



# 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<sup>2</sup>).

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## 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  $\text{Na}_2\text{CO}_3$  above  $1100\text{ }^\circ\text{C}$  [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  $210\text{--}300\text{ }^\circ\text{C}$  [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  $\text{H}_2\text{SO}_4$  [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  $\text{FeSO}_4$  [17]  $\text{Na}_2\text{S}$  [18],  $\text{Ca}_5\text{S}$  [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 ( $105\text{--}400\text{ }^\circ\text{C}$ ), 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%  $\text{Cl}_2$ , *VWR Chemicals*) and  $\text{O}_2$  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  $\text{O}_2$  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

cellulose ester membrane filter ME25 (0.45  $\mu\text{m}$  pore size) and the liquid phase was collected in a closed polyethylene bottle and stored in a refrigerator at approximately 2 °C until elemental analyses could take place. The reduction in L/S and loss of dissolved metals, caused by each sampling of 10 ml samples, is taken into account during calculation of the overall leachability.

Column leaching tests were performed by means of up-flow percolation of the leaching solution through a packed bed of the solid sample. Hereto, between about 500 g and 640 g of the solid sample was packed in a glass column with a diameter of 5 cm. The solid material was wetted with about 10 wt% of the leaching solution prior to introduction in the column to avoid swelling of the material in the column upon contact with the leaching solution. The column leaching was performed by percolating the leaching solution through the column and collecting the percolated liquid fractions for analysis (Fig. 1). The flow of the leaching solution was controlled by a peristaltic pump system and was set at 240 ml/day. The leaching liquor was collected in a closed plastic beaker. For each sample, collected at a certain time, the collection beaker was replaced. The collected sample was weighed and the pH, conductivity and redox potential were measured. Subsequently the liquid sample was filtered over a Whatman mixed cellulose ester membrane filter ME25 (0.45  $\mu\text{m}$  pore size) and conserved for ion coupled plasma atomic emission spectroscopy (ICP-AES) analysis at about 2 °C. Columns and vessels were shielded from light to avoid decomposition of NaOCl.

### 2.3. Analytical methods

The total concentration of Cr and other matrix elements in the leach liquor was determined by ICP-AES (*Thermo Elemental*). Whereas, the chemical composition of solid samples was analysed by one of two X-ray fluorescence (XRF) techniques on powder samples: (i) handheld XRF (*Thermo Scientific*) measurement in air, (ii) energy dispersive X-ray fluorescence (EDXRF) by a HE XEPOS (*Spectro Analytical Systems*) apparatus, which measures in He atmosphere. Mineralogical analyses were performed using X-ray diffraction (XRD, *Philips, X'pert*). For oxidation-reduction potential (ORP) measurements, a SenTix® ORP 900 electrode was used. The measured potential was corrected according to data provided by the

electrode manufacturer, whereby  $U_H = U_{Meas} + U_{Ref}$ .  $U_H$  is the ORP referring to the standard hydrogen electrode (SHE),  $U_{Meas}$  is the measured potential and  $U_{Ref}$  is a temperature dependent voltage of the reference system (3 M KCl) compared to the standard hydrogen electrode. In this work the  $U_H$  is always given, whereby  $U_{Ref}$  is derived by accounting for the measured temperature of the solution ( $T_s$ ) according to  $U_{Ref} = -0.7341T_s + 224.87$ .

## 3. Results and discussion

### 3.1. Characterisation of the slag materials

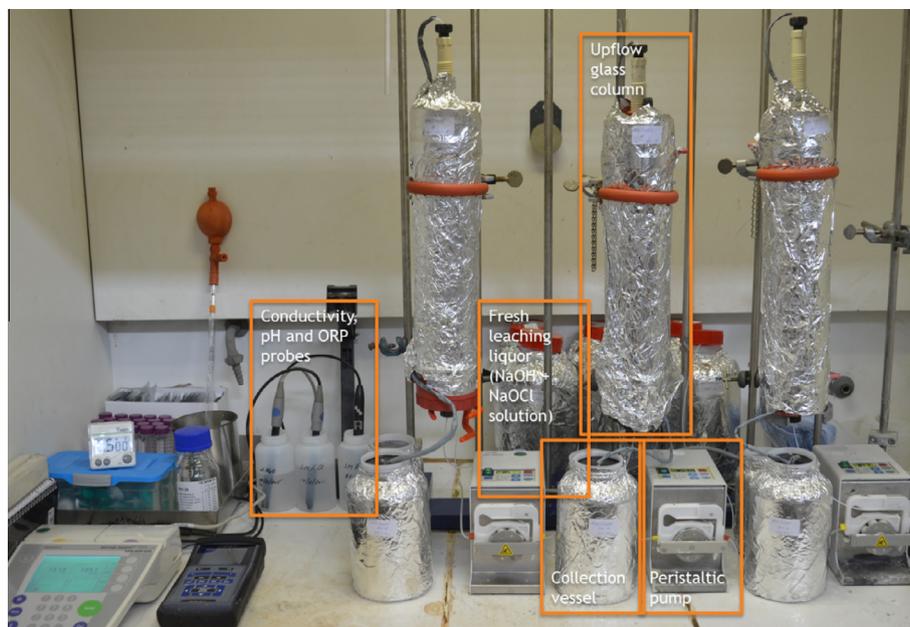
The two slag materials, SS slag and FeCr slag, contain respectively 1.3 wt% and 2.2 wt% Cr, as determined by high performance laboratory EDXRF (Table 1). Furthermore, both slag materials contain a small amount of valuable vanadium (V) with concentrations of 283 ppm and 139 ppm, respectively.

