



Selective recovery of Cr from stainless steel slag by alkaline roasting followed by water leaching



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ABSTRACT

Selective chromium (Cr) leaching from stainless steel slag (SS slag) by alkali roasting followed by water leaching was investigated. The efficiency of the alkali roasting process for Cr leaching was increased by optimizing the mass ratio of alkaline agents (NaOH, and NaOH–NaNO₃) to the slag, roasting temperature and time. At the optimum condition (0.67 mass ratio of NaOH to SS slag, 400 °C, 2 h) of NaOH roasting, chromium leaching was around 83%, while the matrix material was dissolved only to a limited extent (Si 8.0%). Mechanical activation of the SS slag prior to roasting reduced the optimum NaOH to SS slag mass ratio to 0.4. The addition of NaNO₃ as an oxidant to the NaOH salt increased Cr leaching to 89% after roasting at 400 °C for 2 h. The remaining Cr phases in the residue were almost exclusively FeCr alloys. Further chromium dissolution from these alloys is prevented by a passivation layer of Fe oxides as shown by SEM/EDS images. Based on these results, a SS slag recycling process is suggested in which roasting–water leaching followed by water washing to remove Cr yields a residue which has potential for application as a construction material.

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1. Introduction

Global stainless steel production increased from 29.8 million tons in 2007 to 34.7 million tons in 2014 (Outokumpu Annual Report, 2014; World Steel Association, 2014). During the steel production process, stainless steel slag (SS slag) such as electric arc furnace (EAF) slag or argon decarburization (AOD) slag is produced as a byproduct. Approximately one ton of slag is generated per 3 tons of produced stainless steel (Shen et al., 2004; Niemelä and Kauppi, 2007). In Europe, around 48% of steel slag is used as road base aggregates (Euroslag Statistics, 2010) and the remainder is being dumped into landfills or stockpiled for long periods at steel plants. SS slag contains relatively high amounts of chromium (Cr), which is a hazardous material when in oxidation state +6 (Zygmunt and Marta, 2003; Dhal et al., 2013), and lower concentrations of valuable Ni, Mo, and V. Therefore, the removal of such metals from the SS slag matrix would improve the environmental quality of the slag material for further use as cement or construction material while simultaneously recovery of the valuable and critical metal Cr (UNEP Report, 2013) takes place. In fact, the constraints on slag utilization imposed by the high chromium concentrations in the slag (up to 4 wt.%) have been a main driver to study removal or recovery of chromium (Shen and Forsberg, 2003; Shen et al., 2004).

Chromium recovery from primary as well as secondary ores through alkali extraction has been investigated by many researchers. These

processes comprise alkaline roasting with NaOH (Hundley and Olsen, 1985; Yildiz and Sengil, 2004) or Na₂CO₃ (Tathavadkar et al., 2003; Guo et al., 2014), and molten salt process with NaOH(–NaNO₃) (Zhang et al., 2010a, 2010b; Liu et al., 2013b; Wang et al., 2014b, 2015; Zhang et al., 2014) or KOH (Xu et al., 2005; Chen et al., 2013, 2014; Liu et al., 2013a; Sun et al., 2009; Wang et al., 2014a). Previous works on alkaline extraction from secondary ores are summarized in Table 1. The traditional recovery of Cr from chromite ore dominantly involves roasting with Na₂CO₃ above 1100 °C (Ladd and Vanderpool, 1987; Habashi, 1997; Antony et al., 2001; Dhal et al., 2013; Li et al., 2015). However, this process is very energy consuming since it takes place at high temperatures and is therefore not economical for the treatment of low grade ore materials containing only a few percentages of Cr.

Compared to Na₂CO₃ roasting, NaOH or KOH molten salt (Amer and Ibrahim, 1996; Xu et al., 2005, 2006; Wang et al., 2013; Zhang et al., 2014) can decrease the operating temperature (200–450 °C) and the salt can be reused after evaporation. This process, however, requires high pressure (up to 3.2 MPa) and a high concentration of the alkaline agents (60–70 wt.%) resulting in the significant dissolution of matrix elements such as Al and Si. Zhang et al. (2010a) investigated the decomposition of chromite ore in molten NaOH in the presence of NaNO₃ instead of oxygen to decrease decomposition temperature. It was reported that the reaction temperature decreased from above 500 °C to 400 °C without consumption of sodium nitrate, which plays a role as an oxygen carrier according to Eqs. (1)–(3):



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Table 1
Summary of previous works on Cr extraction from secondary resources using alkaline extraction.

