Cadmium Detoxification by Sintering with Ceramic Matrices

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The use of various low-cost and attainable ceramic matrices (amorphous SiO₂, γ-Al₂O₃, α-Fe₂O₃, and Fe₂O₃) to interact with Cd-containing waste is a promising method of Cd stabilization. Heating mixtures of cadmium oxide (CdO) and ceramic matrices at various molar ratios and temperatures (600-1000 °C) for 3 h could achieve the goal of Cd incorporation. Phase transformation was assessed using X-ray diffraction (XRD), and the efficiency of Cd incorporation was quantified through Rietveld analysis of the obtained XRD patterns. The XRD results show that Cd can be crystallochemically incorporated into Cd₅SiO₆, Cd₃SiO₇, Cd₃SiO₉, Cd₄Al₂O₇, and CdFe₂O₄ phases. The treatment temperature greatly affected the Cd incorporation reactions. The Cd incorporation efficiency was quantified and expressed as a transformation ratio according to the weight fractions of crystalline phases in the sintering products. To evaluate the metal stabilization effect of the Cd detoxification process, a series of constant-pH leaching tests was conducted. A remarkable reduction in Cd leachability was achieved by forming different Cd-hosting crystalline products, particularly spinel phase CdFe₂O₄. Overall, the efforts to stabilize Cd by sintering with ceramic matrices suggest a promising strategy for the detoxification of Cd in wastes.

Cadmium pollution control; Ceramic matrices; Detoxification; Leaching tests; Sintering; Thermal stabilization; XRD analysis.
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ABSTRACT

Cadmium (Cd) is often found in industrial sludge, fly ash, slag and flue gas, and it presents serious risks to the environment and biota. Stabilizing and detoxifying Cd in waste streams is thus of great importance. The use of various low-cost and attainable ceramic matrices (amorphous SiO₂, γ-Al₂O₃, α-Fe₂O₃ and Fe₃O₄) to interact with Cd-containing waste is a promising method of Cd stabilization. Heating mixtures of cadmium oxide (CdO) and ceramic matrices at various molar ratios and temperatures (600-1000 °C) for 3 h could achieve the goal of Cd incorporation. Phase transformation was assessed using X-ray diffraction (XRD), and the efficiency of Cd incorporation was quantified through Rietveld analysis of the obtained XRD patterns. The XRD results show that Cd can be crystallochemically incorporated into CdSiO₃, Cd₂SiO₄, Cd₃SiO₅, CdAl₂O₇ and CdFe₂O₄ phases. The treatment temperature greatly affected the Cd incorporation reactions. The Cd incorporation efficiency was quantified and expressed as a transformation ratio according to the weight fractions of crystalline phases in the sintering products. To evaluate the metal stabilization effect of the Cd detoxification process, a series of constant-pH leaching tests was conducted. A remarkable reduction in Cd leachability was achieved by forming different Cd-hosting crystalline products, particularly spinel phase CdFe₂O₄. Overall, the efforts to stabilize Cd by sintering with ceramic matrices suggest a promising strategy for the detoxification of Cd in wastes.

Keywords: Cadmium pollution control; Ceramic matrices; Detoxification; Leaching tests; Sintering; Thermal stabilization; XRD analysis.
ABBREVIATIONS AND NOMENCLATURE

$\text{Al}_2\text{O}_3$ - Alumina

AWWA – American Water Works Association

CPLT – Constant-pH leaching test

$\text{CdAl}_2\text{O}_7$ - Cadmium aluminate

$\text{CdFe}_2\text{O}_4$ - Cadmium ferrite

$\text{CdO}$ - Cadmium oxide

$\text{CdSi}_2\text{O}_3$ - Mono-cadmium silicate

$\text{Cd}_2\text{Si}_2\text{O}_7$ - Di-cadmium silicate

$\text{Cd}_3\text{Si}_5\text{O}_9$ - Tri-cadmium silicate

$d$ - the spacing between the lattice planes of the corresponding phase.

EPA – US Environmental Protection Agency

$G$ - Gibbs free energy

ICDD – International Centre for Diffraction Data

ICP-OES – Inductively coupled plasma optical emission spectrometry

MSW – Municipal solid waste

MSWI – Municipal solid waste incineration

MW – Molecular weight

PDF – Powder Diffraction File

QXRD – Quantitative X-ray diffraction

$S$ - Entropy

$\text{SiO}_2$ - Silicon oxide

SPLP – Synthetic precipitation leaching procedure

$T$ - Temperature

TCLP – Toxicity characteristic leaching procedure

TR – Transformation ratio

$V$ - Volume

WHO – World Health Organization

XRD – X-ray diffraction

$\lambda$ - the applied X-ray wavelength

$\theta$ - the angle between the incident beam and the scattering plane(s)
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1. INTRODUCTION

Contamination of air, water and soil by heavy metals is a pressing global issue that poses huge threats to the environment and public health, due to long- and short-term toxicological effects (1-3). Cadmium (Cd) is a heavy metal that is commonly found in zinc/lead mining waste, alkaline batteries, electroplating products, PVC stabilizers, semiconductors and solar cells (4,5). The release of Cd-containing pollutants from solid waste into the environment causes serious contamination (2,6,7). Cadmium accumulates in food chains and is easily absorbed by the human body, where it exerts toxic effects on health and results in a great number of acute and chronic diseases (including kidney failure, skeletal deformation and lung cancer) (6). In an attempt to eliminate Cd pollution in solid waste and from combustion processes, many techniques (such as solidification/stabilization by cement or sorption by minerals) have been developed (4,8-12). However, most of them have many inconvenient drawbacks, such as their low treatment efficiency, consumption of large amounts of raw materials and formation of undesired products (10,13,14).

