirdly, sewage sludge incineration residues have the potential to replace raw materials in the ceramic industry and eliminate the stress in excessive exploitation of clay minerals in ceramic systems. The other benefit of using sewage sludge as ceramic raw materials is that there's always abundant of sewage sludge in the world. For example, in 2004, Japan produced about $4.14 \times 10^8 \text{m}^3$ of sewage sludge, and the volume increased by 170% from 1990 to 2004. The sewage sludge occupies a lot of space and has long term toxicity, therefore requires instant proper handling. The recycling of sewage sludge incineration residues as ceramic precursor will relieve the environmental burden and provide a ‘waste-to-resource’ strategy to realize the sustainable management of sewage sludge.

In this study, sewage sludge incineration residues were used as ceramic raw materials, and $\text{Cd(NO)}_3$ and $\text{CdO}$ were added to the sewage sludge incineration residues to simulate Cd-laden industrial sludge, which has yet to be stabilized. Sintering temperature range is 500°C-1000°C, and the duration is 2 hours. The
phase constitution of each product will be characterized to explain the phase transformation and cadmium binding mechanism during sintering. The leachability of cadmium will be tested by leaching experiments to further evaluate the stabilizing effect of cadmium in sintered ceramic products.

2. Materials And Methods

The sewage sludge incineration residues were collected from a wastewater treatment plant in Shenzhen, China, which contains sludge after primary and secondary treatment processes. The sewage sludge incineration residues were dried in an oven at 105°C and analyzed via X-ray fluorescence spectrometer (XRF, BRUKER S2 RANGER). The results in Table 1 show that silicon, aluminum, iron and phosphate are main ingredients.

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>P₂O₅</th>
<th>CaO</th>
<th>K₂O</th>
<th>MgO</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight percentage (%)</td>
<td>40.4</td>
<td>27.9</td>
<td>10.5</td>
<td>9.5</td>
<td>2.6</td>
<td>2.0</td>
<td>1.3</td>
<td>5.8</td>
</tr>
</tbody>
</table>

To study the mechanism of stabilization in different cadmium compounds, Cd(NO)₃ (Kermel, Tianjin) and CdO (aladdin, Shanghai) were used in this experiment to simulate the cadmium bearing industrial solid waste. Cd(NO)₃ and CdO was separately mixed with sewage sludge incineration residues with a molar ratio of Cd:Al = 1:1. To ensure mixing uniformly, sewage sludge incineration residues and cadmium compounds were ground with alcohol in an agate mortar for more than 30 minutes, and dried in oven at 105°C for further used. Meanwhile, the effect of the statement of samples was assessed. sewage sludge incineration residues mixed with CdO was pressed into pellets at 12 MPa for 2 min via electric hydraulic press (MSK-YLJ-E60T Kezhida), compared with powder samples. Sewage sludge incineration residues mixed with Cd(NO)₃ was not pressed into pellets because the mixture was too absorbent and hard to form pellets. The samples were sintered in 500°C-1000°C range with a holding time of 2-hour in the muffle furnace at a heating rate of 10°C/min, and then cooled down with furnace control.

After sintering, a part of sample was broken and ground into power for X-ray diffraction (XRD) analysis and leaching experiments. XRD analysis was done via Rigaku Smartlab diffractometer, with Cu Kα radiation (45KV, 200 mA) in 2θ range of 10–80°, a scan speed of 0.12 s/step and a step size of 0.02 °/min. Phase identification was executed by Jade 6.0 via matching powder brag peaks with those listed in the standard powder diffraction database of the International Centre for Diffraction Data (ICDD PDF, Release 2004). The stabilization leaching experiments modified from toxicity characteristic leaching procedure (TCLP, U.S. EPA SW-846 Method 1311). 4 mL of the extraction fluid#2 (pH = 2.88) and 0.2 g of the powder sample were added into each vail, which was then rotated end-over-end at 60 rpm for 18 h. After that, the leachates were filtered through a 0.22 μm membrane, and the concentration of heavy
metals in leachates was measured by an inductively coupled plasma-optical emission spectrometer (ICP-OES, Optima 8000DV PerkinElmer).

