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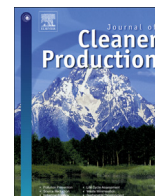
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Vanadium recovery from steel converter slag utilised as an oxygen carrier in oxygen carrier aided combustion (OCAC)

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ABSTRACT

This study investigates vanadium extraction from steel converter slag from the LD (Linz-Donawitz) process. This slag has been used as an active bed material in a biomass boiler in a combustion technique called oxygen carrier aided combustion (OCAC). This usage in the boiler could be compared to the roasting step in the common roasting-leaching method for vanadium extraction. Leaching of LD slag prior to use as an oxygen carrier is undesirable as the materials active in OCAC are removed. This study successfully leached the slag following use in the combustion process. Two methods of leaching were utilised to compare the OCAC slag against traditional methods of vanadium extraction; a continuous flow leaching procedure and a microwave-assisted leaching procedure. It was found that a vanadium extraction efficiency of 22.1% could be achieved from the OCAC slag using 5 M sulphuric acid as a leaching solution following 30 min water leaching followed by 30 min of continuous acid leaching. Using the microwave-assisted method and further optimising leaching conditions, a final efficiency of 49.1% was achieved with 4 M sulphuric acid and particle size within the range of 44–74 μm .

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1. Introduction

Vanadium possesses unique properties and is described as a strategic metal due to its wide application in a number of different industries (Sun et al., 2019). Due to the hardness and ductility of the metal, around 85% of produced vanadium is used as an alloy for steel (Liu et al., 2010; Moskalyk and Alfantazi, 2003). An expanding area of interest in which vanadium could also be utilised is in redox flow batteries for renewable energy storage (Dassisti et al., 2016). The majority of vanadium used today is sourced from vanadium bearing slag, titaniferous magnetite ores or spent catalysts and oil residue, each contributing around 58%, 34% and 8%, respectively (Raja, 2007). LD (Linz-Donawitz) slag - also known as Basic Oxygen Furnace Slag (Hobson et al., 2017) - is a by-product of the steel manufacturing process. The material can reach production rates of

up to 200 kg per tonne of steel (Das et al., 2007; Umadevi et al., 2010). In some regions, such as Scandinavia, due to the vanadium content of the ore, this slag contains significant concentrations of vanadium. This prevents its use for some applications including as a fertilizer due to the toxicity of the metal (Hobson et al., 2018). A number of different vanadium extraction methods from this slag have been studied, typically following the general process of an initial roasting step followed by leaching with an appropriate solution (Jing et al., 2017; Mahdavian et al., 2006; Wang et al., 2020).

Due to LD slag containing high concentrations of iron, it has also been considered as a potential bed material in oxygen carrier aided combustion (OCAC). An oxygen carrier needs to be able to react with both oxygen and reducing fuel gases at temperatures relevant for combustion. Important characteristics also include, having no negative effects on the environment and being fluidizable (Hossain and de Lasa, 2008). From the studies conducted on the utilisation of LD slag as an oxygen carrier (Hildor et al., 2018; Rydén et al., 2018), one found that the vanadium had accumulated on the surface of the particles of this 'OCAC slag' during combustion (Hildor et al., 2019). This may result in increased extraction efficiencies due to the leaching solution having easier access to the present vanadium.

At present, the most common method of vanadium extraction involves roasting of the slag with sodium salts followed by leaching

Abbreviations: LD, Linz-Donawitz; OCAC, Oxygen Carrier Aided Combustion; CFB, Circulating Fluidized Bed; ICP-SFMS/OES, Inductively Coupled Plasma-Sector Field Mass Spectrometry/Optical Emission Spectrometry; L/S, Liquid to Solid Ratio; SEM-EDS, Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy; XRD, X-Ray Diffraction.

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with water (Aarabi-Karagani et al., 2010; Deng et al., 2019; Mahdavian et al., 2006; Xu et al., 2014; Zhao et al., 2018). As well as the extensive consumption of energy associated with this process (Ju et al., 2015), as with any pyrometallurgical steps in a vanadium extraction process, sodium roasting also produces harmful gases (Fang et al., 2015; Gao et al., 2018). Direct leaching of the vanadium bearing slag is another potential method of extraction (Li et al., 2008; Mirazimi et al., 2015; Zhang et al., 2017). However, this process presented difficulties in that the selectivity of vanadium extraction during the leaching process can be low, resulting in a vanadium solution containing other species such as Fe^{2+} , Cr^{3+} and Mn^{2+} . Another proposed method is calcification roasting which involves the addition of calcium containing minerals such as lime, prior to the roasting process in order to aid in the oxidation of the vanadium spinel (Li et al., 2016a; Xiang et al., 2018; Yang et al., 2014; Zhang et al., 2019). Hydrometallurgical extraction processes are also used, however, the overall recovery which can be achieved is often low (Al-Harashsheh and Kingman, 2004).

Attempts to improve the hydrometallurgical process for species extraction has been investigated using novel techniques such as continuous flow and microwave-assisted leaching. Continuous flow-based techniques make leaching easier and more efficient compared to batch reactor leaching techniques (Vainio et al. n.d.). Microwave-assisted leaching aids in improving yields due to unique microwave heating characteristics. These include reduced processing time; direct, selective and volumetric heating and a more controllable heating process (Jafarifar et al., 2005). With the difficulties associated with the pyrometallurgical step in traditional methods of extraction, microwave-assisted leaching of the slag is a potential alternative.

Similarities to the previously mentioned studies highlight the potential to use OCAC slag as a source for vanadium extraction. The roasting procedure can liberate the spinel from its present phase into a more leachable state and does so by first breaking down the surrounding phases which entrap the spinel. The high temperatures in OCAC can potentially have the same effect. The operating conditions in the combustion boiler closely replicate those used in the roasting stage of vanadium extraction. The temperatures typically required for the roasting process are around 800–1000 °C (Liu et al., 2018; Xu et al., 2014; Yang et al., 2014; Zhang et al., 2017), which is similar to combustion in OCAC (Hildor et al., 2019). This allows for the inclusion of a pyrometallurgical step without the need for additional energy usage. The chemical compositions typically present within the boiler also aid in the leaching of OCAC slag. In biofuel combustion systems, the ash present within the boiler contains considerable quantities of sodium originating from the fuel (Zevenhoven et al., 2012). With this, as well as the boiler operating conditions, OCAC of biofuel may be like the sodium roasting processes as biofuel contains high amounts of alkali (Zevenhoven-Onderwater et al., 2006). The composition of the slag also highlights the opportunity to use OCAC slag for vanadium extraction due to its high Ca content of around 30–60% (Hildor et al., 2019; Remus et al., 2013). All these conditions promote the transformation of vanadium into a soluble form, increasing the potential for more efficient extraction. With the accumulation of vanadium to the outer layers of the particles (Hildor et al., 2019), the distance required to be travelled by the leaching solution is significantly reduced which may lead to an enhanced extraction rate and efficiency.

The primary objective of this study was to evaluate the opportunity to utilise OCAC slag as a feedstock for vanadium leaching and, to find the optimal leaching solution for extraction from this slag. The potential for the use of microwave-assisted leaching of OCAC slag to increase recovery and reduce process time was also investigated. In order to evaluate the suitability of using this OCAC

slag as a vanadium source, this study compares its performance against other traditional vanadium extraction methods. With sodium roasting being the most applied extraction technique, typically achieving high extraction efficiencies, this was compared against the OCAC slag. It was also deemed of interest to compare both processes with a direct leaching method.

2. Materials and methods

2.1. Materials

Prior to receiving the material, the LD slag was crushed, dried and sieved to a size fraction of 150–400 μm . Totally a batch of 28 tons was delivered to the boiler. Of this material, roughly 1 m^3 was stored indoors for usage in other experiments. For this study three samples were compared in the leaching experiments: Fresh, OCAC and Roasted. The Fresh sample was simply the LD slag as obtained from SSAB, without undergoing any pre-treatment prior leaching. The OCAC sample was LD slag that had been operated as an active bed material in a 12 MW_{th} circulating Fluidized Bed (CFB) boiler with biomass as fuel. The sample was extracted directly from the boiler after a continuous operation of roughly 46 h. The Roasted sample was treatment involved mixing the LD slag with sodium carbonate and roasting in a tube furnace. Table 1 provides the chemical compositions of the Fresh slag and the OCAC sample obtained with Inductively Coupled Plasma – Sector Field Mass Spectrometry (ICP-SFMS). Here the samples have been dried at 105 °C and correlated to this weight. The samples were then melted with LiBO_2 and dissolved using HNO_3 according to ASTM D3682: 2013, ASTM D4503: 2008 and SS EN 13656: 2003. ICP-SFMS was operated adoring to SS EN OSP 17294-2: 2016 and EPA-method 200.8: 1994. Loss on ignition was 5% for both the samples.

