



Immobilization potential of Cr(VI) in sodium hydroxide activated slag pastes



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HIGHLIGHTS

- Alkali-activated slag cement exhibited effective immobilization for Cr(VI).
- The chromium leachability depended on the final leachate pH.
- Cr(VI) was reduced to Cr(III) by AAS without any additional reductants.
- The CrO₄-U phase was formed as the primary retention phase for unreduced Cr(VI).

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ABSTRACT

This study investigated the immobilization potential of alkali-activated slag (AAS) pastes for Cr(VI) by examining compressive strength, toxicity characteristic leaching procedure (TCLP) and generalized acid neutralization capacity tests. Alkaline digestion, total acid digestion, XRD, FTIR and SEM-EDS were carried out to clarify the immobilization mechanism. The AAS pastes gave high compressive strengths, which contributed to the physical encapsulation of Cr. The addition of Cr(VI) induced an increase in compressive strength compared to Cr(VI)-free pastes. The leaching results showed that AAS pastes exhibited effective immobilization for Cr(VI) and that the leachability was strongly dependent on the NaOH dosage, water to slag ratio, initial Cr(VI) content, leachate pH and curing duration. The initial Cr(VI) content up to 1.5 wt% by weight of slag was well immobilized with the total-Cr leachability below the TCLP regulatory limit of 5 mg/L. The digestion results demonstrated that the reduction of chromium from hexavalent to trivalent played a significant role in the immobilization of Cr(VI) in AAS without any additional reductants. The XRD and SEM-EDS results suggested the formation of a clear CrO₄-U phase as the primary retention phase for unreduced Cr(VI). Therefore, alkali-activated slag binder is effective in the immobilization of Cr(VI)-bearing wastes.

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1. Introduction

Due to the development of industrial activities, large quantities of heavy metal-bearing wastes are generated each year. Most of them are harmful to human health and therefore need to be treated safely prior to contact with the environment. For decades, cement-based immobilization technologies combining interrelated solidification/stabilization (S/S) processes have been widely used for the treatment of heavy metal contaminated wastes to prevent their interactions with the environment. The S/S process is regarded as the best demonstrated available technology for many hazardous wastes by the United States Environmental Protection Agency (US EPA).

Portland cement is the most common binder used for the immobilization process due to its low cost, versatility and high alkaline pH at which many metal contaminants are effectively fixed by precipitation and sorption reactions. Recent works [1,2] have shown that some metal cationic ions such as Pb(II), Cd(II) and Cu(II) are effectively immobilized by Portland cement-based materials. However, it seems to be problematic for Cr(VI) immobilization due to lack of effective chemical fixation. Pandey et al. [3] stated that Cr(VI) was more leachable than other metal ions because it cannot be precipitated by hydroxide or carbonate ions. Wang and Vipulanandan [4] studied the immobilization of Cr(VI) based on K₂CrO₄ with PC matrices. Their results indicated the K₂CrO₄/cement ratio needed to be limited to 0.2 wt% to meet the TCLP limit of 5 mg/L. The addition of Cr(VI) also inhibited the PC hydration process and impaired its mechanical strength development.

In comparison with Cr(VI), the toxicity and mobility of Cr(III) are much lower. Therefore, detoxification and immobilization based

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on the reduction of Cr(VI) to Cr(III) is a promising choice for the treatment of Cr(VI)-containing solid wastes, such as chromite ore processing residue, municipal solid waste fly ash and electroplating sludge. For this purpose, additional reductants such as zero-valent iron, ferrous sulfate and sulfide [5–7] have been used previously.

Ground granulated blast furnace slag (GGBFS) is an industrial by-product of the iron and steel industry with latent hydraulic reactivity that can be activated by a proper alkali activator to produce an alkali activated slag cement. As a potential alternative binder, alkali-activated cement is appealing due to its 70% lower CO₂ emission and 60% less energy consumption compared with Portland cement [8]. In addition, when compared with traditional Portland cement, AAS presents some superior properties, including high mechanical strength, low permeability, high resistances to acid attack and chemical attack, etc. [9,10]. In general, the release of chromium from cement-based matrices is controlled primarily by diffusion. Thus, the above advantageous properties may play positive roles in decreasing Cr outward migration and increasing resistance to external chemical attack. Importantly, it seems that some phases present in GGBFS can control the solubility of Cr(VI) [11]. Many studies [12–14] have reported that the sulfur contained in GGBFS was mainly present in the form of S²⁻ providing a reduction environment, where the Cr(VI) was converted to Cr(III).

In light of the previous mentioned physical and chemical advantages, AAS is expected to be a better binder for the immobilization of Cr(VI). There have only been a few previous reports regarding the treatment of Cr(VI) by AAS. The investigation by Deja [15] showed that AAS exhibited a high degree of Cr(VI) immobilization based on the monolithic tank leaching procedure with deionized water as the extract medium. However, the exact immobilization mechanism was not completely understood. In actual situations, wastes contaminated by heavy metals are generally found in more aggressively acidic environments, for instance, acid rain or landfill conditions. In particular, the pH value usually affects not only the solubility of the heavy metal components but also the redox chemistry, which are crucial for Cr(VI) treatment.

