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Immobilization and encapsulation during vitrification of incineration ashes in a coke bed furnace

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Abstract

A real-scale coke bed furnace system has been successfully applied to vitrify the incineration ashes into glassy slags. The object of this research was to evaluate the effect of the system on the immobilization of metal species in the slag. Ashes and slag specimens were tested to identify their metal phase distribution following a sequential extraction procedure. The mobility of Al, Ca, Cd, Cr, Mg, Mn and Pb was noticeably reduced by vitrification. An important implication is the reduction of Cr^{6+} to Cr^{3+} along with its immobilization with this coke bed furnace. The Ni and Zn contents were relatively low in slag, indicating that their availability of mobile phases in ashes was reduced during vitrification. The XRD analyses identified the major crystalline phase in slag as åkermanite, which is inert and helpful in metal immobilization. The phase distribution analysis also contributed to verify that the incorporation of Ca and Mg enhanced the encapsulation in the slag matrix. The low oxygen content in slag made the structure of silicate resistant to the proton-promoted attack and also enhanced the mobility reduction of matrix elements (Ca, Mg and Al) in the moderately reducible phase and also contributed to the immobilization of other metal species. However, the properties of slag also deserve further studies to ensure its long-term stability and safety.
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1. Introduction

Incineration ashes may give rise to significant environmental pollution on disposal or during use due to the potential risk of releasing toxic organic compounds and/or heavy metals [1]. Vitrification is a promising technology for stabilizing ashes [2] since it can immobilize environmentally relevant metals into quartz-type silica lattices [1,3], reduce dioxin toxicity with a high efficiency (>99%) [4] and meet the criterion of sustainability [5]. It can also cut the ashes volume by 10–15% in bottom ash [6] and 80–85% in fly ash [7]. Among these melting processes, the coke bed furnace system particularly provides a reducing environment during vitrification, similar to that in the

iron-making process [8]. It was also reported that such a condition is preferred for the immobilization of metals in ashes [9].

In the previous research, the fate of heavy metal during vitrification in a coke bed furnace was reported [10]. In this study, the effect of a coke bed furnace with respect to immobilization of heavy metals in ashes was further evaluated by a sequential extraction procedure. The phase distributions of metals and crystalline phase of slag were identified in the investigation to study the stability of slag under a harsh extracting environment.

2. Materials and methods

2.1. Sampling and six-stage sequential extraction

The detailed process of a coke bed furnace was given in the previous report [10]. Ashes and slag were sampled and pulverized to a size that passed through a mesh 100 sieve, precisely

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weighted. The mobility of metals cannot be evaluated well as to their long-term actual performance in the field by current leachability tests. In this study, samples were extracted by a six-stage sequential procedure to identify the following phases and evaluate the immobilization of metals.

I. *Exchangeable cation phase*

Ashes (2 g) and slag (4 g) were added with a 20 mL, 1 M ammonium acetate solution, respectively, and shaken overhead for 2 h. The samples were centrifuged at 1000 rpm for 15 min, filtrated and then analyzed by ICP–AES.

II. *Carbonate phase*

The residuals from step I were extracted by a 20 mL, 1 M sodium acetate solution for 5 h. After overhead shaking, samples were ran through procedures same as step I for centrifuging, filtration and analysis in steps II through V.

III. *Easily reducible phase*

The mixture of a 35 mL, 0.1 M hydroxylammonium chloride solution and residual samples from step II were shaken for 15 h.

IV. *Moderately reducible phase*

The residual from step III and a 35 mL, 0.1 M ammonium oxalate/oxalic acid solution were shaken overhead for 15 h.

V. *Sulfide phase*

The residual samples from step IV were immersed in a 20 mL, 30% hydrogen peroxide solution. After the hydrogen peroxide was completely evaporated, a 20 mL, 1 M ammonium acetate solution was added in and the mixture was shaken overhead for 12 h.

VI. *Residual phase*

The residual samples were hermetically digested in an acid mixture ($HF:HNO_3:HClO_4 = 1:5:10$) in Teflon vessels at 180 °C for 5 h. After cooling, boric acid was added to neutralize excess hydrofluoric acid. The samples were then diluted exactly to 25 mL, filtrated and analyzed.

