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In-situ chromium and vanadium recovery of landfilled ferrochromium and stainless steel slags

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HIGHLIGHTS

- NaOCl assisted alkaline heap leaching of Cr and V from slags was investigated.
- The matrix material of stainless steel slag and ferrochromium slag remains intact.
- 11–19% Cr and 7.0–7.5% V were leached selectively after 64 days.
- A model shows that Cr will leach for 4–5 years at chosen heap leaching conditions.
- Cr and V extraction potentially improves the slags' environmental quality.

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ABSTRACT

A novel heap leaching method was investigated for selective removal of chromium (Cr) and vanadium (V) from ferrochromium (FeCr) and stainless steel (SS) slags. In particular, alkaline oxidative heap leaching was simulated on lab-scale by batch and column leaching tests. The results show a selective leaching of Cr (11–19%) and V (7.0–7.5%) after 64 days of column leaching, with a very low dissolution (<2.2% (FeCr slag) and <0.15% (SS slag)) of matrix elements (e.g. Al, Fe, Si, Mg, Ca), when NaOCl is applied as oxidation agent and NaOH as alkaline agent. Furthermore, the used leaching liquor is reactive for a longer period of time, indicating that circulation of leaching liquor could be possible. Finally, the experimental results were fed into a first-order model which predicts that Cr will continue to leach from the tested slags for 4–5 years at a chosen infiltration rate of 73,000 l/(y m^2).

1. Introduction

1.1. Ferrochromium and stainless steel slags

In the value chain of stainless steel production, significant amounts of chromium (Cr) are lost in ferrochromium (FeCr) slags and stainless steel (SS) slags. FeCr slags are generated during the production of ferrochromium, an intermediate product for stainless steel production (1.1–1.6 tonnes FeCr slag/ton ferrochromium) [1]. In 2013 the global ferrochromium production amounted to 9.93 Mt [2]. Stainless steel slag (SS slag) is a by-product generated during the production of stainless steel, at approximately one ton of slag per 3 tonnes of produced stainless steel. The global stainless steel production was 38 Mt in 2013 [2].

Cr concentrations in FeCr and SS slags are in the range of 2–8% and 1–2%, respectively. Johnson et al. has estimated that in Europe (including Turkey) 74,900 t/y and 18,700 t/y Cr is lost in FeCr slag and SS slag, respectively [3].

Due to its high chromium content as well as poor physical properties, SS slag has almost no utilization. Most of the produced slag is initially stockpiled in the steel plants and sent to slag disposal sites. For instance, at the REMO landfill site in Belgium, about 1 Mt of SS slags were recently reported to be stored in dedicated zones of the landfill [4]. Due to the amounts of Cr, which is a hazardous material (recognised as a human carcinogen) when in oxidation state +6 [5], their disposal is an environmental concern [4]. In the past, research and development with regard to mono-landfills, brownfields and slag ponds containing these slag

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materials have mainly focussed on remediation, stabilisation and pollution prevention both for SS slag and FeCr slag materials [6,7].

Only a small proportion of SS slag is recycled and treated for application in inner plant recycling, cement mixture, and roadbed material [8]. When FeCr slags are used in road construction without extra treatment, the chromium has been found to leach to the environment and be taken up by surrounding life [9]. Apart from relatively high amounts of Cr, SS slag contains also significant concentrations of valuable Ni, Mo, and V. Removal of these metals, together with the Cr from the FeCr and SS slag matrix will improve the environmental quality of the slag material for further use as cement [10] or construction material [11]. Simultaneous recovery of valuable and critical metals could take place. Currently, the recovery of Cr from both FeCr and SS slags occurs mainly by physical separation processes which recover metallic alloys containing Cr [12]. However, the hydrometallurgical recovery of Cr, present in mineral phases other than alloys within the slags, has not been studied extensively.