Recently, a technology inspired by ceramic sintering processes has proved to be effective and reliable for the stabilization of heavy metals (including Ni, Zn, Cu and Pb) (15-19). The interactions of metal-containing waste with a series of inexpensive
and easily attainable ceramic matrices have been explored, and various stable ceramic (crystalline) products with high acid resistance have been formed. This novel technique has suggested a possible method for the stabilization of Cd-containing waste. In addition, studies have demonstrated that cadmium oxide (CdO) can thermally react with certain metal oxides (such as Al₂O₃, SiO₂ and Fe₂O₃) or Al/Si-rich materials (e.g., kaolinite and mullite) (20-25). With thermal treatment, a number of robust crystalline products with particular crystal structures can be harvested. Thermally treating CdO with these ceramic matrices suggests further possible and feasible techniques for Cd incorporation. However, the processing parameters and mechanisms of Cd incorporation should be determined by thorough investigation.

This chapter addresses the sources and toxicity of Cd, methods of Cd detoxification and techniques to evaluate the Cd stabilization effects. The feasibility of using various Al/Fe/Si-based ceramic matrices to detoxify Cd in wastes via a sintering process is investigated. The detoxification and stabilization of Cd can be achieved by transforming it into crystalline products. The influences of operational parameters (i.e., sintering temperature and the molar ratios of reactants) are considered in detail. Quantitative X-ray diffraction and constant-pH leaching test (CPLT) results reveal the metal incorporation efficiencies and metal stabilization effects of this method.

1.2 CADMIUM POLLUTION AND CONTROL TECHNOLOGIES

The rapid development of industrialization has generated a huge amount of solid waste, including mining waste, electronic devices, industrial and domestic sludge and incineration residues like bottom and fly ash (2,26-32). Such solid waste often contains large amounts of heavy metals and is a main source of environmental pollution. The toxicity of heavy metals has been widely studied. Their effects on human health have been well assessed by international organizations, such as the World Health Organization (WHO). The heavy metals Cd, Pb, Hg and Cr and most of their compounds have been classified as highly toxic and are known to be carcinogenic. Heavy metals tend to bioaccumulate in food chains and are eventually assimilated in living tissues (33). As they are non-biodegradable, they are very stable and persistent contaminants. Without adequate treatment, metal-containing waste will
release high levels of toxic metals, leading to air pollution and water and soil contamination (Figure 1).

Figure 1. Heavy metals risk to air, water bodies and soil.

Cadmium can be found in contaminated sites and in solid waste because it is widely used in many fields, including metallurgical alloying, electroplating, alkaline batteries, textile printing industries, metal plating, pigment works and ceramics (6,34-37). In recent years, the use of Cd has been increasing along with its emission to the environment, as Cd-containing products are rarely recycled and are habitually abandoned with household waste. The unstable Cd-containing waste contaminates the environment when it is disposed of in landfill or incinerated (2,35).

Incineration can greatly reduce the mass and volume of municipal solid waste (MSW) (38,39). The process creates a considerable amount of incineration residue, mainly composed of bottom ash and fly ash (39-41). Unlike organic compounds, metal species are not destroyed in high-temperature conditions and remain in the residue. Most of them condense and convert into metallic or metal oxide particles or airborne aerosols. Residues from the incineration of MSW are therefore usually enriched with toxic metals such as Zn, Ni, Cr, Cu, Pb and Cd (4,39-41). Concentrations of Cd from
24-1500 µg/m³ have been reported for flue gas from incinerating MSW, and most of this Cd eventually accumulates in fly ash (4). The largest source of Cd pollutants in MSW is Ni-Cd batteries, which contribute 60-70% of the total Cd, and the second largest source is waste plastics (42). Wan et al. found Cd content of 72 mg/kg in fly ash (43). In the fly ash from two incineration plants in China, the Cd contents were found to be 37 and 276 mg/kg (44,45). Quina et al. reported that the content of Cd in MSW residues ranged from 16 to 1660 mg/kg (46). Using an adsorption process to remove Cd from aqueous solutions produces a significant amount of waste containing Cd, with 98-600 mg Cd adsorbed per gram of adsorbent (47-52). Before disposal, the Cd-containing waste must undergo suitable pretreatment or stabilization to reduce its adverse effects on the environment (38,41,53-56).

