Zinc Stabilization Efficiency of Aluminate Spinel Structure and its Leaching Behavior

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ABSTRACT: The feasibility of immobilizing zinc in contaminated soil was investigated by observing the role of zinc reacting with aluminum-rich materials under thermal conditions. To observe the process of zinc incorporation, mixtures of ZnO with alumina precursors (γ-Al₂O₃ and α-Al₂O₃) were fired at 750–1450 °C. Both precursors crystallographically incorporated zinc into the ZnAl₂O₄ spinel structure. The incorporation efficiencies of a 3 h sintering scheme were first quantitatively determined by Rietveld refinement analysis of X-ray diffraction data. Different zinc incorporation behavior by these two precursors was revealed, although both resulted in nearly 100% transformation at the highest temperature. Different product microstructures and thermal densification effects were found by observing the sintered products from these two precursors. The leaching performances of ZnO and ZnAl₂O₄ were compared by a prolonged acid leaching test for 22 d. The leachability analysis pointed to superiority of the ZnAl₂O₄ structure in stabilizing zinc, suggesting a promising technique for incorporating zinc into the aluminum-rich product. Finally, the sludge collected from water treatment works was calcined and used as an aluminum-rich material to test its ability to stabilize zinc. Successful formation of ZnAl₂O₄ indicated good potential for employing waterworks sludge to thermally immobilize hazardous metals as a promising waste-to-resource strategy.

INTRODUCTION

Metal pollution is becoming an increasingly significant concern due to rapid industrialization in many regions of the world. The release of large quantities of hazardous metals into the natural environment has resulted in various environmental problems. Hazardous metals, such as zinc, copper, and chromium, are not biodegradable and can accumulate in nature, causing various diseases and disorders when exceeding specific limits.¹² The spread of such hazardous metals from mining operations or by the use of agrochemicals, for example,³ can contaminate the soil of surrounding areas.⁴,⁵ Traditional environmental remediation techniques (excavation and landfilling) are expensive, and only limited resources have been allocated to remediation of contaminated sites; thus, alternative techniques are sought.⁶

Many investigators have attempted to immobilize hazardous metals in contaminated soil by adding amendments that are able to adsorb, complex, or (co)precipitate elements in the soil.⁶–⁸ Zinc in soil can be immobilized by precipitation with hydroxides, carbonates, phosphates, and sulfides and by forming complexes with organic ligands.⁶,⁹,¹⁰ However, as a rather mobile element, zinc is easily out-competed by other cations for adsorption.¹¹ Because the mobility of metals is lowest when the soil is near neutral to slightly alkaline,⁶ the immobilization effect will be reduced when the soil pH becomes more acidic. It was demonstrated in our previous work that after the addition of aluminum-rich materials into hazardous metal waste, the metals can be stabilized by spinel structure formation through well-controlled thermal treatment schemes.¹²–¹⁵ By thermally reacting with alumina, hematite, and kaolinite precursors, the nickel and copper in the spinel-type crystalline structure were found to have substantial reduction in their leachability under acidic environments. Formation of zinc aluminate spinel (ZnAl₂O₄) from alumina (Al₂O₃) and zinc oxide (ZnO) has been reported in many high-temperature equilibrium experiments,¹⁶–¹⁸ and has also been found in thermally treated sediments.¹⁹ However, a reliable and applicable metal stabilization strategy requires quantitative understanding of the metal incorporation efficiency at a shorter processing time and more achievable temperatures, the metal leachability and leaching behavior of product, and the influence of different types of precursors.

As a waste-to-resource technology, the use of waste sludge resulting from water and wastewater treatment processes has attracted much attention.²⁰,²¹ In water treatment, for example, all processing systems generate a substantial amount of sludge with the residues of treatment chemicals used as coagulants (commonly aluminum-based), and the use of aluminum-rich
sludge as raw material for ceramic products has shown promise. Therefore, in this study, we attempted to quantify the reaction efficiency between zinc oxide and two types of alumina precursors within a sintering time of 3 h to assist in the exploration of different metal incorporation processes. This was followed by a prolonged leaching experiment to examine the zinc stabilization effect and the leaching behavior of the sintered products. Finally, the water treatment sludge rich in aluminum was reused as a ceramic raw material so that we could evaluate its potential for effectively stabilizing hazardous metals during the sintering process.