1.2. Hydrometallurgical recovery of Cr and V

The traditional recovery of Cr from chromite ore or Cr oxides involves roasting with Na_2CO_3 above 1100 °C [5]. Since this process is very energy consuming, it is not applicable to low-grade ore materials (such as the FeCr and SS slags). Alternatively, a hydrometallurgical method based on caustic soda leaching has been investigated for Cr recovery from chromite ore as well as chromium oxides [13]. Indeed, chromium oxides present in slag can readily dissolve with NaOH/KOH under oxidative pressure (1–3.2 Mpa) at 210–300 °C [14]. This process, however, requires high pressure and a high concentration of alkaline agents (60–70 wt%). An additional disadvantage is the dissolution of matrix elements such as Al and Si which strongly hinders the recycling of the left-over matrix material. Several other studies describe Cr leaching from slag materials in acidic conditions under pressurised H_2SO_4 [15] as well as HCl [16]. However, also those processes simultaneously dissolve the stainless steel slag matrix materials, *i.e.* no selective Cr leaching takes place. Alternatively, landfilling of the materials after stabilisation of soluble Cr(VI) to insoluble Cr(III) by reducing agents such as $FeSO_4$ [17] Na_2S [18], Ca_5S [19] or through biological treatment [12] from low-grade Cr-materials like chromite ore processing residue (COPR), has been studied. This, however, is not a promising process due to the generation of a large amount of waste material and still remaining soluble Cr(VI) by incomplete reduction of Cr posing a long-term risk to the environment. An oxidative leaching environment causes Cr species to more readily dissolve both in acidic as well as in alkaline environments, as we have shown theoretically in previous work [20]. The above overview clearly shows that there is still a great need for an efficient and effective process that can (i) recover most to all of the Cr present in the slag, while (ii) leaving the matrix materials unaffected and ready for further recycling, for example as a construction material. However, in recent studies, an alkaline roasting method [21] and oxidative alkaline leaching methods, such as pressure leaching [20] and NaOCl assisted leaching [22], were developed in which Cr can be selectively leached from a stainless steel slag, allowing for a further valorisation as a construction material of the slags' matrix material. Such methods require batch wise processing steps at elevated temperatures (105–400 °C), that could impede the economics for a sustainable treatment route of these low-grade and low-value waste materials.

Similar to Cr, V can be recovered from low-grade primary and secondary raw materials, such as steel slag, by means of roasting processes [23] or alkaline leaching in the presence of oxidation agents [24]. Generally, the oxidant in V leaching oxidises V(III) and/or V(IV) to V(V) to enhance V dissolution.

1.3. Heap leaching

Heap leaching is traditionally used in the mining industry to extract (precious) metals from low-grade ores [25]. In the mining industry, these low-grade ores are excavated, agglomerated and heaped on an impermeable liner. The ore is then sprinkled with a leach solution for a period of one month up to two years, depending on the treated ore. The pregnant leach solution is collected at the bottom of the heap and the metals (and other elements) are subsequently recovered from it.

Heap leaching has also been investigated as a possible route to remediate heavy metal contaminated soils [26]. Heap leaching technology is low cost and flexible, and could therefore be suitable to treat low-grade mineral waste streams. Commercial heap leaching operations focus on the mining of mainly copper, nickel, uranium and gold by means of acid leaching [25]. However, alkaline leaching has been tested and could be beneficial for high acid consuming ores [27].

In the current study, explorative experiments were set up to simulate alkaline heap leaching from FeCr and SS slag material. The main aim of these experiments is to obtain an efficient and selective Cr, and possibly V, recovery from these slag materials with a minimal dissolution or mineral alteration of the matrix material. By achieving this aim, a critical raw material, namely Cr, could be recovered from a nowadays landfilled waste material. In addition, the bulk materials from these wastes could become environmentally suitable for further use in, for instance, new construction materials.

2. Materials and methods

2.1. Materials

In this work, two types of mineral waste materials were tested: Firstly, a sample of electric arc furnace stainless steel (SS) slag, which is finely grained and obtained after stainless steel recovery by an industrial scale slag treatment installation. Secondly, a FeCr slag, which was produced during FeCr refinery. Both samples were taken at a slag treatment company in Belgium according to the Flemish standard CMA/1/A.14, which is based on the standard CEN/TR 15310 – 1:2006, ensuring a homogeneous and representative sampling [28].

The FeCr slag materials were ground by a planetary ball mill (*Retsch*, *PM 400*), sieved to the desired particle size and/or granulated by an *Eirich mixer R02*. Granulation was performed by introducing the fine grained solid and the leaching liquor with a volume ratio of 5:1 in the Eirich mixer and applying a pan speed of 1 m/s and a mixing speed of 2 m/s for 3 min. The used pre-treatment method for each experiment is clearly mentioned in the results section.

Used reagents include NaOH pellets (min. 99%, *Merck*), NaOCl solution (14% Cl_2, *VWR Chemicals*) and O_2 gas (99.5%, *Air Products*). Solutions were prepared in deionised water.

2.2. Batch and column leaching

Batch leaching tests were performed in a plastic beaker at room temperature which contained 100 g slag material (FeCr slag) and 1 l leaching solution. The leaching solution consisted of 1 M NaOH with either NaOCl (0.197 M) or pure O_2 gas (continuous purging) as oxidising agents. The slurry was magnetically stirred at 200 rpm. At regular intervals the temperature, pH and conductivity (*Mettler Toledo SevenMulti*) and oxidation/reduction potential (*WTW Multi3430*) of the slurry was measured and a 10 ml sample was taken while stirring. Next, this sample was filtered by a Whatman mixed