Cadmium can induce a great number of acute and chronic illnesses, including renal damage, hypertension, emphysema, testicular atrophy and cancers (34,36,57,58). Due to its high toxicity, Cd has been classified as a group 1 carcinogen (59). According to a WHO document, the concentration of Cd in drinking water should not exceed 0.005 mg/L (60).

Cadmium-containing waste requires detoxification and metal stabilization before disposal. The development of novel and environmentally friendly technology should be adopted to control and reduce the harm of Cd-containing waste (37,58,61). A solidification/stabilization (S/S) process is commonly used for the treatment of most metal-containing waste, preventing the hazardous substances from migrating into the surroundings by physically fixing toxic contaminants and/or chemically bonding them to binders (22,62). Figure 2 shows a typical S/S process for toxic metal immobilization. In the S/S process, pollutants can be converted into less mobile, soluble and toxic forms using various stabilizers, additives or binders, such as cement, clay, fly ash, zeolite and red mud (63).
Common S/S technologies using sorption or cementation to immobilize metals may not reliably control metal leaching in a variety of acidic environments because the binding effect is not satisfactory in such environments (64). It is not possible to fix metals, especially highly mobile metals such as Hg, Cd and Pb, for long-term disposal because they are easily leached when the products are in acidic conditions (63). Furthermore, a large amount of cement would be consumed to achieve the goal of stabilization, which may lead to a significant increase in the volume of end-products.

Vitrification is an alternative approach to the treatment metal-containing waste (65-67). After vitrification, the metals are immobilized in glass matrices (67,68). This process can control and reduce the leachability of the harmful constituents of the treated products (69). However, high temperatures (1600-2000 °C) are required (70), causing a large amount of energy consumption. From the economic and environmental viewpoints, the development of energy-saving and cost-effective metal stabilization is of great importance.

1.2 THERMAL STABILIZATION TECHNIQUE
Feasible and effective technology used to detoxify metal-containing waste is urgently needed. Using a ceramic sintering process to thermally convert heavy metals into various robust crystal structures via reacting with ceramic matrices is a novel and promising waste management technique (16,17,19,71) and has become a mainstream research interest in the field of waste management (16,17,19,71).

By sintering mixtures of metal-containing waste and ceramic matrices, heavy metals can be incorporated into specific crystalline phases by driving atoms to their most energetically favorable positions. The crystalline products generally have good mechanical properties and high acid resistance, suggesting their potential for heavy metal stabilization (16,19,72,73). Ceramic sintering is therefore considered to be a good option for the treatment of different types of hazardous waste, including contaminated soil, industrial sludge and fly ash (61). It is important to note that comparing to vitrification method ceramic sintering can effectively incorporate toxic components at relatively low temperature, which makes it attractive from economic and environmental perspectives because less energy is required (74). Studies have demonstrated that waste containing relatively high contents of heavy metals, including Pb and Cd, can be successfully incorporated into ceramic products such as bricks and tiles (74,75). Figure 3 shows a typical ceramic sintering process.

![Figure 3. A typical ceramic sintering process.](image-url)
During the ceramic sintering process, a solid-state reaction occurs among the solid particles to transform the raw materials into a dense product upon heating. The consideration of thermal dynamics is one of the most important factors for the incorporation reaction. When sintering takes place, the free energy in the reactive system varies and such variation generates different driving forces. The driving forces generally include (1) particle surface free energy, (2) external pressure and (3) chemical reaction (76,77). Sintering can be achieved by increasing the driving forces via a physical or chemical process (78).

Sintering requires matter transportation among solid materials. The transportation of matter among solid particles can be triggered by various diffusion processes that involve atoms, ions or molecules (76,79). At the atomic level, diffusion is the process of atoms migrating from one lattice site to another. An intermediate stage with higher energy causes the transformation of different phases (77). In the intermediate stage, the energy barrier must be overcome so that the movement of atoms can occur. The energy required to overcome the energy barrier is the activation energy. The relationship between the energy \( P \) for an atom and the energy barrier \( q \) is expressed as

\[
P = \exp\left(-\frac{q}{kT}\right)
\]  

where \( k \) is the Boltzmann constant and \( T \) is the absolute temperature.

The Gibbs free energy (\( G \)) is an important parameter for the driving force of a reaction and can be used to examine the thermodynamic stability of the reaction. For an irreversible reaction, the change in \( G \) is expressed as

\[
dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp = -SdT + Vdp
\]

where \( S \) is the entropy and \( V \) is the volume of the reactive system (76,79).

In recent years, the synthesis, structure, properties and applications of versatile functional materials have become popular research topics in materials science and engineering. To understand the intrinsic characteristic of a new material, knowledge
of its crystal structure at different levels is essential. The fundamental level is the
electron configuration, which explains characteristics such as the material color,
optical properties, electrical conductivity and magnetic behavior (80). The distribution
of electrons in atoms determines the bonds that can form, which result in differences
in crystal structures. Furthermore, knowing the arrangement of atoms in the crystal
structure is crucial to understanding the mechanical and electronic properties of the
material. During sintering, crystalline and non-crystalline (amorphous) ceramic
products can be formed. In crystalline ceramics the atoms show a periodic
arrangement, and those in the non-crystalline ceramics such as glass do not have long-
range order. Crystals are constructed by regular atomic arrangements in three
dimensions, and such arrangements are repeated by the unit cell. The unit cell is the
smallest repeating unit in the crystal structure that shows the symmetry of the crystal
structure. The crystal systems can be classified as triclinic, monoclinic, orthorhombic,
tetragonal, hexagonal, rhombohedral (also called trigonal) or cubic (81).