### EXPERIMENTAL METHODS

To study the zinc incorporation mechanism, experiments were conducted with samples prepared by firing ZnO separately with two alumina precursors (γ-Al₂O₃ and α-Al₂O₃). A sintering scheme with a 3 h dwelling time at the targeted temperature was used for temperatures ranging from 750 to 1450 °C. The ZnO powder was purchased from Sigma Aldrich, and the surface area was measured by the BET method, yielding 2.91 ± 0.06 m²/g. Qualitative phase identification of HiQ-7223 alumina was confirmed by X-ray diffraction (XRD) as boehmite (AlOOH), which converts to the γ-Al₂O₃ phase upon thermal treatment at 650 °C for 3 h. The α-Al₂O₃ (corundum) used as the other zinc stabilization precursor was obtained by further calcining the as-formed γ-Al₂O₃ at 1500 °C for 6 h (Figure S1 of the Supporting Information (SI)). To evaluate capacity for incorporating zinc under the sintering environment, a water treatment (waterworks) sludge sample collected in Hong Kong was heated for use as an aluminum-rich ceramic precursor. The sludge was dried and fired at 900 °C for 30 min to remove the organic content and then ground into powder for elemental composition analysis by X-ray fluorescence spectroscopy (XRF) (JEOL JSX-3201Z).

Samples for all sintering experiments were prepared by mixing each precursor with ZnO powder for a total dry weight of 60 g at a Zn:Al molar ratio of 1:2. The mixing process was carried out by ball milling the powder in water slurry for 18 h. The slurry was dried and homogenized by mortar grinding, then ground into powder for elemental composition analysis by X-ray fluorescence spectroscopy (XRF) (JEOL JSX-3201Z).

Phase transformation during sintering was monitored using the powder XRD technique. The step-scanned XRD pattern of each powder sample was recorded by a Bruker D8 Advance X-ray powder diffractometer equipped with a Cu Kα₁,₂ X-ray radiation source (40 kV 40 mA) and a LynxEye detector. The 2θ scanning range was 10–130°, and the step size was 0.02° with a scan speed of 0.3 s/step. Qualitative phase identification was executed by matching powder XRD patterns with those retrieved from the standard powder diffraction database of the International Centre for Diffraction Data (ICDD PDF-2, Release 2008). Zinc-containing crystalline phases found in products were ZnO (PDF#36-1451), ZnAl₂O₄ (PDF#05-0669), and corundum (α-Al₂O₃; PDF#10-0173).

Figure 1. XRD patterns of sintering (a) ZnO + γ-Al₂O₃ at 750 to 1450 °C for 3 h and (b) ZnO + corundum at 750–1450 °C for 3 h. The standard patterns retrieved from the ICDD database include ZnO (PDF#36-1451), ZnAl₂O₄ (PDF#05-0669), and corundum (α-Al₂O₃; PDF#10-0173).
The leachability of single-phase ZnO and ZnAl₂O₄ samples was tested by means of a leaching experiment modified from the U.S. EPA Toxicity Characteristic Leaching Procedure (TCLP), with a pH 2.9 acetic acid solution (extraction fluid #2) as the leaching fluid. Each leaching vial was filled with 10 mL of TCLP extraction fluid and 0.5 g of powder. The leaching vials were rotated end-over-end at 60 rpm for agitation periods of 0.75 to 22 d. At the end of each agitation period, the leachates were filtered with 0.2-μm syringe filters, the pH was measured, and the concentrations of all metals were derived from an Optima 3300DV inductively coupled plasma atomic emission spectrometer (PerkinElmer). The sample surface areas were determined from the nitrogen adsorption–desorption isotherms at liquid nitrogen temperature (77K) on a Beckman Coulter SA3100 surface area and pore size analyzer by Brunauer–Emmett–Teller (BET) method.

