Journal of Hazardous Materials 306 (2016) 67–76

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

# Hydration characteristics and environmental friendly performance of a cementitious material composed of calcium silicate slag

Na Zhang[a,b], Hongxu Li[a,b], Yazhao Zhao[a], Xiaoming Liu[a,b,*]

[a] School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China
[b] Beijing Key Laboratory of Rare and Precious Metals Green Recycling and Extraction, University of Science and Technology Beijing, Beijing 100083, China

## HIGHLIGHTS

- Cementitious material was designed according to [$SiO_4$] polymerization degree of raw materials.
- The cementitious material composed of calcium silicate slag yields excellent physical and mechanical properties.
- Amorphous C–A–S–H gel and rod-like ettringite are predominantly responsible for the strength development.
- Leaching toxicity and radioactivity tests show the cementitious material is environmentally acceptable.

## ARTICLE INFO

*Article history:*
Received 14 August 2015
Received in revised form
27 November 2015
Accepted 28 November 2015
Available online 2 December 2015

*Keywords:*
Calcium silicate slag
High-alumina fly ash
Cementitious material
Hydration products
Environmental friendly performance

## ABSTRACT

Calcium silicate slag is an alkali leaching waste generated during the process of extracting $Al_2O_3$ from high-alumina fly ash. In this research, a cementitious material composed of calcium silicate slag was developed, and its mechanical and physical properties, hydration characteristics and environmental friendly performance were investigated. The results show that an optimal design for the cementitious material composed of calcium silicate slag was determined by the specimen CFSC7 containing 30% calcium silicate slag, 5% high-alumina fly ash, 24% blast furnace slag, 35% clinker and 6% FGD gypsum. This blended system yields excellent physical and mechanical properties, confirming the usefulness of CFSC7. The hydration products of CFSC7 are mostly amorphous C–A–S–H gel, rod-like ettringite and hexagonal-sheet $Ca(OH)_2$ with small amount of zeolite-like minerals such as $CaAl_2Si_2O_8{\cdot}4H_2O$ and $Na_2Al_2Si_2O_8{\cdot}H_2O$. As the predominant hydration products, rod-like ettringite and amorphous C–A–S–H gel play a positive role in promoting densification of the paste structure, resulting in strength development of CFSC7 in the early hydration process. The leaching toxicity and radioactivity tests results indicate that the developed cementitious material composed of calcium silicate slag is environmentally acceptable. This study points out a promising direction for the proper utilization of calcium silicate slag in large quantities.



## 1. Introduction

Fly ash is a typical industrial solid waste obtained from thermal power plant. In Inner Mongolia of China, large quantities of fly ash are disposed every year, and most of them are high-alumina fly ash with alumina content as high as 50% [1–3]. It was reported that over 12 million tons of high-alumina fly ash is generated annually in Inner Mongolia, and its stockpile amount has exceeded 100 million tons [4]. Extracting $Al_2O_3$ from this high-alumina fly ash is a good solution for China to relieve the shortage of bauxite resource and develop circular economy. In order to utilize this kind of fly ash resource, Inner Mongolia Datang International Renewable Resources Development Co. Ltd., developed pre-desilication and alkali-lime-calcination process to extract $Al_2O_3$ from high-alumina fly ash [4,5], and a production line with annual capacity of 0.2 million tons of alumina has been built beside Inner Mongolia Datang Togtoh power plant. However, an insoluble residue named calcium silicate slag is generated during the alumina extraction from fly ash. Usually consuming 1 t of high-alumina fly ash generates 1 t of calcium silicate slag and 0.4 t of $Al_2O_3$. Due to NaOH and $Na_2CO_3$ are added during the process of extracting $Al_2O_3$ from high-alumina fly ash by the pre-desilication and alkali-lime-calcination method, calcium silicate slag is an alkali leaching waste containing as high as 5% $Na_2O$. As a corrosively hazardous material, the

* Corresponding author at: Room 810, School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China. Fax: +86 10 62332786.
*E-mail address:* liuxm@ustb.edu.cn (X. Liu).

http://dx.doi.org/10.1016/j.jhazmat.2015.11.055
0304-3894/

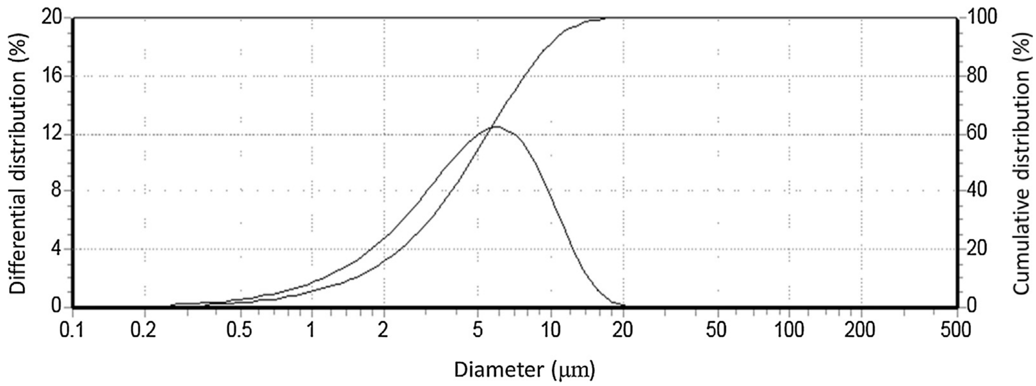


**Fig. 1.** Particle size distribution of dried calcium silicate slag after milling.

discharge of this alkali residue will cause serious environmental problems such as soil contamination and water pollution due to lye leaching. If calcium silicate slag cannot be utilized in an effective way, it will not only seriously influence the local ecological environment of Inner Mongolia of China, but also restrict the application and popularization of extracting $Al_2O_3$ from high-alumina fly ash.

