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Evaluation of alkali-activated blast furnace ferronickel slag as a cementitious material: Reaction mechanism, engineering properties and leaching behaviors

Dengquan Wang, Qiang Wang [*], Shiyu Zhuang, Jun Yang

Department of Civil Engineering, Tsinghua University, Beijing 100084, China

HIGHLIGHTS

- The properties of alkali-activated heavy metal-bearing slag were comprehensively evaluated.
- The activation requires relatively high alkalinity and low silicon modulus.
- The activated heavy metal-bearing slag is environmentally acceptable.

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ABSTRACT

Blast furnace ferronickel slag (BFFS) is a kind of heavy metal-bearing slag with moderate calcium content that is obtained from the production of ferronickel in a blast furnace. The reaction mechanism, engineering properties, and leaching behaviors of alkali-activated BFFS materials were investigated. The results show that the main crystalline phase of the reaction products is strätlingite, and the gel phase is a kind of C-A-S-H with Ca/Si and Al/Si ratios of 0.64–1.65 and 0.57–1.44, respectively. The reaction of BFFS greatly depends on the alkalinity and silicon modulus, with a high alkalinity and low silicon modulus resulting in a rapid initial exothermic rate, a high reaction degree, and a denser pore structure in the alkali-activated BFFS materials. In addition, the compressive strength of the alkali-activated BFFS mortar is comparable to that of the alkali-activated blast furnace slag (BFS); furthermore, the alkali-activated BFFS shows more continuous strength gains from 7 days to 90 days and much lower 7-day autogenous shrinkage. More importantly, the alkali-activation treatment can significantly decrease the leaching amount of Mn, Cr(VI) and Cr(III), and it converts the hazardous BFFS to non-toxic construction materials.

1. Introduction

Ferronickel slag is an industrial waste obtained from ferronickel alloy production. An estimated 0.64 million tons of ferronickel alloy (calculated in contained nickel) are produced annually worldwide, of which China accounts for approximately 48% [1]. The ferronickel industry employs two main smelting technologies: the electric furnace method and the blast furnace method. The electric furnace method is used worldwide and currently represents the primary method in ferronickel alloy production, whereas the blast furnace method was chiefly used in the past and is currently restricted to parts of eastern China because of the lack of nickel-rich minerals and the high demand for ferronickel alloys [2,3]. The distribution of the main ferronickel smelting plants worldwide and in China are summarized in Fig. 1. According to the different smelting technologies, ferronickel slag can be categorized as electric furnace ferronickel slag (EFFS) and blast furnace ferronickel slag (BFFS) with different chemical and mineralogical compositions. The chemical composition of EFFS is mainly composed of SiO_2, MgO, and Fe_2O_3, and its mineral composition is primarily crystalline minerals such as enstatite, forsterite and dropsied. In contrast, BFFS mainly consists of SiO_2, Al_2O_3, and CaO, and moreover, BFFS contains a large amount of amorphous phase [4]. EFFS has been comprehensively studied: this slag can be used in construction as aggregates [5–7], supplementary cementing material [8–10], and as raw material for cement clinker production [5] and geopolymers [11,12]. However, thorough research is not available on BFFS.

As a heavy metal-bearing waste slag, the massively deposited BFFS causes the occupation of farmland and pollution of soil and groundwater because of its Cr and Mn leaching. Cr and Mn are

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[*] Corresponding author.
E-mail address: w-qiang@tsinghua.edu.cn (Q. Wang).

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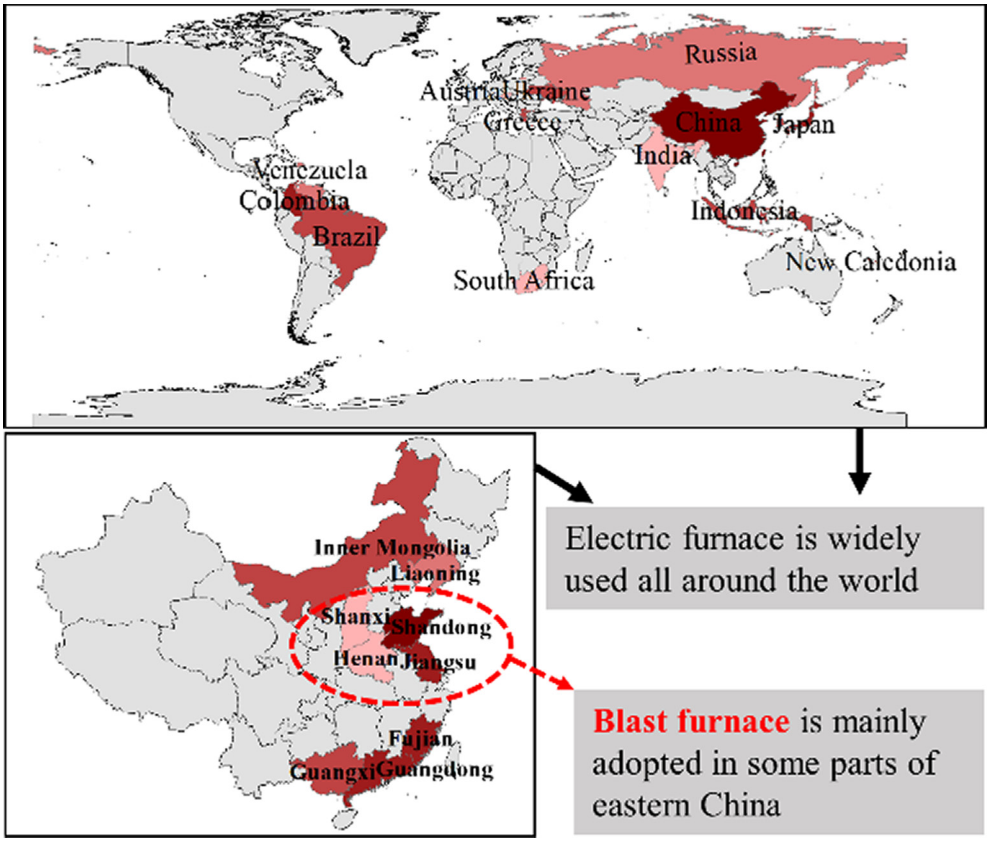

