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FEASIBILITY STUDY FOR CHROMIUM (Cr) RECOVERY FROM STAINLESS STEEL SLAG

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Introduction

Chromium (Cr) containing slags (Cr < 2 wt.%) such as electric arc furnace (EAF) slag or argon decarburisation (AOD) slag are solid wastes generated during melting or refining of stainless steel.[1] Currently, most of these slags are still disposed of in landfills or used as low grade materials in construction applications. Due to changing economic conditions and technological innovations, these types of waste have become potential resources, especially for the Cr as a critical raw material in EU.[2] Through the metal removal the mineral matrix material is cleaned from these contaminants and can be used as a valuable product in the building industry without posing a risk to the environment. Carbonation of the slag mineral matrix enhances the technical and environmental properties of the matrix material and increases its value as a construction material.[3]

This work focusses on the selective leaching of Cr from stainless steel slags by applying several hydrometallurgical methods in order to recover Cr and safely re-use the matrix material.

Material and methods

A representative Cr slag sample, obtained from a stainless steel producer, was used in this study and contained around 1.2 wt.% Cr (Table 1). For this study, the slag was crushed and grinded below 125µm.

The alkaline pressure leaching (APL) experiments were carried out in a 100 mL stainless steel reactor equipped with electric heating and temperature controller. A mechanical agitator with a stirring speed of 200 rpm was applied. As an oxidant, O_2 was added to the reactor at room temperature to a predetermined amount (8.4 bar) and then the reactor was sealed, stirred and heated during 6 hours. For the mechanical activation, milling was carried out using a planetary ball mill for 10, 15 or 30 min at a rotation speed of 3000 min^{-1}.

The total concentration of chromium and other matrix elements in the leach liquor and residue was determined by ICP-MS and XRF, respectively. Mineralogical analyses were performed using XRD. The morphology of the sample and distribution of the Cr in the original sample were determined using SEM/EDS, respectively.

Results and discussion

Sample characterization

In Table 1 the chemical composition based on XRF analysis of the original Cr slag is given.

Table 1: Major elements of Cr slag

Elements	CaO	SiO_2	MgO	Al_2O_3	TiO_2	Total Fe	Total Cr	Total Mn
wt.%	38.50	40.65	14.10	1.80	0.75	0.72	1.18	0.45

Figure 1 shows the X-ray diffraction (XRD) pattern of the stainless steel slag. Merwinite, $Ca_3Mg(SiO_4)_2$, and akermanite, $Ca_2Mg(Si_2O_7)$ are the major crystalline phases and chromium is mainly present in a $Mg(Fe_{0.2}Cr_{1.8})O_4$ spinel structure. Scanning electron microscopy (SEM**)** images of the stainless steel slag are shown in Figure 2. It indicates that Cr is present in both spinel and metal phases. The former phases have small dimensions (<10µm) and are surrounded by calcium silicate matrix phases (Figure 2a), while the latter phases are present as metal droplets (Figure 2b) consisting of iron rich alloys.

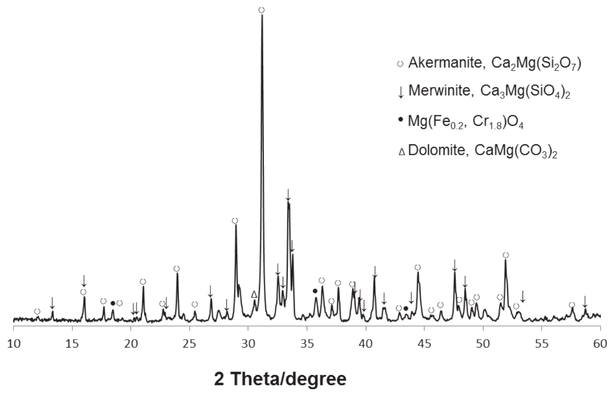

Figure 1: XRD pattern of a Cr-containing stainless steel slag used in this study

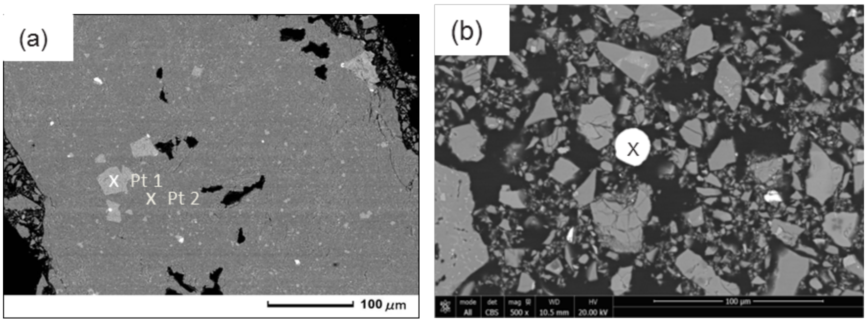

Figure 2: SEM images of raw material: (a) small Cr-oxide (X pt 1) in the silicate matrix (X pt 2), (b) FeCr metals (point x)

Acid leaching

Citric acid leaching in the presence of an oxidant (H_2O_2) at room temperature did not prove successful since the alkaline slag material easily dissolves, causing a low selectivity towards Cr leaching. Also, acid leaching with addition of extra reaction energy, in the form of ultrasound, had a negative effect on the selectivity of Cr leaching, and only increased the dissolution of matrix material (Si, Mg, Ca).

