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# Cadmium stabilization via silicates formation: Efficiency, reaction routes and leaching behavior of products☆

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ABSTRACT

Stabilizing cadmium by incorporating it into crystalline products is an effective approach to detoxify cadmium-containing wastes. In this study, two Si-rich matrices in amorphous and crystalline forms (i.e., silica fume and $\alpha$-quartz, respectively) were employed to incorporate Cd. The processing parameters, namely the type of Si-rich matrix, Cd/Si molar ratio ($\Gamma$) and sintering temperature, were thoroughly investigated using quantitative X-ray diffraction technique. Cd incorporation was more energetically favored when silica fume was used rather than when $\alpha$-quartz was used because of the lower Gibbs free energy of formation for silica fume. The sintering temperature and $\Gamma$ values substantially affected the formation of three cadmium silicates, namely monoclinic $CdSiO_3$, orthorhombic $Cd_2SiO_4$, and tetragonal $Cd_3SiO_5$. $CdSiO_3$ formed only in $\Gamma = 1.0$ systems. $Cd_2SiO_4$ was dominant in all reactive systems. In $\Gamma = 3.0$ systems, $Cd_3SiO_5$ rather than $Cd_2SiO_4$ was the predominant Cd-hosting product at temperatures above 850 °C. Leaching test results demonstrated that $CdSiO_3$ possessed the highest acid resistance among the cadmium silicates. The leachability of $Cd_2SiO_4$ was very similar to that of $Cd_3SiO_5$. $CdSiO_3$ preferred incongruent dissolution, whereas $Cd_2SiO_4$ and $Cd_3SiO_5$ favored near-congruent dissolution. This study delineated the feasibility of cadmium incorporation by Si-rich matrices, identifying a promising approach for cadmium detoxification.



## 1. Introduction

The release of heavy metals into the environment, which causes contamination of air, water, and soil, is an urgent environmental concern that poses huge threats to human health (Järup, 2003; Prabhukumar et al., 2004; Su et al., 2018). Cadmium (Cd) is a heavy metal that is widely used as an industrial raw material in alkaline batteries, pigments, and metallurgical alloying because of its exceptional physical and chemical properties (Clemens et al., 2013; Pan et al., 2010; Wang et al., 2009; Saikia and Kojima, 2011; Fowler, 2009). However, the extensive application of Cd has inevitably led to its environmental release-whether incidentally or intentionally (Ono, 2013). For example, considerable amounts of Cd are often found in incinerator residues, such as those from scrubbers, electrostatic precipitators, bag-filters and fly ashes, because products containing Cd are habitually discarded as municipal solid wastes and most of them end up being incinerated (Ono, 2013; Tang and Steenari, 2016). Cd-rich wastes severely contaminate the environment and pose risks to human health (Järup, 2003; Satarug et al., 2003; Su and Wong, 2004; Tinkov et al., 2018). Cd and most of its

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compounds have shown long- and short-term toxicological effects and have thus been classified as carcinogenic substances since 1990 (NTP, 2014). Therefore, specific considerations and proper treatment of Cd-containing wastes are necessary.

Cement stabilization and vitrification are the two most commonly applied methods used to treat metal-containing wastes; these methods prevent the leaching of metals (Diaz-Somoano and Martínez-Tarazona, 2005; Ma et al., 2017). However, these methods have numerous shortcomings, including low efficiency, large consumption of energy, and generation of undesired products, which have largely impeded their application (Lee et al., 2005; Quina et al., 2008; Chen et al., 2009). The development of an effective and reliable technique to convert metal-containing wastes into crystalline products with superior acid resistance is one of the most urgent challenges in this field currently. Inspired by ceramic sintering processes, a low-cost technology that sinters metal-containing wastes with easy attainable precursors (e.g., alumina, kaolinite, and hematite) has recently been demonstrated to be effective and reliable for metal stabilization (Tang et al., 2011, 2013; Shih et al., 2006a; 2006b). Thermally reacting the metal-containing wastes with aluminum and iron precursors could produce various desired crystalline products with specific crystal structures that possess exceptional mechanical properties and excellent acid resistance ability, which would substantially reduce the release of toxic components into the environment (Matsuzawa et al., 2006). Furthermore, thermally treating metal-containing wastes at a low temperature (e.g., $\leq$1050 °C) associated with high metal incorporation efficiency is highly attractive from economic and environmental perspectives because it consumes less energy (Matsuzawa et al., 2006; Saikia and Kojima, 2011). In a waste-to-resource strategy, the stabilized products could be bricks or tiles intended for further use, as evidenced by extensive studies in which wastes with relatively high contents of heavy metals including Cd and Pb were converted into ceramic products (Saikia and Kojima, 2011).