To identify the optimal conditions for extraction, two leaching procedures were conducted, comparing the effects of an acid and base as leaching solutions. This was also compared to a microwave-assisted leaching method. The samples used and applied methods are detailed in Table 2.

For the acidic and alkali experimental runs, 5 M sulphuric acid and 1.25 M ammonium carbonate solution were used, respectively. These solutions at these concentrations were selected due to their strong performance in vanadium extraction observed in previous studies (Aarabi-Karagani et al., 2010; Li et al., 2016b; Xu et al., 2014). For the roasted sample, the fresh slag was roasted with 20 wt% Na_2CO_3 , again based on high extraction efficiencies achieved using this salt at this ratio in literature (Aarabi-Karagani et al., 2010; Li and Xie, 2012; Mahdavian et al., 2006; Xu et al., 2014).

2.2. Procedure

The procedure for alkali roasting was conducted by mixing the fresh LD slag with 20 wt% Na_2CO_3 . For each sample, 1 g of slag was homogeneously mixed with 0.25 g of Na_2CO_3 prior to being roasted. The roasting process was conducted for 2 h in a tube furnace using air at a flow rate of 100 ml/min at 850 °C, same temperature as the boiler operation.

Similar studies examining leaching conditions, generally tend to conduct leaching as a batch process. The slag sample is typically collected in a flask with the leaching solution and stirred for a given period. This presents difficulties however, as when extracting samples of solution at a given time interval for analysis, the L/S ratio is altered - an important parameter for extraction performance. To avoid such challenges, an alternative method was conducted utilising a continuous leaching process. The basis of this proposed method involves the slag samples (1.25 g for the mixed Roasted sample and 1 g for Fresh and OCAC) being held within a sample

Table 1
Chemical composition of the slags prior to leaching from ICP-SFMS.

Compound	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	MgO	CaO	MnO	P ₂ O ₅	Na ₂ O	V
Fresh (wt.%)	24.4 ± 4.9	12.0 ± 2.3	1.4 ± 0.3	9.8 ± 1.7	44.4 ± 7.4	3.4 ± 0.6	0.56 ± 0.09	0.053 ± 0.011	1.51 ± 0.21
OCAC (wt.%)	21.5 ± 4.3	11.6 ± 2.1	1.5 ± 0.3	8.0 ± 1.4	38.7 ± 6.5	2.9 ± 0.5	0.71 ± 0.12	0.20 ± 0.04	1.47 ± 0.21

Table 2
Experimental matrix for vanadium leaching of various slag materials.

Method	Sample		
Continuous Flow Leaching (Base)	Fresh	OCAC	Roasted
Continuous Flow Leaching (Acid)	Fresh	OCAC	Roasted
Microwave-Assisted Leaching (Acid)	Fresh	OCAC	Roasted

holder with the leaching solution pumped through at a constant flowrate. The slag samples were placed into the sample holder with filter paper to prevent solid particles escaping into the leaching solution. A pump was used in order to provide a continuous flow of leaching solution at around 4.2 ml/min through the sample. The sample holder was held within a water bath set at 60 °C in order to maintain a constant leaching temperature. The experimental setup is provided in Fig. 1, with the final leaching solution being collected at set time intervals.

Following the collection of each sample, the volume collected was noted to allow for extraction efficiencies to be determined. This was calculated using the following equation:

$$\text{Extraction Efficiency}(\%) \text{ at time, } t = \frac{m_{T-t}}{M_T} \times 100\%$$

where, M_T is the total initial mass of vanadium in the slag sample prior to leaching and m_{T-t} is the mass of vanadium in solution at time, t , calculated from the concentration and volume of the sample at this time plus the sum of the mass calculated at the previous time steps.

In order to see the effects of microwave-assisted leaching on the vanadium extraction efficiency, the experiments were repeated with the use of a Milestone™ MicroSYNTH MA143 (600 W) microwave synthesis equipment with the same experimental conditions. The leaching setup, including water bath and the sample holder were placed into the microwave system and the temperature of the water bath was controlled by the temperature sensor of the microwave system.

2.3. Analysis

Following collection of the liquid solution samples,

concentration analysis was conducted using the iCAP 6500 Series ICP-OES (Inductively coupled plasma - optical emission spectrometry) from Thermo Scientific. Following leaching, the remaining solid sample within the sample holder for each run was also collected for further analysis. SEM-EDS (Scanning Electron Microscope-Energy Dispersive X-Ray Spectroscopy) FEI Quanta 200 FEG ESEM was used for imaging and elemental mapping. The samples were first embedded within an epoxy which was further ground and polished in order to investigate the particle cross section for SEM imaging and EDS analysis. A proportion of each sample was also collected for XRD (X-ray Diffraction) analysis using a Bruker™ D8 ADVANCE in the range $2\theta = 15-80^\circ$ with a step size of 0.01 (40 kV, 40 mA). For the proposed chemical reactions, the thermodynamic calculations were made by using FactSage 7.2-Reactions Module.

3. Results

3.1. Phases, structure and elemental distribution after pre-treatment

Fresh LD Slag is quite complex material which consists of several compounds. Detailed phase analysis of the fresh and used LD Slag in OCAC operations can be found in a related study (Hildor et al., 2018). The particle structure of the Fresh slag was analysed using SEM-EDS. Due to the complex nature of the slag, the presence of vanadium in the slag was difficult to detect using XRD analysis. To obtain better conditions for leaching it is important to detect how or where vanadium is present in the slag. Fig. 2 displays the SEM image clearly showing different phases within the particle. The image shows a central white phase surrounded by a darker grey phase, with all of this being encompassed by an outer structure. Point analysis of this image gives an indication of the chemical compositions of these regions. The mean values of points G1, G2 and G3 are presented in Table 3 as the 'Grey' area and points W1, W2 and W3 as the 'White' area. The inner white phase consists primarily of O and Fe with higher concentrations of V. This indicates that the vanadium present within the particles is mainly in the form of vanadium spinel, FeV_2O_4 , as suggested in previous research (Li et al., 2017; Liu et al., 2018; Xu et al., 2014). Within this area,

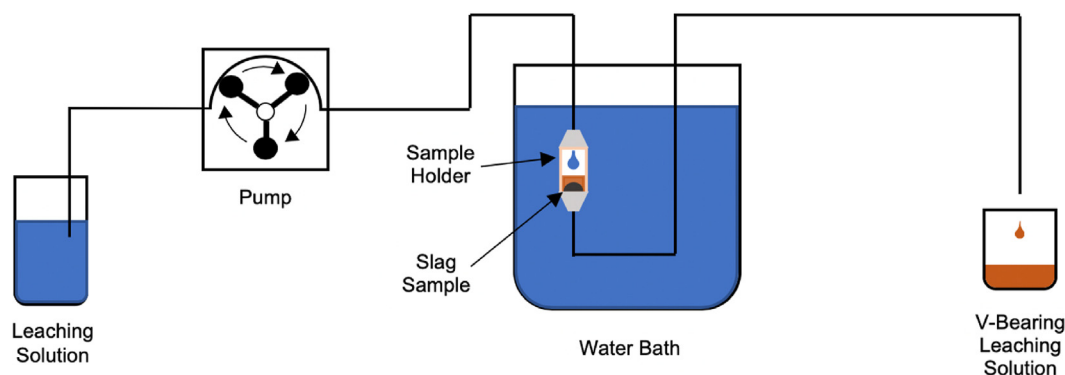


Fig. 1. Diagram of the leaching procedure carried out for vanadium extraction.

