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

E. Kim^{1,2,*}, J. Spooren¹, K. Broos¹, P. Nielsen¹, L. Horckmans¹, R. Geurts¹, K. C. Vrancken^{1,2}, M. Quaghebeur¹

¹VITO – Flemish Institute for Technological Research, Boeretang 200, BE-2400 Mol, Belgium

²Department of Bioengineering, University of Antwerp, Groenenborgerlaan 171, BE-2020 Antwerp, Belgium

*Corresponding author

E-mail address: key7649@gmail.com, eunyoung.kim@vito.be

Address: VITO, Boeretang 200, BE-2400 Mol, Belgium

Tel: +32-14-33-57-35

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E. Kim^{1,2,*}, J. Spooren¹, K. Broos¹, P. Nielsen¹, L. Horckmans¹, R. Geurts¹, K.C. Vrancken^{1,2}, M. Quaghebeur¹

¹VITO – Flemish Institute for Technological Research, Boeretang 200, BE-2400 Mol, Belgium

²Department of Bioengineering, University of Antwerp, Groenenborgerlaan 171, BE-2020 Antwerp, Belgium

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 stabilise the remaining Cr in the matrix material and make the subsequent recycling of the matrix material as a construction material possible.

1. Introduction

Chromium (Cr) containing slags (Cr < 2 wt%) such as electric arc furnace (EAF) slag or argon decarburisation (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 Elevelis, 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 FeSO₄ (Jagupilla et al, 2009), Na₂S (Velasco et al, 2012) and Ca₅S (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 Na₂CO₃ 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 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 H₂SO₄ (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 2⁴⁻¹ 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), silicium (26% SiO₂), magnesium (11% MgO) and aluminum (2.1% Al₂O₃) 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, Ca₃Mg(SiO₄)₂, and akermanite, Ca₂Mg(Si₂O₇) phases. Furthermore, a spinel phase was observed which could possibly be assigned to (Fe,Mg)(Cr,Al,Fe)₂O₄, which contains chromium.

2.2. Alkaline pressure leaching test

Leaching experiments were carried out in a 100 mL stainless steel reactor (Premex reactor ag®) equipped with a digitally controlled electric heating. The reactor was purged and pressurized at room temperature with O₂ 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 to 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.

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 Na₂CO₃ and NaOH, and concentrations of these reagents between 0.02 and 1 M.

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, 6h), 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 (2⁴⁻¹) 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 Cr₂O₃ or spinel structure reaction with alkaline agents or oxygen as an oxidant was calculated using HSC software (2002).

2.3. Environmental and carbonation testing

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.

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 gram 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.

Carbonation test

The APL residue after washing with 0.1M 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 kg_f/cm². The final height of the cylinders was 11 mm, and the bulk density was 2.33 g/cm³. Carbonation of the cylinders was carried out in a reactor at 20 bar pCO₂ (with automatic replenishment of the consumed CO₂) and at 80 °C for 8 h according to the Carbstone process (Quaghebeur et al., 2009; Quaghebeur et al., 2010). The compressive strength of the carbonated cylinders was measured. For the leaching tests the carbonated samples were crushed and milled to obtain a similar grain size as that of the original material (< 125 μm).

2.4. Analytical methods

The total concentration of chromium and other matrix elements in the leach liquor was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo Elemental). The chemical compositions of the residue and raw material samples (< 125 μm) were determined by X-ray fluorescence (XRF, Thermo Scientific) and ICP-AES after microwave digestion of the sample with HCl, HNO₃, and HF (described in method CMA/2/II/A.3, VITO, 2005). Mineralogical analyses were performed using X-ray diffraction (XRD, Philips). The morphology of the sample and distribution of the Cr therein were determined using scanning electron microscopy (SEM, FEI) and energy dispersive X-ray (EDS, Bruker), respectively. For SEM analysis, samples were embedded in an epoxy resin, polished to produce a smooth, flat surface, and coated with a thin PdPt (80:20wt%) layer.

3. Results and discussion

3.1. Slag characterization

SEM images of the stainless steel slag (Fig 1) indicate that Cr is mainly present in both spinel and FeCr alloy phases. The spinel phases have small dimensions (< 10 μm) and are embedded in calcium silicate matrix phases (Fig. 1a), while the FeCr iron rich alloy phases (Fig. 1b) are present as metal droplets (< 20 μm).