**RESULTS AND DISCUSSION**

**ZnAl₂O₄ Formation from Alumina Precursors.** Figure 1 collates the XRD patterns of the sintered samples within the temperature range of 750–1450 °C, and ZnAl₂O₄ is indicated as the predominant product phase after sintering. Therefore, the potential reactions between ZnO and the two alumina precursors (γ-Al₂O₃ and α-Al₂O₃) are expressed as follows:

\[
\text{ZnO} + \gamma\text{-Al}_2\text{O}_3 \rightarrow \text{ZnAl}_2\text{O}_4
\]

\[
\text{ZnO} + \alpha\text{-Al}_2\text{O}_3 \rightarrow \text{ZnAl}_2\text{O}_4
\]

When γ-Al₂O₃ was used as the precursor, the ZnAl₂O₄ spinel phase was clearly initiated with sintered at 750 °C for 3 h. However, when corundum was used as the precursor, the ZnAl₂O₄ spinel was first detected in the sintering product when the temperature reached 950 °C. Once the sintering temperatures were raised above those corresponding to the first appearance of the spinel phase, continuing growth of ZnAl₂O₄ was observed with increased peak intensity. The signals of reactants eventually diminished after 3 h of sintering at 1450 and 1250 °C for the ZnO + γ-Al₂O₃ and ZnO + α-Al₂O₃ systems, respectively.

To further quantify the variation of zinc incorporation efficiency in both precursor systems at different sintering temperatures, the distribution of crystalline phases in the products can be expressed by a "transformation ratio (TR, %)" index defined as follows:

\[
\text{TR(%) = } \frac{\text{wt\% of ZnAl}_2\text{O}_4}{\text{MW of ZnAl}_2\text{O}_4} \times \frac{\text{wt\% of ZnAl}_2\text{O}_4}{\text{MW of ZnAl}_2\text{O}_4} + \frac{\text{wt\% of ZnO}}{\text{MW of ZnO}}
\]

where MW = molecular weight. For TR = 100%, complete transformation of zinc into ZnAl₂O₄ spinel structure occurred.

Figure 2 summarizes the TR values of zinc incorporated into ZnAl₂O₄ phase when ZnO + γ-Al₂O₃ and ZnO + α-Al₂O₃ samples were sintered over the temperature range of 750–1450 °C. The reaction of zinc with γ-Al₂O₃ precursor was strong and even reached over 60% transformation at the lowest sintering temperature (750 °C). The zinc transformation continued to increase with the elevation in sintering temperature and reached nearly full incorporation after sintering at 1450 °C. In contrast, no ZnAl₂O₄ was observed when sintering ZnO with corundum precursor at temperatures below 850 °C. Nevertheless, when the sintering temperature reached 1250 °C, complete transformation of zinc into ZnAl₂O₄ structure (TR ≈ 100%) occurred.
The crossover of the two curves at about 1100 °C suggests that the ZnO and γ-Al2O3 interaction was dominant at lower temperatures, whereas the corundum precursor may greatly facilitate zinc incorporation at higher temperatures. The driving forces for mass transfer during sintering are the differences in chemical potential (free enthalpy or molar Gibbs energy) between fired materials.25 The value of ∆Hf° (standard enthalpy of formation) for γ-Al2O3 is +18.8 kJ/mol higher than that of corundum,26 and thus the reaction between ZnO and γ-Al2O3 is more energetically favored in comparison to that between ZnO and α-Al2O3. This may explain the greater zinc incorporation efficiency by γ-Al2O3 at lower temperatures.

**Influence of Precursors on Products Microstructure.** The product microstructure plays a vital role in affecting the mechanical properties and determining the potential product applications. The different types of alumina precursors were found to generate spinel-containing products with distinct microstructures. Part a of Figure 3 shows the product microstructure resulting from the mixture of ZnO and γ-Al2O3 sintered at 1350 °C for 3 h. On the electron scanning micrograph, the ZnAl2O4 product grains appear tightly associated with each other. The product sintered under the same conditions but with the corundum precursor appears to have finer spinel grains and contains numerous voids (part b of Figure 3). Because greater zinc incorporation efficiency was observed with the use of corundum precursor at higher temperatures (see Figure 2), the product microstructure suggests enhanced incorporation owing to the additional interfacial diffusion in ZnO + α-Al2O3 samples in comparison to the lattice diffusion dominant in sintering ZnO + γ-Al2O3 samples.