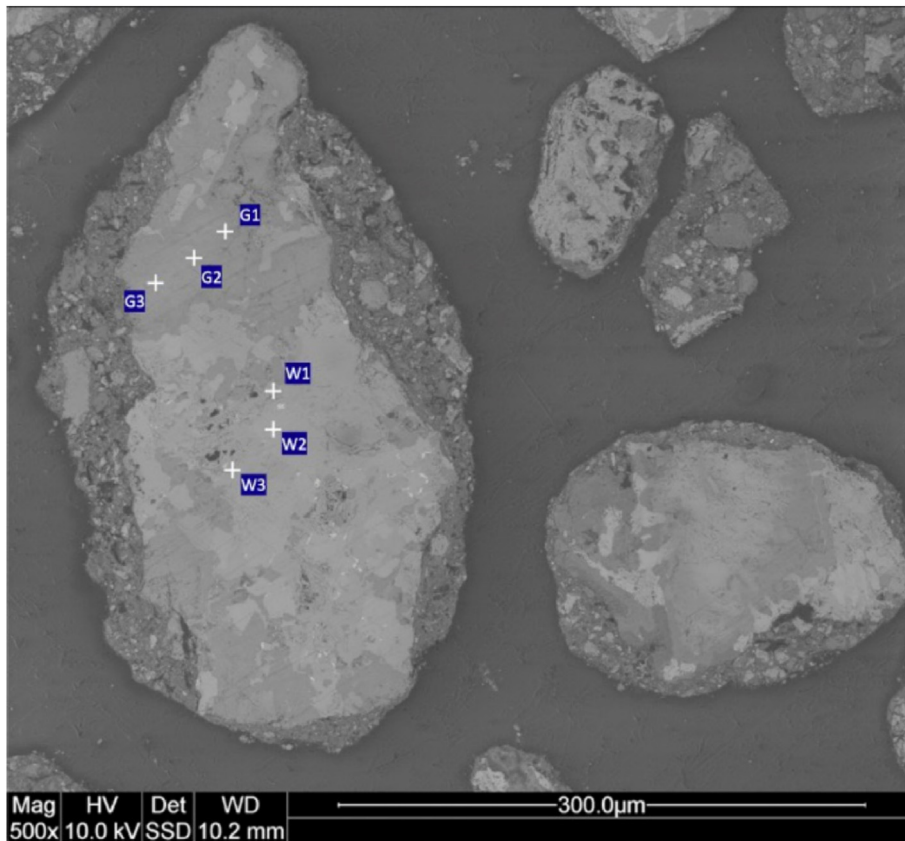


Fig. 2. Backscattered electron SEM image of the cross section of a fresh slag particle with points chosen in the two distinct regions for EDS analysis.

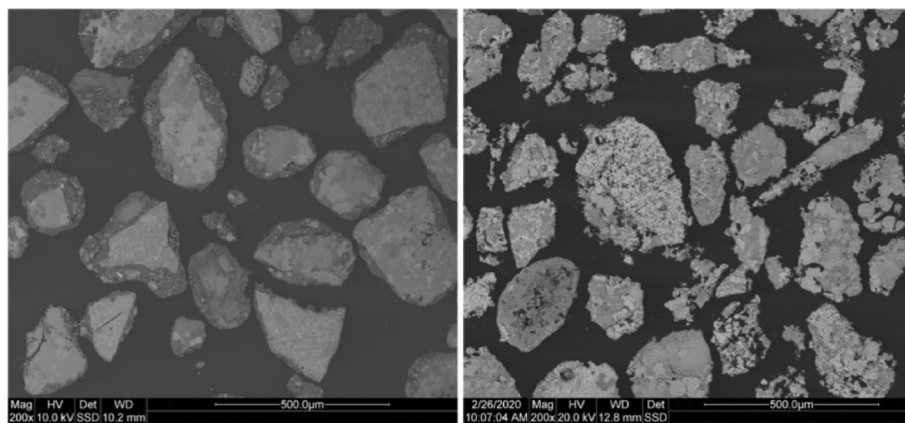


Fig. 3. SEM images of the cross sections of the fresh slag before (left) and after (right) roasting with Na₂CO₃.

Table 3

Energy dispersive x-ray spectroscopy (EDS) analysis of the Grey area (G1, G2 and G3) and the White area (W1, W2 and W3) from Fig. 3.

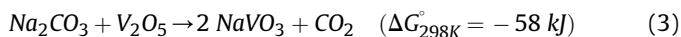
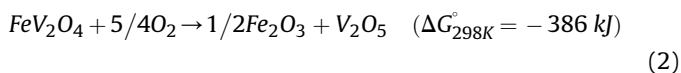
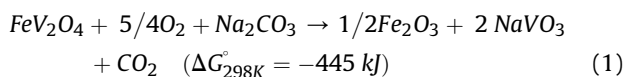
Element (wt.%)													
Area	C	O	Mg	Al	Si	P	S	K	Ca	Ti	V	Mn	Fe
Grey	14.0	38.4	0.4	0.2	9.3	0.3	0.1	0.1	34.9	-	0.4	0.3	1.7
White	11.4	29.5	4.4	0.8	3.0	0.4	0.02	0.1	22.0	2.3	3.0	2.7	21.2

there are also significant quantities of Ca, aligning with the high Ca concentration which may be present in various forms. This highlights the high potential for the formation of calcium vanadates during the OCAC and roasting processes.

Surrounding the vanadium spinel, the grey phase, contains significant quantities of O, Si, and Ca with smaller amounts of Fe. This may suggest the presence of compounds such as calcium silicate (Ca_2SiO_4) or other oxides produced from the reaction between CaO and SiO_2 , as well as minerals such as srebrodolskite ($\text{Ca}_2\text{Fe}_2\text{O}_5$) and olivine ($(\text{Mg,Fe})_2\text{SiO}_4$) in smaller quantities. The presence of these phases surrounding the spinel, limit the direct reaction of the vanadium bearing compounds with oxygen and highlight the importance of a roasting step.

After the fresh slag was roasted in the furnace with 20% Na_2CO_3 , the slag samples were analysed again using SEM-EDS in order to observe the effects of the pyrometallurgical process. Fig. 3 displays backscattered electron images of the slag before and after roasting with 20% Na_2CO_3 at 850 °C for 2 h.

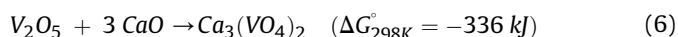
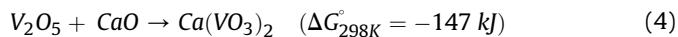
There is a clear physical difference in slag structure caused by the roasting process. Slag particles are evidently broken down due to the high temperatures experienced within the roasting furnace. One of the aims of this process is the breakdown of the surrounding phases around the vanadium and to obtain soluble vanadates (Yin et al., 2015). The new loose structure will allow easier access for oxygen to reach the vanadium spinel and hence the subsequent transformation to a soluble phase. The reactions likely to have occurred during this process are described in Reactions 1–3:



The reaction 1 is thermodynamically more favourable compare to reaction 2–3. From this point of view, alkali roasting enhances the liberation of vanadium from iron vanadate. However, since LD Slag has a complex chemical composition and phase structure, factors such as kinetic parameters, homogeneity and particle size are worth to consider along with the thermodynamic (De Windt et al., 2011).

The initial oxidation of the vanadium spinel occurs through Reaction 1 in order to produce the water-soluble sodium vanadate. The correspondence of the sodium, oxygen and vanadium can be seen in the EDS map analysis of the roasted slag in Figure S1.a in the Supplementary Information. Especially Reaction 1 was also mentioned by the other studies related to vanadium extraction (Kim et al., 2015; Wang et al., 2015). In addition to that, XRD pattern of roasted sample along with the fresh sample can be found in Figure S1.b in the Supplementary Information. Since LD Slag consists of several inorganic compounds, and vanadium content of the slag is not that significant, it is difficult to distinguish the formed vanadium compounds before and after roasting. However, the most significant difference after the roasting was the formation of $\text{Ca}_{1.94}\text{Na}_{0.06}\text{Fe}_2\text{O}_5$. This formation reveals the interaction of Na_2CO_3 with the V-bearing srebrodolskite phase which was identified as white area in Fig. 2 (Table 3).