3.2. Thermodynamic analysis

The changes of standard Gibbs energy for Cr₂O₃ oxidation reaction with oxygen in the absence (Eq. 1) and presence of different alkaline agents (Eqs. 2-3) were calculated at standard states. The results show that the Gibbs free energy of reactions 2 and 3 is negative, meaning that the oxidation of Cr(III) to Cr(VI) occurs relatively easy in the presence of Na₂CO₃ and NaOH. Furthermore, at standard states the presence of NaOH is preferable because the reaction is characterized by a lower Gibbs free energy (Eq. 3). On the other hand, oxidation cannot occur thermodynamically at standard states without an alkaline agent (positive Gibbs free energy for Eq. 1). It shows that an alkaline agent, especially NaOH, is an important factor in oxidative Cr leaching at relatively low temperatures (Zydorczak et al, 2012; Qi et al., 2011; Xu et al, 2005).

However, in the stainless steel slag Cr(III) is not present in Cr_2O_3 but rather in more complex spinel phases. Compared to the Cr_2O_3 phase, the spinel MgCr_2O_4 (Eq. 4) is more stable having less negative Gibbs free energy during oxidation in the presence of NaOH, while FeCr_2O_4 (Eq. 5) is more easily dissolved than Cr_2O_3 . Furthermore, the change in Gibbs free energy of Cr(VI) in CaCrO_4 (Eq. 6) upon reaction with NaOH is less negative than for Eq. (4) and (5), which indicates that CaCrO_4 is more stable and difficult to dissolve. These trends are also shown in the E-pH diagrams in Fig. 2. The Cr(III) solid phases, Cr_2O_3 (Fig. 2a), MgCr_2O_4 (Fig. 2c) and FeCr_2O_4 (Fig. 2d) are very stable in the entire pH region except under strong acidic conditions ($\text{pH} < 2$). This indicates that an oxidation regime is needed to dissolve these phases.

3.3. Alkaline pressure leaching (APL)

Zydorczka et al. (2012) have shown that at atmospheric conditions the alkaline leaching of Cr(III) from oxides is very low and the reaction is slow. Therefore, we investigated Cr leaching in oxidative pressurized conditions at elevated temperature, which should improve the thermodynamics and kinetics of Cr dissolution. In 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, in order to establish the preferred reagent and concentration range for a further design of experiment. The obtained Cr leachabilities in these preliminary tests are shown in the supplementary data (SD) section (Fig. 1). As predicted by the thermodynamic analysis (Eqs. 1-3), Cr leaching was not efficient in the presence of only oxygen. The addition of Na_2CO_3 and NaOH at stoichiometric amounts according to Eq. 2 and 3 slightly increased the Cr leachability to 5.5% and 6.0%, respectively. However, when the concentration of NaOH was increased to 1 M, Cr leaching was drastically enhanced to 20% due to increasing ionic activity and diffusivity of NaOH.

Based on the preliminary results described above, the influence of reaction parameters and conditions on selective Cr leaching in the presence of NaOH and O_2 were assessed by a DOE method. Mechanical activation (MA) was introduced as a parameter, since MA by milling is well known to improve the extraction of metal components from minerals (Baláž, 2000). Mechanical activation leads to amorphization of the mineral material by disordering its crystal structure or inducing phase transitions, causing a more facile decomposition (Baláž, 2000). Also, the decomposition temperature of minerals can be reduced by MA during milling (Baláž, 2000, 2008). Zhang et al. (2010) enhanced Cr leaching from chromite ore in molten NaOH by applying MA. They observed an extraction efficiency of 97% after MA for 10 min and leaching for 200 min.

Table 1 presents the used DOE arrangement and the obtained response (Cr leaching (%) results). The ANOVA test was used to analyze the importance of each term in the regression model as well as the lack of fit and curvature significance. The test shows that the factors temperature and MA have a significant effect ($p < 0.05$) on Cr leaching. For the factors time ($p = 0.085$) and NaOH concentration ($p = 0.14$) no significant effect could be concluded at a 95% confidence level. After removal of the non-significant parameters, time and NaOH concentration, a final regression model is made which yields the following equation in coded variables:

$$\text{Cr leaching (\%)} = 22.63 + 11.46 \times \text{Temperature} + 5.31 \times \text{MA} \quad (7)$$

This relation shows that the temperature (coefficient 11.46) has the most significant effect on Cr leaching, followed by mechanical activation time (coefficient 5.31). Since both coefficients are positive, both factors show an increase of Cr leaching when increased (Fig. 3). The results of the ANOVA test on the regression model are reported in the supplementary data (Table I). The linear model above can explain the observations for 64% as is indicated by the adjusted R^2 . Also, the lack-of-fit is considered non-significant ($p=0.206$), indicating a good fit of the observed data to the regression model. However, the ANOVA test also indicates that a significant curvature is present ($p=0.012<0.05$). This is reflected in an underestimation of the Cr leaching at the center point.