XRD (Fig. 2) and SEM analyses (not reported here) show that in both materials Cr is present in spinel phases as well as in FeCr alloy particles, which are embedded in the mineral matrix material. The matrix material of both slag materials consists mainly of Ca-Mg-(Al-)silicates and also periclase (MgO) is present. Furthermore, the fine SS slag contains a considerable amount of portlandite ( $\text{Ca}(\text{OH})_2$ ), calcite ( $\text{CaCO}_3$ ) and cuspidine ( $\text{Ca}_4\text{Si}_2\text{O}_7\text{F}_2$ ) phases.

**Table 1**

Total concentration of the major elements in the studied slag materials, measured by EDXRF.

Element	Unit	Fine SS slag	FeCr slag
Mg	wt%	5.0	8.0
Al	wt%	1.2	3.6
Si	wt%	13	16
Ca	wt%	35	31
Ti	wt%	0.55	0.08
V	mg/kg	283	139
Cr	wt%	1.3	2.2
Mn	wt%	0.58	0.08
Fe	wt%	0.49	0.36



**Fig. 1.** Setup of the column leaching experiments.

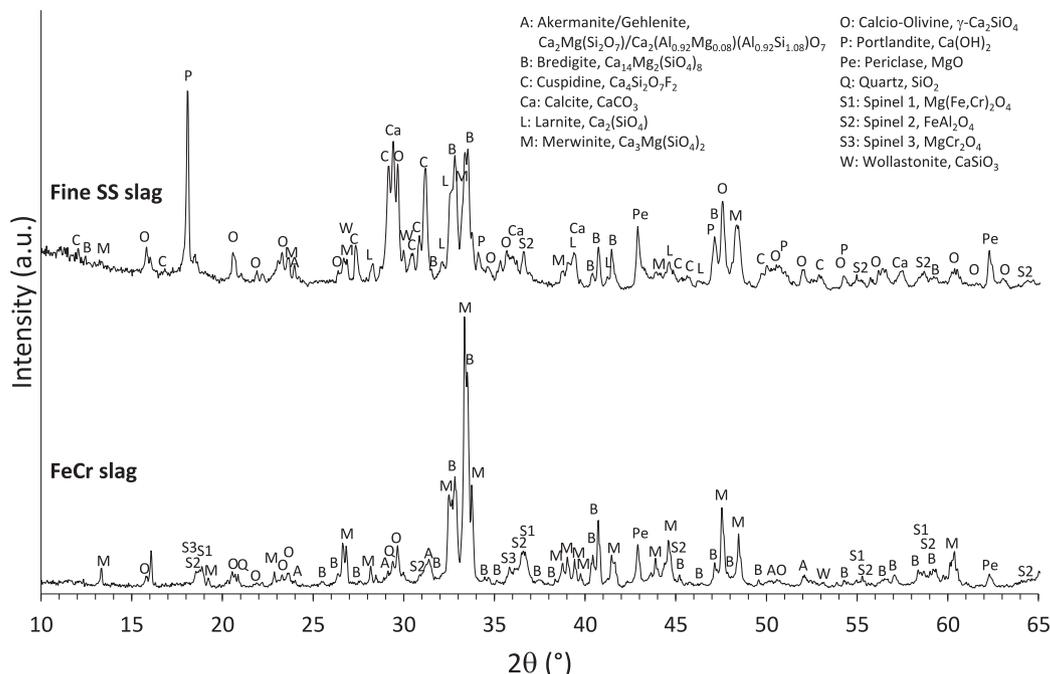


Fig. 2. Powder XRD diffractograms of the studied fine FeCr slag and SS slag.

### 3.2. Batch leaching experiments of FeCr slag

Two batch leaching experiments were performed on the FeCr slag material, which was milled and sieved to  $<150\ \mu\text{m}$ . In the first experiment (B1(NaOCl)), NaOCl (0.197 M) was used as an oxidation agent, while in the second experiment (B2(O<sub>2</sub>)) pure O<sub>2</sub> gas was purged through the reaction solution. The liquid-to-solid ratio (L/S) was 10 for both experiments. Both experiments ran for 25 days. Throughout both experiments the pH and conductivity of the slurry remained constant at about 13.5 and 185 mS/cm, respectively. The pH and conductivity are mainly imposed by the NaOH in solution. However, the oxidation-reduction potential (ORP) strongly depends on the oxidising agent used. In the case of NaOCl, the ORP remained constant at about 666 mV<sub>SHE</sub>, showing that no decrease in oxidation potential occurred over time. In the case of purging with O<sub>2</sub>, the ORP remained close to about 220 mV<sub>SHE</sub>, indicating that a lower oxidising environment was present in the B2(O<sub>2</sub>) experiment.

Clearly the presence of NaOCl in the leaching solution enhanced the alkaline Cr leachability with respect to O<sub>2</sub> purging (Fig. 3). Over time, the leached Cr concentration increased for both experiments,

indicating that the leaching liquor remained reactive for the whole duration of the experiments. At the end of the NaOCl assisted leaching experiment (B1(NaOCl)), 9% of Cr was leached, while only 0.5% Cr leached in the B2(O<sub>2</sub>) experiment. Furthermore, the V leachability proceeds in a similar fashion as a function of time as that of Cr and 7% of V was leached in B1(NaOCl) and 1% in B2(O<sub>2</sub>) (Fig. 3).

Other elements, such as Al, Si and Ca also dissolved slightly, but their leachability remained limited to  $<1\%$  and clearly a selective Cr leaching took place in both experiments (see Table 2). Furthermore, the concentrations of Al, Si, Mn, and Fe in the leaching solution were observed to steadily increase upon increasing leaching time (data not shown), while the concentration of dissolved Ca decreased with time (Fig. 4). Given the high pH, the dissolved Ca<sup>2+</sup> ion probably precipitates as Ca(OH)<sub>2</sub> or CaCO<sub>3</sub> over time.