4. CERAMIC MATRICES FOR CADMIUM DETOXIFICATION

It has been reported that some oxides (including SiO₂, γ-Al₂O₃ and α-Fe₂O₃) and
mineral compounds (including kaolinite and montmorillonite) can thermally react
with CdO to produce different Cd-hosting crystalline product phases. For the reaction
between CdO and SiO₂, an equilibrium diagram of a Cd-B-Si-O system was reported
(23). It can be seen from the phase diagram that three types of cadmium silicate can
be obtained after sintering mixtures of CdO and SiO₂ with different molar ratios of
Cd/Si. The phase diagram of a Cd-Al-O system shows that cadmium aluminates (e.g.,
CdAl₂O₄, CdAl₄O₇ and CdAl₁₂O₁₉) may be formed when sintering CdO with alumina.
This may offer an opportunity for Cd stabilization with alumina. According to
Kurihara and Suib (82), it is possible to obtain CdAl₂O₄ via a two-step synthetic
process (sol-gel and sintering). CdAl₄O₇ can be prepared via conventional solid-state
reactions by sintering mixtures of CdO and alumina (21). Few studies have mentioned
the formation of CdAl₁₂O₁₉, although Colin (21) stated that CdAl₁₂O₁₉ may be formed
by analogy with products from the reactions between β-Al₂O₃ and oxides (e.g., CaO,
BaO and PbO) under thermal conditions. Studies have indicated that CdFe₂O₄ can
form a Cd-Fe-O system by sintering CdO with α-Fe₂O₃ (83).
Silicon (Si) is the second most abundant element (after oxygen) in the Earth’s crust (84,85). Silica (SiO₂), the oxide form of Si, has many applications in science and engineering because it is chemically inert, thermodynamic stable, non-toxic and low-cost (86). Silica can be crystalline and non-crystalline. In crystalline silica, the Si and O atoms are arranged in a geometric structure. In non-crystalline (amorphous) silica, no spatial ordering of Si and O atoms is observed. Crystalline forms of silica include quartz, cristobalite and tridymite (87). Of these, quartz is the most common and is easily attainable from natural sources, such as rocks and soil, including arable loess and clay soils. The three types of amorphous silica are naturally occurring silica, silica formed under uncontrolled conditions and synthetic silica (87). Silica fumes comprising very fine amorphous silica particles are a by-product of the manufacture of silicon and ferrosilicon (88). Studies have demonstrated that silica fumes can fix heavy metals due to their large specific surface area and high amorphous silica content (89-91). Amorphous and crystalline silicon compounds are also commonly present in sewage sludge ash and MSW fly ash (92). Most silicates have good physical and chemical stability and thus have a wide range of industrial applications (93). Silicates can be prepared by various methods, including sol-gel, sintering and solid-state diffusion. It has been reported that Cd can react with silicates via solid-state reactions, forming different silicate products (23,94), and thus the use of silicates to stabilize Cd can be a promising strategy.

Aluminum (Al) is the third most abundant element in the Earth’s crust and accounts for 8 wt.% of its solid surface (95). Alumina (Al₂O₃) is the oxide form of Al. The common forms of alumina are α, γ, η, δ, θ, κ and γ forms. α-Al₂O₃ is the most stable phase and the other forms can be obtained by the thermal decomposition of aluminum hydroxides or oxyhydroxides (96). Aluminas are widely applied as raw materials in the manufacturing of various functional and conventional ceramic products. Among these aluminas, γ-Al₂O₃ is the most common oxide form of Al in nature. It has great application potential in many fields because of its unique crystal structure, large surface area, highly reactive nature, low cost and attainability (97,98). γ-Al₂O₃ has a cubic lattice in space group Fd3. Its crystal structure is often defective, which may promote the incorporation of metals (99-102).
Iron (Fe) is also one of the most abundant elements on Earth, and is common in the raw materials of ceramic manufacturing (17,103). Several iron oxides exist, including hematite (α-Fe₂O₃), magnetite (Fe₃O₄), maghemite (γ-Fe₂O₃), β-Fe₂O₃, ε-Fe₂O₃ and wustite (FeO). Both β-Fe₂O₃ and ε-Fe₂O₃ are uncommon in nature (104). Wustite is an intermediate in the reduction process of iron ores and is not thermodynamically stable (103-105). Hematite and magnetite are the two most widespread iron oxides in nature (103,104). Hematite has a corundum structure, and is the most thermodynamically stable of all the iron oxides. The close-packed arrangement of Fe and O atoms in hematite means that is has no charge excess or deficit. Magnetite is an inverse spinel and can be easily oxidized to maghemite and finally turned into hematite (103,104,106). Few studies have revealed the effects of different iron oxides on the formation of CdFe₂O₄. Hence, it will be of great interest to investigate the reaction of different iron oxides with Cd to form ceramic products.

