



Research article

Recovery of Al, Cr and V from steel slag by bioleaching: Batch and column experiments

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ABSTRACT

Steel slag is a major by-product of the steel industry and a potential resource of technology critical elements. For this study, a basic oxygen furnace (BOF) steel slag was tested for bacterial leaching and recovery of aluminium (Al), chromium (Cr), and vanadium (V). Mixed acidophilic bacteria were adapted to the steel slag up to 5% (w/v). In the batch tests, Al, Cr, and V were bioleached significantly more from steel slag than in control treatments. No statistical difference was observed arising from the duration of the leaching (3 vs 6 d) in the batch tests. Al and Cr concentrations in the leachate were higher for the smaller particle size of the steel slag (< 75 μm), but no difference was observed for V. In the column tests, no statistical difference was found for pH, Al, Cr and V between the live culture (one-step bioleaching) and the supernatant (two-step bioleaching). The results show that the culture supernatant can be effectively used in an upscaled industrial application for metal recovery. If bioleaching is used in the 170–250 million tonnes of steel slag produced per year globally, significant recoveries of metals (100% of Al, 84% of Cr and 8% of V) can be achieved, depending on the slag composition. The removal and recovery percentages of metals from the leachate with Amberlite[®]IRA-400 are relatively modest (< 67% and < 5%, respectively), due to the high concentration of competing ions (SO₄²⁻, PO₄³⁻) in the culture medium. Other ion exchange resins can be better suited for the leachate or methods such as selective precipitation could improve the performance of the resin. Further research is needed to minimise interference and maximise metal recovery.

1. Introduction

In 2016, the global steel production was 1360 million tonnes (WSA, 2017), generating around 170 to 250 million tonnes of steel slag as a major by-product (Gomes et al., 2016b; USGS, 2017a). Recycling of this slag as construction materials has long been a research focus and an established afteruse, with up to 70% of slag in Europe reused (48% in road construction, 10% in metallurgical processes, 6% in cement production, 3% in hydraulic engineering and 3% as fertilizer, in 2010) (Euroslag, 2017; Fakhri and Ahmadi, 2017; Gajda et al., 2017; Garg and Singh, 2016; Gutierrez et al., 2016; Zhao et al., 2017). Although metal recovery from wastes is becoming a key process in the context of a circular economy (Haas et al., 2015; Hagelüken et al., 2016), metal recovery from steel slag has been largely confined to bench scale studies thus far (Gomes et al., 2017). Also, several obstacles can limit full implementation, such as regulatory constraints (e.g. definition of waste, environmental permits), ownership (slag belongs to the aggregate

company, but the leachate is the responsibility of the producer), and liabilities arising from past action and owners (Deutz et al., 2017). Without a sustainable technology for large scale processing of slags, stockpiling in heaps and tailings is the usual management practice, potentially causing environmental problems due to dust generation and accidental leakage of alkaline drainage (pH > 12) (Gomes et al., 2016b; Kaksonen et al., 2017).

Bioleaching is a mature hydrometallurgical technology, which relies on microorganisms to solubilise metals primarily through the production of a mineral or organic acid, and it is widely employed commercially for processing pyrite-rich, low-grade copper sulphide ores (Reed et al., 2016; Rodrigues et al., 2016). The approach benefits from low energy input, low capital cost and it requires only unskilled labour, and this has underpinned increasing research focus onto bioleaching in recent years (Funari et al., 2017; Rastegar et al., 2015; Reed et al., 2016). Bioleaching has only recently been investigated as a potential route for the valorisation of alkaline wastes, as a pre-treatment to mineral

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carbonation or for removal of toxic metals which facilitates further reuse or valorisation (Chiang et al., 2013). Steel slag can be a valuable secondary resource if processed with low energy consumption and minimal environmental impacts for secured supply of metals (Hocheng et al., 2014).

There are few studies on metal bioleaching from steel slag. Pure cultures such as *Acidithiobacillus ferrooxidans* were tested in blast furnace sludge and flue dust (Banerjee, 2007). Bioleaching of smelter slag was tested using a mixed culture enriched from a sulphide ore mine site, which contained *Acidithiobacillus* spp. and *Leptospirillum* spp. for the recovery of Zn and Fe (Vestola et al., 2010). In all these studies, one step bioleaching was performed where the microorganism is inoculated together with the slag in the medium and microbial growth, and metal leaching co-occur (Pandey and Natarajan, 2015). In two-step bioleaching (or spent medium leaching), after the maximum growth of the microorganism and consequent maximum production of metabolites occurred, the suspension is filtered, and only the filtrate is used for leaching (Pandey and Natarajan, 2015). Culture supernatants of *Acidithiobacillus thiooxidans*, *Acidithiobacillus ferrooxidans*, and *Aspergillus niger* were used with electric arc furnace (EAF) slag for two-step bioleaching (Hocheng et al., 2014). *Acidithiobacillus thiooxidans*, *Pseudomonas putida* and *Aspergillus niger* were tested with roasted Linz-Dona-witz converter slag for vanadium recovery (Mirazimi et al., 2015) in one and two-step bioleaching. However, further research is needed to determine: which culture or mixed cultures enhance steel slag bioleaching; if one-step or two-step bioleaching is more effective; the optimal time of exposure; and how to recover metals from the bioleachate.