### 3.3. Column leaching experiments

Three experiments were performed by means of a column leaching test (Table 3), whereby fresh leaching liquor was fed constantly to the column with an average flow rate of about 240 ml/d.

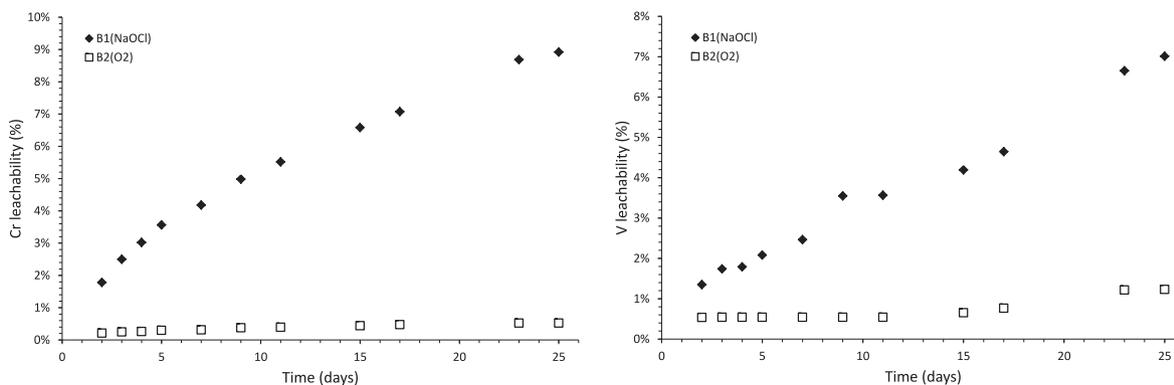
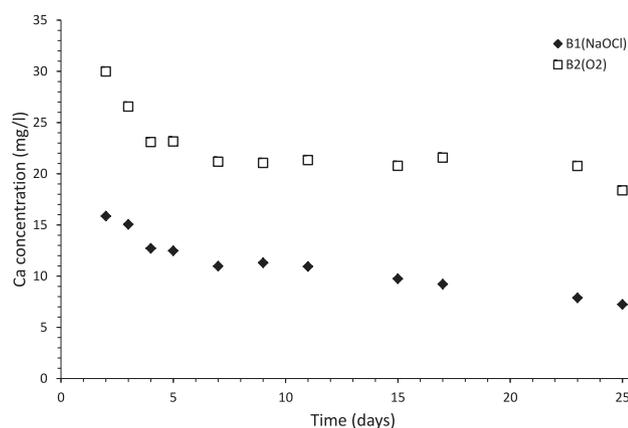


Fig. 3. Cr leachability (left) and V leachability (right) from FeCr slag during two batch leaching experiments. In B1(NaOCl), NaOCl was used as an oxidation agent whereas in B2(O<sub>2</sub>) pure O<sub>2</sub> was used.

**Table 2**  
Leached amount of elements at the end of the batch leaching tests.

Element	B1(NaOCl)		B2(O2)	
	Concentration (µg/l)	Leachability (%)	Concentration (µg/l)	Leachability (%)
Mg	<10	/	<10	/
Al	30535	0.81	7342	0.20
Si	68125	0.39	40650	0.24
Ca	7228	0.02	18366	0.06
Ti	<25	/	<25	/
V	1032	7.0	180	1.2
Cr	206144	8.9	11873	0.52
Mn	27	0.03	40	0.05
Fe	59	0.02	<25	/



**Fig. 4.** Ca concentration in the leaching liquor during batch leaching experiments.

Both FeCr slag and Fine SS slag were tested. In experiments Col1 (FeCr 1 mm) and Col3(SS 1 mm) the FeCr and SS slag materials were granulated and sieved to <1 mm before being introduced in the column. While in experiment Col2(FeCr 150 µm), the FeCr slag sample was milled to <150 µm. All three column leaching experiments ran for 64 days. During the last four weeks of the Col3(SS 1 mm) experiment it was difficult to maintain a constant flow of the leaching solution through the column due to transport of very fine particles to the top of the column, which caused clogging of the column and tubing system. Therefore, the flow rate decreased drastically near the end of experiment Col3(SS 1 mm) and on a few occasions leakage occurred due to blocked tubing, leading to a 50% lower cumulative liquid to solid ratio (L/S). A similar phenomenon occurred in Col1(FeCr 1 mm) on a single occasion. Table 3 reports the average measured flow rates during the column leaching tests which were derived by measuring the volume of the collected fractions and the time period during which each fraction was collected. These values reflect the encountered permeability difficulties during the column testing, where in particular the flow rate of experiment Col3(SS 1 mm) is much reduced and has a large variation due to decrease of flow rate as described above.