1.4 XRD-BASED QUALITATIVE AND QUANTITATIVE ANALYSIS

Since the diffraction of X-rays was discovered in 1912, X-ray diffraction (XRD) has become an effective and reliable technique for phase analysis (107). XRD analysis can provide both qualitative and quantitative information on the phases in a tested sample (108,109). XRD is a reliable, precise and reproducible method that can identify the crystalline phases in solids (e.g., minerals and inorganic compounds) and reveal structural details of their phases (81,109,110). Consequently, XRD is extensively used to characterize natural and industrial materials with the support of detailed database information.

Every crystalline phase has a distinctive diffraction pattern. By analyzing the peak positions (corresponding to d values) and peak intensities in the XRD pattern, the crystalline phases in the sample can be identified. The phase analysis of XRD data is based on Bragg’s law (108) (Eq. 3) and indicates the peaks of crystal lattice scattering on the basis of two conditions: (i) the angle of the incident beam is equal to the angle of the scattered beam, and (ii) the path length difference is equal to an integer number of wavelengths.
\[ d = \frac{n \cdot \lambda}{2 \cdot \sin \theta} \]  

where \( n \) is an integer, \( \lambda \) is the applied X-ray wavelength, \( \theta \) is the angle between the incident beam and the scattering plane(s) and \( d \) is the spacing between the lattice planes of the corresponding phase.

With the fast development of computer science, the quantification of XRD data is now well developed (111,112). In addition to qualitative analysis, another very important feature of the XRD technique is that it can quantify the weight fractions of crystalline phases in the samples. Quantitative X-ray diffraction (QXRD) analysis is able to quantify the weight fractions of phases in a mixture by refining the XRD data following particular algorithms (113). QXRD analysis refines the lattice parameters of a unit cell, including coordinates, factors of temperature, atomic occupancies, profile parameters, 2\( \theta \) displacements, preferred orientation, background radiation parameters, extinction and micro-absorption (113). The orientation factors and scale factors of each phase are included in the refinement process.

![Diagram of XRD process](image)

Figure 4. Quantitative X-ray diffraction analysis with Rietveld refinement method for phase composition determination.
The methods of QXRD analysis include the reference intensity ratio (RIR) method, Rietveld method, profile stripping (or pattern subtraction) and full-pattern fitting (114-116). The Rietveld method is the most widely used for phase quantitative analysis and is used in combination with crystal structure models to calculate the XRD pattern for each individual component in the mixture (Figure 4). With a good refinement, the calculated pattern fits well to the observed diffraction pattern and the weight fraction data of crystalline phases can be obtained. The Rietveld refinement method provides not only the weight fractions of crystalline phases but also information about the refined crystal structure, such as lattice parameters, atomic occupancies and crystal size. The Rietveld method refines structures by minimizing a quantity with Newton-Raphson algorithms (113).

Ceramic sintering via solid-state reactions is one of the most effective and reliable ways to incorporate metals into crystalline products. The phase transformations that occur via solid-state reactions among CdO and ceramic matrices can be monitored and quantified by a combination of the XRD technique and Rietveld refinement method. The QXRD results can be used to assess the metal incorporation level and efficiency, as well as the stabilization mechanisms.

1.5 LEACHING TESTS FOR EVALUATING METAL STABILIZATION EFFECTS

Most pollution caused by metal-containing waste is due to the leaching of metals. The chemical durability of treated products should be examined by a series of leaching tests to assess metal stabilization (117).

Leaching is a relatively complicated reaction (118). A number of factors, such as chemical composition, pH, redox potential, complexation, liquid-to-solid ratio and contact time, influence the release rate and leaching behavior of the constituents of waste in different conditions (e.g., acidic or alkaline) (118,119). So far, over 50 leaching tests have been developed. Some of them (such as the toxicity characteristic leaching procedure (TCLP), SPLP and column leaching test) have been frequently used to evaluate the environmental consequences of MSW or industrial waste. The TCLP is one of the most commonly used methods for evaluating the leachability of
toxic metals from waste (120). It is a batch test developed by the United States Environmental Protection Agency for the assessment of the leachability of toxic metals from wastes (63). The pH significantly influences the substance surface potential, proton competition on surface binding sites and mineral dissolution (121). However, during leaching tests, the pH value is not constant, which may impede the leaching process and/or re-precipitation of metal compound(s) (122).

The constant-pH leaching test (CPLT) developed in our recent work can largely overcome the shortcomings of non-constant pH in other leaching tests. The CPLT can effectively examine the chemical durability of the tested materials and products due to its simplicity, improved reproducibility and shorter time requirements (123,124). It can be used to compare the dissolution or leaching behavior of test samples. The test is performed at a constant pH and no buffer solution is involved. Adding buffer solutions is a facile method of controlling the mobility of metals in the leaching system. However, the compounds in buffer solutions may form complexes with the metals, thus influencing the leaching performance of the tested sample (125). Therefore, the CPLT without buffer solutions can rapidly and precisely assess the leaching performance of the products of a well-controlled thermal treatment scheme.