This study investigates steel slag bioleaching for the removal of Al, Cr and V in batch and column tests using a mixed culture of acidophilic bacteria and its cell-free supernatant applied for the first time to steel slag, under different experimental configurations. Recovery performances of those metals from the bioleachates were tested using an anion exchange resin to determine the value chain potential and establish a testing ground for a large-scale rollout. The main objectives were to i) determine the bioleaching yields in column and batch experiments; ii) assess if the particle size affected the steel slag bioleaching; iii) assess if the duration of the experiments influenced bioleaching; and iv) evaluate recovery of metals from the bioleachate using a commercial ion exchange resin.

2. Materials and methods

2.1. Materials and chemicals

Basic oxygen furnace (BOF) steel slag was collected from Yarborough, Scunthorpe, UK (53°35'07.3"N 0°35'35.5"W) in December 2016. The primary sample was ground (fly press and vibrating mill Siebtechnik) and sieved into three different fractions: < 75 µm, < 2 mm, and 4 < size > 10 mm (typically used for pipe bedding). The first two fractions were used in the batch tests, and the third for the column tests to investigate a granulometry that would not require as much mechanical crushing before leaching.

The bacteria mixed culture was cultivated in a modified 9 K medium (Funari et al., 2017; Silverman and Lundgren, 1959) containing (NH₄)₂SO₄ 3.0 g L⁻¹, K₂HPO₄ 0.5 g L⁻¹, MgSO₄·7H₂O 0.5 g L⁻¹, KCl 0.1 g L⁻¹, Ca(NO₃)₂ 0.01 g L⁻¹, FeSO₄·7H₂O 22.5 g L⁻¹ and 10.0 g L⁻¹ S⁰. The modified 9 K medium was adjusted to pH 2.0 with concentrated H₂SO₄. All reagents used were of analytical grade.

The ion exchange resin used for assessing the metal recovery was Amberlite®IRA-400 (Sigma-Aldrich), which is a strong base anion exchange resin with quaternary ammonium functional groups (-N+R3) in a polystyrene matrix, and particle sizes of 600–750 µm. Before use, the resin was converted to the hydroxide form according to Gomes et al. (2017).

2.2. Adaptation of the bacteria culture

The mixed acidophilic culture used for the bioleaching experiments was obtained by combining several samples from overflows and ponds of the Libiola Fe-Cu mine area (Ligurian Apennines, Italy), collected at the sediment-water interface. The pH of the original liquid samples varied between 1 and 3 and the samples contained red-brown iron(III) precipitates (not analysed in this study) (Dinelli et al., 2001). *Acidithiobacillus thiooxidans* and *Acidithiobacillus ferrooxidans* are the dominant strains in the natural culture. A preliminary terminal restriction enzyme fragment length polymorphism (T-RFLP) analysis report is presented in Table S1 (Supplementary Information). Initial conditioning of the original culture, which comprised a turbid suspension of water, minerals, and biomass, was performed in flasks containing 90% (v/v) modified 9 K medium on a shaker incubator (Infors HT Multitron Standard). The pH was maintained below 2.5 using concentrated H₂SO₄, as required. The total volume of H₂SO₄ added in the three rounds of adaptation was 330 µL per flask. The culture was incubated at 150 rpm and 30 °C. To enhance the cell activity, the culture was renewed every 15 days by inoculating 10% (v/v) of former cultivation and 90% (v/v) of the modified 9 K medium.

The original acidophilic culture was adapted to tolerate the presence of steel slag, and the adaptation phase was conducted in 250 mL Erlenmeyer flasks containing 90 mL of the modified 9 K medium. Flasks were inoculated with the acidophilic culture (10% v/v) followed by the addition of the steel slag. Before the adaptation, the steel slag was autoclaved for 30 min at 135 °C, assuring that no other microorganisms than those inoculated were present. The pH was adjusted to 2.0 with concentrated H₂SO₄, and flasks were incubated on the same incubator (150 rpm, 30 °C). Growth of bacteria was monitored by measuring pH and redox potential. If a spontaneous decrease in pH was observed during 15 days due to the growth and activity of the sulphur oxidising acid-generating bacteria, a new modified 9 K medium with an increased amount of steel slag was prepared and inoculated with the previous solution (10% v/v) of the adaptation phase. As part of the adaptation process, the quantities of slag were increased three times (1, 2, and 5%) of L/S ratio. The culture successfully tolerated the addition of up to 5% steel slag, and that adapted inoculum was used for the experiments.