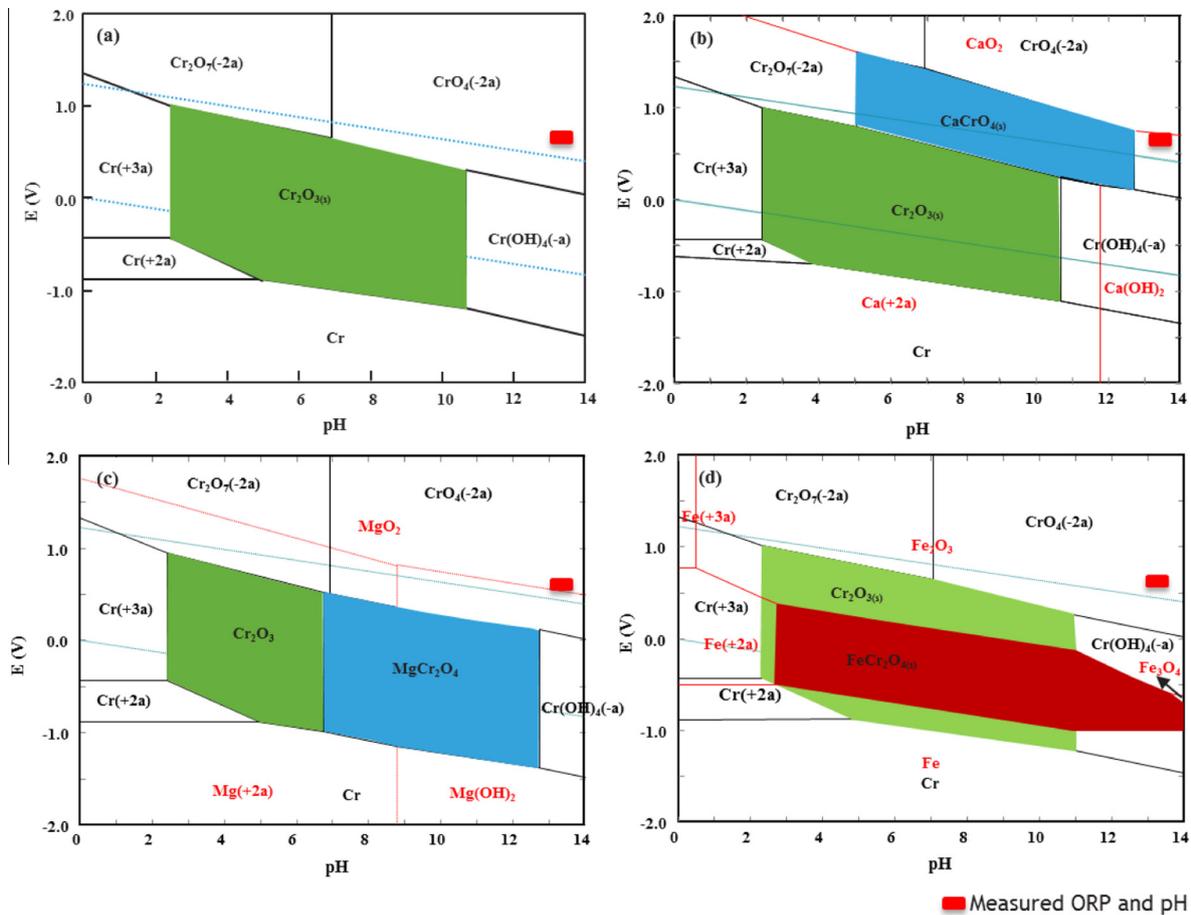
**Table 3**  
Column leaching experiment parameters used.

Experiment	Col1(FeCr 1 mm)	Col2(FeCr 150 µm)	Col3(SS 1 mm)
Sample	FeCr slag	FeCr slag	Fine SS slag
Pre-treatment	Granulated to <1 mm	Milled and sieved to <150 µm	Granulated to <1 mm
Sample weight (g)	551 (incl. 10 wt% moisture)	499 (incl. 10 wt% moisture)	707 (incl. 10 wt% moisture)
NaOCl (M)	0.66	0.66	0.66
NaOH (M)	0.67	0.67	0.67
Set flow rate (mL/day)	±240	±240	±240
Average measured flow rate (mL/day)	222 (±30)	229 (±46)	161 (±94)

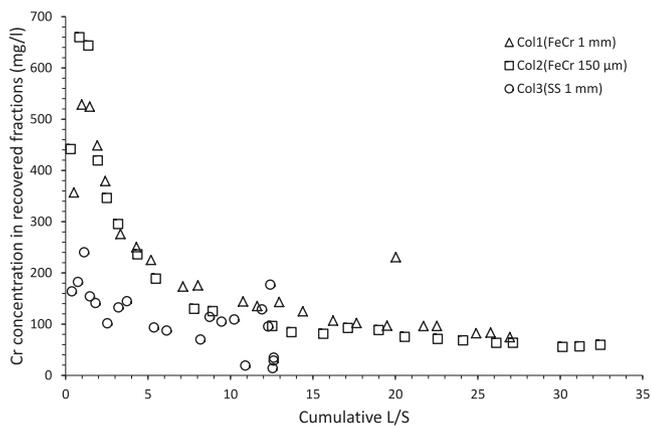
All the collected leaching fractions for the three column leaching experiments show an identical constant pH of 13.4 as a function of cumulative L/S with a standard deviation of ±0.1 for Col1 (FeCr 1 mm) and Col3(SS 1 mm) and of ±0.2 for Col2(FeCr 150 µm). Similarly, the measured conductivity of the collected leaching fractions remains constant at about 187 mS/cm. The ORP remains relatively stable during experiment Col1(FeCr 1 mm) (ORP = 673 ± 24 mV<sub>SHE</sub>) and Col2(FeCr 150 µm) (ORP = 687 ± 17 mV<sub>SHE</sub>), while the ORP of Col3(SS 1 mm) (ORP = 671 ± 30 mV<sub>SHE</sub>) slightly decreases near the end of the experiment. This decrease is probably caused by a longer residence time of the leaching liquor in the packed bed of the column due to a decrease in the flow rate as a result of the decreased flow rate by blockage as described above. It needs to be noted that for all three experiments, the pH range 13.0–13.6 and ORP range 626–712 mV<sub>SHE</sub> lie within the stability area of dissolved CrO<sub>4</sub><sup>2-</sup> in the E-pH diagram (calculated by HSC Chemistry software [29]) of relevant Cr-containing systems (Fig. 5) for the studied materials, namely Cr in spinel phases containing Mg, Ca and/or Fe. Therefore, an increased Cr solubility (from spinel phases) should be expected.

