Chemosphere 167 (2017) 360–366

Contents lists available at ScienceDirect

Chemosphere

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

Mineralogical determination and geo-chemical modeling of chromium release from AOD slag: Distribution and leachability aspects

Junguo Li*, Bao Liu, Yanan Zeng, Ziming Wang

College of Metallurgy and Energy, North China University of Science and Technology, Tangshan 063009, PR China

HIGHLIGHTS

- Mineralogical composition of AOD slag were identified via X-ray and SEM.
- Larnite, merwinite, pyroxene and periclase with Cr dispersed were the main minerals.
- Chromium concentration in leachates obtained by EN12457-2 were measured.
- Geochemical model was established by PHREEQC simulation combined with FactSage.
- Cr leaching from AOD slag was controlled by Cr(III)-hydroxide.

ARTICLE INFO

Article history:
Received 18 March 2016
Received in revised form
28 September 2016
Accepted 7 October 2016
Available online 12 October 2016

Handling Editor: X. Cao

Keywords:
AOD slag
Mineral analysis
FactSage
PHREEQC
Leaching toxicity

ABSTRACT

AOD (argon oxygen decarburization) slag, which is the by-product of the stainless steel refining process, is a recyclable slag because of its high content of calcium and silicon. The leaching toxicity cannot be ignored in the recycling process because the slag contains a certain amount of Cr. In this study, the mineral analysis, batch leaching tests and thermodynamic and kinetic modeling by PHREEQC combined with FactSage software were performed to explore the influence of the dissolution of primary minerals and the precipitation of secondary minerals on the elution of Cr from AOD slag. The results indicated that the main minerals in the original AOD slag are larnite, merwinite, pyroxene and periclase. Cr was dispersed in the mineral phases mentioned above. The simulation of Cr leaching controlled by Cr(III)-hydroxide corresponded better to the batch leaching tests, while the Cr leaching controlled by chromite or double control was underestimated. Increasing the L/S ratio enhances the pH of the leachate and restrains the elution of Cr from the AOD slag.

1. Introduction

AOD (argon oxygen decarburization) slag is the by-product of the stainless steel refining process, with an estimated 1 million tons generated annually. Presently, AOD slag is reused as slag cement or building materials because of its high content of calcium and silicon, whose content is similar to that of cement. The high content of chromium in AOD slag can be leached out and enters into soil and water bodies under the leaching function of rainwater, which limits its valorization. In particular, hexavalent chromium easily enters into human body through the food chain and then causes harm to the respiratory and digestive system because of its high oxidation capacity. Therefore, it is extremely important to find effective measures to describe the releasing capacity of chromium from AOD slag and to reduce the leaching toxicity of such chromium.

Several studies have illustrated that some factors, such as the mineral phases of AOD slag and the electrochemical characteristics of the leachate, should significantly influence the releasing capacity of Cr from slag (Wang et al., 2011; Kuo et al., 2008). Moreover, environmental factors such as pH, redox potential and dissolved oxygen should impact the speciation of chromium ions in the effluent and the transfer and transformation tendency of the chromium ions (Han, 2010; Wang et al., 2009). Furthermore, the influence of the spinel phases in the original slags and the secondary phases formed during the leaching process on the

---

* Corresponding author.
E-mail address: lijg99@163.com (J. Li).

http://dx.doi.org/10.1016/j.chemosphere.2016.10.020
0045-6535/

chromium released from slags has also been described by Aarabi-Karasgani and Kuhn (Karasgani et al., 2010; Kuhn and Mudersbach, 2004).

Several models have been developed to describe the leaching behavior of elements from some industrial solid wastes using different thermal software packages (De Windt et al., 2011; Cheryl et al., 2005; Huijgen and Comans, 2006). De Windt et al. established the models for some elements, such as Ca, Mg, Cr, and V, from BOF slag using HYTEC (De Windt et al., 2011). Cheryl et al. provided the leaching models of Pb, Cd, As and Cr from cementitious waste using PHREEQC (Cheryl et al., 2005). Huijgen and Comans investigated the carbonation of BOF slag and the pH-dependent leaching behavior of the major and trace elements (Huijgen and Comans, 2006).

These studies provide several effective means to describe the leaching process of chromium from AOD slag. The chromium leaching speciations and transformation mechanism during the leaching process have been explored in our previous study (Bao et al., 2016). However, the influence of mineralogical components on chromium leaching concentrations was not specifically clarified. This work aimed at developing a leaching model of chromium from AOD slag using PHREEQC combined with FactSage software based on the influence of the dissolution of the original minerals and precipitation of the secondary phases on chromium leaching. Moreover, EN12457-2 batch leaching tests were performed to correspond to the simulation.