Materials	Mineralogy	Methods	Reaction conditions	Leaching (%)	Reference
Vanadium slag (V ₂ O ₅ 10.2%, Cr ₂ O ₃ 4.2%)	Spinel (Mn,Fe)(V,Cr) ₂ O ₄ , SiO ₂ , fayalite Fe ₂ SiO ₄	Molten NaOH salt (40 wt.%) + electro-oxidation	120 °C, 6 h, current density 750 A/m ²	V 95%, Cr 90%	Wang et al. (2015)
Vanadium slag (V ₂ O ₅ 10.6%, Cr ₂ O ₃ 3.8%)	Spinel (Mn,Fe)(V,Cr) ₂ O ₄ , SiO ₂ , fayalite Fe ₂ SiO ₄	Molten KOH (70–75 wt.%) salt	180 °C, 5 h, O ₂ /air 1 L/min at 1 atm	V 95%, Cr 90%	Liu et al. (2013a)
Vanadium slag	Spinel (Mn,Fe)(V,Cr) ₂ O ₄ , SiO ₂ , fayalite Fe ₂ SiO ₄	Molten salt 1) NaOH 80% 2) KOH 70–75% 3) NaOH–NaNO ₃	180–375 °C, 6 h, O ₂ 1 L/min	V 95%, Cr 90% in KOH molten salt	Wang et al. (2014b)
Vanadium slag (V ₂ O ₅ 10.2%, Cr ₂ O ₃ 4.2%)	(Mn,Fe)(V,Cr) ₂ O ₄ , Fe ₂ SiO ₄ , SiO ₂	NaOH–NaNO ₃ molten salt	350–450 °C, 6 h, NaNO ₃	V 94%, Cr 88%	Liu et al. (2013b)
*COPR (Cr ₂ O ₃ 14.0%)	Mg(Al,Cr) ₂ O ₄ , γ-Fe ₂ O ₃ , Cr ₂ O ₃	Na ₂ CO ₃ roasting	1150 °C, 1 atm air	Cr 85%	Antony et al. (2001)
Spent Cr–Fe catalyst (6% Cr, 62% Fe as oxides)	Cr ₂ O ₃	NaOH or Na ₂ CO ₃ roasting (+ H ₂ O ₂)	600–700 °C, 2 h, 1 atm air	Cr > 89.7%	Stubbs and Jong (1988)
Laterite ore (Cr ₂ O ₃ 5.0%)	FeOOH, Fe ₂ O ₃ , Fe ₃ O ₄ , Al(OH) ₃ , (Mg,Fe)(Cr,Al) ₂ O ₄ , MnO(OH)	Na ₂ CO ₃ roasting	1000 °C, 1 atm air	Cr 99%, Al 82%	Guo et al. (2014)
Limonitic laterite ore (Cr ₂ O ₃ 3.3%)	FeOOH, Fe ₂ O ₃ , Fe ₃ O ₄ , Al(OH) ₃ , (Mg,Fe)(Cr,Al) ₂ O ₄ , MnO(OH)	NaOH roasting	700 °C, 1 atm air	Cr 96%, Al 84%, Si 40%	Guo et al. (2012)
Cu–Cr catalyst (Cu 42.4%, 36.2% Cr)	CuCrO ₂ , CuCr ₂ O ₄ , Cu ₈ O	Mechanical activation followed by NaOH roasting	850 °C, 2 h, 1 atm air	Cr 92%	Swaroop et al. (2013)
Synthesized vanadium slag (Cr ₂ O ₃ 35.3–46%)	Fe _x Cr _{3-x} O ₄ , Mg _x (Fe,Cr) _{3-x} O ₄ , (Fe,Mn) ₂ SiO ₄ , (Mn,Mg)SiO ₃	Na ₂ CO ₃ roasting	1000 °C, 2 h, 1 atm air	Cr 90%	Fang et al. (2012)

* COPR: chromite ore processing residue.