Although the change in product pellet size can be influenced by factors such as impurities, powder particle size, and sintering conditions, understanding the basic effect on pellet size caused by the zinc incorporation reaction is important. The overall densification or thermal expansion will reflect an increase or decrease in pellet sizes. Figure 4 demonstrates the pellet size variation after 3 h sintering, showing the different thermal effects when γ-Al2O3 and corundum were used as precursors. Interaction between ZnO and γ-Al2O3 led to a decrease in pellet diameters after sintering. Shrinkage due to the thermal densification of samples continued until the end of the sintering process, consistent with the increased zinc transformation into ZnAl2O4 phase shown in Figure 2. However, when corundum was used, the pellet diameters increased with increases in temperature through the same sintering process as with γ-Al2O3 as the precursor. The most significant expansion appeared at the temperature range of 950–1150 °C, and the pellet reached its largest size after complete zinc transformation was achieved, as
shown in Figure 2. In porous compacts, such as powder-pressed pellets, mass transport from grain boundaries to pores leads to densification. As a more efficient transport mechanism during sintering, grain boundary diffusion is determined by its intrinsic mobility and drag forces from pores. The pore drag is substantial at high porosity, and it decreases during densification. If the drag force falls below the required minimum, grain boundaries and pores become separated, and intragranular pore entrapment occurs. Because the surface area of $\gamma$-Al$_2$O$_3$ (204.8 m$^2$/g) is substantially greater than that of corundum (1.645 m$^2$/g), the larger pore drag forces in the $\gamma$-Al$_2$O$_3$ precursor system may lead to the stronger densification effect after sintering.

**Leaching Performance of ZnO and ZnAl$_2$O$_4$** To investigate the effect of zinc immobilization after incorporation by the spinel structure, the inherent leachability of the two zinc-containing phases, i.e., ZnO and ZnAl$_2$O$_4$, was evaluated through the prolonged TCLP leaching procedure. The as-received ZnO powder was used for the leaching experiment. To produce a powder sample with ZnAl$_2$O$_4$, as the single phase, a mixture of ZnO and $\gamma$-Al$_2$O$_3$ powders was prepared at a Zn/Al molar ratio equal to 1:2, pelletized, and sintered at 1350 °C for 48 h before being ground into powder form. The extended sintering time was to further ensure a complete reaction and homogeneity of the spinel formation. The XRD pattern of this synthesized ZnAl$_2$O$_4$ powder sample is shown in SI Figure S2. It illustrates the successful achievement of ZnAl$_2$O$_4$ phase without any peaks of reactant phases (ZnO or Al$_2$O$_3$) observed in the sample. The BET surface area of the ZnAl$_2$O$_4$ powder was 0.830 ± 0.022 m$^2$/g.

Throughout the 22 day leaching experiment, the pH values of ZnO and ZnAl$_2$O$_4$ leachates were monitored, as shown in part a of Figure 5, and the greater pH increase of ZnO leachate was revealed. Within the first 18 h, the pH of ZnO leachate increased substantially from 2.9 to 6.3, and then it remained at approximately 6.5 throughout the rest of the leaching period. In contrast, the pH of the ZnAl$_2$O$_4$ leachate remained at its initial value throughout the entire leaching period. The increase in the leachate pH may be due to the dissolution of cations through ion exchange with protons in the solution, accompanied by the destruction of crystals at the solid surface by the acidic leaching fluid. The results indicate that ZnAl$_2$O$_4$ is of higher inherent resistance to such acidic attack and that ZnO may be much more vulnerable to proton-mediated dissolution.

