Behaviour and fate of vanadium during the aerobic neutralisation of hyperalkaline slag leachate

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HIGHLIGHTS

- V present in leachates as the vanadate oxyanion
- V removed downstream by a mechanism contemporaneous with $CaCO_3$ precipitation
- V initially attenuated due to incorporation into neoformed $CaCO_3$
- At lower pH adsorption to Fe (oxy)hydroxides are most important sink for V.
- Removal of V from solution may lead to a corresponding enrichment in sediments.

GRAPHICAL ABSTRACT
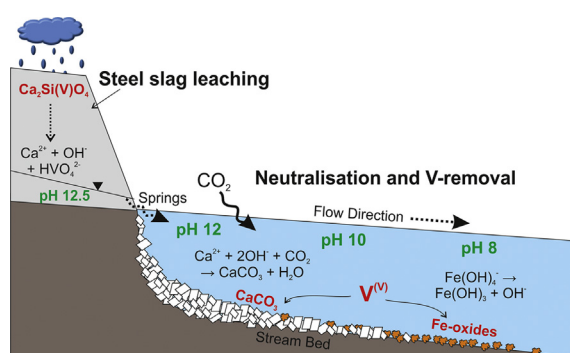
ARTICLE INFO

ABSTRACT

Vanadium is a toxic metal present in alkaline leachates produced during the weathering of steel slags. Slag leaching can therefore have deleterious effects on local watercourses due to metal toxicity, the effects of the high pH (9–12.5) and rapid carbonation (leading to smothering of benthic communities). We studied the fate and behaviour of V in slag leachate both through field observations of a heavily affected stream (Howden Burn, Consett UK) and in controlled laboratory experiments where slag leachates were neutralised by CO_2 ingassing from air. V was found to be removed from leachates downstream from the Howden Burn source contemporaneously with a fall in pH, Ca, Al and Fe concentrations. In the neutralisation experiments pH reduced from $12 \rightarrow 8$, and limited quantities of V were incorporated into precipitated $CaCO_3$. The presence of kaolinite clay (i.e. SiOH and AlOH surfaces) during neutralisation experiments had no measureable effect on V uptake in the alkaline to circumneutral pH range. XANES analysis showed that V was present in precipitates recovered from experiments as adsorbed or incorporated $V^{(V)}$ indicating its likely presence in leachates as the vanadate oxyanion (HVO_4^{2-}). Nano-scale particles of 2-line ferrihydrite also formed in the neutralised leachates potentially providing an additional sorption surface for V uptake. Indeed, removal of V from leachates was significantly enhanced by the addition of goethite (i.e. FeOOH surfaces) to experiments. EXAFS analysis of recovered goethite samples showed HVO_4^{2-} was adsorbed by the formation of strong inner-sphere complexes, facilitating V removal from solution at pH < 10. Results show that carbonate formation leads to V removal from leachates during

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leachate neutralisation, and the presence of both naturally occurring and neoformed Fe (oxy)hydroxides provide a potent sink for V in slag leachates, preventing the spread of V in the environment.

1. Introduction

Vanadium is a redox active transition metal commonly present in natural samples in the +3, +4 and +5 oxidation states (Peacock and Sherman, 2004; Wanty and Goldhaber, 1992). V speciation in natural systems depends strongly on pH and Eh, and $V^{(IV)}$ and $V^{(V)}$ are the dominant species present in natural waters. $V^{(V)}$ species are stable across a wide pH range and are the dominant species in oxic environments at low pH and both oxic and anoxic systems above pH 8 (Huang et al., 2015; Takeno, 2005). At high pH, $V^{(V)}$ is normally present as the vanadate oxyanion (HVO_4^{2-}) (Wehrli and Stumm, 1989). In general, the toxicity of V increases with oxidation state with $V^{(V)}$ species being the most toxic (Barceloux and Barceloux, 1999).

Naturally occurring V (i.e. derived from parent rocks) is the most common source of V in surface environments (Guagliardi et al., 2016), but this V is often present bound in low solubility minerals as $V^{(III)}$ (Huang et al., 2015). Naturally occurring V is therefore relatively immobile in water and of less environmental concern. In contrast, V associated with anthropogenic sources, such as fossil fuel burning and steel making, is more commonly present as $V^{(V)}$, and therefore forms a problematic component in the resultant residues and slags (Chaurand et al., 2007a; Proctor et al., 2000; Roadcap et al., 2005). Weathering of steel slags can therefore be a significant source of leachable V, which is often found at high concentrations in associated leachates (Hull et al., 2014; Koryak et al., 2002).