With the results above and the chosen experimental design it is impossible to find the optimum parameters for Cr leaching. For this purpose, the design should be extended to a response surface design (e.g. central composite or Box-Behnken) for which additional experiments will have to be carried out in a follow-up study.

An additional experiment was performed in which MA was carried out for 10, 15 and 30 minutes to investigate whether the MA time could be reduced without having a large effect on Cr leaching was investigated (Fig. IIa in SD) in the highest Cr recovery in DOE (i.e. 240 °C, 6 h and 1.0 M NaOH). The Cr leaching increases from 31% to 46% by increasing the MA time from 10 to 30 min. After a MA time of 15 minutes the Cr leaching already reached 43%. 15 minutes of MA is thus sufficient to obtain similar results as with 30 minutes MA. The particle size distribution after 15 and 30 minutes MA are similar (Fig. IIb in SD). The effect of MA on the crystallinity of the composing minerals of the SS slag was investigated and is shown in the supplementary data section (Fig. III). As the MA time was increased the XRD peaks were broadened and less intense, which indicates a decrease of crystallinity (and crystal sizes) and thus amorphization of the material (Baláž, 2000, 2008).

The effect of particle size (without MA) was investigated by comparing Cr leaching from the SS slag after sieving the raw material below 32 μm to the < 125 μm fraction used elsewhere (Fig. IIa in SD). It was shown that the Cr leaching for the <32 μm SS slag was higher (34%) than that of <125 μm fraction (24%), and similar to that when MA of 10 min was applied on the raw (<125 μm) material (31%) (Fig. IIa in SD). Therefore, it can be concluded that the main effect of MA on the Cr leachability is due to a decrease in particle size, or rather the increase of the effective surface area of Cr oxides by liberation. This is confirmed by the particle size (Fig. IIb in SD) which is similar for the < 32 μm and MA 10 min samples, whereas the < 125 μm sample is much coarser. The increase of Cr leaching in MA 15 min to 43% may be attributed to amorphization (i.e. structure disordering or defects). This is confirmed by XRD analyses in function of MA time (Fig. III in SD) indicating decreased intensity and broadening of peaks as of MA 15 min.

Furthermore, the effect of liquid to solid (L/S) ratio was investigated by decreasing L/S ratio from 10 to 5. An decreased L/S ratio can reduce both the reagent consumption and required reactor size, leading to better economics of the process. Generally, L/S ratio can be optimized after the affecting parameters and conditions of the process are optimized and selected (Gupta and Mukherjee, 1990; Habashi, 1997). So, the effect of the L/S ratio on Cr leaching was studied at the maximum Cr leaching condition in our study (240 °C, 1M NaOH, MA 30 min, 6 h). These experiments were not included in the DOE design. The experiments show that the leaching of Cr drastically decreased from 46.0%, to 32.6% and 23.8% as the L/S ratio decreased from 10 to 6 and 5, respectively. Therefore, a lower L/S is disadvantageous for Cr leaching and L/S 10 is the optimum L/S ratio within the tested range.

During the APL at optimal condition (240 °C, 6 h, MA 30 min, 1 M NaOH, L/S 10, 8.4 bar pO_2), the leachability of other elements present in the slag was analyzed (Table II in SD). These analyses showed that most of the elements were not dissolved from the slag. The maximum leaching was observed for Al reaching 2.88%. The presence of Na in the residue originates from the used alkaline agent, NaOH, which remained in concentrations of around 0.8%.

3.4. Residue utilization

3.4.1. Residue analysis

As observed with the SEM, Cr is mainly present in spinel structures and Fe alloys, which are evenly distributed in the silicate matrix of the SS slag (Fig. 1). Shen et al (2004) reported that in stainless steel slag more than 70% of Fe and Cr are generally present in the form of oxides (spinel). The alloy phases are stable in alkaline conditions because a passivation layer of Cr(III) oxide or Fe oxides (Kim et al., 2015) is formed. This is also in accordance with the E-pH diagram presented in Fig. 2.