Fig. 6 shows the measured Cr concentration in the recovered fractions during the three column leaching tests as a function of cumulative L/S of the leaching liquor percolated through the packed materials. The Cr concentration in the first fraction is low with respect to the following two fractions since a saturation time is required for all the solid material to equilibrate with the leaching liquor. In fact, the standard column leaching procedure with water as leaching solution (CMA/2/II/A.9.1 [30], NBN CEN/TS 14405 [31]) foresees a saturation period of 18–72 h in order to equilibrate the system before starting percolation. However, this procedure was not followed here. Upon increasing L/S, and thus leaching time, the Cr concentration in the recovered leaching fractions decreases. Due to the difficult control of the flow rate for experiment Col3(SS 1 mm), the Cr concentrations near the end of the experiment are inconsistent. This is due to the strong variation in contact time between the leaching liquor and the solid material, caused by slower flow rates of the leaching liquor. The same effect is observed in experiment Col1(FeCr 1 mm) for the recovered fraction at L/S ≈ 20, where the flow rate decreased drastically with respect to the set flow rate due to a temporary clogging of a transport tube for the leaching liquor.

Fig. 7 (left) shows the cumulative Cr leachability for the three experiments as a function of cumulative L/S. Clearly in all three experiments the Cr leaching proceeds in a similar fashion. The Cr leaching behaviour from the granulated and milled FeCr slag is very similar and at the end of the experiment 19% and 18% of Cr was leached, respectively. While, the amount of leached Cr from the fine SS slag at the end of the experiment lies around 11%, because percolation problems hindered the set amount (flow) of leaching solution to pass from the column. However, the observed leaching behaviour as a function of L/S is similar for both the FeCr and SS slag materials. Contrastingly, the leaching behaviour of V differs clearly for both materials (Fig. 7, right). Whereas the cumulative leaching of V from FeCr slag as a function of L/S follows



**Fig. 5.** E-pH diagram at 25 °C, 1 atm, [Metal] = 0.1 M: (a) Cr-H<sub>2</sub>O system, (b) Cr-Ca-H<sub>2</sub>O system, (c) Cr-Mg-H<sub>2</sub>O system, (d) Cr-Fe-H<sub>2</sub>O system [29]. The red square in each figure indicates the pH-ORP zone in which the investigated experiments were located.



**Fig. 6.** Cr concentration of the recovered fractions during column leaching experiments.

somewhat a sigmoidal curve, the V leaching from SS slag increases steeply with increasing L/S. The cumulative leaching of the matrix elements Al, Si and Ca remained low during the column leaching tests for both the FeCr slag and fine SS slag materials (Fig. 8). Mg and Fe leaching were so low that their concentrations in the recovered leaching liquor fractions were mostly below the detection limit (*i.e.* 10 μg/l and 20 μg/l, respectively) of the ICP-AES apparatus. The leachability of Mn proceeds in a different manner for the

FeCr slag and fine SS slag materials, possibly due to the difference in initial Mn concentration (*i.e.* 0.08 wt% and 0.58 wt%, respectively) and resulting Mn speciation.

The total leachability of Cr and other elements was calculated based upon the cumulative leached amount of the elements in the leaching liquors (Table 4). The leachability of elements from the FeCr slag in Col1(FeCr 1 mm) and Col2(FeCr 150 μm) is similar. The leachability of both Al and Si is about an order of magnitude higher for the FeCr slag (Al 1.0–2.2%, Si 0.57–1.1%) than for the fine SS slag (Al 0.12%, Si 0.15%). The original FeCr slag material contains a higher concentration of Al and likely aluminosilicates dissolve slightly more from the FeCr slag. In fact, Si and Al are known to show a synchronised leaching behaviour from aluminosilicates in slags in alkaline environments [32]. The Cr leachability of the FeCr slag in the studied system is between 18 and 19%, while the Cr leachability of the fine SS slag (experiment Col3(SS 1 mm)) is 11%. Iron, magnesium, manganese and titanium are elements that generally co-exist in the same spinel structure as chromium [21]. In this context, it needs to be noted that iron does not leach by the used alkaline leaching liquor and the Mn and Ti leachabilities are far lower than that of Cr. However, it needs to be noted that the Mn-leachability reaches 0.45% for the FeCr slag and 1.4% for the SS slag. Furthermore, the XRD analyses of the residues do not show a clear decrease in the presence of spinel phases, which could be associated with Cr leaching. Therefore, it remains unclear which reaction pathway is followed for Cr-leaching from spinel phases. Finally, XRD analyses show an intense peak for portlandite (Ca(OH)<sub>2</sub>) in SS slag before leaching, which diminished substantially after leaching and disappeared completely after water-washing

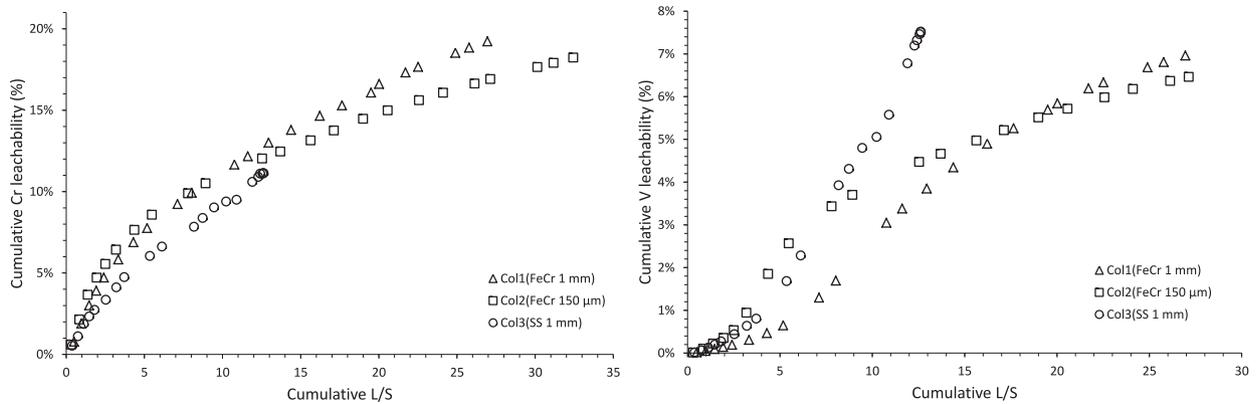


Fig. 7. Cumulative Cr (left) and V (right) leachability during column leaching experiments.