Significant quantities of calcium present within the fresh slag also leads to the formation of calcium metavanadate within this process, as shown in Reactions 4–6. These peripheral vanadates are all known to be water insoluble.



In order to compare the effects of the OCAC process to sodium roasting, SEM-EDS analysis was again used for the OCAC sample. During operation as an oxygen carrier, the sample experiences temperatures of around 850–860 °C for a long period of time all whilst being exposed to ash, physical stress as well as oxidation and reduction.

From Fig. 4, the OCAC process is observed to have had an effect on slag structure, with the particles again broken down due to the high temperatures and mechanical collisions in the boiler. The severity of which, however, is significantly less than that observed for the sodium roasted slag, which was more effectively broken down despite undergoing a considerably shorter process. But one must keep in mind that fines and small particles are removed with the fly ash during the operation in the boiler, hence there are only the larger fraction left.

Similar to the roasting process, Reactions 4–8 are thought to occur during OCAC with the spinel being oxidised again through Reaction 2 and the subsequent reactions hypothesised to take place converting vanadium into various vanadate compounds. In this case, however, due to the limited concentrations of sodium present compared to the sodium roasting process, Reaction 3 is less likely to occur. This causes most of the vanadium to be transformed into calcium vanadates as opposed to sodium vanadates. This is indicated through Fig. 5 and Table 4, with Ca, O and V present together at Points 1, 2 and 3, as well as Mg and Mn suggesting that the formation of calcium, magnesium and manganese vanadates has occurred during the combustion process. However, it should be noted that Reaction 4–6 are thermodynamically more favourable than Reaction 7–8 (Zhang et al., 2015).

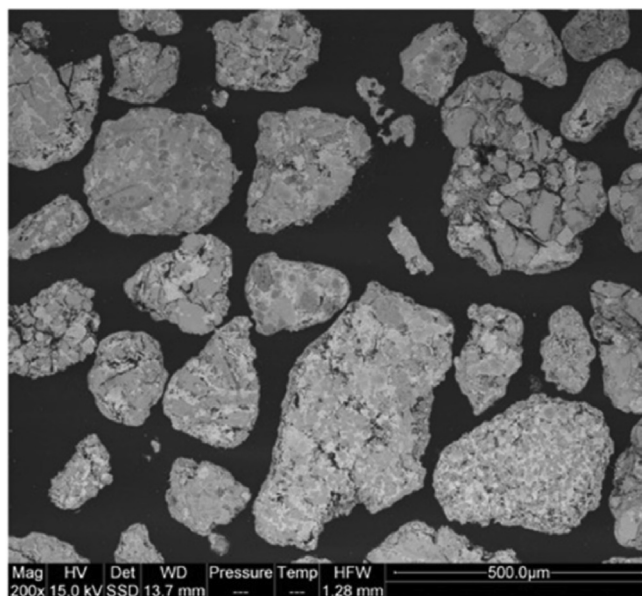


Fig. 4. SEM image of the cross section of the OCAC sample; LD slag that have been operated as an oxygen carrier in a 12MW_{th} CFB boiler for 46 h.

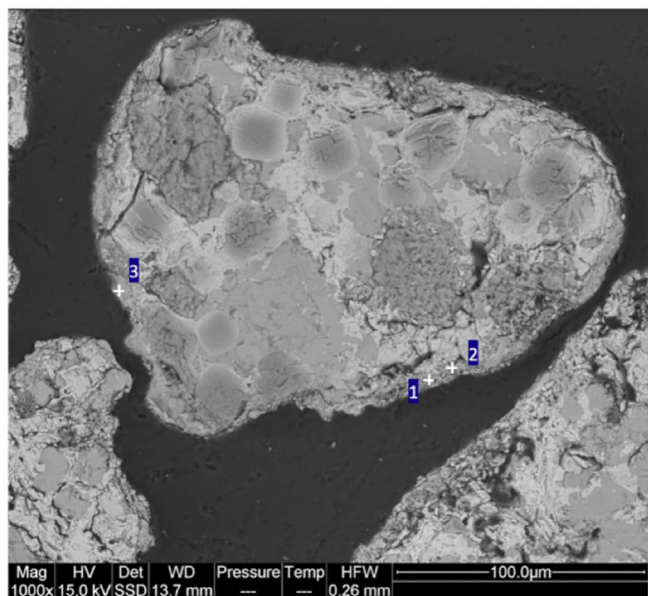


Fig. 5. SEM-EDS image of cross section of OCAC sample before leaching. Point analysis are provided in the surface of the particle at areas with higher V concentration.

Table 4
EDS analysis of Points 1, 2, and 3 from Fig. 5.

Point	Element (wt.%)										
	O	Mg	P	S	Cl	K	Ca	Ti	V	Mn	Fe
1	32.7	6.05	1.21	0.28	0.14	0.50	35.1	0.83	4.36	2.41	16.4
2	33.0	5.71	0.52	0.24	0.15	0.66	33.9	0.56	2.06	4.09	19.2
3	28.5	11.4	2.52	0.43	0.08	0.79	33.1	0.36	5.16	3.55	14.2



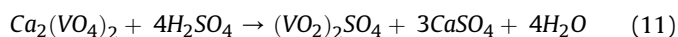
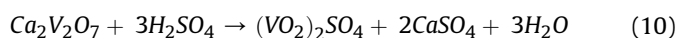
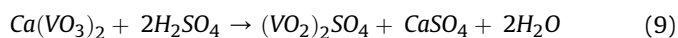
SEM-EDS map analysis of the slag shows the elemental distribution within the OCAC particles, Fig. 6. As discovered in previous research (Hildor et al., 2019), vanadium migrates to the edges of the slag particles. Phosphorus is seen to be distributed in regions similar to that of the vanadium, also present in the outer layers of the particle. Again, due to its significant quantities, calcium is present alongside these two elements around the particle edge as well as throughout the slag. Fig. 6 also confirms the presence of Mg and Mn within the OCAC particles. These latter three elements are likely to be present in the form of their water insoluble vanadates following the OCAC process according to Reactions 4–8.

Although the OCAC process operates at similar temperatures as the roasting furnace, the slag particles aren't broken down as much in this process as in roasting, and those which are cannot be collected, which may be detrimental to the leaching potential. With little breakdown in structure in comparison to the roasted slag (or the removal of these broken-down particles with the fly ash), difficulties may be faced in the oxidation of the vanadium spinel to produce V_2O_5 and hence, the formation of vanadates. This may be compensated, however, by the formation of this outer vanadium layer as the leaching solution has easier access to the vanadium present.

3.2. Leaching efficiency

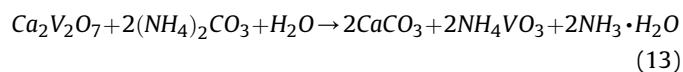
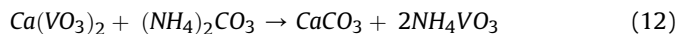
In determining the most effective leaching solution for vanadium extraction from OCAC slag, the sample was leached with 5 M sulphuric acid and 1.25 M ammonium carbonate solution. The extraction results are displayed in Fig. 7 below. The extraction curve is split into two distinct phases separated by the dotted line. The first 30 min shows an initial stage of water leaching, which is followed by the introduction of the sulphuric acid/ammonium carbonate which results in an immediate spike in extraction efficiency, showing that water is greatly ineffective in comparison to both the acid and basic solutions as there are no significant amounts of water-soluble vanadates present. Due to the complex conditions within the combustion boiler, the formation of calcium vanadates as well as sodium vanadates during OCAC causes difficulties as both differ in solubility. The pre-leaching with water allows for extraction of vanadium from its water-soluble states. Following 60 min of leaching, sulphuric acid is observed to be the superior leaching solution for OCAC slag with an extraction efficiency exceeding 19% compared to around 13% achieved with the basic solution.

During acidic leaching, based on previous literature (Li et al., 2016b; Yang et al., 2014), it is theorised that the present calcium vanadates are leached into the sulphuric acid through the following mechanisms:



To support these mechanisms, XRD analysis was carried out on the residues after the leaching (Figure S2). As expected, CaSO_4 was observed in all acidic leaching experiments within the residues. There is more CaO present in the fresh LD slag than the OCAC or the roasted slag, since Ca would interact further with other compounds during a heat treatment like an OCAC or a roasting. Due to this reason, CaSO_4 formation was dominant in the residue after the leaching of the fresh slag. The used slag in the OCAC process and the roasted slag showed similar phase analysis in the residue samples which supports the idea of the using OCAC process as a roasting in this way.