Because the leaching of a solid is likely dominated by surface reactions, such reactions are expected to be proportional to the sample surface area. In addition, because samples of the same weight (0.5 g) were always used, the total zinc content in each sample, subject to the different zinc phases, can be normalized for comparison. Part b of Figure 5 summarizes the amounts of leached zinc normalized with respect to the surface areas and the total zinc content of tested samples. After such normalization, the amount of leached zinc in the ZnO leachate was about 3 orders of magnitude greater than that in the ZnAl$_2$O$_4$. In comparison to ZnO, the ZnAl$_2$O$_4$ spinel demonstrated much higher inherent resistance to acidic attack, and thus the spinel incorporation strategy proved to be beneficial in stabilizing zinc. The inset of part b of Figure 5 further provides the details of the normalized zinc content in the ZnAl$_2$O$_4$ leachate.

When the pH of ZnO leachate reached about 6.5, the zinc concentration in the leachate stabilized at about 3000 mg/L (10$^{-13}$ M). As a general assumption of the cation-proton exchange mechanism, the destruction of zinc oxide by the acidic attack of the solution can be expressed as follows:

$$\text{ZnO}(s) + 2\text{H}^+(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{H}_2\text{O}$$  \hspace{1cm} (3)

However, the concentration of zinc ions in the solution [$\text{Zn}^{2+}(aq)$] is limited by the potential precipitation/dissolution reactions, such as in respect to Zn(OH)$_2(s)$:

$$\text{Zn(OH)}_2(s) \Leftrightarrow 2\text{Zn}^{2+}(aq) + 2\text{OH}^-(aq)$$  \hspace{1cm} (4)

where the solubility constant $(K_{sp})$ of eq 4 is 10$^{-16.35}$. At pH 6.5, the product of $[\text{Zn}^{2+}(aq)] \times [\text{OH}^-(aq)]^2$ was found to be 10$^{-16.3}$, which is very close to the $K_{sp}$ of Zn(OH)$_2(s)$. This indicates that the system was in equilibrium with Zn(OH)$_2(s)$ and explains why the zinc concentration stabilized at about 3000 mg/L after the substantial increase in the leachate pH during the first 18 h of leaching.

When leaching the ZnAl$_2$O$_4$ phase, a “congruent dissolution” through the cation-proton exchange reaction can be written as follows:

$$\text{ZnAl}_2\text{O}_4(s) + 8\text{H}^+(aq) \rightarrow \text{Zn}^{2+}(aq) + 2\text{Al}^{3+}(aq) + 4\text{H}_2\text{O}$$  \hspace{1cm} (5)

Such congruent dissolution would usually result in a theoretical $[\text{Al}^{3+}(aq)]/[\text{Zn}^{2+}(aq)]$ molar ratio of 2.0 in the leachates. However, this ratio was observed at 0.60—0.95 in the leachate of ZnAl$_2$O$_4$ as shown in part c of Figure 5. Because the system was maintained in a more acidic environment (about pH 2.9) and the zinc concentration was much lower than that in the ZnO leachate, the zinc concentrations in the leachates of ZnAl$_2$O$_4$ should be all considerably under-saturated with respect to the Zn(OH)$_2(s)$. Furthermore, the maximum aluminum concentrations measured in the ZnAl$_2$O$_4$ leachates were about 0.91 mg/L (10$^{-3.47}$ M), and the reaction of amorphous aluminum hydroxide (am $\cdot$ Al(OH)$_3(s)$) precipitation/dissolution is expressed as follows:

$$\text{am} \cdot \text{Al(OH)}_3(s) \rightarrow \text{Al}^{3+}(aq) + 3\text{OH}^-(eq)$$  \hspace{1cm} (6)

where the solubility constant $(K_{sp})$ of eq 6 is 10$^{-32.7}$. The product of $[\text{Al}^{3+}(aq)] \times [\text{OH}^-(aq)]^3$ was found to be 10$^{-37.8}$ in the leaching system, and it did not reach the saturation $(([\text{Al}^{3+}(aq)] \times [\text{OH}^-(aq)]^3) = 10^{-32.7})$ of amorphous Al(OH)$_3(s)$. Therefore, neither zinc nor aluminum ions were subject to reprecipitation from the leachates, and the observed $[\text{Al}^{3+}(aq)]/[\text{Zn}^{2+}(aq)]$ ratio may indicate incongruent dissolution of ZnAl$_2$O$_4$ in the leaching experiment, where the majority of the Al—O bonds still remained on the ZnAl$_2$O$_4$ spinel surface. Although some previous studies also suggested the possibility of surface reorganization of remaining molecules during the incongruent dissolution process, the overall result suggests the accumulation of aluminum-rich substance(s) on the surface of leached ZnAl$_2$O$_4$, which may also be beneficial for preventing further leaching of Zn from the spinel product.

