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Studies on the solidification mechanisms of Ni and Cd in cement clinker during cement kiln co-processing of hazardous wastes

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HIGHLIGHTS

- Cd concentrated in Cao phases but distributed mainly in C_3S phases.
- Ni was mainly formed $MgNiO_2$, also present in C_4AF and C_3S.
- Cd and Ni solidified by isomorphous replacement and formation of a new or interstitial solid solution.
- Ca–Cd–O sosoloid and Ni–Mg compound were formed in solidification.
- Cd and Ni incorporated in C_3S by substituting Ca and in C_4AF by inter lattice space.

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ABSTRACT

To clarify the solidification mechanisms of heavy metals in cement clinker during the cement kiln co-processing of hazardous wastes, cement clinker samples were produced. EPMA[1] and XANES[2] spectroscopy were employed to acquire information on the microstructure and the Cd and Ni species formed in the cement system. The average Cd concentrations in CaO, C_4AF[3] and C_3S[4] were 3.92%, 1.21% and 0.75%, respectively, but Cd was mostly present in C_3S in clinker (71.0%). The solidification methods of Cd during the calcination process included the formation of a Ca–Cd–O sosoloid, substitution for Ca in C_3S and C_4AF (isomorphous replacement) and inter the space of the lattice (interstitial solid solution). Ni was combined mainly with Mg in the form of a new Ni–Mg compound (distribution ratio of 61.2%), which was $MgNiO_2$, as confirmed by XANES analysis. Ni was also present in C_3S and C_4AF (distribution ratios of 24.9% and 10.3%, respectively) by replacement of Ca^{2+} in C_3S and substituting Fe in C_4AF (isomorphous replacement), and also by inter the spaces of the C_4AF lattice (interstitial solid solution).

1. Introduction

Cement kilns possess inherent features that suit the treatment of hazardous wastes. These features include high temperatures and long residence times (greater than 1200 °C for several seconds), surplus oxygen during and after combustion, good turbulence and mixing conditions, and no generation of by-products such as slag, ashes, or liquid residues [1–3]. The co-processing of waste using cement kilns has been widely and successfully employed in the United States, Europe, Japan and other developed countries for several decades, and more recently in developing countries [4,5]. As far as wastes containing heavy metals are concerned, heavy metals are discharged to the atmosphere through gaseous emissions, but in the main, the metals reside in the cement clinker. Studies have indicated that the leaching rate of heavy metals in cement derived from the co-processing of waste is low [6–8]. The key reason for this is that the heavy metals in cement clinker and cement products have been solidified and are relatively inert to leaching.

The solidification of heavy metals in cement kiln co-processing wastes typically occurs by two processes, cement hydration and

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Abbreviations: EPMA, electron probe microanalysis; XANES, X-ray absorption near-edge structure; C_4AF, tetracalcium aluminoferrite; C_3S, tricalcium silicate; C_2S, bicalcium silicate; C–S–H, calcium silicate hydrate.

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[1] Electron probe microanalysis.
[2] X-ray absorption near-edge structure.
[3] Tetracalcium aluminoferrite.
[4] Tricalcium silicate.

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calcination. There has been much research on the solidification theory of heavy metals as a result of hydration [9]. In the cement hydration process, Cd is solidified by the formation of a mixed Ca/Cd hydroxide or Cd undergoes an exchange with Ca in a C–S–H gel [10,11]. Vespa et al. used unhydrated cement to condition a nitrate solution containing Ni. Results of X-ray absorption spectroscopy and scanning electron microscopy revealed that the main form of Ni in the cement-based solidified/stabilized wastes was a mixture of a Ni–Al layered double hydroxide phase and Ni $(OH)_2$ [9]. Sheidegger et al. also demonstrated that the formation of Ni- and Al-containing hydrotalcite-like layered double hydroxides is a relevant binding mechanism for Ni in cement [12].

Currently, several solidification effects of heavy metals in cement clinker have been reported. Barros studied the incorporation ratio of ZnO, PbO and CdO when the heavy metals were added to clinker raw material [13]. Additionally, when a galvanic sludge containing Cu and Ni was added to clinker raw material, at a ratio of 2.4 wt% and 1.2 wt%, these metals were totally incorporated into the clinker [14].

There have been relatively few studies on the solidification mechanism of heavy metal in cement clinker for the calcination process. Murat studied the effect of large additions of heavy metals to cement raw material on the composition and properties of the cement clinker. The results showed that Cd^{2+} enters the C_3S lattice by replacing Ca^{2+} in C_3S, Pb forms $PbSO_4$ and dissolves in C_3S and C_2S, and Cr is mainly distributed in C_2S [15]. Investigations by Zhang showed that, in the case of As, Cd, Pb and Zn, for calcinations in a cement rotary kiln and then hydration during cement application, the metals were more effectively fixed than in the case of cement-based solidification [16]. Clearly, the different retention mechanisms for co-processing and cement hydration result in different fixation effects for the heavy metals. As can be seen, the physical and chemical changes for heavy metals that occur in the calcination processes have not been fully characterized.