As well as this, it is thought that the magnesium and manganese vanadates are also leached, again producing $(\text{VO}_2)_2\text{SO}_4$. For the basic leaching process, ammonium carbonate reacts with the vanadates according to Reactions 12 and 13. Vanadium is extracted in the form of NH_4VO_3 which is highly soluble in aqueous solutions.



Similar to the acidic leaching, XRD analysis was carried out on the residues after the alkaline leaching (Figure S2). Phase composition of the residues was almost the same for the fresh sample, the sample used in OCAC and the roasted slag after the leaching. It is clear from the extraction efficiencies of the two processes displayed in Fig. 7 that acid is the most effective of the two solutions for the leaching of vanadium. The reasons for which may be attributed to the effect on the structure of the slag particles caused by both solutions. The sulphuric acid solution was more effective in physically breaking down the slag particles than ammonium carbonate. This

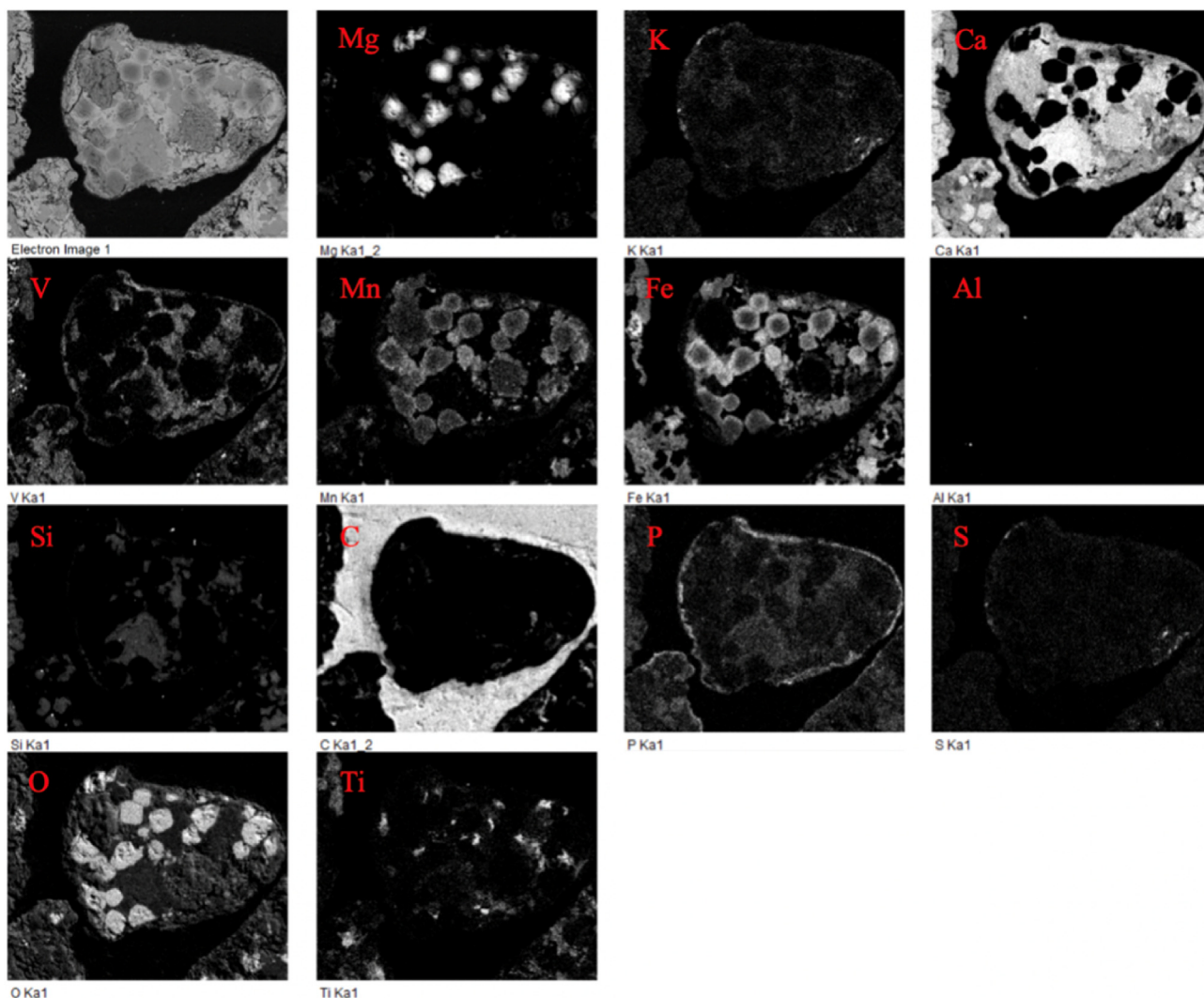


Fig. 6. Elemental map provided through SEM-EDS analysis of the OCAC slag showing V, P and K enrichment on the surface of the particles.

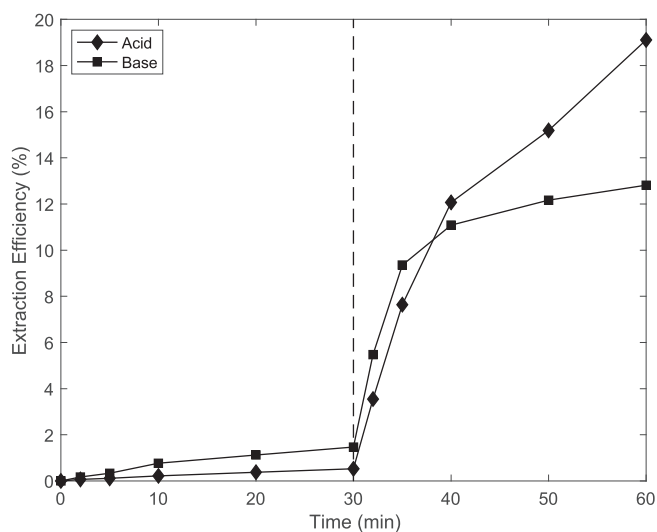
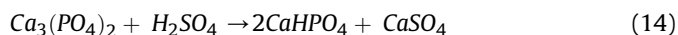


Fig. 7. Vanadium extraction efficiency against time for OCAC slag with left of the dotted line being water leached and right of the line being acid/base leached.

allows for an increased surface area for reaction and further ease of access for the sulphuric acid to reach the vanadates that are still trapped within the slag particles. Figure S3 in the Supplementary Information displays SEM images of the OCAC slag particles after both acid and basic leaching.

Although a better vanadium extraction performance is achieved through acidic leaching, there are other concerns that may influence the choice of leaching solution. Basic leaching is often employed over acidic leaching due to its selectivity in extraction of vanadium over phosphorus. During the acidic leaching process, phosphorus is thought to be leached into the solution through Reactions 14 and 15:



As discussed by Li et al. (2016b), the presence of these phosphate ions can inhibit vanadium extraction and limit overall extraction efficiency following purification. Alternatively, the corresponding reaction in basic leaching does not occur:



This is due to the difference in solubility product constant, K_{sp} , of $Ca_3(PO_4)_2$ and $CaCO_3$ with the former being significantly smaller and hence, the reaction will not take place. Evidence of this can be seen through the difference in produced phosphorus concentrations in the acidic and basic leaching solutions of OCAC slag obtained from ICP-OES analysis. Fig. 8 displays the resultant phosphorus concentrations from each leaching solution. In the first half of the run, whilst leaching with water, the concentrations are relatively similar. This significantly changes once the acidic and basic solutions are introduced after 30 min, with the phosphorus concentration in the basic leaching solution being significantly lower than that observed in the acidic leaching solution.