Others have investigated Cr leaching from chromite ore using sulfuric acid (60–80 wt.%) at elevated temperature (160–240 °C) with or without HClO₄ as an oxidant (Amer, 1992; Vardar et al., 1994; Geveci et al., 2002; Jiang et al., 2014; Zhao et al., 2014). However, since slag materials are generally composed of alkaline mineral phases such as CaO, Al₂O₃ and MgO, acid leaching will dissolve the stainless steel slag matrix materials as well as cause a high consumption of acid solution. Recently, it was shown that alkali pressure leaching could recover Cr selectively from SS slag material with a modest yield (48%), without dissolving or altering the matrix material drastically (Kim et al., 2015).

As an alternative, roasting with NaOH (Hundley and Olsen, 1985; Stubbs and Jong, 1988; Guo et al., 2012) instead of Na₂CO₃ was studied in chromite ore as well as secondary resources. This process has the advantage that it can operate at lower temperatures (550–850 °C) than Na₂CO₃ roasting at atmospheric pressure in air. Compared to the molten slag process, consumption of alkali reagent is decreased, but the operating temperature remains higher.

In this study, alkali roasting with a relatively low concentration of alkaline salt, followed by water leaching, was applied in order to selectively recover Cr from stainless steel slag. The effect of process parameters (i.e. roasting temperature and time, mass ratio of alkaline agents to the slag) and pretreatment (i.e. mechanical activation prior to roasting) on leaching behavior was studied. The effect of these parameter optimizations to reduce both the reaction temperature and the required amount of alkaline reagent is studied, in order to improve the economics of the process.

2. Experimental

2.1. Materials

A representative stainless steel slag (SS slag) sample, containing around 1.2 wt.% Cr (Table 2), was obtained from a historic slag mono-landfill. For this study, the slag was crushed and ground below 125 μm.

For the mechanical activation (MA), a planetary ball mill (Retsch, PM 400) with an overall capacity of 500 mL was used. Mechanical activation took place by dry milling of the slag (<125 μm) at a rotation speed of 400 rpm for 15 min based on previous results (Kim et al., 2015). The milling chamber contained 100 g of sample together with 5 tungsten carbide balls of 30 mm diameter. After milling, the activated sample directly went to the alkaline roasting step.

2.2. Alkali roasting and water leaching

The roasting of the stainless steel slag was carried out in an alumina crucible, which was placed in a temperature controlled muffle furnace. Before, 3.0 g of SS slag sample (<125 μm) was mixed homogeneously with a predetermined amount of alkaline agents (NaOH, or NaOH–NaNO₃) and placed in the crucible. Then 4 mL of water was added to the mixture to dissolve the alkali reagent before roasting. This reaction mixture was heated in the muffle furnace at a heating rate of 2 °C/min until the set roasting temperature (300 °C–400 °C). Then the set roasting temperature was maintained for 2, 4 or 6 h. During the roasting, no gas injection system was applied to enhance the roast.

To determine the Cr extractability, the roasted material was manually ground by mortar and pestle. Then water leaching of the roasted product took place in a 100 mL Pyrex beaker with magnetic stirring for 1 h at 50 °C at an L/S of 10 which was selected by preliminary leaching tests. After vacuum filtration, the Cr concentration in the solution was measured, and other elements such as Al, Si, Ca, Mg were analyzed in the solid residue to determine Cr leachability and selectivity among the other elements.

2.3. Analytical methods

Particle size distributions were measured using powder laser diffraction (Microtrac S3500). Therefore, the sample was prepared and

Table 2
Major compounds of the studied SS slag.

Elements	CaO	SiO ₂	MgO	Al ₂ O ₃	TiO ₂	Total Fe	Total Cr	Total Mn
Wt.%	40.30	31.23	6.01	1.74	1.13	0.64	1.18	0.54

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