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Stabilization/solidification on chromium (III) wastes by C_3A and C_3A hydrated matrix

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HIGHLIGHTS

- The Cr leaching content of Cr-doped C_3A was higher than hydrated C_3A matrix in $Cr(NO_3)_3$ solution.
- Part of Cr^{3+} was oxidized to Cr^{6+} in the clinkering process and identified as $Ca_4Al_6O_{12}CrO_4$.
- The oxidant Cr^{3+} to Cr^{6+} resulted in the higher leaching of hydrated matrix of Cr-doped C_3A.

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ABSTRACT

Hazardous wastes are usually used in the Portland cement production in order to save energy, costs and/or stabilize toxic substances and heavy metals inside the clinker. This work focus on the stabilization/solidification on chromium (III) wastes by C_3A and C_3A hydrated matrix. The immobilization rate of chromium in C_3A and the leaching characteristics of the C_3A hydrated matrixes containing chromium were investigated by ICP-AES. The results indicated that C_3A had a good solidifying effect on chromium using the clinkering process, however, the Cr leaching content of Cr-doped C_3A was higher than that of hydrated C_3A matrix in $Cr(NO_3)_3$ solution and was lower than that of the hydrated C_3A matrix in K_2CrO_4 solution, no matter the leachant was sulphuric acid & nitric acid or water. To explain this, C_3A formation, chemical valence states of chromium in C_3A, hydration products and Cr distribution in the C_3A-gypsum hydrated matrixes were studied by XRD, XPS and FESEM-EDS. The investigation showed that part of Cr^{3+} was oxidized to Cr^{6+} in the clinkering process and identified as the chromium compounds $Ca_4Al_6O_{12}CrO_4$ ($3CaO{\cdot}Al_2O_3{\cdot}CaCrO_4$), which resulted in the higher leaching of hydrated matrix of Cr-doped C_3A.

1. Introduction

With the increasing contamination of the natural environment, the problem of heavy metal immobilization becomes more and more significant. Various technologies have been developed to render a waste non-toxic or to reduce the potential for the release of toxic species into the environment. Solidification/stabilization (S/S) processes using cement-based materials are one of the particularly appropriate ways to dispose heavy metal-contained wastes [1–4]. Heavy metals stabilization with traditional cement S/S process relies on the formation of calcium silicate hydrate ($CaO{\cdot}SiO_2{\cdot}nH_2O$, briefed as CSH), ettringite hydrate ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$, abbreviated as AFt) and monosulfate ($3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}12H_2O$, abbreviated as AFm) in the matrix [5]. Recently, utilization of heavy metal-contained wastes as raw materials in the clinkering process has been investigated substantially [6–12]. However, in order to effectively utilize the heavy metal-contained waste in cement-manufacturing processes, mechanism and environmental aspects on stabilization/solidification of these wastes must be known.

Tricalcium aluminate (C_3A) is one of the main constituents of Portland cement. Even though it is typically less than 10% of the total composition, its uncontrolled reaction with water can lead to rapid setting. The hydration of C_3A-gypsum system leads to the formation of ettringite [13]. Many studies have been done on the incorporation of heavy metals in synthesized ettringite or ettringite-based solidification systems. X.C. Qiao [14] investigated the influence of individual heavy metal on the hydration reactions of major cement clinker phases (C_3S and C_3A). V. Albino [15] reported potential of ettringite generating systems in the stabilization processes of hazardous wastes, and results indicated that sulphoaluminate phase crystals were able to accommodate part of the metal in each case. Results also showed that Al^{3+} can be replaced

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Table 1
Mix proportion of C_3A hydrated matrix (wt%).

No.	C_3A	Gypsum	W/C	Chromium type	Chromium content
A*	28	72	0.8	–	–
B	28	72	0.8	$Cr(NO_3)_3{\cdot}9H_2O$	1.79
C*	28	72	0.8	–	–
D	28	72	0.8	K_2CrO_4	0.87

* A is the pure C_3A; C is Cr-doped C_3A (1%Cr_2O_3).

by some trivalent ions like Fe^{3+}, Cr^{3+} and Mn^{3+}, Ca^{2+} can be substituted by bivalent ions as Zn^{2+}, Mn^{2+}, Co^{2+} or Ni^{2+}. Moreover, SO_4^{2-} can be replaced by SeO_4^{2-}, CrO_4^{2-} etc. [16–22].

Chromium is a common heavy metal present in cement clinkers, and its possible sources are raw materials, mineral admixtures, fuels, chromium-containing waste and kiln refractory bricks [23]. It is known that chromium has a wide range of oxidation states, in which Cr(III) and Cr(VI) are the most common. D. Rai [24] reported that Cr(VI) has higher toxicity, solubility, and mobility than Cr(III), so it is much more harmful to human health and the environment. Suthatip Sinyoung [25] had found that the valence of chromium might oxide into +4.6, +5, and +6 during the production of cement clinker at the presence of Cr_2O_3. Frías [26] also noted that Cr(III) can be partly oxidized to Cr(VI) during the clinker burning process, which significantly increases the harmfulness of the residual chromium in the clinkers. Several studies have shown that there is a lack of chemical fixation of the concentrations of Cr(VI) in cement based S/S technology [27,28]. Trivalent chromium is more likely to be precipitated or sorbed than hexavalent chromium under most conditions [4]. So, the relationship between the chemical forms and the leaching or migration characteristics of chromium in C_3A and C_3A hydrated matrixes must be known.