2. EXPERIMENTAL METHODS

2.1 MATERIALS AND CHEMICALS

Cadmium oxide (CdO) was used to simulate the Cd source in the waste streams. Silica fumes (amorphous SiO₂), γ-Al₂O₃, α-Fe₂O₃ and Fe₃O₄ were selected as the ceramic matrices for Cd incorporation. γ-Al₂O₃ was prepared via thermally treating alumina powder (Pural SB (Sasol)) at 650°C for 3 h. Other ceramic matrices were used as received without further purification.

2.2 CADMIUM INCORPORATION

To examine the ability of ceramic matrices to incorporate Cd, CdO powder was individually mixed with the ceramic matrices at desired molar ratios of Cd/Si (1/1, 2/1 and 3/1), Cd/Al (1/4) and Cd/Fe (1/2). The mixtures were well mixed in a total weight
of 10 g by mortar grinding for 30 min in the presence of absolute ethanol. The mixtures were dried at 105 °C for 24 h in a vacuum oven, and then further homogenized by mortar grinding. Subsequently, the homogenous dried powder was pelletized into Φ 20 mm pellets at a pressure of 250 MPa. The pellets were subjected to a well-controlled thermal treatment scheme. The sintering temperature of the scheme was in the range of 600-1000 °C and the dwelling time was set at 3 h.

2.3 QUALITATIVE AND QUANTITATIVE XRD ANALYSIS

The fired pellets were cooled in air and then ground into powder for the XRD test. The step-scanned diffraction data of each powder sample were recorded on a Bruker D8 Advance X-ray powder diffractometer equipped with Cu Kα1,2 X-ray radiation and a LynxEye detector. The 2θ scanning range was from 10° to 80°. The step size was 0.02° and the scan speed was 0.5 per step. The phase analyses were performed by matching the collected XRD patterns with those derived from the standard powder diffraction database of the International Centre for Diffraction Data (ICDD PDF-2 Release 2008). With Rietveld refinement of the XRD patterns, the weight fractions (in percentages) of the phases in the sample were obtained. The refinement was performed on a TOPAS V4.0 program (Bruker AXS, Karlsruhe). A transformation ratio (TR) index was developed to assess the efficiency of Cd incorporation into Cd-hosting product phase(s). The TR was calculated as follows:

$$TR(\%) = \frac{\sum \text{wt\% of Cd-hosting product phase(s)} \times \text{MW of Cd-hosting product phase(s)}}{\sum \text{wt\% of Cd-hosting product phase(s)} \times \text{MW of Cd-hosting product phase(s)} + \text{wt\% of CdO} \times \text{MW of CdO}}$$ (8)

where MW is the molecular weight of the phase, g/mol. A TR of 0% indicates that no Cd was incorporated and a TR of 100% indicates complete transformation of Cd into the Cd-hosting products.

2.4 STABILIZATION EFFECT EVALUATION
The leaching performance of Cd-bearing samples (CdO, CdSiO₃, Cd₂SiO₄, Cd₃SiO₅, CdAl₄O₇ and CdFe₂O₄) were tested by the CPLT so that Cd leachability could be evaluated under acidic conditions. Nitric acid (HNO₃) aqueous solution (pH 4.0) was used as the leaching fluid and the pH of the leaching system was maintained at 4.0 ± 0.2 with the compensation of HNO₃ aqueous solution (1 M) in negligible volume (ca. 20 µL for each adjustment). The CPLT was implemented in a jar with 500 mL of leaching fluid. The weight of tested powders for each CPLT was 0.5 g. During the CPLT, the system was mechanically stirred at 200 rpm and 5 mL of leachate was removed at 10 min intervals. The leachate was filtered with a 0.2 µm syringe filter and then stored in a vial for the determination of metal concentrations by an inductively coupled plasma optical emission spectrometer (ICP-OES 800, Perkin Elmer). A standard for Cd was determined before and periodically during each sampling event to generate a satisfactory calibration curve.