The purpose of this study was to clarify the solidification mechanisms of heavy metals in cement clinker during the cement kiln co-processing of hazardous wastes. Experiments were conducted for the simulation of the high-temperature calcination of cement raw material with the heavy metals of Cd and Ni. Microanalytical methods including electron probe microanalysis (EPMA) and X-ray absorption near-edge structure (XANES) analysis were employed to obtain information on microstructure and the species of heavy metals formed in the cement clinker.

2. Materials and methods

2.1. Characterization of raw materials

The cement raw materials, including limestone, clay and iron powder, were supplied by a local cement plant. The chemical compositions of the raw materials are listed in Table 1.

2.2. Sample preparation

The clinker was made in a laboratory furnace using industrial raw materials and heavy-metal compounds. Limestone, clay and iron powder were thoroughly mixed at a weight ratio of 76.5:21.0:2.5 and homogenized. The addition of heavy metals was based on considerations of current industrial practice and measurement requirements for EPMA and XANES analysis. Heavy-metal compounds were thoroughly mixed with the cement raw materials in accordance with the ratios listed in Table 2. The table also gives the total contents of heavy metals in mixed raw materials. Each mixture was calcined in the furnace at 1450 °C for 1 h to prepare the clinker, which was then smashed and milled to a powder having specific surface area of 310 m^2/kg.

Table 1
Chemical compositions of raw materials (%).

Material	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	Cd (mg/kg)	Ni (mg/kg)
Limestone	0.18	0.04	0.04	55.64	0.05	6.13	27.9
Clay	62.14	9.10	16.17	1.63	0.00	35.0	26.6
Iron powder	34.98	50.56	4.95	1.34	0.84	9.95	27.1

2.3. EPMA-EDS

The prepared clinker powder was compacted to clinker flake (thickness, 10 mm) using a press with pressure of 8 t/cm^2. The head of the press was polished to ensure that the clinker flake surface was smooth to facilitate EPMA. Energy dispersive spectrometry (EDS) was employed to determine the elemental content.

A JEOL JXA8800R EPMA analyzer and an Oxford ISIS300 X-ray energy spectrometer were used for analyses. The high voltage employed was 15 keV and the electron beam current employed was 2×10^{-8} A. Backscattered-electron images and X-ray images (elemental distribution images) were acquired. Standard samples of oxides and silicates were used for quality control of EPMA measurements.

The overall features of the clinker mineral phase were first observed with EPMA under low-power magnification (scale of 200 μm), and then typical mineral phases were measured under medium-power magnification (scale of 50–100 μm) in surface, line and point mode. Some mineral phases with fine particles were transferred to the high-power lens (scale of 20 μm) for further measurement.

2.4. XANES measurements

Cd and Ni K-edge XANES spectra were collected at the Beijing Synchrotron Radiation Facility. The typical energy of the storage ring was 2.5 GeV with the current decreasing from 250 to 160 mA during runs. Spectra for standard samples of CdO, $CdSO_4$, $CdCO_3$, $CdCl_2$–$2.5H_2O$, NiO, Ni_2O_3, $Ni(OH)_2$, $NiCO_3$–$Ni(OH)_2$–$6H_2O$, $NiSO_4$–$6H_2O$ and $NiCl_2$–$4H_2O$ were recorded in transmission mode. Clinker samples were measured in fluorescence mode. All standards were ground to fine grains and pressed to form wafers (diameter, 1.0 mm). Data processing of the XANES spectra was performed with FEFF8.0 software [17].

3. Results and discussion

3.1. Solidification process

The solidification of a heavy metal by cement clinker may be characterized by the fixation ration, which is expressed as

Table 2
Addition of heavy-metal compounds and heavy-metal content in mixture.

Items	Cd	Ni
Heavy metal compound	CdO	Ni_2O_3
Heavy metal addition ratio (%)	1	1
Amount added (g/kg)	22.84	28.18
Amount of raw material (kg)	1.98	1.97
Heavy metal content (mg/kg)	10,012	10,027

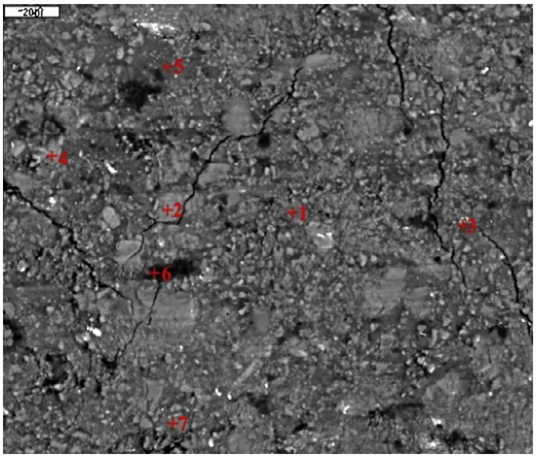

Fig. 1. Morphology of cement clinker with sites for analysis.