The SEM/BSE images and EDS mappings of the APL residue (Fig. IV in SD) clearly show that the surface layer of the slag particles has been leached and subsequently covered by new precipitates. The leached layer is the darker (less dense) layer at the surface of the slag particles. The new precipitates, on the other hand, are denser (lighter colored in the SEM/BSE images) than the slag particles. These precipitates are rich in Ca, Al and Si, but contain no or very little Mg. Based on the SEM/BSE images (high density and crystal form), the SEM/EDS mapping and the XRD pattern of the residue (Fig. V in SD) it can be concluded that these precipitates are most likely hibschite, $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_2(\text{OH})_4$. Hibschite may form during APL by hydrothermal reaction with the slag particles. The precipitation of this mineral has been shown to induce hydrothermal solidification of blast furnace slag (Hosokawa et al., 2014). Here, hibschite seems to form a layer around the slag particles, which may hamper the leaching of the underlying slag particles.

XRD patterns of the raw SS slag, and the residue after APL and carbonation are all shown in the supplementary data section (Fig. V). In the APL residue the remains of the silicate minerals akermanite, $\text{Ca}_2\text{Mg}(\text{Si}_2\text{O}_7)$, and monticelite, CaMgSiO_4 can still be observed. Other silicates such as merwinite, $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$ have almost disappeared completely. In the residue also newly formed mineral phases such as hibschite, $\text{Ca}_3\text{Al}_2\text{Si}_2\text{O}_8(\text{OH})_4$ and calcium silicate hydrate phases are present.

3.4.2. Leachability test

The environmental impact of the residue was investigated by performing a one-stage leaching test to investigate Cr leachability of the residue after APL (1 M NaOH, 240 °C, 6 h, MA 30 min, L/S 10). Before the leaching test the APL residue was washed with various washing agents such as water with sonication (No. 1) in an ultrasonic bath, 0.1 M NaOH (No. 2), and 0.1 M HCl (No. 3) to remove adsorbed or unrinsed Cr(VI). The results of these tests are shown in Table III (in SD). Clearly, water washing assisted by sonication was the most effective method for Cr removal. During NaOH washing the amount of Cr in the leachate (washing water) is 40% lower than for the water washed material. However, during NaOH washing far less Ca leaching is observed. Because Ca is as an important resource for the carbonation reactions that bind the slag particles together to produce a brick like building material, NaOH washing is considered more promising. NaOH has also been reported to enhance carbonation, either by enhancing the extraction of Ca- and/or Mg-ions from silicate structures (Blencoe et al., 2004) or by enhancing CO_2 dissolution and precipitation of carbonates (Montes-Hernandez et al., 2012), thus if some NaOH remains in the residue this may also be beneficial for the subsequent carbonation process.

After washing the residue under different conditions, a one-stage leaching test was performed by stirring the residue in water (L/S 10) for 24 h in accordance with EN 12457-2 (2002). The results for the water washed and NaOH washed samples were compared (Table 2). Both alkali pressure leached and subsequently washed materials (No. 1,2) exceeded the legal limit value for Cr leaching for reuse as construction materials in the Flemish region of Belgium (0.5 mg/kg dm). However, washing with 0.1 M NaOH (No. 2) was the most effective treatment to reduce Cr leaching to 0.84 mg/kg dm. Note, that the leaching results of the EN 12457-2 batch leaching test can only be used as an indicative value for comparison with the Flemish leaching limit values. To test whether a material complies with the Flemish leaching limit values a column leaching test in accordance with NEN 7373 (2003) has to be performed. The NEN 7373 and EN 12457-2 leaching tests are both carried out at a L/S ratio of 10, with material < 4 mm. The major difference is that the EN 12457-2 test is carried out under

vigorous shaking during 24 hours, while the NEN 7373 test is a column leaching test that takes 21 days to perform. In many cases the leaching concentrations obtained by both tests are comparable if the same L/S ratio is applied (Grathwohl and Susset, 2009).

3.4.3. Carbonation of the residue

XRD patterns before and after carbonation were measured and are shown in the supplementary data section (Fig. V). The hydroxyl form, hirschildite, disappeared after carbonation indicating that the Ca present in hirschildite was converted to carbonates, which was confirmed by the increasing intensity of the CaCO_3 diffraction peaks. The intensities of the akermanite diffraction peaks, on the other hand, were not affected by the carbonation process.

Compressive strength is one of the most important mechanical properties of building materials. The compressive strength of the carbonated sample was 38 MPa. The minimum compressive strength of limestone building stones varies from approximately 17 MPa to 55 MPa based on the density (Ingham, 2011). The carbonated sample thus fulfills the criteria for low and medium density limestones (> 28 MPa). Therefore, it could be applied for various building applications.