Alkaline pressure leaching (APL)

Cr leaching was investigated in oxidative pressurized conditions at elevated temperatures. As a preliminary test, Cr slag was leached with different alkaline agents, such as Na_2CO_3 and NaOH, and at various NaOH concentrations in the presence of oxygen gas. Figure 3 shows the Cr leachability of the stainless steel slag with different alkaline agents and concentrations. Cr leaching was not efficient in presence of only oxygen. The addition of Na_2CO_3 and NaOH at stoichiometric amounts according to Eq. 1 and 2, slightly increased the Cr leachability to 5.5 and 6.0 %, respectively. However, when the concentration of NaOH was increased to 1M, Cr leaching was drastically enhanced to 20%.

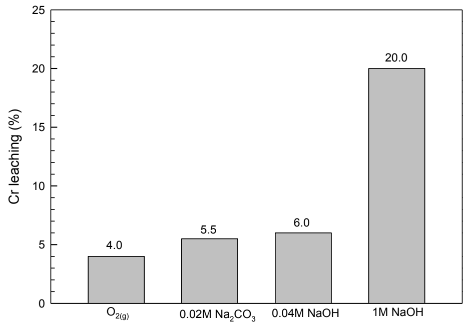

Figure 3: Leaching of Cr (%) with different alkaline concentrations (pO_2 8.4 bar, 240°C, 6hr)

$Cr_2O_3 + 1.5O_{2(g)} + 2Na_2CO_3 = 2Na_2CrO_4 + 2CO_{2(g)}$ $\Delta G_{298K} = -26.11$ kcal (1)

$Cr_2O_3 + 1.5O_{2(g)} + 4NaOH = 2Na_2CrO_4 + 2H_2O$ $\Delta G_{298K} = -89.01$ kcal (2)

Based on the previous results (Figure 3), APL leaching of Cr slag was investigated after different mechanical activation (MA) times to optimize it. As shown in Figure 4, Cr leaching was increased with the milling time to 46%.

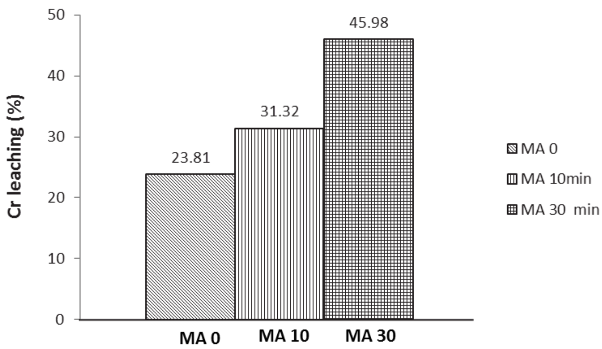

Figure 4: Effect of mechanical activation time

Conclusions

In this work, to develop an effective hydrometallurgical recovery of Cr from stainless steel slags, selective Cr leaching by several methods including APL combined mechanical activation was investigated. Based on the experimental results, the following conclusions are drawn.

- The stainless steel slag is composed of more than 90 wt.% calcium silicate matrix with merwinite ($Ca_3Mg(SiO_4)_2$) and akermanite, ($Ca_2Mg(Si_2O_7)$) as major phases and 1.2 wt.% chromium is mainly embedded in the matrix material as fine amorphous oxides or droplets of FeCr metal.
- Acid leaching by citric acid in H_2O_2 assisted with ultrasound was not selective for Cr leaching and also dissolved the matrix materials.
- The leaching efficiency of Cr under alkaline oxidized conditions increased with temperature and mechanical activation (MA) time. The Cr leaching after MA increased from 24% (no milling) to 48% after 30 minutes of milling.

References

1. H. Zhang, X. Hong, "An overview for the utilization of wastes from stainless steel industries", *Resour.Conserv.Recy.*, **55** 745-754 (2011).
2. UNEP report, Metal recycling-opportunities, limits, infrastructure (2013).
3. M. Quaghebeur, P. Nielsen, B. Laenen, E. Nguyen, & D. van Mechelen, "Carbstone: sustainable valorisation technology for fine grained steel slags and CO_2". *Refractories Worldforum,* **2** 75-79 (2010).