2.2. Instrumentation

Metal species analysis in extracts was carried out by an inductively coupled plasma–atomic emission spectrometer (Jobin Yvon JY-38 Plus ICP–AES). The concentrations of nine metal elements, including Al, Ca, Cd, Cr, Mg, Mn, Ni, Pb and Zn, in each sample were determined. In this study, each sample was tested in triplicates under the same sequential procedure.

The X-ray diffraction (XRD) analysis was performed to identify the crystalline phase of slag. It was carried out under 20 μm particle size, at 3°/min, in the $2\theta = 5$–75° range by a powder diffractometer (Geigerflex 3063) with Ni-filtered Cu Kα radiation on powders.

3. Results and discussion

3.1. Phase distributions of anthropogenic metal species

The composition of metal species in ashes and slag shown in Table 1 was excerpted from the previous study [10]. The phase

Table 1
Metal compositions in ashes and slag

Element	Ashes average (μg/g) (R.S.D., %)	Slag average (μg/g) (R.S.D., %)
Al	30200 (14.4)	64900 (16.8)
Ca	180000 (27.6)	189200 (4.43)
Cd	70.4 (13.4)	2.53 (26.6)
Cr	133 (21.4)	13.3 (29.6)
Mg	10500 (3.20)	21500 (7.91)
Mn	658 (9.16)	1130 (7.51)
Ni	80.6 (22.0)	8.99 (52.7)
Pb	4570 (33.5)	33.2 (15.6)
Zn	6090 (10.8)	2.55 (31.9)

distribution, the major concern in this research, of anthropogenic metal species (Cd, Cr, Mn, Ni, Pb and Zn) in ashes and slag were shown in Fig. 1 sequentially.

In ashes, the fractions of exchangeable cation, carbonate, easily reducible and moderately reducible phase of Cd were $44.9 \pm 6.4, 14.1 \pm 2.2, 21.1 \pm 9.0$ and $12.3 \pm 1.2\%$, respectively. With respect to slag, 16.5 ± 2.4 and $58.9 \pm 4.2\%$ Cd was found in the sulfide and residual phase, respectively. The results imply that when choosing a Cd immobilizing process a coke bed furnace seemed to be more preferable to the electric arc vitrification [6].

Chromium was distributed predominantly in the moderately reducible phase ($26.9 \pm 3.4\%$) and residual phase ($60.0 \pm 4.2\%$) in slag. In comparison to ashes, less availability of Cr was found in the first three phases. This is of environmental importance because easily reducible and mobile Cr^{6+} was reduced to Cr^{3+} which is much less toxic [6].

Manganese was available in the easily reducible phase ($14.5 \pm 5.6\%$), the moderately reducible phase ($29.8 \pm 4.8\%$) and the residual phase ($41.8 \pm 8.5\%$) in ashes. Most of Mn in slag was retained in the residual slag matrix ($86.6 \pm 2.4\%$) and a conspicuous reduction of the mobility was observed.

Nickel in ashes and slag were similarly distributed in the moderately reducible phase ($29.4 \pm 4.8, 18.5 \pm 1.3\%$) and in the residual phase ($58.6 \pm 12.3, 67.5 \pm 2.3\%$). The total Ni content of the first three phases in slag was trace (<1 mg/kg), indicating that the availability of mobile Ni in ashes was reduced during vitrification.

Lead in ashes mainly stayed in both the carbonate phase ($40.8 \pm 1.5\%$) and the residual phase ($38.7 \pm 1.5\%$). The fraction of Pb bound to the residual phase increased drastically to $75.1 \pm 1.8\%$ due to thermal decomposition of the carbonate.