3.3. Effect of acid concentration, microwave leaching and particle size

5 M sulphuric acid was initially selected due to its performance in previous literature (Aarabi-Karaszgani et al., 2010), however, the strength of the acid at this concentration results in increased concentrations of impurities leached with the vanadium into solution. Therefore, the effect of reducing the acid concentration to 4 M on vanadium extraction efficiency was investigated (Fig. 9). During the entirety of the leaching experiment, the 4 M sulphuric acid solution performed slightly better than the 5 M solution, with a final vanadium extraction efficiency ~22%. It is also likely that this less concentrated acidic solution will leach less impurities with the vanadium such as phosphorus. With this lower impurity extraction and increased extraction efficiency, 4 M sulphuric acid is believed to be a better suited leaching solution for the extraction of vanadium from OCAC slag.

With the 4 M sulphuric acid solution proving the most effective in terms of vanadium extraction of OCAC slag, this solution was then used in the comparison of the slag samples with three different types of pre-treatment.

Fig. 10 displays the extraction of vanadium using 4 M sulphuric acid from OCAC, fresh and roasted slag samples. During the water leaching stage, the roasted slag performs significantly better than the other slag samples. This is most likely due to the formation of sodium vanadates during the roasting process which can be easily liberated from the samples due to their solubility in water. The vanadium present within the other samples is predominantly in

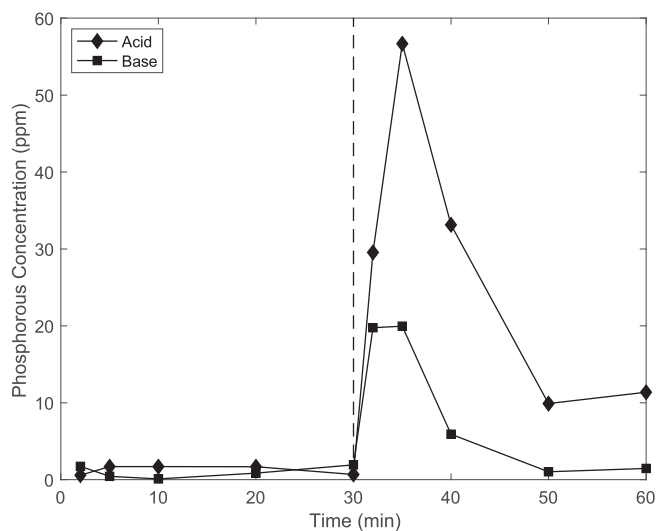


Fig. 8. Phosphorus concentration in the leached solution samples at set time intervals from the OCAC slag against time with left of the dotted line being water leached and right of the line being acid/base leached.

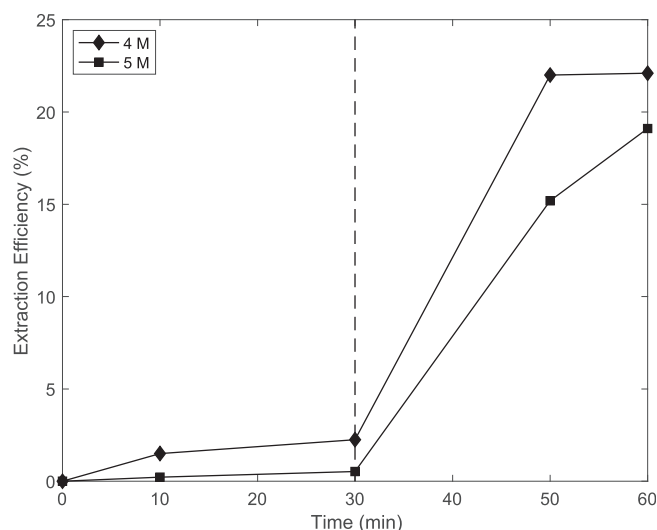


Fig. 9. Vanadium extraction efficiency of OCAC slag following leaching with 4 M and 5 M sulphuric acid.

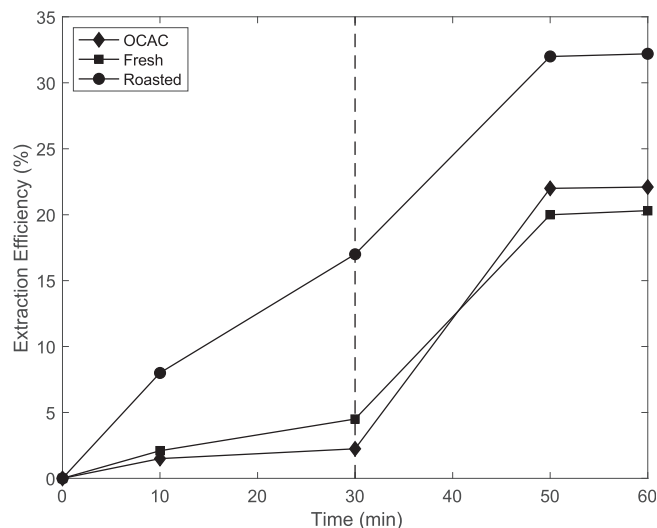


Fig. 10. Vanadium extraction efficiency against time for OCAC, Fresh and Roasted slag with left of the dotted line being water leached and right of the line being 4 M sulphuric acid leached.

the form of water insoluble calcium vanadates, hence the low extraction efficiencies in the first 30 min. Despite performing better than the fresh sample, the OCAC slag produced an efficiency lower than that of the roasted slag. Following 60 min of leaching, the OCAC samples achieved an extraction efficiency of 22.1% compared to around 32.2% and 20.3% achieved by the roasted and fresh samples respectively. The reason for this may be partly attributed to the limited breakdown of OCAC slag structure as previously discussed, preventing sufficient reaction of the vanadium spinel to produce the soluble vanadates. Following XRD analysis of the solid residues remaining after leaching, $CaSO_4$ was observed in all three samples. A similar outcome was observed (Figure S4 in the Supplementary Information) following basic leaching with the OCAC sample again performing slightly better than the fresh and the roasted producing a significantly higher extraction than both.

Further analysis of the OCAC slag sample following acid leaching using SEM-EDS mapping also provides an explanation for its poor performance, presented in Fig. 11. Similar to the elemental maps