2.3. Batch experiments

The leaching experiments (one-step bioleaching) were carried out in triplicate in 500 mL Erlenmeyer flasks with 1.0 g of steel slag (< 75 µm and < 2 mm fractions), with 90 mL of culture medium and 10 mL of the adapted inoculum. The flasks were shaken on an incubator shaker (Infors HT Multitron Standard) at 150 rpm at 30 °C for 3 and 6 d, as maximum metal extraction was achieved in six days by *At. thiooxidans* culture supernatant (Hocheng et al., 2014). Then, 10 mL of the mixture was sampled for further analysis. Control tests without inocula (mixed acidophilic culture) were performed under the same conditions.

2.4. Column experiments

Column experiments were conducted in a 1.8 cm diameter × 35 cm height acrylic (Plexiglas) tube in which 100 g of steel slag (4 mm < size > 10 mm) was packed. The experiments lasted 22 days. The column experiments were carried out at controlled temperature (28 ± 1 °C). All columns were fed from the top from a 2 L flask at a flow rate of 5 mL min⁻¹, which was controlled by a peristaltic pump (Watson-Marlow, Falmouth, UK) and the feeding solution was then recirculated (closed-loop tests). We ran a set of column experiments to assess the yields between one-step bioleaching and two-step bioleaching. In experiment A (two-step bioleaching), the leaching solution was 1 L of the supernatant of the cultures after filter sterilisation (vacuum filtration, cellulose nitrate filters Sartorius Stedim Biotech 0.22 µm). In experiment B (one-step bioleaching), the leaching solution

was 1 L of bacterial culture, after adaptation. In experiment C (control test), the feeding solution was the sterile culture medium, as described in 2.1. Samples of the column effluent were collected periodically (days 0, 1, 2, 3, 5, 6, 7, 8, 11, 13, 16, 20 and 22) and analysed to determine metal concentrations.

2.5. Recovery with ion exchange resins

Batch tests were performed with Amberlite®IRA-400 to assess the possibility of using the ion exchange resin to recover the metals, following successful tests with V (Gomes et al., 2016a, 2017). One gram of hydrated resin in the hydroxide form was stirred at 150 rpm for 30 min with 20 mL of the columns leachate obtained at the end of the experiments. The solution was decanted off and sampled for elemental analysis. The resin was then mixed with 20 mL of NaOH 2 M and stirred for 30 min for elution and assess the metal recovery. The NaOH was decanted off and analysed for elemental analysis.

2.6. Chemical analysis

All aqueous samples (10 mL) were filtered (0.45 µm, MCE Membrane Millex HA) and preserved with a few drops of HNO₃ (Romil SpATM Super Purity Acid). Trace metal analysis was done using a Perkin Elmer Optima 5300 DV Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). A certified reference material (estuarine sediment solution, CRM-ES AT-1529, lot number 1319108) was used for quality control with recoveries of 99.5 ± 3% of Al, 97.0 ± 6% of Cr and 102.0 ± 7% of V. In the column tests, pH, Eh, and conductivity were also measured daily in a Jenway 3540 pH and conductivity meter.

A representative sample of the dried solid steel slag was weighed into an Xpress microwave digestion vessel (CEM MARS microwave digestion system, CEM Corporation, Milton Keynes, UK) and 5 mL nitric acid (Romil SpA trace metal, SpA, grade, Romil Ltd, Cambridge, UK) was added. The samples were left to slowly digest at room temperature at least overnight with the vessel sealed, and vented before microwave extraction. The microwave heating was programmed to heat to 200 °C in 15 min, then held at that temperature for a further 15 min. When cooled to room temperature, the gaseous products from the vessels were vented into a fume cupboard, and then the digests were diluted by weight with pure water (Elga Purelab, 18 Megohm conductivity) into tared 50 mL sample vials. Analysis on ICP-OES for 69 elements under high argon purge conditions was against a calibration of 10 ppm for all elements. X-ray powder diffraction was performed on a PANalytical Empyrean X-ray diffractometer (XRD) operating in Bragg-Brentano geometry using copper K α_1 radiation ($\lambda = 1.54056 \text{ \AA}$), and a PIXEL detector, in the range $3 \leq 2\theta / ^\circ \leq 70$ with a step size of 0.0393° and counting time 240s per step.