Although much of the V present in steel slag is incorporated into relatively unreactive dicalcium aluminoferrite phases (Chaurand et al., 2007a; Hobson et al., 2017), significant concentrations of V are also found as $V^{(V)}$ in dicalcium silicate phases (e.g. larnite; Hobson et al., 2017). Hydration and dissolution of dicalcium silicate (Eq. (1)) can therefore result in V release to solution. $V^{(V)}$ is very soluble as the vanadate ion (Wehrli and Stumm, 1989), which at the high pH produced by dissolution of associated CaO (typically 11.5 to 12.5; Eq. (2)) interacts poorly with mineral surfaces, thus enabling its release to the wider environment.

$$Ca_2SiO_4 + 2H_2O \rightarrow 2Ca^{2+} + H_2SiO_4{}^{2-} + 2OH^- \qquad (1)$$

$$CaO + H_2O \rightarrow Ca^{2+} + 2OH^- \qquad (2)$$
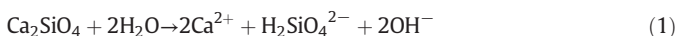
Slag weathering produces a highly alkaline leachate with high Ca^{2+} concentrations. Ingress of atmospheric CO_2 leads to the leachate immediately becoming supersaturated with respect to $CaCO_3$, which precipitates readily onto existing solid surfaces (Boylan et al., 2017; Ford and Williams, 1989; Eq. (3)). This reaction consumes OH^- ions leading to a progressive fall in pH contemporaneous with precipitation of Ca downstream of the leachate source. The rate of Ca precipitation generally varies proportionally with leachate aeration (Gomes et al., 2017; Mayes et al., 2008) but is also affected by mixing with carbonate alkalinity present in surface waters. Where both are high, $CaCO_3$ deposition rates up to 100 g day^{-1} m^{-2} have been estimated (Mayes et al., 2008).

$$Ca^{2+} + CO_2 + 2OH^- \rightarrow CaCO_3 + H_2O \qquad (3)$$
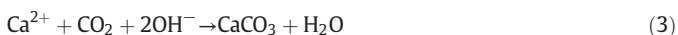
A significant ecological impact from leachates has been observed at legacy sites, where a decrease in biological diversity has been observed as pH and metal loadings increase closer to the leachate source (Hull et al., 2014; Koryak et al., 2002). Steel slag leachate is an ecological stressor in a number of ways. The high pH of leachate (pH > 10.5) is considered toxic to aquatic organisms (Wilkie and Wood, 1996). In addition, rapid precipitation of $CaCO_3$ forms hardpans that can smother benthic ecosystems and prevent light from reaching primary producers (Effler, 1987; Fjellheim and Raddum, 1995). Furthermore, a large range of potentially problematic trace metals have been reported to be present in alkaline steel slag leachates including Al, Fe, As, Pb, Mn, Mo, and V (Hull et al., 2014; Roadcap et al., 2005).

Long term monitoring of steel slag leachate shows a general decline in both pH and Ca concentrations over time as available CaO and Ca-silicate phases are depleted and weathering rinds that are comprised of Ca-Si-H and carbonate minerals are formed (Costa et al., 2016; Riley and Mayes, 2015). It has been observed that the high pH, Ca-dominated leachate formed during the early stages of slag weathering inhibits V release due to the inverse relationship between Ca and V concentrations imposed by Ca-Vanadate solubility limits (Cornelis et al., 2008; De Windt et al., 2011; Hobson et al., 2017; Huijgen and Comans, 2006). However, when Ca concentrations are reduced, V concentrations can significantly increase in leachates (Hobson et al., 2017). Therefore a decline in pH and Ca concentrations over time may not necessarily lead to a corresponding fall in V concentrations, and may in fact allow higher concentrations of V to accumulate in leachate.

The behaviour and fate of leached V in environments affected by steel slag leachates has not been widely studied. Therefore, regulatory bodies (such as the UK Environment Agency) have adopted highly precautionary approaches when dealing with disposal of steel slag (Environment Agency, 2014) which may lead to unnecessarily onerous monitoring requirements at landfill and legacy sites. Improving understanding of the behaviour of leached V will enable the environmental risks posed by legacy slag heaps to be fully assessed and assist in the implementation of effective remedial measures if required.