2. Materials and methods

2.1. Materials

AOD slag was collected from Tangshan stainless steel factory after air cooling and spraying with water; then the AOD slag was sieved with a 75-μm (200 mesh) sieve. The undersized slag was used for mineralogical analysis and batch leaching tests after drying for 6 h at 105 °C to remove the free moisture adsorbed during the air-cooling and water-spraying processes. The slag composition was determined by chemical analysis YBT140-1998 (Method for chemical analysis of steel slag in cement, China), as presented in Table 1.

AOD slag is an alkaline waste with a ternary basicity ($(CaO + MgO)/SiO_2$) of 2.50. The major components in this slag are CaO (55.90%), which originated from the addition of lime as flux during the smelting and refining process, and SiO_2 (24.67%), which is used for preventing chromium oxidation during the melting process and is formed due to the reaction of oxygen and silicon dissolved in the steel. The chemical analysis results are similar to the XRF analysis results obtained by Zhao (53.27% CaO and 27.54% SiO_2) (Zhao et al., 2013). The weight content of MgO, which is the third most dominant oxide, is 5.85%. Slight amounts of FeO, TiO_2, MnO and Al_2O_3 were contained in this slag. Chromium is a trace element with a weight content of 0.35% and occurs as Cr_2O_3 (0.51%).

2.2. Batch leaching test

The batch leaching test used in this research was EN12457-2, as recommended by the European Committee for Standardization, which was the preferred choice to conduct the compliance test for the leaching of granular waste materials and sludges because of its simplicity, reproducibility and reliability. First, 100 g of AOD slag was weighed and then transferred into a conical flask. After a certain amount of leachate was added, the conical flask was sealed with a lid to prevent the intrusion of carbon dioxide and oxygen; the flask was then vibrated at a speed of 10 rpm at 25 °C. The batch leaching test was performed at liquid-to-solid (L/S) ratios of 10 and 100 for 20 days. During the leaching tests, a small volume of leachate was sampled every 24 h, and the same volume of pure water was supplemented to maintain the L/S ratio. The sampled leachates were filtered through 0.22-μm membrane filters and then analyzed using UV–visible spectrophotometry by diphenylcarbazide method (GB/T 15555.4–1995. Hexavalent chromium and total chromium concentrations were determined by diphenylcarbazide spectrophotography in conjunction with oxidation of ammonium peroxydisulfate (Chen and Tian, 2008; Ronnald, 1997). The concentration of trivalent chromium was determined by the difference method.

2.3. Mineralogical analysis

Mineralogical compositions of the original and hydrolyzed AOD slag were determined by X-ray diffraction (XRD). Measurements were performed on a D/MAX2500PC automatic diffractometer with a continuous scanning device using Cu-Kα radiation at 100 mA and 40 kV, a scanning velocity of $10^\circ\ 2\theta\ min^{-1}$, and a 2θ range of 10–90°. Mineral identification and micro-morphology of the AOD slag were performed in a previous study (Wang et al., 2013). In this work, the SEM-BSE (Scanning Electron Microscope Backscatter Electron, Hitachi, S-4800, Japan) images of AOD original slag were obtained to evaluate the diameters of different primary minerals, which could be used to calculate the mineral reaction surface (A). EDS (Energy Dispersive Spectrometer, Thermo Fisher, Noran 7, America) was coupled to SEM-BSE to determine the composition of minerals. The XRD patterns of the original and hydrolyzed AOD slag were analyzed using Jade 6.0 which is a mineralogical analysis software based on the mineralogical database of PDF-2004.

FactSage version 6.4 thermodynamic software (Bale et al., 2009) was also used to simulate the mineralogical compositions of original and hydrolyzed slags. FactSage, which is one of the largest fully integrated database computing systems in the chemical thermodynamic domain, can provide thermodynamic data regarding the thousands of compounds existing in all types of metallurgical slags. The Equilib module in FactSage can simulate the primary phases initially in the slag after cooling down and the secondary phases generated and precipitated in leachate provided that the chemical components of slags were known. The database used in FactSage simulation was the FToxid database. Since the mineral thermodynamic constant contained in FToxid database is incomplete. The thermodynamic constant of calcium silicate hydrates (CSH) was obtained from the thermoddem database of HSC 5.0 database and added them into FactSage database. After FactSage simulation, a comparison between the measured and simulated results was performed to improve the accuracy of mineralogical analysis.

2.4. PHREEQC simulation

PHREEQC version 2.0 can be used to model chemical reactions

Table 1
Chemical composition of the AOD slag.

Components	CaO	SiO_2	MgO	TiO_2	MnO	FeO	Cr_2O_3	Al_2O_3	V_2O_5	S	P
Content/wt.%	55.90	24.67	5.85	0.69	0.16	1.15	0.51	1.07	0.008	0.06	0.01