2.7. Data analysis

Statistical analysis was carried out in RStudio (R Development Core Team, 2017), using the Mann-Whitney-Wilcoxon matched pair test to compare data from the batch tests. The column data equality of variance was analysed with Levene's test using the "car" package (Fox and Weisberg, 2011). Since the data were homogeneous ($p < 0.05$), except for pH, we used the non-parametric Mood's Median Test using the "RVAideMemoire" package (Hervé, 2017). A posthoc analysis was performed using the Pairwise Mood's Median Tests function and the Benjamini, Hochberg, and Yekutieli method with the "rcompanion" package (Mangiafico, 2017). When the concentrations were below the detection limit, we assume that the value was half of the detection limit (Croghan and Egeghy, 2003).

The software PHREEQC Interactive v.3.4.012927 (USGS) with MINTEQA V4 database was used to determine the speciation of the metals.

Table 1

Average values and standard deviations ($n = 3$) of selected elements present in the acid digested steel slag samples studied.

Major elements (%)	
Mg	29.4 ± 6.9
Ca	20.0 ± 5.2
Fe	1.1 ± 0.2
Si	0.6 ± 0.1
Al	0.4 ± 0.07
P	0.05 ± 0.04
Trace elements (mg kg ⁻¹)	
As	10 ± 4
Ba	30 ± 10
Cd	1.6 ± 0.3
Cr	100 ± 20
Cu	20 ± 4
Ga	10 ± 2
Li	4 ± 1
K	200 ± 200
Mn	1000 ± 20
Mo	2 ± 1
Na	300 ± 70
Ni	40 ± 20
Pb	500 ± 200
Ti	0.002 ± 0.0003
V	40 ± 10
Sr	30 ± 10
Zn	30 ± 4

The elements marked in bold were the ones targeted in the study Al, Cr and V.

3. Results and discussion

3.1. Steel slag characterisation

The Yarborough basic oxygen furnace (BOF) slag was dominated by magnesium (29.4 ± 6.9 wt. %), calcium (20.0 ± 5.2 wt. %), iron (1.1 ± 0.2 wt. %), silicon (0.6 ± 0.1 wt. %), and aluminium (0.4 ± 0.07 wt. %) (Table 1). Other trace elements accounted for < 1.2 wt. % of the total slag content (Table 1). XRD analyses confirmed the presence of magnesium oxide (MgO), C, and CaOH with trace amounts of CaCO₃, Al₂O₃, in the slag. The concentrations are lower than the ones reported for the typical composition of BOF slag, as the typical Si content of BOF slag ranges from 3.3 to 8.4%, while Al and Mg are in the expected 0.2–7.4% and 0.3–2.4% ranges, respectively (Yildirim and Prezzi, 2011). The presence of calcium hydroxide and calcium carbonate is consistent with the weathering of the slag before reuse as construction material and results of the presence of free lime, used in the process for the conversion from iron to steel.

3.2. Batch tests

Fig. 1 displays the average concentrations and standard deviations of Al, Cr and V in the leaching experiments, comparing the < 75 µm and < 2 mm fractions, and the presence and absence of the mixed culture inocula. The Mann-Whitney-Wilcoxon Test indicates that concentrations with inocula were statistically enhanced in the treatments for all metals compared to the control experiments ($U = 144$, $p < 0.001$). Al concentrations were, on average, 8 times greater than in the control experiments, while Cr and V were 40 and 15 times higher when compared with the control. No statistical difference was observed for the duration of the leaching (3 vs 6 d). This is consistent with previous results that showed maximum bioleaching yields occur within the first 3 days for sulphur and iron oxidising bacteria (Funari et al., 2017). Al and Cr concentrations were higher for the finer grain size of the steel slag (< 75 µm, $p = 0.03$), but no difference was observed for V between size fractions ($p = 0.156$).