3. Results And Discussion

3.1 Phase transformation and cadmium incorporation during sintering

Figure 1 displays the XRD patterns of sintered samples (500–1000°C) of Cd:Al with molar ratio 1:1, where cadmium is provided by Cd(NO)_3. CdO is the main form of cadmium compounds at 500°C-700°C. At the same time, six silicon-contained phases (SiO_2, CaAl_2Si_2O_8, Ca_3Al_2Si_3O_12, CaSiO_3, Ca_2SiO_4, FeSiO_3) were identified in XRD patterns at 500°C-700°C. The peak of SiO_2 decreased obviously as temperatures increased, due to the incorporation of SiO_2 into other silicon-contained phases. Ca_3Al_2Si_3O_12 disappeared when the samples were sintered at 800°C, which may relate to its involvement in the formation of new phases. FeSiO_3 disappeared while Fe_2O_3 was observed at a sintering temperature of 800°C. In addition, CdO disappeared and new cadmium contained phases (CdSiO_3, CdAl_2Si_2O_8) were observed at 800°C. At 800°C-1000°C, the silicon-contained phases were identified as SiO_2, CaAl_2Si_2O_8, Ca_3Al_2Si_3O_12, CaSiO_3, CdSiO_3, CaAl_2Si_2O_8. The complex cadmium aluminum silicate CdAl_2Si_2O_8 has been reported in previous study when the mixture of cadmium vapor and aluminosilicate substrate was thermally treated at 800°C, and it is stable at a temperature above 900°C. Peak intensities of CdAl_2Si_2O_8 become higher with increased temperatures, indicating continuous reaction to generate CdAl_2Si_2O_8. [27, 28]

Figure 2 illustrates the XRD patterns of sintered samples (500–1000°C) of Cd:Al with molar ratio 1:1, where cadmium is provided by CdO. The peak of CdO was identified in XRD patterns at 500°C-700°C, but the peak intensity of CdO significantly declined at 700°C and disappeared when the sintering temperature was increased beyond 800°C, due to the involvement in the formation of new phase (CdAl_2Si_2O_8). Ca_3SiO_5 was observed as intermediate product at 800°C. CdAl_2Si_2O_8 phase was identified in samples after sintering at 900°C and 1000°C. In addition, SiO_2 disappeared in 900°C-sintered sample due to the participation in formation of new silicon phased mentioned above. The reaction equations for the formation of Si and Ca/Cd-containing product phases (CdSiO_3, Cd_2SiO_4, CdAl_2Si_2O_8, CaSiO_3, Ca_2SiO_4, CaAl_2Si_2O_8, Ca_3Al_2Si_3O_12) can be expressed as follows: [29–35]

CdO + SiO_2 → CdSiO_3 (1)

2CdO + SiO_2 → Cd_2SiO_4 (2)

CaO + SiO_2 → CaSiO_3 (3)

2CaO + SiO_2 → Ca_2SiO_4 (4)
CdO + Al₂O₃ + 2SiO₂ → CdO·Al₂O₃·2SiO₂ (CdAl₂Si₂O₈) (5)

CaO + 2SiO₂ + Al₂O₃ → CaAl₂Si₂O₈ (6)

3CaO + 3SiO₂ + Al₂O₃ → Ca₃Al₂Si₃O₁₂ (7)

3.2 Leaching behavior of cadmium from the samples after sintering

The TCLP experiments were conducted to evaluate the stabilization effect of cadmium caused by reactant types and samples statement. Figure 3 shows cadmium concentration in the leachates and leachate ratio of cadmium. Leachate ratio of cadmium is calculated with the amount of cadmium in leachate divided by the total amount of cadmium in 0.2 g of the corresponding sample. Both of Fig. 3 (a) and (b) show obviously decrease of cadmium concentration in the leachates with the formation of CdAl₂Si₂O₈. In ‘Cd(NO)₃ + sewage sludge incineration residues’ reaction system, the concentration of cadmium is 5085.0 mg/L at 500°C, and declined to 1518.6 mg/L at 1000°C. In ‘CdO + sewage sludge incineration residues’ reaction system, the concentration of cadmium is 3233.3 mg/L at 500°C, then reduced to 1153.3 mg/L at 1000°C. Figure 3 (c) and (d) reveals the reduction in leachates ratio of cadmium, where the trends are in accordance with that of cadmium concentration in the leachates. After thermal treatment, leachate ratio of cadmium can be reduced to 12.97% in ‘Cd(NO)₃ + sewage sludge incineration residues’ reaction system at 1000°C. Moreover, ‘CdO + sewage sludge incineration residues’ reaction system showed even lower leachate ratio, with powder samples achieving 9.21% and pellets samples achieving 6.12%, indicating better immobilization effect of cadmium in pellets samples. Compared with Cd(NO)₃, CdO compound is easier to form stable aluminosilicate substrate (CdO·Al₂O₃·2SiO₂) and therefore leads to lower cadmium leachates ratio in ‘CdO + sewage sludge incineration residues’ reaction system. Pellets samples shows lower leachates ration than powder sample, due to higher density of pellets after pressed process, thus higher rate of reaction to form stable cadmium crystal phases.[36]