The main purpose of this paper is to investigate the stabilization/solidification technologies for chromium, as a raw material containing chromium when producing cement clinker. The valorization of chromium in cement kilns is also considered because some heavy metals may affect the burning property of cement clinker and some of them may evaporate during the process of sintering. The Cr immobilization rate of chromium in C_3A and the leaching characteristics of the C_3A hydrated matrixes containing chromium were investigated by ICP-AES. In order to explain the leaching or migration mechanism of Cr in the C_3A clinkering and hydration process, C_3A formation, chemical valence states of chromium in C_3A, hydration products and Cr distribution in the C_3A-gypsum hydrated matrixes were studied by XRD, XPS and FESEM-EDS. The data can provide a useful basis for further utilizing the chromium wastes in cement kilns or others industries with high-efficiency and safety.

2. Experimental

2.1. Samples preparation

Pure C_3A was produced by sintering stoichiometric amounts of $Ca(OH)_2$ and Al_2O_3 (reagent grade) by a molar ratio of 3:1 in a ball mill for 12 h. The mixtures were pressed and molded into discs forms, then the molded specimens were sintered three times at 1320 °C, each time for 3 h. Cr-doped C_3A sample was produced from pure C_3A, which were mixed with the 1, 3, 5, 10 wt% Cr_2O_3 (Cr, introduced as Cr_2O_3) and then burned twice for 3 h and ground to <125 μm. Between the intervals, the samples were ground and remolded into discs with anhydrous alcohol.

In order to investigate stabilization/solidification on the chromium (III) wastes by C_3A mineral and C_3A hydrated matrix, the C_3A doped chromium (C), the pure C_3A sample containing $Cr(NO_3)_3{\cdot}9H_2O$ (B) and K_2CrO_4 (D) for the leaching and hydration characteristics were prepared as shown in Table 1. The hydration samples were performed at 25 °C and at a water to cement ratio of 1:1, pastes were cured for 3d and 7d in sealed containers to avoid being carbonized.

2.2. Methods

Free CaO of the sintered samples was determined according to Glycerin–ethanol method. The X-ray diffraction (XRD) patterns of C_3A and the hydrated matrixes were examined by a D/max-IIIA X-ray diffractometer, using Cu Kα radiation and a position sensitive detector. Immobilization rate of Cr in C_3A phase was calculated by the change of the Cr concentration.

The Cr-doped C_3A samples were dissolved by a mixture of $HCl–HNO_3–HClO_4–HF$ and the Cr concentration of the dissolved solutions was determined by means of an Optima 4300DV Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).

Chemical valence states of Cr in the sintered C_3A samples were investigated by X-ray photoelectron spectroscopy (XPS) analyses, which were carried out using a Kratos XSAM 800 photoelectron spectrometer fitted to a custom-built vacuum chamber. A portion of the bulk sample was ground into a fine powder and pressed into a stainless steel sample holder. The analysis chamber was maintained at 6×10^{-7} Pa. Mg Kα radiation (1253.6 eV) was employed throughout the experiment.

The morphology of the hydrated C_3A matrixes were carried out with a JEM-2100F field-emission high resolution transmission electron microscopy (FESEM) and the accelerating voltage was maintained at 160–200 kV. The elemental micro-analyses of the samples were identified by an energy dispersive X-ray spectroscopy (EDS) coupled with the FESEM system. The resolution power of EDS is 132 eV and the testing time is set to 50 s.

Two leachants were used to identified the leaching toxicity of the 3d and 7d hydrated pastes. One was determined according to Chinese National Standard Solid Waste-Extraction procedure for leaching toxicity-sulphuric acid & nitric acid method (HJ/T 299-2007) [29] which was to modify the acid rain condition, another leachant was water, and the detailed procedure was the same with HJ/T 299-2007. The concentration of Cr ions in the filtrate solution was determined by ICP-AES.

3. Results and discussions

3.1. Free CaO (f-CaO) and immobilization rate of Cr

The f-CaO content of C_3A is a good indicator to evaluate burnability of the sintered samples. A reduce of f-CaO content means an improvement in the burnability incorporating some metals with the specific concentration. In contrast, a rise of f-CaO means deterioration on the burnability [30]. The effect of Cr on f-CaO content of the sintered samples was given in Table 2.

The f-CaO of all C_3A samples decreased with the subsequent increase of sintered times and chromium content. After sintered 3 times, f-CaO of the pure C_3A and the C_3A doped 1% chromium were only 0.48% and 0.28%, respectively. The results indicated that the incorporation of chromium could reduce the sintering temperature and was favorable to the burnability of C_3A.

Cr did not fully solidify in C_3A mineral phase, however, the immobilization rate of chromium in the Cr-doped C_3A increased with the increasing of the chromium content. Immobilization rate of the sample containing 1% chromium reached 82.42%. These demonstrated that C_3A had a good solidifying effect on chromium in the clinkering process.