When the one-stage leaching test was performed on the carbonated sample, the Cr leaching was reduced to 0.43 mg/kg dm, which is below the legal leaching limit value of 0.5 mg/kg dm in the Flemish region of Belgium (VLAREMA, 2012). This indicates that reuse as a construction material may be possible in the Flemish region of Belgium (Spooren et al., 2013). This also clearly shows that besides the technical benefits, carbonation also enhances the stabilization of Cr in the residue and thereby decreases the associated environmental risks.

3.5. Suggested process

Based on the results of the Cr leaching experiments, we propose a SS slag recycling process as shown in Fig. 4. This process will result in the recovery of valuable Cr as well as the matrix material from which the Cr content, a hazardous pollutant, is reduced. This matrix material can be further recycled after washing steps with alkali and water by means of a carbonation process. Carbonation allows for Ca- and Mg-containing slag materials to be shaped and solidified to generate strong building products, whereby Ca- and Mg-carbonates act as a binding agent. Furthermore, the remaining Cr in the matrix is stabilized by this process and leaching is reduced below legal limit values for the Flemish region of Belgium. Chromium can be recovered from the leachate and the alkali/water washing solution by a Cr recovery processes, such as ion exchange (Sengupta et al., 1986; Gode and Pehlivan 2005) or (electro-)reduction/precipitation (Golder et al., 2011; Ramakrishnaiah, 2012).

4. Conclusions

In this study an effective hydrometallurgical recovery of Cr from historic stainless steel slags was developed. Selective Cr leaching by alkaline pressurized oxidation, combined with a mechanical activation pre-treatment step was investigated. Based on the experimental results, the following conclusions are drawn.

- (1) The stainless steel slag matrix is composed of more than 90 wt% calcium silicates containing crystalline phases such as merwinite, $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$, and akermanite, $\text{Ca}_2\text{Mg}(\text{Si}_2\text{O}_7)$. Embedded in the matrix, 1.2 wt% chromium is present, mainly as fine grained oxides (spinel) or FeCr metallic droplets.
- (2) The leaching efficiency of Cr under alkaline oxidizing conditions increased with temperature and MA time, which were determined to be the most significant parameters by a DOE. Maximum Cr leaching was 46% at the condition of 240 °C, 6 h, MA 30 min, 1 M NaOH, L/S 10, 8.4 bar pO_2 with limited dissolution of matrix elements (Al 2.88%, Si 0.12%, Ca 0.05%).
- (3) In the leaching residue, precipitation of hirschildite on the surface of the leached slag particles was observed. These precipitates may hamper further Cr leaching of the underlying slag particles during APL.
- (4) For a complete recycling of the stainless steel slag, we propose a recycling process which closes the full material loop. After Cr leaching by the MA assisted APL technique and a subsequent washing step the leftover matrix material can be used for the production of building materials through a carbonation step.

Chromium can be recovered from the leachate and alkali/water washing solution by ion exchange or precipitation.

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Fig. 1. SEM images of raw material: (a) small oxide (pt 1: spinel in Cr) in the silicate matrix (pt 2), (b) FeCr alloy (point x)

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Fig 4. Suggested process flow sheet for recycling of Cr containing slag.

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Table 1. Design arrangements and Cr leaching (%) result (L/S ratio 10)

Run	Temp(° C)	Time(hr)	NaOH(M)	MA (min)	Cr leaching (%)
1	160	6	1.0	0	6.9
2	240	3	1.0	0	23.8
3	160	3	0.5	0	2.0
4	240	6	1.0	30	46.0
5	160	6	0.5	30	12.6
6	160	3	1.0	30	11.5
7	240	3	0.5	30	30.0
8	200	4.5	0.75	15	33.2
9	200	4.5	0.75	15	35.4
10	240	6	0.5	0	24.9

Table 2. Leaching result of the one-stage leaching test (EN 12357-2) performed on three solid samples obtained after specific washing steps or carbonation (unit: mg/kg dm slag)

Sample	Cr	Fe	Mn	Ca	Mg	Si	Al	Ti	V
No. 1 (ultrasonic+H ₂ O)	1.7	<DL	<DL	951	4.9	675	0.4	<DL	ND
No. 2 (NaOH washing)	0.8	<DL	<DL	934	0.3	58	0.3	<DL	ND
Carbonation of No. 2	0.4	<DL	<DL	158	22.4	345	0.6	<DL	0.3

DL: Below detection limit

ND: Not determined