Zinc in ashes spread among the exchangeable cation phase ($15.1 \pm 0.5\%$), the carbonate phase ($25.0 \pm 3.9\%$), the easily reducible phase ($10.9 \pm 4.6\%$), the moderately reducible phase ($12.6 \pm 1.6\%$) and the residual phase ($32.5 \pm 1.7\%$). After the thermal treatment, the Zn content in slag was only trace in comparison to ashes. This can be explained by evaporation during vitrification in a high-temperature environment [10]. Therefore, the immobilization of Zn in slag was not crucial for the stability of slag.
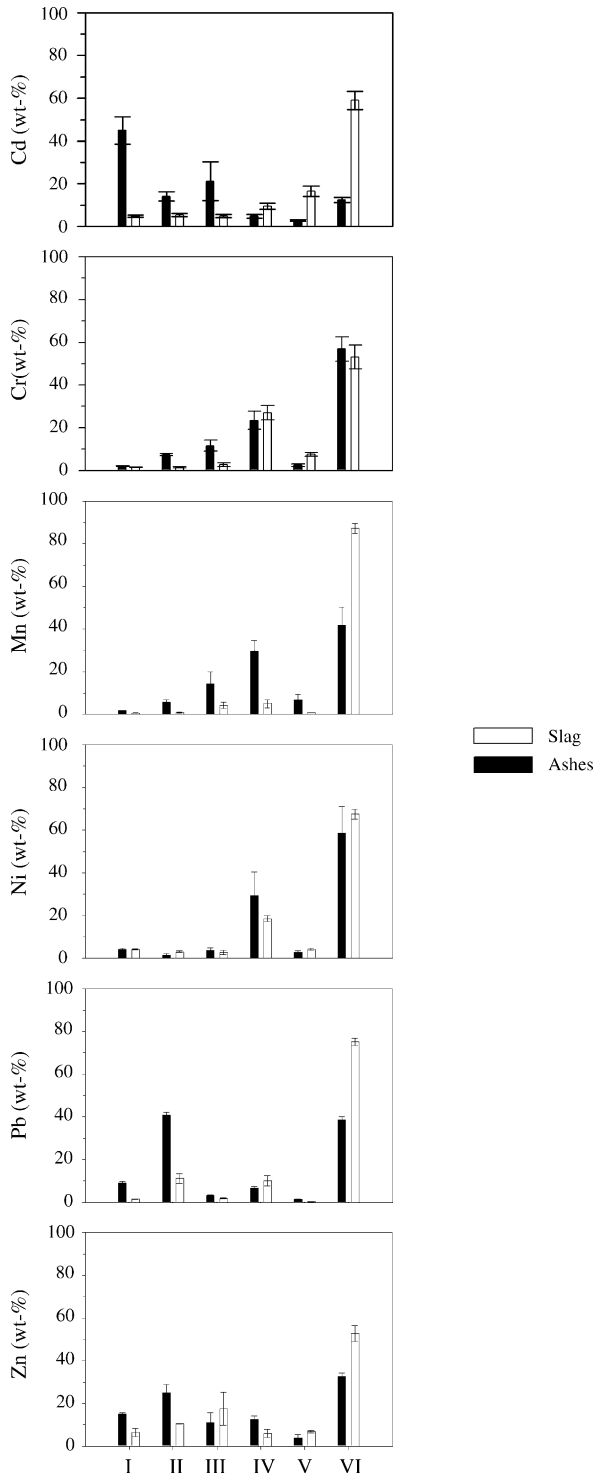
Fig. 1. Phase distribution of anthropogenic metal.

Fig. 2. Phase distribution of crust metal.

3.2. Phase distributions of crust metal species

The phase distributions of crust metal species, including Al, Ca and Mg, in ashes and slag are shown in Fig. 2, respectively. The fractions of the exchangeable cations, carbonates, easily reducible and sulfide phase contained relatively little Al in both ashes and slag. The ashes had most of Al mass in the moderately reducible phase ($71.3 \pm 6.1\%$) and the residual phase ($25.7 \pm 5.6\%$). Vitrification process raised the level of residual phase up to $83.4 \pm 1.2\%$.
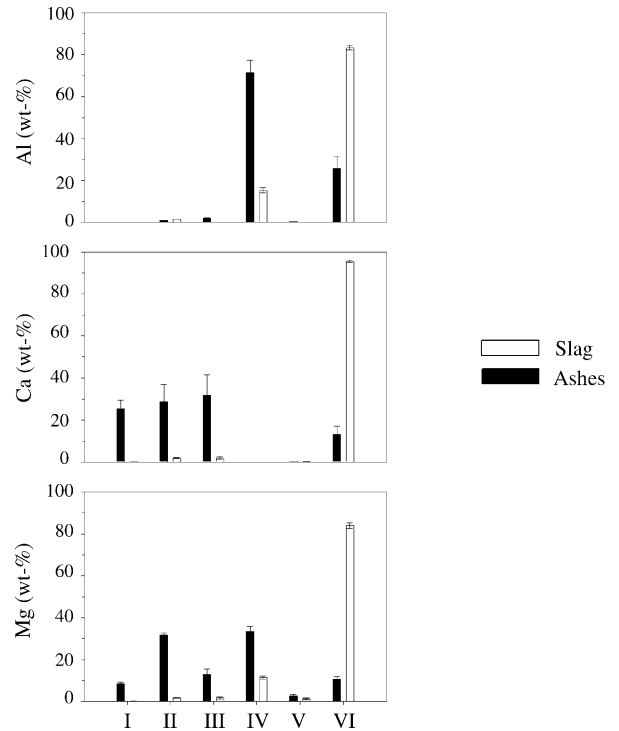
The fractions of the first three phases of Ca in ashes were 25.3 ± 4.2, 28.8 ± 7.9 and $32.0 \pm 9.3\%$, while the slag had $95.6 \pm 0.6\%$ of Ca mass in the residual phase. The leaching of Ca deserves more attention because it could lead to deterioration of the ashes structure and thus cause further leaching of hazardous metals.