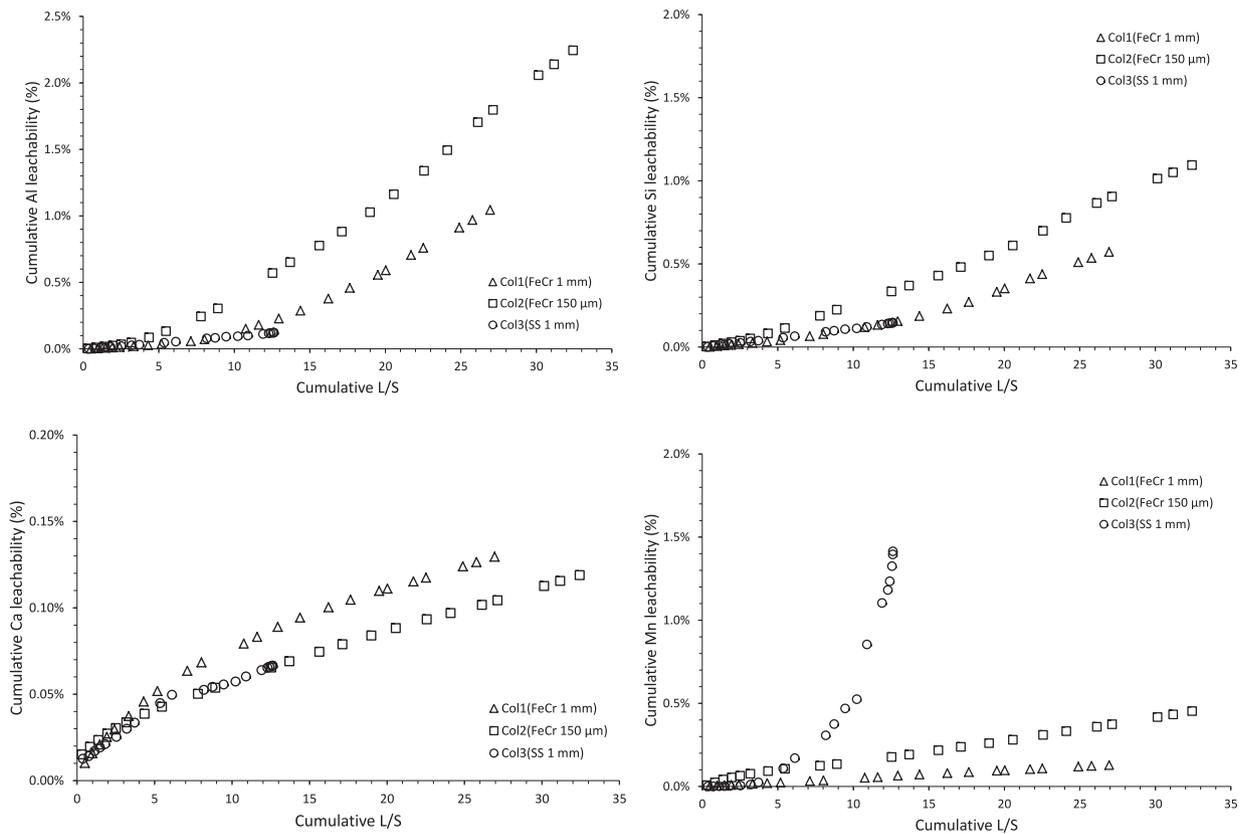


Fig. 8. Cumulative leachability of Al (top left), Si (top right), Ca (bottom left) and Mn (bottom right) as a function of the cumulative L/S measured during column leaching tests Col1(FeCr 1 mm), Col2(FeCr 150 μm) and Col3(SS 1 mm).

Table 4

Cumulative leached amount of elements at the end of the column leaching tests based on the XRF analyses of the washed residues and on the ICP analyses of the leaching liquors.

Element	Col1(FeCr 1 mm) Leachability (%)	Col2(FeCr 150 μm) Leachability (%)	Col3(SS 1 mm) Leachability (%)
Mg	0.0	0.0	0.0
Al	1.0	2.2	0.12
Si	0.57	1.1	0.15
Ca	0.13	0.12	0.07
Ti	0.10	0.10	0.01
V	7.0	6.9	7.5
Cr	19	18	11
Mn	0.13	0.45	1.4
Fe	0.0	0.0	0.0

of the residue (Fig. 9, bottom). At the same time an increase of calcite ( $\text{CaCO}_3$ ) is observed in the residue, indicating carbonation of portlandite or other Ca-containing phases (e.g. Ca-Mg-silicates) to calcite. Actually, increased calcite content is also observed in the FeCr slag leaching residues.