As calcium silicate slag is mainly composed of CaO, $SiO_2$, $Al_2O_3$ and $Na_2O$, it is thought that using calcium silicate slag in cement production is an efficient method for large-scale recycling of this solid waste. In the past few years, using calcium silicate slag in cement clinker has been widely carried out in China [6–9]. It was reported that calcium silicate slag can improve burnability of raw meal during the preparation of cement clinker [8,9]. However, it is noticed that the calcium silicate slag used in the production of cement clinker contains small amount of alkali ($Na_2O + 0.658K_2O$) [10]. Due to the alkali content of raw meal needs to be controlled in a low level, the calcium silicate slag is required to be pretreated by dealkalization and after that it can be used for producing cement clinker. Generally, calcium silicate slag is dealkalized through adding lime milk, washing and filtering process. It was reported that the optimal dealkalization process for the calcium silicate slag derived from Inner Mongolia Datang International Renewable Resources Development Co. Ltd., was lime milk addition of 10%, temperature of 85 °C for 3 h and washing twice, and subsequently the alkali content of dealkalized calcium silicate slag was 0.83% (comparing to the original alkali content of 4.12%) in experimental investigation [11]. Moreover, preparation of cement clinker requires a high temperature between 1350 °C and 1450 °C consuming lots of energy. Yang et al. [5] conducted an investigation on using raw calcium silicate slag and dealkalized calcium silicate slag respectively as an admixture in Portland cement, and it showed that the early-age compressive strength of cement composed of raw calcium silicate slag is higher than that of cement composed of dealkalized calcium silicate slag, but the dealkalized calcium silicate slag is more beneficial to maintain the long-term strength, lower the hydration heat and reduce the dry shrinkage of the cement comparing with the raw calcium silicate slag. As a matter of fact, the high amount of $Na_2O$ in calcium silicate slag without dealkalization restricts its large-scale utilization in cement production.

Red mud is a typical industrial waste obtained from alumina production with high amount of $Na_2O$ (2.0–6.0%) [12]. Many efforts have been made in our research team to find effective ways of utilizing red mud. We have carried out some investigations on using bauxite-calcination-method red mud, coal gangue, blast furnace slag, clinker and gypsum as raw materials to produce cementitious materials [12–14]. It has been demonstrated that the developed red mud-coal gangue based cementitious material has good physical and mechanical properties [12], and fibrous C–A–S–H gels and needle-shaped/rod-like ettringite are mainly formed in the early hydration period, and then the fibrous intertwined C–A–S–H gels gradually grow into amorphous phase and further into network shape with increasing of the hydration time [13]. Feng found out that C–A–S–H gel with low Ca/Si ratio was formed in the hydrated paste of silica-alumina based cementitious material composed of red mud [15], and due to $Na^+$ balanced the negative charges which were caused by the substitution of Al for Si, this kind of hydration product had high capability of $Na^+$ solidification. The usefulness of red mud based cementitious materials has been confirmed through these investigations [12–17], which provides important guidance for using calcium silicate slag to prepare cementitious materials.

In this paper, according to [$SiO_4$] polymerization degree of raw materials, calcium silicate slag was blended with high degree of [$SiO_4$] polymerization material (high-alumina fly ash), middle degree of [$SiO_4$] polymerization material (blast furnace slag), and low degree of [$SiO_4$] polymerization material (clinker) as main compositions to produce cementitious material. The aim of the present study is to investigate the feasibility of the developed cementitious material composed of calcium silicate slag, including its mechanical and physical properties, hydration products, hydration kinetics and environmental friendly performance. Instrumental techniques such as X-ray diffraction (XRD), Fourier transform infrared (FTIR) and scanning electron microscopy (SEM) were applied to obtain useful information on the hydration products of cementitious material composed of calcium silicate slag.

## 2. Experimental

### 2.1. Materials

Calcium silicate slag, high-alumina fly ash and FGD gypsum were obtained from Inner Mongolia Datang International Renewable Resources Development Co. Ltd. The calcium silicate slag used in this work was original without dealkalization. Granulated blast furnace slag (BFS) was supplied by Tangshan steel refining plant, and clinker was provided by Inner Mongolia Mengxi cement plant. The chemical composition (analyzed using XRF-1800 sequential X-ray fluorescence spectrometer) and specific surface area of raw materials are presented in Table 1. The mineralogical phases (determined by XRD) of raw materials are presented in Table 2.

### 2.2. Experimental procedure

Calcium silicate slag was dried at 105 °C in an oven and ground in a laboratory ball mill for 20 min. The size distribution, SEM observation and thermal analysis of the dried calcium silicate slag after milling were performed. The calcium silicate slag was blended with