Fig. 1. Distributions of major ferronickel smelting plants worldwide and in China (darker red regions indicate higher ferronickel production) [1,3,27].

considered hazardous substances on the ATSDR 2017 Substance Priority List [13]. Cr has acute toxicity, delayed manifestations and even genotoxicity [14,15]. Generally, Cr(VI) is considered more toxic than Cr(III) and should receive more attention [16]. Mn toxicity is associated with several cellular dysfunctions, and neurobehavioral effects and reproductive dysfunction in response to this toxicity have been reported in humans [17,18]. Thus, the efficient treatment and usage of BFFS is a critically important subject for resource conservation and environmental sustainability.

Alkali-activation technology is receiving increasing attention worldwide for the production of alternative binders to Portland cement. This technology can successfully use industrial solid wastes, such as commonly used blast furnace slag (BFS) and fly ash [19], red mud [20], electric furnace ferronickel slag [11,21], Cu-Ni slag [22], and lead slag [23]. There are some construction applications of alkali-activation technology, such as Melton library and Salmon Street bridge in Melbourne, and some residential houses in Russia [24]. Generally, alkali-activated binders are promising materials because of their high strength, high durability and low environmental impact [25]. However, alkali-activated binder also has some limitations, such as fast setting and large shrinkage deformation [24]. Calcium in the amorphous phase plays an important role in the activity of the slag because it can lead to an increased tendency toward framework disorder and decrease the polymerization degree of raw material [26]. Thus, BFS, a type of high-calcium slag, is commonly considered the most promising slag for alkali activation. BFFS is mainly composed of SiO_2, CaO, Al_2O_3 and MgO; it is similar to BFS in its main chemical compositions but contains less CaO and more Al_2O_3. As a result, BFFS can be classified as a type of intermedium-calcium slag, and theoretically it also has potential reaction activity for alkali-activation.

This paper aims to use alkali-activation technology to efficiently use BFFS (as shown in Fig. 2). The reaction products and process are discussed in detail to reveal the reaction mechanism of this type of alkali-activated intermedium-calcium slag. The compressive strength and autogenous shrinkage were tested to evaluate the engineering properties of alkali-activated BFFS concrete, and alkali-activated BFS concrete was used as a reference because it is considered one of the most promising alkali-activated materials for engineering applications. More importantly, leaching tests were performed to evaluate the environmental performance of the alkali-activated BFFS cementitious material.

2. Experimental

2.1. Raw materials

The density of BFFS and BFS was 2.98 g/cm^3 and 3.03 g/cm^3, respectively. The specific surface area of BFFS and BFS was 397 m^2/kg and 374 m^2/kg, respectively. The chemical compositions (analyzed via an X-ray fluorescence spectrometer) of BFFS and typical BFS are summarized in Table 1. BFFS contains less CaO but more Al_2O_3 than BFS. The mineralogical phases (analyzed via an X-ray diffractometer) are shown in Fig. 3. There is a hump at approximately 25–35° (2θ) in both BFFS and BFS raw materials, which is considered the amorphous phase (calcium aluminosilicate framework) and indicates their potential activities. However, compared with BFS, BFFS has obvious crystalline phases in the pattern: spinel and forsterite. These phases are considered unreacted parts because of their stable structures. Theoretically, BFFS shows lower activity than BFS based on chemical and mineralogical compositions. The particle size distributions (analyzed via a laser particle size analyzer) of BFFS and BFS, which were milled to similar particle sizes, are shown in Fig. 4. The element distribution (analyzed via a scanning electron microscope with an electron probe) of BFFS is shown in Fig. 5. The heavy metal elements Cr and Mn are uniformly distributed in BFFS particles. Sodium hydroxide (analytical reagent) and industrial water glass ($Na_2O{\cdot}2SiO_2$) were used as alkali activators. ISO reference sand and crushed limestone aggregates were used as fine aggregates and coarse aggregates, respectively.