At the end of the leaching experiments the solid residues were removed from the column and dried at 40 °C in a drying oven. The elemental composition of the solid residues was determined by a handheld XRF device (Table 5). These analyses show a substantial increase of chloride content in the residues with respect to the original samples. XRD analyses (Fig. 9) confirm the deposition of NaCl on the residues. Sodium chloride can be produced during decomposition or reduction of NaOCl. Since no decrease of oxidation power in the leaching solution was observed and indeed Cr

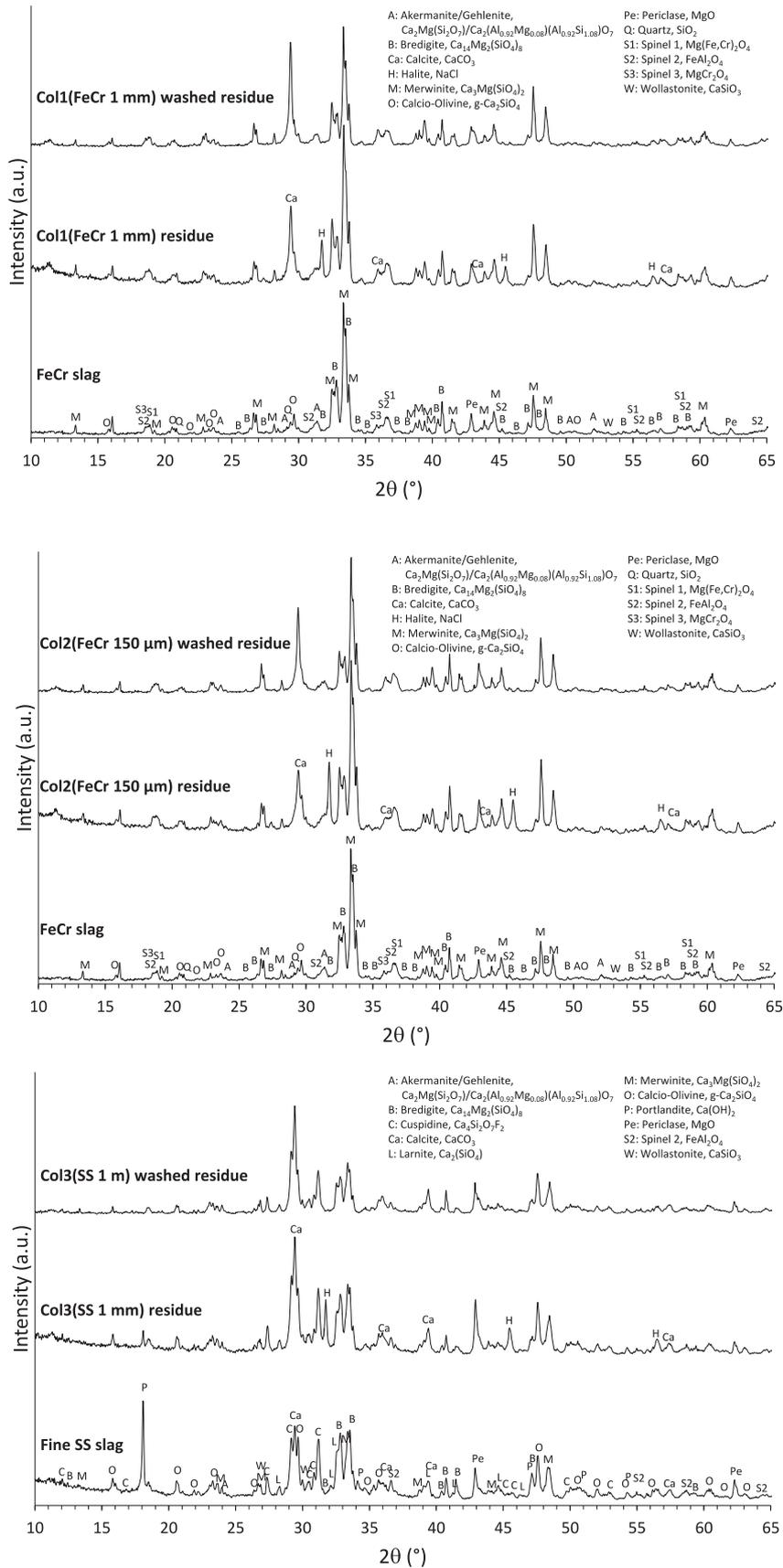


Fig. 9. XRD diffractograms of the residues and water-washed residues for column leaching experiments Col1(FeCr 1 mm) (top); Col2(FeCr 150 μm) (middle); and Col3(SS 1 mm) (bottom).

**Table 5**

Comparison of the total concentration of main elements of the residues recovered from the column after leaching (R) and the washed residues (W), measured by a handheld XRF device.

Element	Col1(FeCr 1 mm)		Col2(FeCr 150 µm)		Col3(SS 1 mm)	
	R (wt%)	W (wt%)	R (wt%)	W (wt%)	R (wt%)	W (wt%)
Mg	2.7	3.9	3.0	4.4	2.5	2.2
Al	1.4	1.8	1.3	1.6	0.59	0.60
Si	8.9	9.7	9.1	9.7	8.3	8.9
Ca	31	33	30	33	35	37
Ti	0.07	0.07	0.05	0.08	0.47	0.53
Cr	1.8	1.9	1.8	2.0	0.89	1.0
Mn	0.06	dl	0.02	0.04	0.52	0.59
Fe	0.44	0.53	0.43	0.52	0.43	0.55
Cl	2.1	0.08	3.0	0.06	2.3	0.06

dl = below detection limit.

oxidation does take place, as evidenced by a substantial Cr-leachability, reduction of NaOCl according to Eq. (1) is the most likely route for NaCl production in the studied systems.



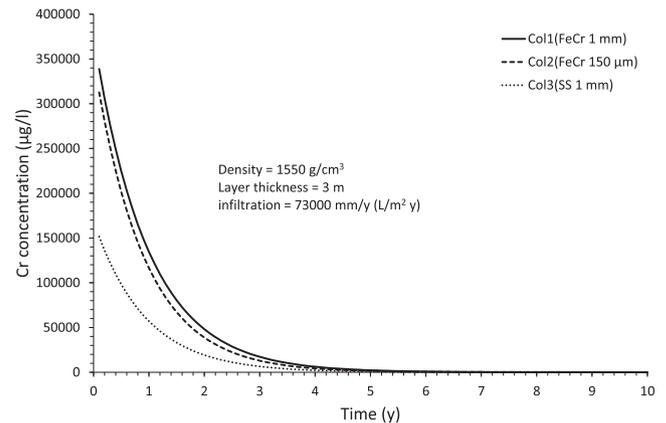
NaCl could be removed by washing the residues three times with deionised water at an L/S of about 12.5. The measured mass loss after washing was 4.1% for the Col1(FeCr 1 mm) residue, 7.1% for the Col2(FeCr 150 µm) residue and 5.1% for the Col3(SS 1 mm) residue. The elemental composition of the washed residue is given in Table 5 and the mineral composition in Fig. 9. Clearly, the chloride amount is reduced in the washed sample.