3. RESULTS AND DISCUSSION

3.1 CRYSTALLINE PRODUCT FORMATION FOR CADMIUM DETOXIFICATION

By sintering CdO with silica fume (amorphous SiO₂), γ-Al₂O₃, α-Fe₂O₃ and Fe₂O₄ at 900 °C for 3 h, cadmium silicate (CdSiO₃, Cd₂SiO₄ and Cd₃SiO₅), cadmium aluminate (CdAl₄O₇) and cadmium ferrite (CdFe₂O₄) phases were formed (Figure 5). For the system of CdO + SiO₂, the Cd-hosting product phases were identified to be monoclinic CdSiO₃ (Eq. 9), orthorhombic Cd₂SiO₄ (Eq. 10) and tetragonal Cd₃SiO₅ (Eq. 11). The Cd incorporation by amorphous SiO₂ was highly influenced by the mixing ratios of the raw materials and by the sintering temperature. In the CdO + γ-Al₂O₃ system, the product phase was only CdAl₄O₇ with a monoclinic structure (Eq. 12), after 900 °C treatment for 3 h (126). In the CdO + α-Fe₂O₃ and CdO + Fe₂O₄ systems, only CdFe₂O₄ spinel was formed as a Cd-hosting product (Eq. 13) (127).

\[
\text{CdO} + \text{SiO}_2 \rightarrow \text{CdSiO}_3 \quad (9)
\]

\[
2\text{CdO} + \text{SiO}_2 \rightarrow \text{Cd}_2\text{SiO}_4 \quad (10)
\]

\[
3\text{CdO} + \text{SiO}_2 \rightarrow \text{Cd}_3\text{SiO}_5 \quad (11)
\]
\[ \text{CdO} + 2 \gamma\text{-Al}_2\text{O}_3 \rightarrow \text{CdAl}_4\text{O}_7 \]  
\[ \text{CdO} + \alpha\text{-Fe}_2\text{O}_3 \rightarrow \text{CdFe}_2\text{O}_4 \] 

Figure 5. X-ray diffraction patterns of sintered CdO + amorphous SiO\(_2\) (Cd/Si = 1/1, 2/1, 3/1), CdO + \gamma\text{-Al}_2\text{O}_3 (\text{Cd/Al} = 1/4) and CdO + \alpha\text{-Fe}_2\text{O}_3 (\text{Cd/Fe} = 1/2) at 900 °C for 3 h, showing the formation of Cd silicates, Cd aluminate and Cd ferrite for Cd incorporation by different ceramic matrices.
The transformation ratios for Cd incorporation are summarized in Figure 6 along with the weight fractions of crystalline phases in the sintered sample. The Cd incorporation started at 600 °C and was fully incorporated at 850 °C, when hematite and magnetite were used as ceramic matrices. At low temperatures, magnetite showed the highest Cd-incorporation efficiency; the TRs derived from the CdO + Fe$_3$O$_4$ system were much higher than those of other incorporation systems. The interactions between CdO and amorphous SiO$_2$ were triggered at 700 °C. Note that the transformation ratios for the CdO + amorphous SiO$_2$ system are the sum of the TRs for converting Cd into a specified Cd silicate, as it was found that the systems often contained more than one type of Cd silicate (Figure 5). Amorphous SiO$_2$ could effectively incorporate Cd at relatively low temperatures, as high TRs were achieved. The Cd-hosting product phase of the CdO + γ-Al$_2$O$_3$ system was CdAl$_2$O$_4$, which starts to form at 850 °C. This temperature is over 200 °C higher than those observed in the CdO + α-Fe$_2$O$_3$ and CdO + Fe$_3$O$_4$ systems. The ceramic matrices used in this study were able to completely incorporate Cd into various crystalline product phase(s). On the basis of these quantitative results, it can be inferred that although a relatively high incorporation efficiency was achieved by γ-Al$_2$O$_3$, more energy may be required to fully incorporate Cd when using γ-Al$_2$O$_3$ as matrix, as compared with other ceramic matrices.
Figure 6. Transformation ratios (TR) of different Cd detoxification systems. The SiO₂ represents silica fumes in amorphous phase.

For a solid-state reaction, the driving forces for mass transfer are related to the differences in the chemical potentials of the reactants. The standard Gibbs free energies of formation ($\Delta G^\circ_f$) for amorphous SiO₂, γ-Al₂O₃, α-Fe₂O₃ and Fe₃O₄ are -849.44 kJ/mol (128), -1563.85 kJ/mol (129), -774.4 kJ/mol (130) and -1012.7 kJ/mol (130), respectively. Among these values, the $\Delta G^\circ_f$ for α-Fe₂O₃ is the highest and thus it can be expected that the reaction between CdO and α-Fe₂O₃ is the most energetically favored. This may explain why α-Fe₂O₃ shows a greater Cd incorporation efficiency than do the systems using amorphous SiO₂ and γ-Al₂O₃ as matrices. Note that Fe₃O₄ will transform into α-Fe₂O₃ at low temperatures in the presence of oxygen and that the crystal size of newly formed α-Fe₂O₃ is generally much smaller than that of Fe₃O₄ (127). Reactants with small crystal size can stimulate the reactions and allow fast reaction kinetics. Therefore, higher TRs were obtained for Cd incorporation by Fe₃O₄ at temperatures below 750 °C.
3.2 EVALUATION OF METAL STABILIZATION EFFECT