Comparing the metal removal percentages (Fig. 2) with previous

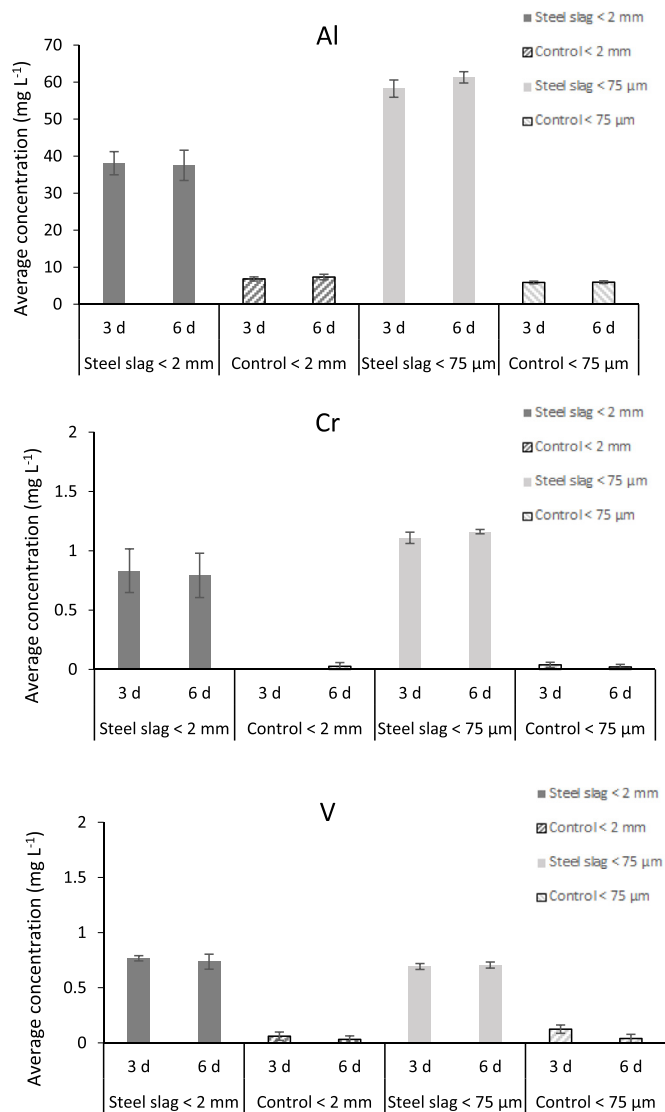


Fig. 1. Metal concentration (Al, Cr and V) in the leachate after 3 and 6 d using the mix bacteria culture and the culture medium (control), with steel slag particle size < 2 mm and < 75 μm . Data plotted as average concentrations; error bars indicate standard deviation.

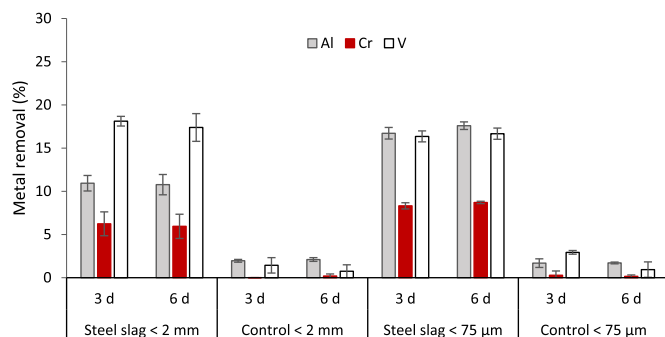


Fig. 2. Metal removal percentages (Al, Cr and V) in the leachate after 3 and 6 d using the mix bacteria culture and the culture medium (control), with steel slag particle size < 2 mm and < 75 μm . Data plotted as average percentages; error bars indicate standard deviation.

studies, it can be seen that the values are consistent with the leaching of electric arc furnace (EAF) slag by culture supernatants of *At. thiooxidans*, *At. ferrooxidans* and *A. niger* (Hocheng et al., 2014), being slightly

higher for Al (18% for slag < 75 μm vs 10% in the literature). Cr removal percentages also agree with values reported from the bioleaching of similar wastes (Hocheng et al., 2014; Karwowska et al., 2015). However, V removal is much lower than the 90% of vanadium reported for slag concentrations of 1–5 g L^{-1} after 15 days (Mirazimi et al., 2015).

The pre-treatment of the Linz-Donawits (LD) converter slag through roasting (1000 $^{\circ}\text{C}$ temperature for 2 h and 20 wt% sodium carbonate additions), the smaller size (< 37 μm), and the longer contact time (15 d) seems to have enhanced vanadium removal (Mirazimi et al., 2015). The unsatisfactory bioleaching performance of BOF slag is attributed to its high basicity, due to substantial CaO content (Chiang et al., 2013). During the tests, the pH increased from 3.3 ± 0.6 to 9.4 ± 0.1 . The use of pre-treatments, such as washing to decrease the pH (Hocheng et al., 2014), and roasting (Mirazimi et al., 2015) could improve the bioleaching efficacy, but are also energy and water demanding.

3.3. Column tests

The column test data are presented in Fig. 3, showing the pH variation and the cumulative mass of metals in the solution for the full duration of the experiments. The statistical analysis using the Mood's median test showed that the pH median is significantly different between experiments ($p < 0.001$), as well as the cumulative mass of the metals considered. The pH values are lower in experiments A (supernatant) and B (culture) when compared with the control (Exp. C, culture medium), but the initial pH was also lower (pH < 1). Bioleaching by acidophile bacteria follows two pathways: the thiosulfate and the polysulfide pathways (Vera et al., 2013). In both, bacteria contribute to mineral dissolution by the generation of the iron(III) ions (oxidising agent), and by subsequent oxidation of sulphur to sulphuric acid. In this study, bioleaching occurred through polysulfide pathway, in which the microorganisms oxidise Fe(II) to Fe(III) ions, which serve as oxidants for the production of sulphuric acid according to the following reaction:



The reaction decreases the pH and dissolves metal oxides. The alteration in basicity of alkaline wastes is usually accompanied by an alteration of mineralogy, with enhanced solubilisation–precipitation and decline of primary phases, and an increase of secondary phases (e.g. calcite), as well as increased specific surface areas (Chiang et al., 2013). Semi-quantitative analysis of the X-ray powder diffraction patterns of steel slag from Exp. A and B (Fig. S1, Supplementary Information) shows that the crystalline component was an approximately equal mixture by mass of gypsum [$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$] (PDF 01-074-7326) and jarosite [$(\text{K}_{1-x}(\text{H}_3\text{O})_x)\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$ (where $x \sim 0.3\text{--}0.1$)] (PDF 01-075-9735). Various jarosite compositions matched the recorded diffraction pattern reasonably; the composition range above represents the best-fitting of these. The X-ray powder pattern of Exp. C is markedly different (Fig. S2). There is still gypsum present, but this is the only major crystalline phase. The colour of the sample (brick red) and the rising background in the X-ray pattern suggest the presence of iron in each of these samples. However, the likely iron in the sample from Exp. C is not present in a crystalline phase.

The metals leached in the control experiment are minor when compared with the experiments A and B, with the supernatant and the mixed culture, respectively. The pairwise comparison for pH, Al, Cr and V revealed that the results from the experiments A (supernatant) and B (culture) are not significantly different ($p > 0.05$), and the difference was only significant when compared with the control ($p < 0.001$). The leaching of Al reached 95% and 109% in Exp. A and B, while the control (Exp. C) only leached 1%. For vanadium, the percentage leached was 8% in Exp. A, B and 1% in Exp. C. The percentages of chromium leached from the steel slag were 84%, 64% and 0.02% in Exp. A, B and C,

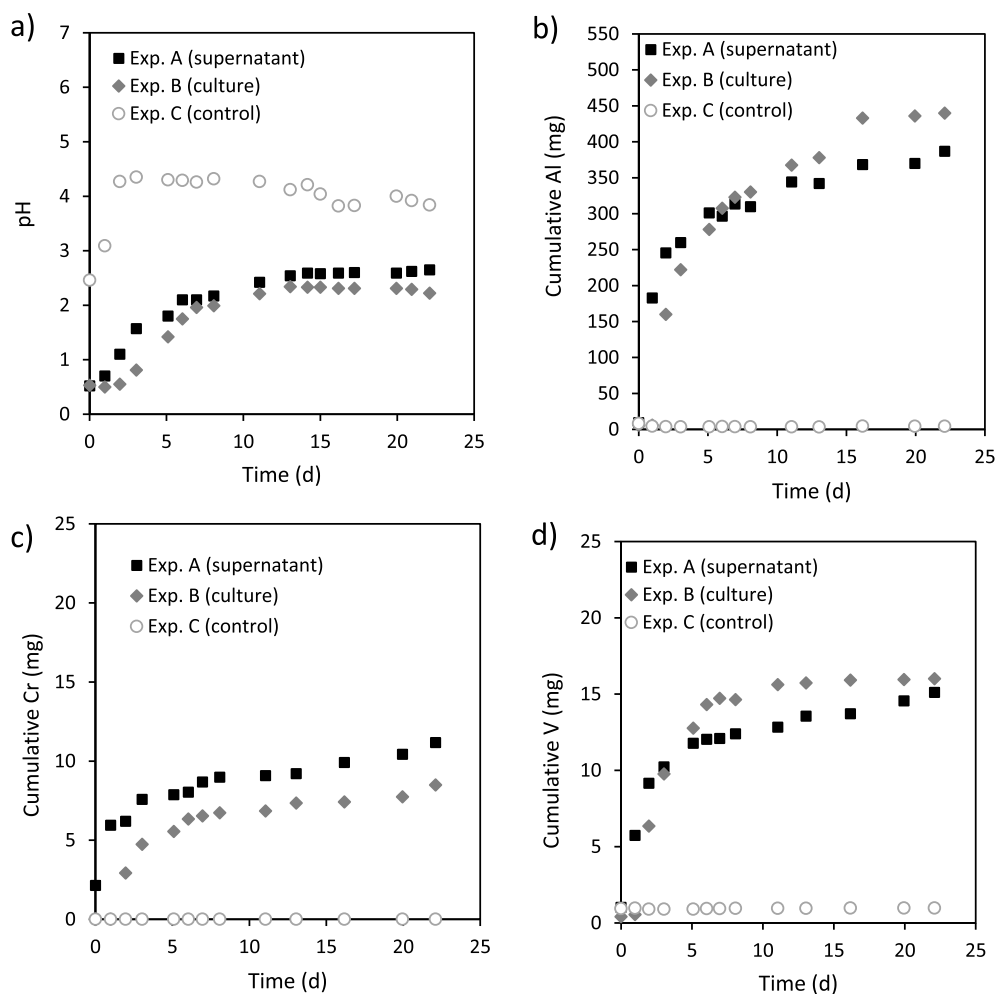


Fig. 3. a) Variation of pH in the column experiments and cumulative mass of b) aluminium, c) chromium and d) vanadium in the 22 days of the experiment. In experiment A, the leaching solution was the supernatant of the cultures after filter sterilisation. In experiment B, the leaching solution was the bacterial culture, after adaptation. In the control test (Exp. C), the feeding solution was the sterilised culture medium.

