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Double-Barrier mechanism for chromium immobilization: A quantitative study of crystallization and leachability

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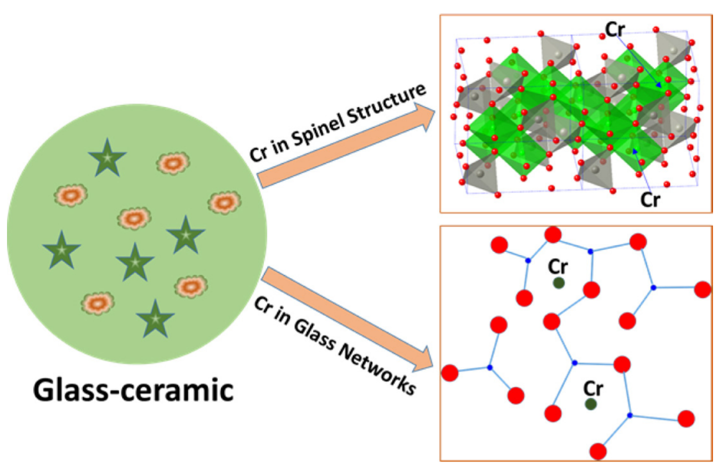
HIGHLIGHTS

- The glass-ceramic samples were proven to be excellent in immobilizing Cr.
- Glass-ceramic was successfully synthesized in CaO-MgO-SiO_2-Al_2O_3 -Cr_2O_3 system.
- Both crystalline and glass phases were quantified by Rietveld quantitative XRD.
- The partitioning ratio of Cr into spinel in the glass-ceramic can be up to 90%.

GRAPHICAL ABSTRACT



Schematic illustration of chromium incorporating in the glass-ceramic matrix. Most chromium contents are incorporated into spinel structure where the residual chromium are resided in the glass networks.

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ABSTRACT

Glass-ceramics are well known for the excellent combination properties provided by their components, a glassy matrix and crystalline phases, and have promising applications in the immobilization and detoxification of solid waste containing toxic metals. Glass-ceramic products were successfully synthesized in CaO-MgO-SiO_2-Al_2O_3 -Cr_2O_3 system. Two key measures – partitioning ratio of Cr in the spinel and Cr leaching ratio – were used to investigate the mechanism of Cr immobilization in the glass-ceramic products. The results of powder X-ray diffraction revealed that both spinel and diopside were major crystalline phases in the products. The value of x in the $MgCr_xAl_{2-x}O_4$ spinel was highly related to the amount of Cr_2O_3 added to the glass-ceramic system. As Cr_2O_3 content increased, the proportion of spinel phase increased, while that of glass phase decreased. The partitioning ratio of Cr in spinel phase was about 70% for 2 wt.% Cr_2O_3, and increased to 90% when loaded with 10 wt.% of Cr_2O_3. According to the results of the

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prolonged toxicity characteristic leaching procedure, the Cr leaching ratio decreased with the increase of Cr partitioning ratio into the spinel phase. The findings of this study clearly indicate that glass-ceramic formed by spinel structure and residual glass successfully immobilized Cr.

1. Introduction

Millions of tons of chromium (Cr) slag worldwide have been dumped and spread over large areas without receiving appropriate treatment at industrial sites. This has caused severe environmental problems in many countries [1]. The continuous leaching of hexavalent Cr, Cr(VI), from Cr slag can seriously contaminate the surrounding environment, such as soil, sediment, underground water, and surface water [2–4]. For example, the Cr concentration of soil and sediment at contaminated source sites may be very high—in some cases exceeding 10,000 mg kg^{-1} [5]. Environmental Cr contamination poses a serious threat to humans, plants and animals. Therefore, an effective method of treating Cr slag is urgently required to protect the environment and human health. In the environment, Cr(III) and Cr(VI) are the two common oxidation states. Generally, Cr(VI) is much more mobile and more toxic than Cr(III) [6,7]. In addition to the hazards caused by their strong oxidation properties, chromate ions ($CrO_4{}^{2-}$) pass through cellular membranes many orders of magnitude faster than do Cr(III) species, resulting in much greater toxic effects on cells [8,9]. All Cr waste must be treated properly before being reused or released to the environment. Stabilization/solidification (S/S) treatment can reduce the mobility of heavy metals by converting hazardous waste into chemically stable solids [10–12]. However, S/S processes have rarely been successfully used to prevent the leaching of toxic metals in acidic environments [12].