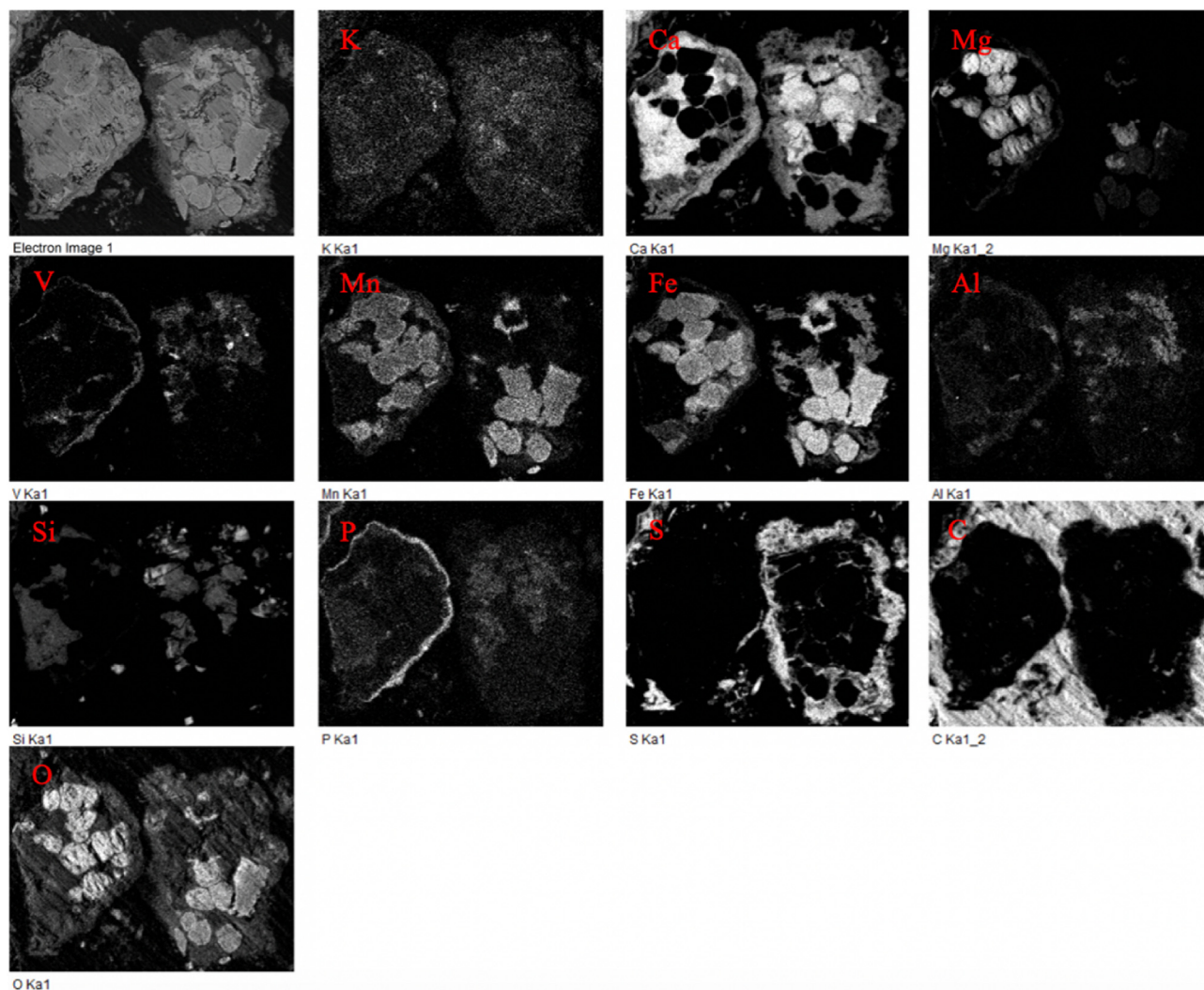


Fig. 11. Elemental map provided through SEM-EDS analysis of cross section of the OCAC slag following sulphuric acid leaching. It can be noted that V and P is clearly accumulated on the surface of the left particle even after leaching.

produced from the OCAC slag prior to leaching, vanadium and phosphorus are again observed to be present together around the surface of the particles. The components seemingly remain together despite the significant time spent being leached with sulphuric acid. The limited extraction performance may be caused by the formation of V-P based heteropolyacid anions. Present calcium phosphates in the slag may react with H_2SO_4 during the leaching to form dicalcium phosphates or calcium biphosphates. Later on, these phosphates can combine with vanadate ions to form V-P based heteropolyacid anions which inhibits the recovering of vanadates (Alonso and Livage, 1999; Li et al., 2016a). V and P bearing phases could not be directly detected in the phase analysis of the residue after the leaching, most likely due to the low amount of these components. However, different Ca based compounds such as $Ca_2Fe_{1.94}Mg_{0.06}O_5$ and $Ca_2Mg_{0.3}Fe_{1.4}Si_{0.3}O_5$ along with $Mg_{0.4}Mn_{0.6}Fe_2O_4$ were observed in the residue. Calcium silicates may also react with H_2SO_4 to produce $CaSO_4$ and silicic acid. It has reported that the both products could prevent vanadates to be extracted further (Yang et al., 2014).

The use of microwave radiation for mineral liberation to induce the phase transformation of minerals for selective leaching has been reported by other studies. Since microwave heating enables

the rapid and selective heating of materials, it may increase the extraction efficiency of the materials which have higher microwave absorption coefficient (Al-Harshesh and Kingman, 2004; Kingman and Rowson, 1998). In addition to this, the increase of the extraction efficiency of vanadium from slags by using microwave assisted synthesis has been reported recently (Tian et al., 2019; Wang et al., 2017, 2018). In order to increase the V extraction efficiency of the OCAC slag, microwave-assisted leaching was carried out. Fig. 12 displays the result comparing the continuous flow leaching method to the microwave-assisted method for OCAC slag.

It was found that the microwave-assisted procedure aided in improving overall vanadium extraction compared to continuous flow leaching, increasing the final efficiency 1.5% from 22.1% to 23.6%. This method was successful in improving efficiency and reducing extraction time from the OCAC slag and was hence used to compare this slag's performance against that from the fresh and roasted samples. Figure S5 in the Supplementary Information shows the vanadium extraction efficiency achieved from the OCAC, fresh and roasted slags utilising the microwave-assisted leaching procedure with 4 M sulphuric acid. Similar results to the continuous flow method were achieved with the OCAC sample again performing better than the fresh slag but not as effective as the

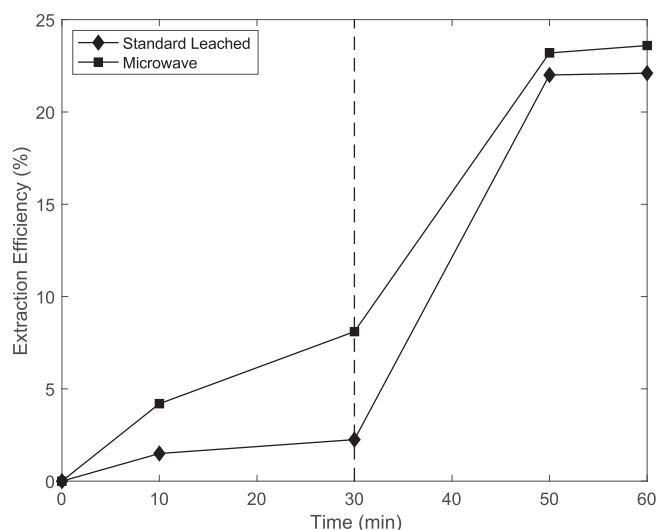


Fig. 12. Vanadium extraction efficiency from the OCAC slag leached with 4 M sulphuric acid from the continuous flow leaching method and the microwave-assisted method.

roasted, with all samples' vanadium extraction improving with the use of the microwave. The microwave-assisted method aided in allowing the leaching solution to more effectively reach the held vanadium within the OCAC slag and at a higher rate, resulting in an increased extraction efficiency. The reasons for this improved extraction rate caused by microwave-assisted leaching has been discussed by Al-Harashseh & Kingman (Al-Harashseh and Kingman, 2004), which suggests that the microwave causes a non-thermal effect to exist which reduces the reactions activation energy. In related literature studies, the activation energies of the reactions observed were lower in the microwave assisted leaching than the conventional leaching (Tian et al., 2019; Wang et al., 2018). Also, the increase of the extraction efficiency in microwave assisted leaching experiments was reported as a result of the formed temperature gradient during the microwave heating and the superheating effect at the solid-liquid interface (Ma et al., 2015). It is also thought that the super heating effect occurring during dielectric heating makes the temperature no longer representative of the reaction conditions. This method only affected the rate at which the extraction occurs and therefore XRD analysis produced the same results as observed from the continuous flow leaching method.

Previous studies have found that reducing the sample particle size can have a significant effect on vanadium extraction (Gao et al., 2018; Xiao et al., 2010). With the limited extraction efficiencies achieved from the OCAC slag compared to previous studies on vanadium extraction, despite the microwave-assisted method improving efficiency, the effect of the sample particle size was also investigated. The slag samples were further ground to size ranges of 44–74 μm and 74–149 μm to compare against the 150–400 μm used originally (Fig. 13). These samples were again leached using the microwave-assisted method and 4 M sulphuric acid. This was observed to be greatly effective in improving the extraction efficiency as OCAC slag with a size fraction of 44–74 μm was found to be 49.1%, nearly double that of the original sample. This reduced particle size allows for a greatly increased surface area for extraction and therefore easier access for the leaching solution to reach the held vanadium within the particles. The positive effects of reducing particle size were also observed in the fresh and roasted samples. Figure S6 in the Supplementary Information shows the effect of particle size on all three samples. The OCAC slag is again found to perform better than the fresh slag however, an extraction

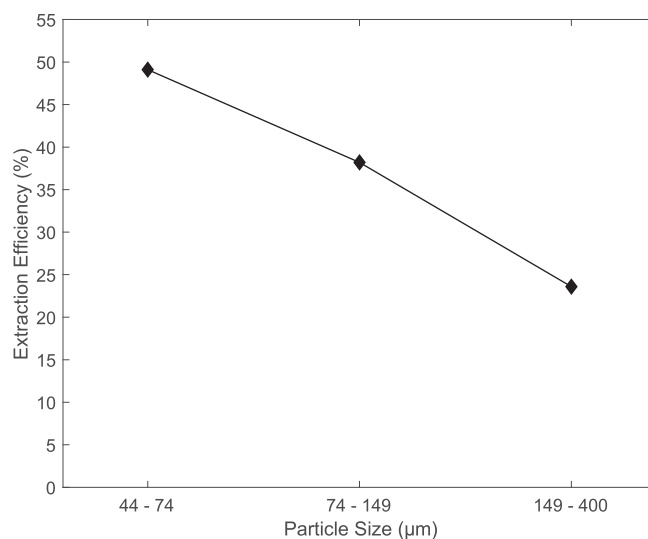


Fig. 13. Vanadium extraction efficiency achieved from OCAC slag of varying size fractions after 60 min of microwave-assisted leaching with 4 M sulphuric acid.

efficiency equal to that of the roasted slag still could not be achieved.