This study investigated the persistence of V in streams affected by slag leachate downstream of a legacy slag heap, and determined the environmental behaviour of V during aerobic neutralisation of leachate in the presence of different mineral surfaces. Field observations of a stream affected by leachate from slag heaps at the former site of the Consett steelworks, Co. Durham were used to understand the range of processes occurring in natural watercourses. Laboratory experiments were then used to determine the mechanism of V removal occurring when both real and synthetic slag leachates were neutralised by ingress of atmospheric CO_2. To determine its fate in solids, V speciation and coordination environment was determined in precipitates recovered after neutralisation using a combination of X-ray absorption spectroscopy (XAS) and high resolution electron microscopy. Finally, these data were used to develop a new understanding of the implications of V behaviour in rivers affected by hyperalkaline slag leachates.

2. Methods

2.1. Study site

Howden Burn drains slag heaps present in the northern part of the former Consett Iron and Steel Works located in the Hownsgill Valley, County Durham UK (source 54°51′12.9″N 1°51′41.1″W; Fig. 1). Waters in Howden Burn are characterised by high pH (9.0–12.5) and high Ca concentrations (median of 149 mg L^{-1} between 1978 and 2004, $n =$ 86; Riley and Mayes (2015)) which decline downstream due to $CaCO_3$ precipitation. $SI_{calcite}$ values between 1.76 and 2.25 have been calculated corresponding to Ca deposition rates of between 14.0 and
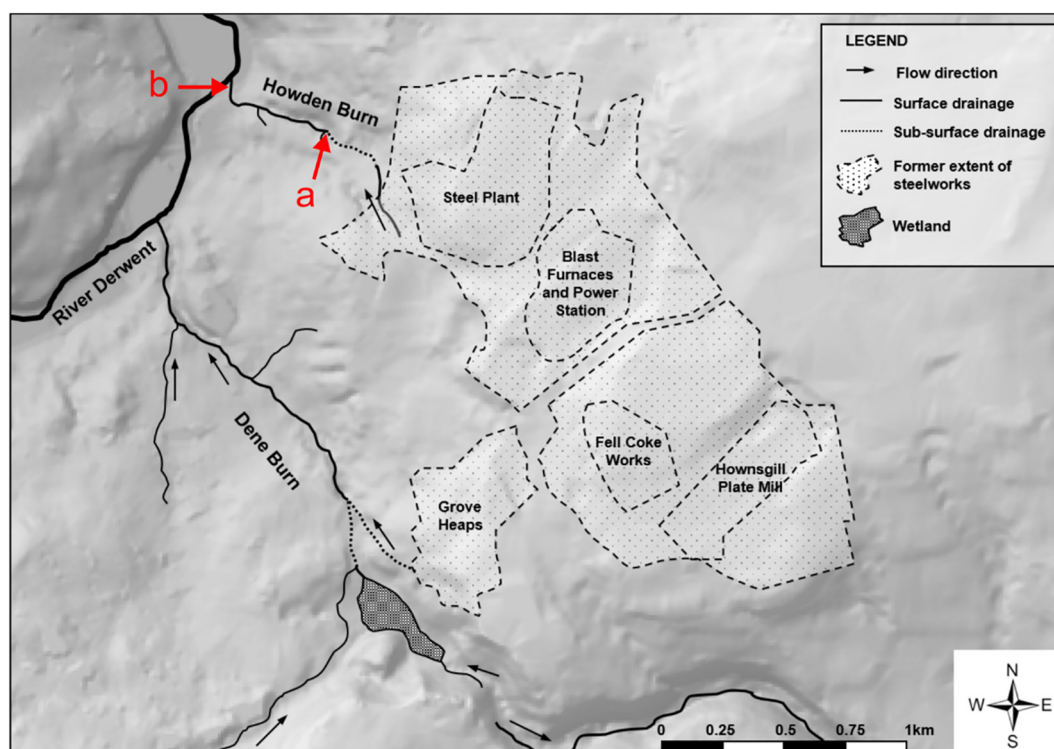
Fig. 1. Site plan for former Consett Iron and Steel Works showing drainage streams including Howden Burn. Red arrows represent a) maximum upstream field sampling locations and sampling point for leachate neutralisation experiments and b) maximum downstream field sampling locations (after Mayes et al. (2008) and Hull et al. (2014)). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

48.2 g day^{-1} m^{-2}. Vanadium concentrations are reported to decrease downstream (Mayes et al., 2008).