Therefore, the objectives of this study were to (1) investigate the immobilization potential of Cr(VI) by AAS, (2) examine the influence of the pH value on the leachability and oxidation state of chromium, and (3) discuss the immobilization mechanism of Cr(VI) in AAS.

2. Materials and methods

2.1. Materials

The GGBFS with a Blaine specific surface area of 4500 cm²/g was supplied by Chongqing Iron & Steel (Group) Co., Ltd., Chongqing, China. Its chemical composition is summarized in Table 1. The X-ray diffractogram of the GGBFS (Fig. 1) shows a diffused XRD pattern (a hump) between 25° and 35° (2θ), indicating that the GGBFS is mainly amorphous. Traces of some crystalline phases, such as gehlenite (Ca₂Al₂SiO₇, PDF# 035-0755) and merwinite (Ca₃Mg(SiO₄)₂, PDF# 074-0382), are observed. Industrial grade NaOH was used to prepare the activator solution. Na₂CrO₄·4H₂O as the source of Cr(VI) and other chemicals for determination were of analytical reagent grade. Ultra-pure water was used for all sample preparations and dilutions.

2.2. Sample preparation

Thirteen paste samples were prepared to investigate the effects of the NaOH dosage, water to GGBFS ratio (W/G) and Cr(VI) concentration on the leachability of chromium after immobilization in AAS. The detailed mix proportions are presented in Table 2.

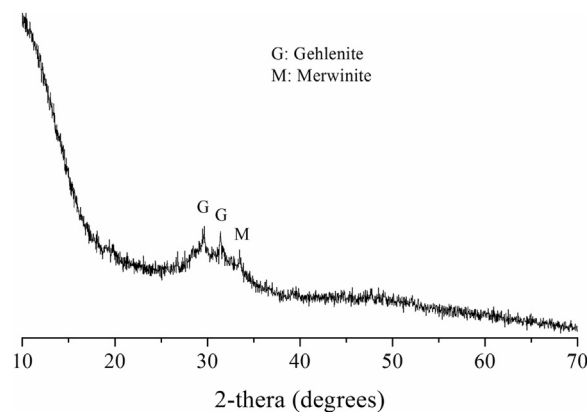


Fig. 1. XRD patterns of GGBFS.

For all pastes, the water incorporated in Na₂CrO₄·4H₂O was considered part of the total water for paste preparation. NaOH and Na₂CrO₄·4H₂O were dissolved in ultra-pure water and cooled to 20 °C prior to mixing with GGBFS to have a homogeneous distribution. The mixed GGBFS powders were then combined with the solutions and fully mixed for 5 min according to the Chinese standard procedure GB/T 1346–2001 to guarantee uniformity of the pastes. The specimens were cast in 40 × 40 × 40 mm metal cubic moulds and vibrated for 2 min to remove large air bubbles. After 1 day, the specimens were removed from the moulds and sealed in plastic bags. All samples were cured at 20 °C and 98% relative humidity prior to the tests.

2.3. Compressive strength tests

The compressive strength was measured at the ages of 28, 90 and 180 days in triplicate in accordance with Chinese National Standard GB/T 17671–1999. After this, the solids were crushed for leaching tests and microstructure analysis.

2.4. Leaching tests

The toxicity characteristic leaching procedure (TCLP) test was conducted according to the EPA 1311 method. The crushed sample was sieved to between 4 and 9.5 mm and extracted for 18 h using a 0.1 M acetic solution (pH = 2.88) with a liquid/solid ratio (L/S) of 20. The generalized acid neutralization capacity test (GANC) was a single batch procedure that utilizes various equivalents of acetic acid per kilogram of crushed solids. In the present work, nine parallel extractions were carried out for 7 days. The L/S was 20, and the particle size passed through a 200-mesh sieve. After the extractions, suspensions were filtered through 0.45 μm membrane filters. The Cr(VI) and total-Cr concentrations in TCLP and GANC tests were measured colorimetrically using the 1,5-diphenyl carbazide method and a UV–vis spectrophotometer (TU-190, China). Ca, Mg, Na, Si, Al and total-S were determined in GANC tests using inductively coupled plasma optical emission spectroscopy (ICP-OES), while SO₄²⁻ was analysed using ion chromatography (IC). Each leachate was analysed in triplicate, and the mean values were reported. The pH values and oxidation reduction potentials (ORPs) were analysed by a pH meter (pHS-3C, China).

2.5. Reduction ratio tests

To assess the reduction efficiency of the AAS, the amounts of Cr(VI) and total Cr in AAS immobilized solid at different curing durations were determined following an alkaline digestion procedure

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