Deriving excellent properties from the combination of a glassy matrix and embedded crystalline phases, [13] marketable glass-ceramics have been prepared from blast-furnace slag, fly ash, sludge, and glass cullet. [14–17] Converting waste to useful glass-ceramics is considered a promising method of protecting the environment and promoting sustainable development. Glass-ceramics are usually produced from the controlled crystallization and devitrification of glass [18], and nucleation processes are critical throughout their fabrication. [19–21] The major components of Cr slag have been shown to be calcium (Ca), magnesium (Mg), silicon (Si), and aluminum (Al) [7], which make up the glass-ceramic matrix. In addition, Cr_2O_3 has been found to be an effective crystallization nucleant during glass production in a quartz sand-dolomite-magnesite system [22] and an SiO_2-Al_2O_3-CaO-Fe_2O_3 system [23]. Barbieri et al. [24] also found that $MgCr_2O_4$ spinel crystallites act as heterogeneous nucleation sites for diopside and anorthite phases after the addition of Cr_2O_3 to an SiO_2-Al_2O_3-CaO-MgO system. However, the above work did not point out the distribution of Cr in glass-ceramic products nor the formed Cr-bearing phases. To ensure the safe and effective reuse of Cr slag as marketable glass-ceramics, Cr should be immobilized to ensure that very little can leach out when the glass-ceramic products are used in the environment. Based on the major reported components of Cr waste, a simulated Cr slag with the system of CaO-MgO-SiO_2-Al_2O_3-Cr_2O_3 was designed in this study [25]. Previous research has shown the promising performance of spinel structures in hosting hazardous metals, and that the metal leachability of the spinel phase is several orders lower than that of metal oxides [26–29]. Therefore, the reported formation of Cr spinel in the CaO-MgO-SiO_2-Al_2O_3-Cr_2O_3 system [25] is expected to greatly facilitate the immobilization of Cr in glass-ceramic products.

Crystalline-phase parameters have been reported to be one of the most important factors affecting the properties of glass-ceramics [30,31], and the formation of crystalline phases is acknowledged to be critical to metal stabilization in glass-ceramics [18,32,33]. Therefore, it is essential to identify the structure and quantify the crystalline phases in glass-ceramic products. Rietveld quantitative X-ray diffraction (QXRD) analysis with spiking a standard reference material (such as Al_2O_3 or CaF_2) is a powerful tool to quantify compositions of both crystalline and amorphous phases in the glass-ceramic samples [34–39]. In the CaO-MgO-SiO_2-Al_2O_3-Cr_2O_3 system mentioned above, the Cr-spinel is expected to form a solid solution due to the complexity of the system [40]. The precise chemical compositions, especially the distribution of hazardous metals between crystalline and glass phases, are highly beneficial to discuss the capacity of glass-ceramics to accommodate the hazardous metals. Transmission electron microscopy-energy dispersive X-ray spectroscopy (TEM-EDX) can be used to obtain detailed information at nano level without interference from other areas [41], ensuring that accurate data are acquired from both crystal and residual glass. Thus, it is powerful to determine the chemical composition of the spinel solid solution in the glass-ceramic matrix.

In this study, simulated Cr slag with varying Cr_2O_3 content in a CaO-MgO-SiO_2-Al_2O_3-Cr_2O_3 system was treated to synthesize glass-ceramic products. To obtain the precise chemical compositions of the crystals in the glass-ceramics, the spinel crystals were probed by the TEM-EDX. The phase components were qualitatively identified by powder XRD, and quantitatively determined by Rietveld quantitative phase analysis with spiking standard reference. A prolonged leaching procedure was also carried out to examine the stabilization of Cr in the glass-ceramics products. Two measures – the Cr partitioning ratio (PR) and the Cr leaching ratio – were used to investigate Cr distribution in the glass-ceramic matrix and the extent of the immobilization of Cr in the glass-ceramic products.

2. Materials and methods

2.1. Preparation of Cr-bearing glass-ceramics

To simulate common Cr-containing slag, a mixture of CaO, MgO, SiO_2, Al_2O_3, and Cr_2O_3 was prepared. The chemical composition of the starting mixture (Table 1) was near the eutectic point of the $CaMgSi_2O_6$-$CaAl_2Si_2O_8$ pseudo-binary phase Diagram [25] to give the lowest possible melting temperature in the final CaO-MgO-SiO_2-Al_2O_3-Cr_2O_3 system. A mixture of reagent-grade oxides (MgO, SiO_2, Al_2O_3, and Cr_2O_3) and calcium carbonate ($CaCO_3$) with about

Table 1
Chemical compositions of the simulated chromium-containing slag (in wt.%) with different Cr_2O_3 contents in the starting materials.

Sample Name	Chemical Compositions (wt.%)				
	MgO	CaO	SiO_2	Al_2O_3	Cr_2O_3
P2	11.62	23.02	49.34	14.02	2.00
P4	11.86	22.43	48.06	13.66	4.00
P6	12.10	21.83	46.78	13.30	6.00
P8	12.34	21.23	45.50	12.93	8.00
P10	12.59	20.63	44.22	12.57	10.00