Single phases of CdSiO₃, Cd₂SiO₄, Cd₃SiO₅, CdAl₄O₇, CdFe₂O₄ and CdO were prepared by mixing with SiO₂, γ-Al₂O₃ and α-Fe₂O₃ powders at defined stoichiometric molar ratios of Cd/Si (1/1, 2/1, 3/1), Cd/Al (1/4) and Cd/Fe (1/2). The well-mixed materials were pressed into pellets and then sintered in a temperature range of 850-1100 °C for various durations. The homogenization, pelletization and sintering processes were repeated to further ensure the complete reaction and homogeneity of the crystalline product phases. Their purity and crystallographic features were assessed by XRD (Figure 7). The XRD patterns further confirmed the successful synthesis of CdSiO₃, Cd₂SiO₄, Cd₃SiO₅, CdAl₄O₇ and CdFe₂O₄ phases. No diffraction peaks of the reactants were observed. The CPLT was used to examine the products' ability to resist acid attack.
Figure 7. X-ray diffraction patterns of the single phases of CdSiO$_3$, Cd$_2$SiO$_4$, Cd$_3$SiO$_5$, CdAl$_4$O$_7$ and CdFe$_2$O$_4$ for the constant-pH leaching test.

The Cd concentrations in the leachates of CdSiO$_3$, Cd$_2$SiO$_4$, Cd$_3$SiO$_5$, CdAl$_4$O$_7$ and CdFe$_2$O$_4$ phases are shown in Figure 8. The CPLT results show that the concentrations of Cd in the leachates of these product phases, particularly for CdSiO$_3$
and CdFe$_2$O$_4$, were remarkably lower than that in the leachate of CdO after 120 min leaching by nitric acid at constant pH 4.0. This indicates that superior stabilization and detoxification could be achieved by the formation of silicates, aluminate and spinel crystal structures. The leachability of Cd$_2$SiO$_4$ and Cd$_3$SiO$_5$ phases is more significant than that of other Cd-hosting product phases. The leaching behavior of Cd$_2$SiO$_4$ and Cd$_3$SiO$_5$ phases tends toward congruent dissolution, whereas the others (CdSiO$_3$, CdAl$_2$O$_7$ and CdFe$_2$O$_4$) display incongruent dissolution. The crystal structures of Cd$_2$SiO$_4$ and Cd$_3$SiO$_5$ together with the high content of Cd (over 70 wt.%) in these two phases suggests that Cd atoms may be more exposed to the leaching fluid, which may lead to a high dissolution of Cd from Cd$_2$SiO$_4$ and Cd$_3$SiO$_5$ phases. For Cd detoxification, converting Cd into CdSiO$_3$ and CdFe$_2$O$_4$ can reliably prevent Cd leaching under acidic conditions, compared with the CdO phase and other Cd-hosting product phases.

Figure 8. Leached Cd concentrations in the leachates of Cd-hosting products at the end of the constant-pH leaching test (120 min).
4. CONCLUSION

This chapter summarizes the emergence of heavy metal contamination, particularly Cd contamination, the current and new technologies for the control of Cd pollution, the potential ceramic matrices for Cd detoxification and quantitative approaches to assessments of Cd incorporation and detoxification. The possibility and feasibility of beneficially using various cost-effective and easily attainable ceramic matrices to convert Cd-bearing waste into stable crystal structures via a ceramic sintering process is considered. Ceramic sintering (a type of thermal treatment process) has been demonstrated to be a reliable strategy for transforming metal-contaminated substances into preferable crystalline phases. Four types of common ceramic matrix (SiO₂, γ-Al₂O₃, α-Fe₂O₃ and Fe₃O₄) were thermally reacted with Cd and their incorporation capabilities were quantified with a combination of the XRD technique and the Rietveld refinement method. The results show that CdAl₆O₁₇ was the only Cd-hosting product of sintering with γ-Al₂O₃. Silicates CdSiO₃, Cd₃SiO₄ and Cd₃SiO₅ were the predominant Cd-hosting product phases in the CdO + SiO₂ system. The formation of silicates was greatly affected by the sintering temperature and the Cd/Si molar ratios (1/1, 2/1 or 3/1). CdFe₂O₄ spinel was the only Cd-hosting product phase in sintered CdO + α-Fe₂O₃ and CdO + Fe₃O₄ systems. The CPLT results revealed that CdFe₂O₄ spinel is the most stable phase, suggesting that the formation of CdFe₂O₄ spinel is the most appropriate for Cd detoxification.
GLOSSARY

Cadmium: A minor metallic element, one of the naturally occurring components in the earth’s crust and waters, and present everywhere in our environment.

Ceramic matrices: Materials like clay that can be converted to ceramics after high temperature treatment.

Detoxification: The act of detoxifying.

Heavy metal: A general term which applies to the group of metals and metalloids and it has an atomic density more prominent than 4000 kg/m³.

Pollution control: A wide range of techniques, solutions, practices and services for treating wastewater and waste.

Sintering: Using heat or pressure to form a solid mass of material, without melting the material to the point of liquefying.

Solidification/stabilization (S/S): The process utilizes chemically reactive formulations that, together with the water and other components in sludges and other aqueous hazardous wastes, form stable solids.

Thermal stabilization: A heating process for metal incorporation into certain stable products.

XRD analysis: A technique can provide both qualitative and quantitative information on the phases in a tested sample.
REFERENCES


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