2.2. Howden Burn leachate and sediment sampling

Water samples were collected on a total of 4 occasions from Howden Burn between November 2006 and May 2015. Leachate pH (±0.3 pH units) was measured in-situ using a Myron L Ultrameter® calibrated using pH 12.4, 10, 7 and 4 buffer solutions. Samples were filtered (0.45 μm, cellulose – nitrate) and aqueous V concentrations were determined using a Perkin Elmer Elan DRCII inductively coupled plasma mass spectrometer (ICP-MS; detection limits 1 ppb) and all other elements were determined on a Perkin Elmer Optima 5300 inductively coupled plasma optical emission spectrometer (ICP-OES; detection limits 10–100 ppb). Both instruments were calibrated with 3 standards (0.1, 1, 10 ppm) and a blank which were run every 15 samples and the calibration cross-checked with a trace metal Certified Reference Material (NIST1646A) with all values within $\pm5\%$.

Sediment samples ($n = 10$) were collected from the Howden Burn stream bed in September 2015. Sediments were dried overnight at 40 °C and sieved to remove the coarse (>2 mm) size fraction. Representative samples were ground to <150 μm and their V concentration determined (with an absolute uncertainty versus certified sediment standards of <$\pm10\%$) using an Olympus X-5000 X-ray fluorescence (XRF) analyser.

2.3. Leachate neutralisation experiments

Leachate emerging at Howden Burn was collected for use in neutralisation experiments from the source of Howden Burn in September 2015 (hereafter referred to as HB source water). Basic oxygen furnace (BOF) slag leachate was generated by leaching of two $2 \times 2 \times 1$ cm blocks of BOF slag in 2 L Milli-Q water over 6 months under air excluded conditions (block leachate) (see Hobson et al., 2017 for details). Synthetic leachate was made under air excluded conditions by diluting saturated Ca(OH)$_2$ by a factor of ten with nitrogen purged deionised water before adding an aliquot of 100 ppm NaVO$_3$ solution to achieve a final concentration of 2500 ppb V.

Leachate neutralisation experiments were established in triplicate 500 mL Erlenmeyer flasks that contained 200 mL of either HB source leachate, block leachate or synthetic leachate with:

1. No mineral surface (unamended),
2. 1.0 or 0.2 g L^{-1} α-FeOOH (goethite-amended) and
3. 1.0 or 0.2 g L^{-1} kaolinite (kaolinite-amended).

Excess kaolinite and goethite (relative to real stream concentrations) were added to ensure interactions with these minerals were not masked by effects of carbonation. Flasks were loosely capped to allow ingress of air and were shaken at 175 rpm on an orbital shaker. At 2–3 hour intervals (until leachate reached ~pH 8), 3 mL aliquots of suspension were removed and filtered (0.2 μm, PES). The pH of the filtrate was determined (±0.3 pH units) using an Orion DualStar pH/ISE benchtop meter (Thermo Scientific, USA) with electrodes that were calibrated daily using pH 4, 7 and 10 buffer solutions. Aqueous metal concentrations were determined (with an analytical uncertainty of <$\pm3\%$) from acidified filtrate (0.2 μm filtered; 0.1 M HNO$_3$) either on a Thermo iCAP 7400 radial ion-coupled plasma optical emission spectrometer (ICP-OES; major elements), or on a Thermo iCAP Qc ion-coupled plasma mass spectrometer (ICP-MS; minor elements). Calibration was against certified multi-element standards and check samples were analysed every tenth sample to check for calibration drift.

Table 1
Aqueous composition of all site waters and leachates used in neutralisation experiments.

	HB source (average of all site data)	HB source (sample used in experiments)	Block (BL)	Synthetic (SL) (average)
pH	11.9 ± 0.5	11.9	11.9	12.0 ± 0.1
Major ions (ppm)				
Ca	104 ± 31	194	85	79
Si	1.3 ± 0.3	2.5	30	
Mg	0.6 ± 0.3	<LOD[a]	0.1	
K	127 ± 57	149	0.4	
Na	33 ± 8	99	2.4	
Minor ions (ppb)				
Al	129 ± 39	<LOD[a]	390	
Cr	5 ± 2	7	10	
Fe	58 ± 8	166	251	
Li	448 ± 175	709	<0.1	
Mn	15 ± 3	39	13	
V	37 ± 14	35	493	2495

[a] LOD, Limit of detection.