Silicon (Si) is the second most naturally abundant element on earth (Imtiaz et al., 2016). Silicon oxides ($SiO_2$) are commonly present in many ceramic raw materials. $SiO_2$ can be amorphous or crystalline. Silica fume in amorphous form and $\alpha$-quartz in crystalline form are two typical types of silica (Nowak et al., 2013; Rodella et al., 2017). Previous studies have indicated that cadmium can react with silica via solid-state reactions under heating conditions, thereby forming various cadmium silicates (e.g., $CdSiO_3$, $Cd_2SiO_4$, and $Cd_3SiO_5$) (Glasser, 1965; Lonsdale and Whitaker, 1978). Silicates generally have high chemical and physical stability; therefore, they are prevalent in many industrial fields (Qu et al., 2009). Moreover, silica has been reported to exhibit versatile capabilities in heavy metal fixation (Li et al., 2014; Khan and Siddique, 2011; Huang and Huang, 2008), which suggests that using Si-rich matrices to thermally incorporate cadmium into silicates is a valuable technique. However, few studies have reported the mechanisms of cadmium incorporation and phase transformation when different types of silica (e.g., amorphous and crystalline phases) are used as matrices. Therefore, quantitatively evaluating how this factor plays a crucial role in cadmium stabilization through sintering with common Si-rich raw materials is necessary. The chemical durability of crystalline products should also be evaluated.

In the present study, we quantitatively elucidated the roles of amorphous $SiO_2$ (silica fume) and crystalline $SiO_2$ ($\alpha$-quartz) in cadmium incorporation under thermal conditions. The incorporation efficiency was quantified through quantitative X-ray diffraction (QXRD) analysis based on the Rietveld refinement method, and thus the incorporation routes occurred during the sintering process were delineated. The metal stabilization effects were examined through the constant-pH leaching test (CPLT). The CPLT results revealed the leachability and leaching behavior of product phases.

## 2. Experimental

### 2.1. Materials and sample preparation

Commercially available chemicals were purchased and used without further purification in this study. Cadmium oxide (CdO, Fisher Scientific) was used as a cadmium source, representing its major form in presintered wastes. The boiling (sublimation) point of crystalline CdO is 1559 °C (Inchem, 2017). The Si-rich matrices used in this study were amorphous and crystalline $SiO_2$. The amorphous $SiO_2$ was silica fume (99.8 wt.%) and the crystalline $SiO_2$ was $\alpha$-quartz (99.6 wt.%). Both were obtained from Sigma-Aldrich. Their intrinsic crystallographic qualities were confirmed through X-ray diffraction (XRD), as shown in Fig. A1. The specific Brunauer–Emmett–Teller (BET) surface areas ($S_{BET}$) of as-received CdO, silica fume and $\alpha$-quartz were $2.63 \pm 0.05$, $251.08 \pm 0.86$, and $6.05 \pm 0.07$ $m^2/g$, respectively. The $S_{BET}$ were measured using a Beckman Coulter SA3100 Surface Area and Pore Size Analyzer at 77 K and by employing the BET method. In practice, metal-contaminated wastes can be incorporated into ceramic products at very low levels to retain the desired properties of such products. However, to investigate the mechanism of cadmium incorporation, the precursors in this study were tailored by alternatively mixing CdO with silica fume or $\alpha$-quartz at Cd/Si molar ratios ($\Gamma$) of 1.0, 2.0, and 3.0. The mixtures were thoroughly blended using an agate mortar and pestle for 30 min. The well-blended mixtures were dried in a vacuum oven at 105 °C for 24 h and then homogenized again through mortar grinding. Subsequently, the mixtures were pressed into $\Phi$20 mm pellets (approximately 1.5 g per pellet) by applying a uniaxial pressure of 250 MPa without any binder. A 3 h sintering process at defined temperatures ranging from 700 to 1000 °C was performed. The adopted temperature range in this study has been proved to be capable of safely stabilizing cadmium (Su et al., 2015, 2018). During sintering, the temperature was increased and decreased at 10 °C per min.

### 2.2. XRD analysis

Powder XRD using filtered copper radiation was employed to characterize the phases of the sintered products. The fired samples were air-quenched and ground into powder form for powder XRD analysis. The step-scanned XRD pattern of each powder sample was recorded using a Bruker D8 Advance X-ray diffractometer equipped with a Cu $K\alpha_{1,2}$ X-ray radiation source and LynxEye detector. The diffraction data were collected with a step size of 0.02° and counting time of 0.5 s per step within a $2\theta$ range of 10°–90°. Qualitative phase identification was executed by matching the collected powder XRD patterns with those retrieved from the standard powder diffraction database of the International Centre for Diffraction Data (ICDD PDF-2 Release, 2008). Through phase analysis, four cadmium-hosting phases, namely CdO (PDF no. 75-0592), $CdSiO_3$ (PDF no. 35-0810), $Cd_2SiO_4$ (PDF no. 89-0218) and $Cd_3SiO_5$ (PDF no. 85-0575) were identified. These phases were used to quantify the efficiency of cadmium incorporation into silicate products. The crystal structure was refined and the phase compositions were quantified through the Rietveld refinement method by using the TOPAS V4.0 program (Bruker AXS, Karlsruhe). The weight fractions of the crystalline phases in each sintered sample are expressed as percentages (%) in this paper.

The efficiency of incorporating cadmium by Si-rich matrices through thermal reactions to produce the cadmium silicates $CdSiO_3$, $Cd_2SiO_4$ and $Cd_3SiO_5$ is expressed as a transformation ratio (TR, %) index. The TR is calculated as follows: