



## Valorization of stainless steel slag by selective chromium recovery and subsequent carbonation of the matrix material



E. Kim<sup>a, b, \*</sup>, J. Spooren<sup>a</sup>, K. Broos<sup>a</sup>, P. Nielsen<sup>a</sup>, L. Horckmans<sup>a</sup>, R. Geurts<sup>a</sup>,  
K.C. Vrancken<sup>a, b</sup>, M. Quaghebeur<sup>a</sup>

<sup>a</sup> VITO – Flemish Institute for Technological Research, Boeretang 200, BE-2400 Mol, Belgium

<sup>b</sup> Department of Bioengineering, University of Antwerp, Groenenborgerlaan 171, BE-2020 Antwerp, Belgium

### ARTICLE INFO

#### Article history:

Received 7 April 2015

Received in revised form

13 January 2016

Accepted 15 January 2016

Available online 23 January 2016

#### Keywords:

Cr (Chromium)

Alkaline pressure leaching

Mechanical activation

Carbonation

Hydrometallurgy

### ABSTRACT

This study focuses on the recycling of stainless steel (SS) slags containing about 1.2 wt% of chromium (Cr). The selective recovery of Cr from SS slag by a hydrometallurgical method (alkaline pressure leaching) was investigated. Leaching experiments were carried out based on  $2^{4-1}$  factorial design of experiment (DOE) with the following parameters: NaOH concentration, temperature, leaching time, and mechanical activation (MA). Results show that temperature and MA are the most influencing factors for an enhanced Cr leaching. The maximum Cr leaching was 46% at 1 M NaOH, 240 °C, 6 h, MA 30 min, while the matrix material was dissolved only to a limited extent (Al 2.88%, Si 0.12%, Ca 0.05%). After Cr leaching followed by alkali washing, a carbonation treatment is proposed to stabilize the remaining Cr in the matrix material and make the subsequent recycling of the matrix material as a construction material possible.

© 2016 Elsevier Ltd. All rights reserved.

### 1. Introduction

Chromium (Cr) containing slags (Cr <2 wt%) such as electric arc furnace (EAF) slag or argon decarburization (AOD) slag generated during melting or refining of stainless steel manufacturing are classified as hazardous waste (Yi et al., 2012; Zhang and Hong, 2011; Shen et al., 2004; Shen and Forssberg, 2003). Their disposal is a major environmental concern (Spooren et al., 2013; Parasad, 2010). Currently most of these materials are still disposed of in landfills or used as low-grade construction materials (Sheen et al., 2014; Gencel et al., 2013; Zhang et al., 2013; Mesei and Elevliis, 2012).

When these waste materials are landfilled, the slag material needs to be stabilized to avoid the release of contaminants to the groundwater or soil. In the case of Cr, several stabilization routes have been studied to transform the soluble Cr(VI) to insoluble Cr(III) by reducing agents, such as FeSO<sub>4</sub> (Jagupilla et al., 2009), Na<sub>2</sub>S (Velasco et al., 2012) and Ca<sub>5</sub>S (Wazne et al., 2007), or through biological treatment (Dhal et al., 2013; Yu et al., 2012). However,

stabilization to landfill is not a promising process due to the generation of large amounts of waste material, being an environmental and economic burden, and the presence of remaining soluble Cr(VI) by incomplete reduction of the Cr.

Furthermore, due to changing economic conditions and technological innovations, these types of waste have become potential resources for the recycling and recovery of various valuable metals and critical raw materials, such as chromium (UNEP, 2013). In 2000, it was estimated that worldwide 46,000 tons of Cr were lost in stainless steel slags and 637,000 tons in chromite ore process residues (COPR) (Jhonson et al., 2006). When the leachable Cr is removed from the mineral matrix material, this material can be used as a valuable product/resource in the building industry without posing a risk to the environment (Salman et al., 2014; Reuter et al., 2004; Shen and Forssberg, 2003). One possible route to turn slags into new building materials is through a carbonation process, which enhances the technical and environmental properties of the slag and increases its value as a construction material (Sheen et al., 2014; Quaghebeur et al., 2010; Teir et al., 2005).

The traditional recovery of Cr from chromite ore or Cr oxides involves roasting with Na<sub>2</sub>CO<sub>3</sub> above 1100 °C (Dhal et al., 2013; Antony et al., 2001; Habashi, 1997; Ladd and Vanderpool, 1987). Since this process is very energy consuming, it is not applicable to low-grade ore materials. A hydrometallurgical method, based on

\* Corresponding author. VITO, Boeretang 200, BE-2400 Mol, Belgium. Tel.: +32 14 33 57 35.

E-mail addresses: [key7649@gmail.com](mailto:key7649@gmail.com), [eunyoung.kim@vito.be](mailto:eunyoung.kim@vito.be) (E. Kim).

caustic soda leaching has been applied to Cr recovery from chromite ore as well as chromium oxides (Habashi, 1997; Gupta and Mukherjee, 1990). Chromium oxides present in slags readily dissolve with NaOH/KOH under oxidative pressure (1–3.2 Mpa) at 210–300 °C (Zhang et al., 2014; Xu et al., 2005, 2006; Amer and Ibrhim, 1996; Gupta and Mukherjee, 1990). This process, however, requires high pressure and a high concentration of alkaline agents (60–70 wt%). An additional disadvantage is that this process is not applicable for subsequent matrix recycling due to the dissolution of matrix elements such as Al and Si. In fact, several authors have also studied Cr leaching from slag materials in acidic conditions under pressurized H<sub>2</sub>SO<sub>4</sub> (Jiang et al., 2014; Zhao et al., 2014) as well as HCl (Yang et al., 2008). However, those processes also simultaneously dissolve the stainless steel slag matrix materials, i.e. no selective Cr leaching takes place.

The aim of this study is to selectively remove Cr from a historic stainless steel (SS) slag material in order to (i) recover Cr from this low-grade (secondary) ore and (ii) reuse the matrix material as a resource for the production of construction materials. Alkaline pressure leaching was studied for the recovery of Cr using a 2<sup>4-1</sup> factorial design to reveal the most important parameters for Cr leaching.

## 2. Material and methods

### 2.1. Material

A representative SS slag sample was obtained from a historic slag monolandfill. At the site, samples were collected at different positions and depths to obtain a total sample of 300 kg. The 300 kg batch sample was mixed and subsamples were taken for further analysis and experiments. For this study, the slag was crushed and ground below 125 µm. The slags main chemical composition consists of calcium (42% CaO), silicon (26% SiO<sub>2</sub>), magnesium (11% MgO) and aluminum (2.1% Al<sub>2</sub>O<sub>3</sub>) and some minor, but still considerable, amounts of d-block metals, such as chromium (1.18% Cr), titanium (0.50% Ti), iron (0.72% Fe), and manganese (0.45% Mn). The mineralogical composition of the slag consists mainly of merwinite, Ca<sub>3</sub>Mg(SiO<sub>4</sub>)<sub>2</sub>, and akermanite, Ca<sub>2</sub>Mg(Si<sub>2</sub>O<sub>7</sub>) phases. Furthermore, a spinel phase was observed which could possibly be assigned to (Fe,Mg)(Cr,Al,Fe)<sub>2</sub>O<sub>4</sub>, which contains chromium.

### 2.2. Alkaline pressure leaching test

Leaching experiments were carried out in a 100 mL stainless steel reactor (Premex reactor ag<sup>®</sup>) equipped with a digitally controlled electric heating. The reactor was purged and pressurized at room temperature with O<sub>2</sub> as an oxidant to a predetermined amount (8.4 bar) after which the reactor was sealed. A mechanical agitator with a stirring speed of 200 rpm was applied, and the reactor was heated to the desired temperature within 20 min (saturated water vapor pressure: 6.8 bar at 160 °C, 18.5 bar at 200 °C, and 43.0 bar at 240 °C). During the leaching test, the pressure, consisting of the partial oxygen pressure and the autogenous water vapor pressure (measured vapor pressure: 15 bar at 160 °C, 24 bar at 200 °C, and 36 bar at 240 °C), and temperature were digitally monitored and logged. After the imposed reaction time (3–6 h), the reactor was cooled down to room temperature in 4 h. Subsequently, the reactor was opened and the recovered suspension was separated in a liquid and a solid fraction by centrifuging and filtering.

For the mechanical activation (MA), dry milling was carried out using a planetary ball mill (Retsch, PM 400) with an overall capacity of 500 mL for 10, 15 or 30 min at a rotation speed of 400 rpm. After milling, the activated sample directly went to the alkaline pressure

leaching step. Particle size analyses were carried out by powder laser diffraction (Microtrac S3500). Samples were analyzed by the wet method through dispersion in deionized water (L/S 20) after sonication for 5 min.

#### 2.2.1. Preliminary test

In order to select the most suitable reagent and concentration range for the experimental design, alkaline leaching was investigated with different alkaline agents, such as Na<sub>2</sub>CO<sub>3</sub> and NaOH, and concentrations of these reagents between 0.02 and 1 M.

#### 2.2.2. Experimental design

Based on the preliminary results, further Cr leaching experiments with SS slag were performed according to a design of experiment (DOE). The applied design includes 4 independent parameters that are each tested at two levels (low and high, coded –1 and +1 respectively), namely temperature (160, 240 °C), leaching time (3, 6 h), NaOH concentration (0.5, 1 M), and mechanical activation (MA) time (0, 30 min). The aim of this design model is to identify which factors have a significant effect on Cr leaching. Therefore a fractional factorial (2<sup>4-1</sup>) design of experiments was adopted, requiring just 8 experiments. This implies that higher order effects like three-way interactions are negligible compared to the main effects, a concept known as *sparsity*. In addition, two center point (replicate) observations (parameter values in between high and low values, coded 0) were added to the design to assess the linearity assumption. The obtained experimental results were processed using the Minitab 14 statistical software. The analysis of variance (ANOVA) was performed to assess the main effects of the investigated factors, their importance in the regression model as well as the lack of fit and curvature significance.

The change of standard Gibbs energy for Cr<sub>2</sub>O<sub>3</sub> or spinel structure reaction with alkaline agents or oxygen as an oxidant was calculated using HSC software (2002).

### 2.3. Environmental and carbonation testing

#### 2.3.1. Preliminary washing

The obtained residue after APL was washed at a liquid to solid (L/S) ratio of 20 with various washing agents, such as water with sonication in an ultrasonic bath, NaOH, and HCl at 25 °C for 1 h. Subsequently, the washed residue was dried at 105 °C for 6 h prior to performing a one stage leaching test.

#### 2.3.2. One stage leaching test

In order to determine the metal leachability from the residues of the APL before and after carbonation of the residue, batch leaching tests were performed based on the European Standard EN 12457-2 (2002) leaching test method. During this test 2.0 g of solid material was mixed with 20 mL ultrapure water (18.2 MΩ cm) (L/S ratio 10) in a 100 mL Pyrex beaker, and stirred with a magnetic stir bar at 200 rpm, 25 °C for 24 h. The leaching solution was filtered with a 0.45 µm membrane filter for subsequent ICP-AES analysis.

#### 2.3.3. Carbonation test

The APL residue after washing with 0.1 M NaOH and drying was used for the carbonation experiments. The leaching residue was mixed with 10 wt% water and compressed in a cylindrical mold with a diameter of 25 mm using a compaction force of 175 kgf/cm<sup>2</sup>. The final height of the cylinders was 11 mm, and the bulk density was 2.33 g/cm<sup>3</sup>. Carbonation of the cylinders was carried out in a reactor at 20 bar pCO<sub>2</sub> (with automatic replenishment of the consumed CO<sub>2</sub>) and at 80 °C for 8 h according to the Carbstone process (Quaghebeur et al., 2009, 2010). The compressive strength

Download English Version:

<https://daneshyari.com/en/article/8102610>

Download Persian Version:

<https://daneshyari.com/article/8102610>

[Daneshyari.com](https://daneshyari.com)