Experiments were stopped following stabilisation of solution pH (24–65 h after starting). Leachates were vacuum filtered (0.2 μm, polycarbonate). Residues were dried in an oven at 40 °C prior to further analysis described below.

2.4. Transmission electron microscopy (TEM) analysis

Approximately 10 mg dried solid residue from the HB source leachate experiment was suspended in ethanol, placed on a Cu support grid with holey carbon support film and air dried prior to analysis. The specimen was examined using an FEI Tecnai TF20: FEGTEM Field emission gun TEM/STEM fitted with HAADF detector. Semi-quantitative elemental analysis was preformed using Oxford Instruments INCA 350 EDX system/80 mm X-Max SDD detector and Gatan Orius SC600A CCD camera using AZtec data acquisition software. The element and sample specific limit of detection for elemental analysis was between 0.1 and 0.5 wt%.

2.5. X-ray absorption spectroscopy (XAS)

XAS spectra were collected from solid residues recovered from leachate neutralisation experiments at the V K-edge (5465 eV) on beamline I18, Diamond Light Source, UK in February 2016. Spectra were also collected from a range of V-containing laboratory chemicals and an aqueous vanadate solution (1000 ppm). Kaolinite and goethite V sorption standards were prepared by adding 20 mL 100 ppm $NaVO_3$ dropwise over 20 min to 0.2 g goethite or kaolinite suspended in 2 L Milli-Q DIW to achieve a sorbed V concentration of ~1 wt%. Solution pH was maintained at pH 8 by adding 0.1 M HCl or 0.1 M NaOH as required. Once all $NaVO_3$ had been added the suspension was left overnight prior to vacuum filtering at 0.2 μm. The residue was dried in an oven at 40 °C for 24 h. All solid samples were analysed as pressed pellets (diluted with cellulose as required) and held in Kapton™ tape. Multiple spectra were averaged to improve signal to noise ratio, normalised and plotted in the XANES data region (−50–100 eV; with a resolution of 0.25 eV) using Athena v0.9.24 (Ravel and Newville, 2005). For selected samples (with sufficiently high V concentrations) V K-edge EXAFS data was also collected and fit to molecular coordination models using Artemis v0.9.24 using reduced chi-squared and R values as measures of goodness of fit.

3. Results and discussion

3.1. Leachate composition and downstream trends in Howden Burn

Average composition of groundwater emerging at the Howden Burn source is shown in Table 1. Water pH values varied between 11.5 and 12.7 and contained elevated concentrations of Ca with trace concentrations of Al, V, K, Fe and Si. These concentrations are consistent with reported elemental compositions of leachate generated during
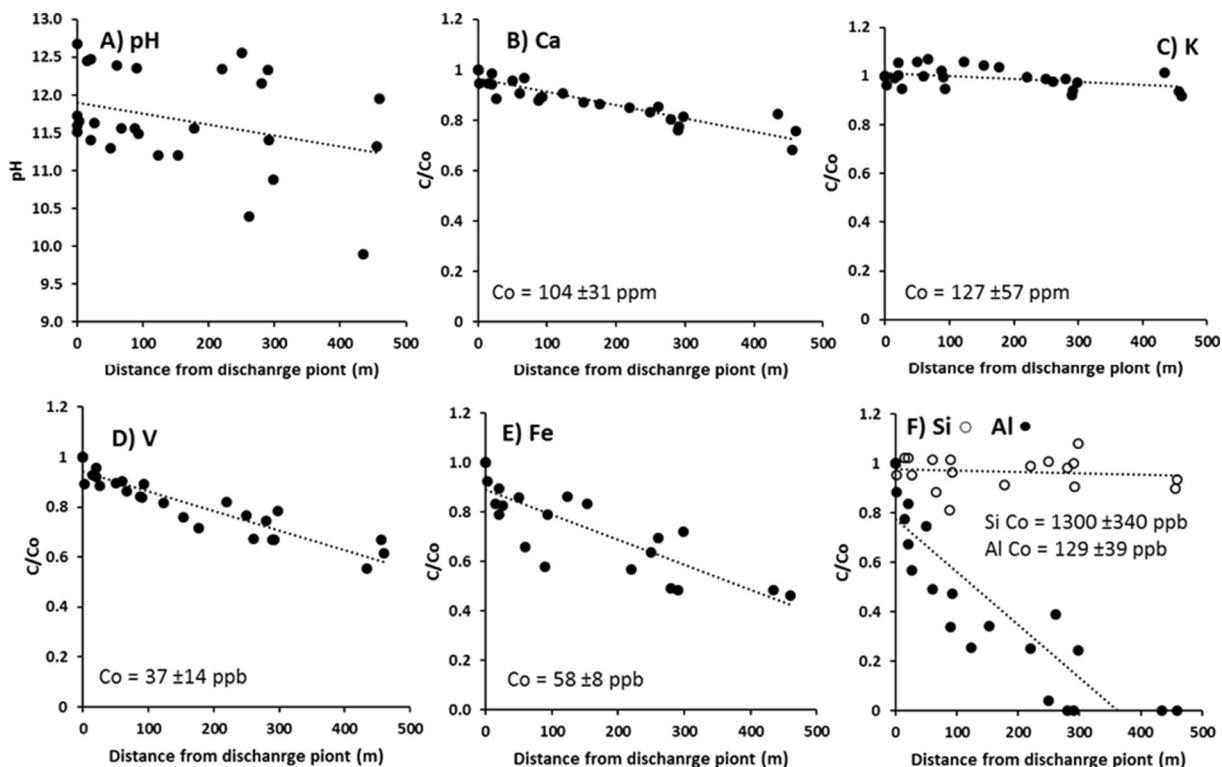
Fig. 2. Relative changes in pH and selected elements concentrations in Howden Burn, Consett, UK, for water samples (filtered at 0.45 μm) collected downstream from a culvert feed by groundwater in contact with mixed iron and steel slags. Data from Mayes et al. (2008); Riley and Mayes (2015). Dashed best fit lines are added to guide the eye.
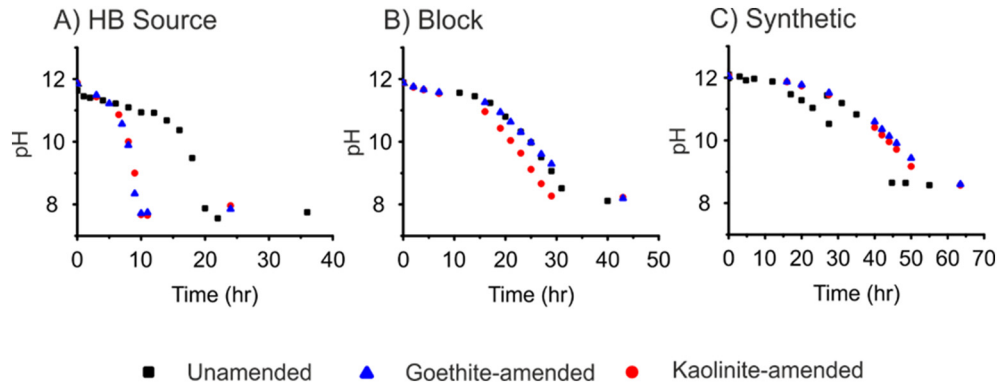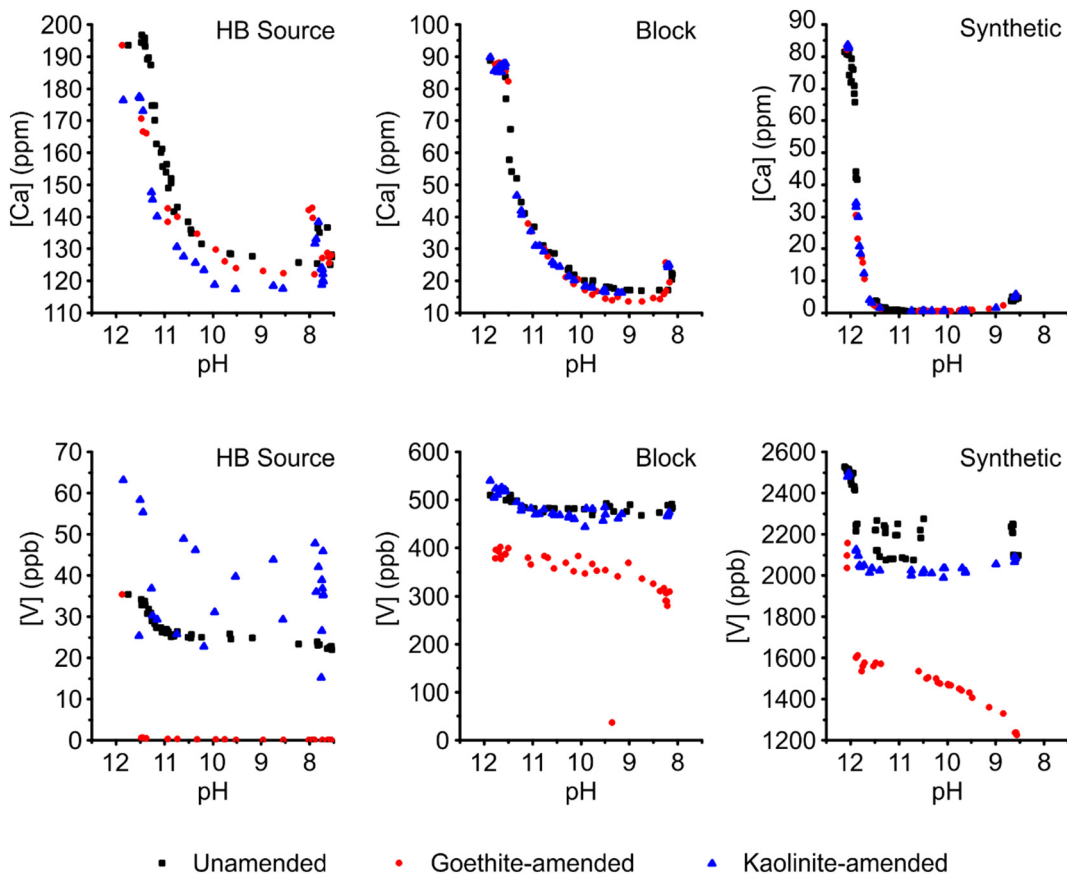
Fig. 3. pH measurements over time during neutralisation of slag leachates. Initial conditions in goethite and kaolinite-amended systems: A) 1.0 g L^{-1} goethite/kaolinite; B) and C) 0.2 g L^{-1} goethite/kaolinite. Data points represent mean values from triplicate measurements.