The column leaching test was performed following similar procedures that are applied to measure the leaching behaviour of inorganic constituents from granular waste, as described in e.g. NBN CEN/TS 14405:2004 [31]. Such basic characterisation test subjects the granular material to percolation with water as a function of liquid to solid ratio under specific percolation conditions. The material is leached under hydraulically dynamic conditions in an up flow column system, wherein the column is water saturated. Although the up flow leaching does not simulate a specific scenario, such as down flow leaching in e.g. heap leaching, the test provides reliable information on the leaching behaviour of the tested elements. Therefore, the principles of the environmental characterisation test are in agreement with the above described leaching tests that apply an oxidising alkaline leaching agent instead of water. Based on modelling principles of the environmental column leaching tests, the results of the above described experiments can be used to make an estimate of the Cr leaching behaviour over time for a hypothetical heap leaching setup, presuming a heap of 3 m height and a leaching solution infiltration rate of 73,000 mm/y. Hereto, we can exploit the fact that leaching of elements often takes place according to a first-order reaction described by the equation  $C = C_0 e^{-\kappa L/S}$ , whereby  $C$  is the measured concentration in a collected fraction at a given cumulative L/S, where L/S is the cumulative liquid to solid ratio,  $C_0$  is the (extrapolated) initial concentration of the element in the leaching solution at L/S = 0 and  $\kappa$  is a constant (kg/l) [33]. The  $\kappa$  value describes the shape of the leaching curve and gives an indication of the rate of leaching of a certain element. The  $\kappa$  value depends both on the element and the material from which the element leaches. A similar equation exists to express the concentration of a leached element as a function of leaching time, namely  $C = C_0 e^{-\kappa' t}$ , whereby  $\kappa'$  is related to the  $\kappa$  value of the L/S dependent equation according to  $\kappa' = (\kappa * q) / (\rho * h)$  and  $q$  gives the infiltration of leaching liquor,  $\rho$  is the density of the solid material and  $h$  gives the layer thickness through which the leaching liquor filtrates. Through fitting the natural logarithm of the measured concentrations as a function of cumulative L/S, the factors  $C_0$  and  $\kappa$  can be determined (Table 6).

**Table 6**

The Cr leaching constants  $\kappa$  and  $C_0$  for the column leaching experiments determined by linear fitting of the data  $\ln(C)$  vs  $L/S$ . The  $R^2$  values of the fitting are also given and the derived  $\kappa'$  value by presuming  $q = 73,000 \text{ mm/y}$ ,  $h = 3 \text{ m}$ ,  $\rho = 1550 \text{ g/cm}^3$ .

	$\kappa$	$\ln(C_0)$	$C_0$	$R^2$	$\kappa'$
Col1(FeCr 1 mm)	0.0633	12.8	375,000	0.7952	1.0269
Col2(FeCr 150 µm)	0.0677	12.8	349,000	0.8122	1.0982
Col3(SS 1 mm)	0.0669	12.0	169,000	0.4792	1.0853



**Fig. 10.** Calculated time-dependent leaching of Cr, determined by three column leaching experiments and presumption of some heap leaching parameters (given in the figure).

From the fitted  $\kappa$  value,  $\kappa'$  can be calculated in which the following constants were presumed:  $q = 73,000 \text{ mm/y}$ ,  $h = 3 \text{ m}$ ,  $\rho = 1550 \text{ g/cm}^3$ . The calculated  $\kappa'$  for each element can then be used in the time-dependent equation  $C = C_0 e^{-\kappa' t}$  in order to obtain a time estimate of the leachability of the measured elements. It must be noted that the coefficient of determination ( $R^2$ ) of fitting the chosen model to the experimental data for each of the three column leaching tests lies only between 0.5 and 0.8 (Table 6). Therefore, the derived Cr leaching time (Fig. 10), based on the calculated  $\kappa'$  values, should be considered as a first rough estimate in need of further optimisation to improve the validity of the proposed models. From these estimations it can be deduced that, at the presumed infiltration rate and heap height, both the FeCr slag and fine SS slag material could leach Cr for 4–5 years.

#### 4. Conclusions

This paper reports on preliminary lab-scale batch and column leaching experiments to investigate the possibility to heap leach Cr and V selectively from FeCr slag and finely grained SS slag by an oxidative alkaline leaching procedure. It was shown that NaOCl is an efficient oxidising agent, which increases the Cr and V leachability. Furthermore, the tested leaching solution, a mixture of NaOH and NaOCl, remained active throughout the 25 days duration of the batch leaching experiment, indicating that circulation of leaching liquor in heap leaching should be possible.

Column leaching tests on both FeCr and SS slag materials reached a cumulative Cr leaching of up to 19% for the FeCr slag materials and 11% for the SS slag after 64 days. The V leaching behaviour seems to differ for both slag materials and reached 7.0% for the FeCr slag and 7.5% for the SS slag. Based on the column leaching results an estimated Cr-leaching time of about 4–5 years was derived for a hypothetical heap leaching setup. Furthermore, it was shown that transport of fines particles during leaching can cause considerable permeability problems, highlighting the need

for an adequate pre-treatment such as granulation. In situ recovery of Cr and V from the studied waste materials reduces potential leaching of these metals to the environment.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2016.05.128>.

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