respectively. Considering the global annual production of 170–250 million tonnes of steel slag (USGS, 2017b) and the varied composition of slag with average values of Al_2O_3 of 7.5%, Cr of 5 g kg^{-1} (Piatak et al., 2015), and V 2 g kg^{-1} (Oty, 2015), significant recoveries of metals can be achieved, if secondary bioleaching is introduced at an industrial scale.

These results imply that the use of the culture supernatant in a two-step bioleaching process can be at least as effective as the use of the bacterial culture for an upscale industrial application. In the first step of this process, organisms are grown in the absence of slag and, in the second step, the metabolites produced are used for bioleaching (Mirazimi et al., 2015; Mishra et al., 2007; Panda et al., 2013). As biogenic substances such as organic acids and exopolysaccharides are the major metabolites, the two-step bioleaching can be optimised to generate higher amounts of biogenic substances prior to the addition of materials to be treated (Chiang et al., 2013) and poisoning of microbial biomass can be avoided (Mishra et al., 2007). Moreover, as the bacteria are not in direct contact with the metal-containing waste, the latter can be more easily recycled or reused, as it is not contaminated by microbial biomass (Mirazimi et al., 2015; Mishra et al., 2007). Other advantages of this process include a higher waste processing capacity when compared with the one-step process, where the microorganisms' tolerance to the waste substrate affects the processing capacity, and the potential increase of the reaction temperature as the temperature of the leaching step can be different from the growth phase (Mirazimi et al., 2015; Mishra et al., 2007). On the other hand, obtaining enough

supernatant to process high waste quantities requires large areas and the generation of considerable amounts of biomass.

In Exp. A, the leaching kinetics in the columns had an initial rapid period in the first 5 days (Fig. 3) and then becomes a slow regime. A possible explanation for this might be that there is a depletion of easily available reacting species, especially in the supernatant experiments, formation of a product layer and intra-particle limited diffusion, or a combination of all these factors (Rastegar et al., 2015). With slag leaching, the role of amorphous C-S-H (calcium silicate hydrate) gels armouring the surface of weathered slag have been shown to limit subsequent V leaching (Hobson et al., 2017). On the other hand, in Exp. B, the mass of vanadium and aluminium removed keeps increasing until day 10 and then slows down. This suggests that the inoculated culture is capable of selectively leaching out metals.

Three kinetic models were fitted to the results of the columns experiments (Table 2). Bioleaching of Al is determined by a chemical reaction at the particle's surface (first-order rate constant) in Exp. A (supernatant), and by the Stokes regime in Exp. B (culture). This means that leaching is not affected by the presence of an impermeable product layer, so the amount of reacting material is proportional to the available surface of the unreacted core and the reacting particle would be shrinking during the reaction, until the solid phase disappears (Chen et al., 2015; Mishra et al., 2008). For both chromium and vanadium, in both Exp. A and B, the best-fitted model is the shrinking core model theory (Table 2), which assumes that bioleaching kinetics is controlled by a solid product layer diffusion, and it is usually the best model to

Table 2
Kinetic models applied to the column experiments A (supernatant) and B (culture).

Model	Equation (Chen et al., 2015)	Experiment	Coefficient of determination (R ²)		
			Al	Cr	V
Shrinking core theory	$k_t = 1 - \frac{2}{3}F_t - (1 - F_t)^{2/3}$	A	0.9227	0.9375	0.8191
		B	0.9304	0.9842	0.8263
First order kinetics	$k_t = 1 - (1 - F_t)^{1/3}$	A	0.9451	0.8522	0.5810
		B	0.9186	0.7432	0.6311
Stokes regime	$k_t = 1 - (1 - F_t)^{2/3}$	A	0.7688	0.7920	0.6278
		B	0.9405	0.7067	0.5789

F_t represents the fraction of metal mobilized; t is the leaching time, and k the rate constant.

explain bioleaching of metals (Chen et al., 2015; Mishra et al., 2008; Rastegar et al., 2015). So, the leachability of Cr and V is likely controlled by product layer diffusion as the core shrinks, and enzymatic reactions of the microbial biomass at the surface of the unreacted core. An alternative kinetic model is that the same diffusive path mechanism which underpins the shrinking core model is induced by the gypsum-dominated permeable secondary crust we observed developing in the experiments. As this secondary crust and a permeable reacted halo around a shrinking core would induce very similar leaching regime, it is not possible to distinguish between these two similar mechanisms in this experiment.