Ashes had 8.47 ± 0.8, 31.7 ± 1.0, 12.9 ± 2.7, 33.4 ± 2.4 and $10.8 \pm 1.2\%$ of Mg mass in the exchangeable cations, carbonates, easily reducible, moderately reducible and residual phase sequentially. The melting process transformed the biggest fraction of Mg mass into the residual phase ($83.9 \pm 1.3\%$).

Fig. 3 shows the XRD analyses for slag, and identifies the major crystalline phase as åkermanite ($Ca_2Mg(Si_2O_7)$), which
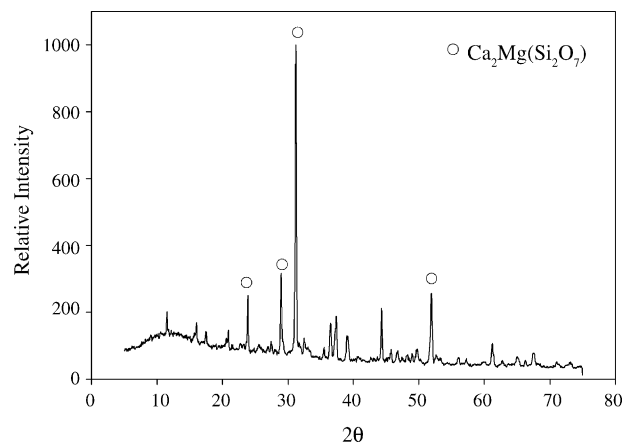

Fig. 3. XRD analysis for slag.

is inert material. In the melting process, åkermanite was found in a calcium-rich environment [7] and the Ca content was identified to be a critical factor in the formation of crystalline phase formation [7,11,12]. Lime elevates the melting point of mixed ashes [13] and also enhances the formation of double metal oxides, such as $CaSiO_3$ and Fe_2CaO_4 [14]. This furnace provides an energy-intensive environment (>1300 °C) which improves the chemical and physical property of slag [11] and promotes the formation of further more complex mineral to modify the glass network in slag and encapsulation of silica [15]. The crystalline phase was formed at the moment of quenching while encapsulation occurred simultaneously. XRD analyses and phase distributions of Mg and Ca point out that incorporation of these two metals strengthen the slag glass network and helps formation of an inert crystalline phase, hence suppress further leaching of hazardous metals.

The oxygen content (~10%) of slag was relatively low in comparison to that of other vitrification processes [10,16]. The characteristic of leaching step IV is the combination of proton-promoted dissolution and ligand-promoted detachment. The proton attack of oxygen bridging in the crystalline silicates was proportionally alleviated [6]. Hence, the availability of Al, Ca, and Mg in moderately reducible phase were reasonably lower than other oxygen-rich vitrification processes [6].

4. Conclusion

The anthropogenic metal species are either at trace levels or well immobilized in slag after vitrification of this coke bed furnace. The phase distribution of these metals can probably serve as an index for leaching deleterious metals. The mobility of matrix metals and crystalline phase analysis further verified the stabilization of slag. The relatively low oxygen content in slag under reducing conditions made the bridging of basic atoms in the slag matrix more resistant to proton-promoted dissolution and thus also contributed to the immobilization of metal species. However, for environmental and ecological concern, properties including the crystalline phase, the mobility of hazardous metals and slag matrix element deserve further studies to ensure the long-term stability and safety of slag.

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