4. Discussion

In the present study, the effect of the used LD Slag in an OCAC process, instead of fresh LD-Slag was investigated in a manner of vanadium extraction. The motivation of the study was the similar natures of the traditional alkali roasting and the OCAC process. The traditional alkali roasting is a pyrometallurgical step where an alkali agent, generally Na_2CO_3 , is used for roasting and generally it takes place above 800 $^\circ\text{C}$ (Kim et al., 2015; Wang et al., 2015). Therefore, this process is highly energy consuming. Different alkali salts like NaOH or KOH can also be used to reduce the roasting temperature; however, the high concentration of alkalis and the high pressures (up to 3.2 MPa) are necessary in this case (Wang et al., 2014). OCAC process is a type of combustion that would enable carbon capture without significant costs for gas separation (Rydén et al., 2018). LD-Slag is a good candidate to be used in OCAC, since it has relatively high concentration of iron (Hildor et al., 2019). From this point of view, OCAC process was taken instead of a traditional roasting step to compare the extraction efficiencies of vanadium in the both processes. The continuous flow leaching was used as a leaching method, and microwave-assisted leaching was also investigated as a method for comparison in the study.

In the study, the continuous flow leaching method was applied which enables to keep the L/S value constant during the experiment. Due to the limited sampling volume of the setup, a small mass of sample was used in each experiment. Since LD Slag is quite non-homogeneous material, it is worth to note that this may affect the evaluation of the results from batch to batch. To minimize this possible effect, the samples were mixed very well before the experiments.

When the extraction efficiency of vanadium in OCAC sample and fresh slag were compared in 4 M H_2SO_4 leaching, OCAC sample performed a slightly better performance than the fresh slag. But, OCAC sample could not perform better than the roasted slag. This result may seem surprising since OCAC sample has more alkali content due to the biomass fired boiler; and the OCAC process would be similar to the traditional alkali roasting. However, it is known that the alkali species most likely interact with the slag

components during the OCAC process and form quite stable Na/K-Ca-Al-Silicates. It was also reported where LD slag was used as an oxygen carrier in a biomass-fired OCAC process, potassium and silica form bridges between the particles (Hildor et al., 2019). With OCAC process, more species are added (mostly high amount of Si, Ca and alkali depending on the fuel) to the mixture which may create more complex phase structures at OCAC operation temperatures (Yilmaz and Leion, 2020). Most likely, more stable Ca-silicates formed with time during the OCAC process, and these formations led V bearing components be trapped. Even though, the V-bearing compounds deposit on the outer layer of the particle after OCAC process, these compounds may have limited solubility in acids or the reason can be the incomplete transformation of vanadium into acid-soluble compounds (Xiang et al., 2018). In addition to this, presence of phosphate ions may also affect the extraction of vanadium via forming V-P based heteropolyacid anions (Li et al., 2016a). It is well known that Fe oxide content in the slag has a positive effect on the extraction of vanadium (Yan et al., 2018). However, Fe oxides interact with other slag components during the OCAC process, and form Ca-Fe based complex compounds which may prevent vanadium to be extracted easily. From this point of view, multistep leaching processes would be beneficial to increase the extraction efficiency (Xiang et al., 2018).

It is evident that the performance of sulphuric acid for the extraction of vanadium is desirable in that high extraction efficiencies are achieved in comparison to ammonium carbonate and water leaching solutions. There are concerns, however, due to the lack of selectivity to vanadium achieved by the acid resulting in a leaching solution containing a range of different species including phosphorus, potentially causing difficulties downstream during purification. In potential future use of OCAC slag for vanadium extraction - during the selection of an appropriate leaching solution - this must first be carefully considered.

Microwave assisted leaching was proposed as a proper method to increase the vanadium extraction efficiency in the study. The extraction efficiency increased compare to the continuous flow leaching when the microwave assisted leaching was carried out, most likely due to the kinetic factors such as fast heating rate and lower activation energies (Tian et al., 2019; Wang et al., 2018; Zhang et al., 2013). H₂SO₄ was used as a leaching agent which is known as a microwave absorber (Wang et al., 2017). Also, LD Slag has several different compounds which have different microwave absorption capacities. From this point of view, most likely a temperature gradient would form along with the superheated zone at the solid-liquid interface which was also reported in a similar study (Ma et al., 2015). The vanadium extraction efficiency would be increased if the related process parameters such as microwave power, leaching time would change. However, there is no optimization study was carried out within the scope of the paper. The leaching time was kept constant in the microwave assisted leaching experiment to be able to compare the results with the continuous flow leaching. Later on, the particle size which was reported as an efficient parameter in vanadium extraction (Yang et al., 2014), was taken as a parameter to increase the extraction efficiency. This was most likely the result of the increased surface area (Peng et al., 2018).

The focus in the study was given to the acid leaching of the used LD slag in an OCAC process. Since LD Slag is rich of calcium-based species, a high amount of CaSO₄ was observed in the residues after the acid leaching. This would make the acid-waste handling and disposal process easier after the leaching. In addition to this, when the benefits of both vanadium recovery from the slag, and the further utilisation of the used LD Slag considered, the costs of acid handling/disposal steps after leaching can be afforded.

5. Conclusion

From this study, it was for the first time possible to successfully leach vanadium from LD slag used as a bed material in OCAC. Extraction of vanadium from this material allows both the valuable metal to be used and the remaining material to be accessible for use in a more efficient way than landfill.

The OCAC process and its effect on the slag particle structure was compared to the sodium roasting process. It was deemed that although the OCAC slag did exhibit some positive effects due to the combustion conditions this was not as effective as the roasting for preparation of the slag in order to get effective leaching. Despite the accumulation of vanadium on the surface of the particles, the accessibility of the vanadium was limited. The limited solubility of the vanadium rich phases after OCAC utilisation resulted in a significant portion of the vanadium remaining trapped within the slag. This was also supported by the increased extraction yield when the particle size was decreased. OCAC particles that were effectively broken down in the combustion boiler, were most likely removed with the fly ash and therefore could not be collected for extraction. It is also thought that an interaction between the vanadium and phosphorus within the slag during the OCAC process, hinders the extraction of vanadium which can be achieved from the slag.

The leaching procedure carried out for this study was successful in extracting vanadium from the slag following all three pre-treatment methods. The novel continuous leaching process worked effectively in conducting the extraction of vanadium from the samples, eliminating the difficulties typically faced using the batch process. For the OCAC slag, an extraction efficiency of 22.1% was achieved using the continuous flow leaching method with 4 M sulphuric acid after 30 min of water leaching followed by 30 min of acid leaching. The microwave-assisted leaching method and decreasing of the particle size were successful in further reducing the extraction time and improving the extraction performance of the OCAC slag. A final vanadium recovery of 49.1% was achieved using a microwave-assisted leaching with 4 M sulphuric acid and a particle range of 44–74 μm. In both cases the OCAC slag proved to be better than the Fresh sample but not as effective as the roasted slag.

CRediT authorship contribution statement

Martin Attah: Conceptualization, Investigation, Writing - original draft, Visualization. **Fredrik Hildor:** Methodology, Validation, Resources, Funding acquisition, Writing - review & editing. **Duygu Yilmaz:** Methodology, Validation, Resources, Funding acquisition, Writing - review & editing. **Henrik Leion:** Project administration, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jclepro.2021.126159>.

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