The XRD results of the precipitates in the column recovered through filtration indicate that gypsum [CaSO₄·2(H₂O)] and jarosite [(K_{1-x}(H₃O)_x)Fe₃(SO₄)₂(OH)₆ (where $x \sim 0.3-0.1$)] are the predominant minerals, which is similar to the secondary crust materials indicating coherent origin of these two materials. This shows that the calcium mobilized from the slag reacts with the sulphates from the culture medium (H₂SO₄, (NH₄)₂SO₄, MgSO₄·7H₂O, FeSO₄·7H₂O) producing hydrated calcium sulphate. The calcium-rich minerals initially present in the steel slag are being transformed into hydrated calcium sulphate that can be reused in gypsum based applications. On similar studies, Chiang et al. (2013) observed an increase in calcite (CaCO₃) in the bioleaching of EAF slag, due to the carbonation of degradation products of calcium silicates. Calcite was not detected in the samples analysed in the XRD, but it could be present in very low concentrations or formed in the steel slag surface coating inside the column.

3.4. Recovery of metals with ion exchange resins

The removal percentages of metals with Amberlite®IRA-400 from the leachate are $9 \pm 1\%$ and $13 \pm 1\%$, for Al in Exp. A and B, respectively. In Experiment A (supernatant), the removal percentages of Cr are $67 \pm 5\%$ and $43 \pm 3\%$ for V, while in Exp. B (culture) are $44 \pm 1\%$ for Cr and $20 \pm 1\%$ for V. The highest removal percentages correspond to the leaching with the cell free acid supernatant (Experiment A), which may indicate potential interference with microbial biomass (Guo et al., 2009), or with other particles > 22 μm. The recovery from the resin after elution with 2 M NaOH was residual for Al and Cr (< 1%), and only $4 \pm 1\%$ in Exp. A (supernatant) and $5 \pm 0.4\%$ for V in Exp. B (culture). These recovery values are low considering that 57–72% of vanadium was recovered with the same ion exchange resin from steel slag leachate (alkaline drainage) (Gomes et al., 2017).

For maximum efficacy of the ion exchange resin, the metals of interest must bind more strongly to the resin than the displaced OH⁻ and the competing ions present in the leachate. Anion exchange resins generally show affinity for SO₄²⁻ > NO₃⁻ > Br⁻ > Cl⁻ > HCO₃⁻ (Gomes et al., 2017; Harland, 1994). Amberlite®IRA-400, in particular, shows affinity for AsO₄³⁻ > PO₄³⁻ > SO₄²⁻ > Cl⁻ > OH⁻ (Korkisch, 1989; Tang et al., 2013). As arsenic concentrations are below the detection limit (< 0.02 mg L⁻¹), the performance of the resin is mainly limited by the presence of interference anions such as PO₄³⁻

and SO₄²⁻ in high concentrations in the culture medium (Korkisch, 1989; Tang et al., 2013). The concentrations of P and S in the column eluate by the end of Exp. A were 8.5 mg L⁻¹ and 21 g L⁻¹, while in Exp. B were 6.9 mg L⁻¹ and 20 g L⁻¹, respectively. The removal of the possible interference anions through selective precipitation could improve the performance of the resin. Other strong basic anion exchange resins were capable to recover V in sulphuric acid leach solution (Nguyen and Lee, 2014), so further research is needed to minimise interference and maximise metal recovery. The results of the PHREEQC Interactive v.3.4.012927 (USGS) simulation with MINTEQA4 database show that the metals are present as cations, in the third oxidation state (Al³⁺, Cr³⁺ and V³⁺), which can also explain the poor performance of the resin. A cation exchange resin would be more selective and effective for the removal and recovery of the metals considered.

4. Conclusions

The use of a mixed culture for the bioleaching of metals was effective for the bioleaching of Al, Cr and V from basic oxygen furnace (BOF) steel slag. In the batch tests, all the metals considered were significantly more leached from steel slag than in the control experiment. The duration of the experiment (3 vs 6 d) did not affect the removal of metals. Both Al and Cr were significantly more leached with slag < 75 μm. The column tests demonstrated that the mixed cultures could be cultivated previously in controlled conditions and their supernatant can be used successfully to remove metals in a two-step process. Given the production and composition of the steel slag, this is relevant for industrial application, where bioleaching for metal recovery could be implemented before bulk reuse of the steel slag, simultaneously adding value to the by-product and minimising the leachate environmental impact. The recovery percentage of metals from the leachate using ion exchange resins was not very encouraging, so further developments are needed to separate the metals for recovery and recycling.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jenvman.2018.05.056>.

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