**Potential of Using Waterworks Sludge for Zinc Stabilization.** Water treatment works in Hong Kong use aluminum-based coagulants (aluminum sulfate, aluminum chloride, poly aluminum sulfate, etc.) to facilitate particulate sedimentation. Because aluminum-rich ceramic raw materials ($\gamma$-Al$_2$O$_3$ and corundum) have shown high efficiency in the incorporation of zinc into spinel structure, the use of waterworks sludge as a precursor material to facilitate stabilization of zinc under thermal conditions may be a promising waste-to-resource strategy.
ZnO are not observable in the XRD patterns, whereas the ZnAl₂O₄ spinel is the predominant Zn-containing phase observed in the sample. Virtually all known drinking water processing systems generate enormous amounts of residual sludge, and what to do with this rapidly increasing waste stream in a beneficial and environmentally sustainable manner remains an important issue.²¹ In this study, the successful incorporation of zinc into the ZnAl₂O₄ structure by waterworks sludge at an attainable sintering temperature indicates that such sludge may be economically reused as an aluminum-rich material to immobilize hazardous metals in soils under thermal conditions. The waste-to-resource strategy of using waterworks sludge material, together with its role in facilitating natural resource remediation, may provide a strategy to further protect public health and enhance environmental sustainability.

■ ASSOCIATED CONTENT

* Supporting Information. Two tables and six figures demonstrating the powder XRD patterns of precursor materials, selected sintered products, and Rietveld refinement. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES


The weight losses of dry sludge heated at different temperatures are shown in SI Figure S3. The weight loss continued until the temperature reached 600 °C, when the maximum weight loss was around 47%. The sludge was further heated at 900 °C for 30 min so that the elemental compositions could be obtained via XRF. Normalization into metal oxides (SI Figure S4) shows aluminum to be the predominant constituent, and the XRD pattern (part a of Figure 6) further indicates that the aluminum component may exist as mullite and poor-crystalline phase(s) in the calcined sludge. A strong quartz signal was also found, which may reflect the second-largest component (silicon) detected by XRF.

At temperatures above 1150 °C, significant zinc incorporation was observed by alumina precursors, and therefore a sintering temperature range of 1150–1350 °C was used to investigate the incorporation of zinc into the sludge precursor. A mixture of ZnO and 900 °C calcined waterworks sludge at a Zn:Al molar ratio of 1.2 was prepared for the 3-h sintering scheme, and the XRD patterns show the success of incorporating zinc into the ZnAl₂O₄ spinel structure (part b of Figure 6). The diffraction peaks of ZnO are not observable in the XRD patterns, whereas the ZnAl₂O₄ spinel is the predominant Zn-containing phase observed in the sample. Virtually all known drinking water processing systems generate enormous amounts of residual sludge, and what to do with this rapidly increasing waste stream in a beneficial and environmentally sustainable manner remains an important issue. In this study, the successful incorporation of zinc into the ZnAl₂O₄ structure by waterworks sludge at an attainable sintering temperature indicates that such sludge may be economically reused as an aluminum-rich material to immobilize hazardous metals in soils under thermal conditions. The waste-to-resource strategy of using waterworks sludge material, together with its role in facilitating natural resource remediation, may provide a strategy to further protect public health and enhance environmental sustainability.

![Figure 6. XRD patterns of waterworks sludge sintered at (a) 900 °C for 30 min and ZnO + sludge mixture sintered at (b) 1150 to 1350 °C for 3 h. The standard patterns retrieved from the ICDD database include quartz (SiO₂, PDF#47-1144), mullite (3Al₂O₃·2SiO₂, PDF#79-1455), ZnAl₂O₄ (PDF#05-0669), and cristobalite (SiO₂ PDF#76-0938).](image-url)