4. Conclusion

With abundant aluminum and silicon, the sewage sludge incineration residues were reused as ceramic raw materials to stabilize cadmium in cadmium-bearing waste by incorporating into the ceramic matrix. After a 2 h sintering scheme within the temperature range of 500°C-700°C, CdO, SiO₂, CaAl₂Si₂O₈, Ca₃Al₂Si₃O₁₂, CaSiO₃, Ca₂SiO₄ were found in ‘Cd(NO)₃ + sewage sludge incineration residues’ reaction system, while CdO, SiO₂, CaAl₂Si₂O₈ were found in ‘CdO + sewage sludge incineration residues’ reaction system. At the range of 800–1000°C in ‘Cd(NO)₃ + sewage sludge incineration residues’ reaction system and 900–1000°C in ‘CdO + sewage sludge incineration residues’ reaction system, cadmium from Cd(NO)₃ and CdO were found to be eventually incorporated into a CdAl₂Si₂O₈ due to the coexistence of aluminum and silicon in the ceramic matrix. The leachability of cadmium was the highest at 500°C and decreased
apparently with the formation of CdAl$_2$Si$_2$O$_8$ at elevated temperatures. Statement of samples on stabilization was also considered in this study. In ‘CdO + sewage sludge incineration residues’ reaction system, the stabilization effect of cadmium was better in samples that has been pressed into pellets. It is related to higher density of pellets after pressed process, which leads to higher rate of reaction to form stable cadmium crystal phases.

Through this study, cadmium can be successfully stabilized by aluminum ceramic matrix of the residues from sewage sludge incineration. It provides a sustainable method for the stabilization of heavy metals in ceramic systems, which promotes the reuse of sewage sludge incineration residues effectively.

**Declarations**

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**Availability of data and materials**

All data and materials of this study have been included in this manuscript or upon request from the corresponding authors.

**Competing interests**

There are no competing interests involved in this study.

**Authors' contributions**

Zhong Lyu conducted the experiments and drafted the manuscript. Fanling Meng assisted the analysis of experimental data and helped to revise the manuscript. Yuanyuan Tang and Kaimin Shih provided the research concept and supervised the study, and all authors independently reviewed and approved the final draft manuscript.

**References**


Figures

![Figure 1](image-url)
XRD patterns of the samples sintered from Cd(NO)3 + sewage sludge incineration residues at temperatures ranging from 500 to 1000℃, with phases identified as: Monteponite (CdO, PDF#75-0592); Quartz (SiO2, PDF#83-2465); Hematite (Fe2O3, PDF#33-0664); Wollastonite (CaSiO3, PDF#27-0088); Orthoferrosilite (FeSiO3, PDF#17-0547); Cadmium Silicate(2SiO4, PDF#49-1673); Cadmium Silicate (CdSiO3, PDF#02-0719); Dmisteinbergite (CaAl2Si2O8, PDF#74-0814); Cadmium Aluminum Silicate (CdAl2Si2O8, PDF#31-0217).

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Figure 2

XRD patterns of powder samples sintered from CdO + sewage sludge incineration residues at temperatures ranging from 500 to 1000°C, with phases identified as: Monteponite (CdO, PDF#05-0640); Quartz (SiO₂, PDF#83-2465); Hatrurite (Ca₃SiO₅, PDF#16-0406); Cadmium Silicate (Cd₂SiO₄, PDF#17-0258); Dmisteinbergite (CaAl₂Si₂O₈, PDF#74-0814); A; Cadmium Aluminum Silicate (CdAl₂Si₂O₈, PDF#31-0217)
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Cadmium concentrations in the leachates with the mixture of (a) Cd(NO)₃ + incineration residues and (b) CdO + incineration residues with two kinds of samples statement, after treated with 500-1000°C and 2 hours sintering processes. (c) leachate ratio of cadmium in Cd(NO)₃ + incineration residues reaction system. (d) leachate ratio of cadmium in CdO + incineration residues reaction system.
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