weathering of steelmaking waste (Mayes et al., 2008; Roadcap et al., 2005). The source water was Ca(OH)$_2$ dominated in composition and the presence of elevated Si concentrations indicated that it was primarily formed via hydration and dissolution of Ca-silicate phases and free lime under relatively CO$_2$-free conditions (De Windt et al., 2011; Roadcap et al., 2005). The presence of other trace elements, including V, Fe and Al, is likely to be due to the release of impurities present in Ca-silicates (Chaurand et al., 2007a; De Windt et al., 2011; Hobson et al., 2017).

When normalised to allow for variation in source concentrations over time, the Ca, V, Fe, and Al concentrations showed distinct declining trends downstream from the Howden Burn (Fig. 2). V concentrations declined from 37 ± 14 ppb at the source to 24 ± 8 close to the junction with the River Derwent. Ca and Fe concentrations fell from 104 ±

31 ppm and 58 ± 8 ppb, to 79 ± 22 and 33 ± 14 over the same distance. Al had an initial concentration of 129 ± 39 ppb and was completely removed from solution at a point 400 m downstream from the source. Si and K showed little variation decreasing only slightly from 1300 ± 340 ppb and 127 ± 57 ppm to 1280 ± 480 and 123 ± 60 respectively. The pH was generally high but fell from 11.9 ± 0.5 to 11.01 ± 0.9 before the River Derwent was reached. V concentrations in the stream sediments ranged from 13 to 48 ppm (mean = 34 ± 11 ppm). As tufa formations are observed in the stream bed it is likely that in-gassing of atmospheric CO$_2$ resulted in Ca being precipitated from solution as CaCO$_3$ (Eq. (3)). This reaction consumes OH$^-$ ions, thus contributing to the fall in pH.

Si concentrations were relatively constant along the Burn despite the changes in pH. This is likely due to undersaturation with respect to SiO$_2$

Fig. 4. Ca and V concentrations from all leachate systems. Data points represent samples from individual flasks. Initial conditions in goethite and kaolinite-amended systems: in HB source water: 1.0 g L^{-1} goethite/kaolinite; in block and synthetic leachates: 0.2 g L^{-1} goethite/kaolinite.
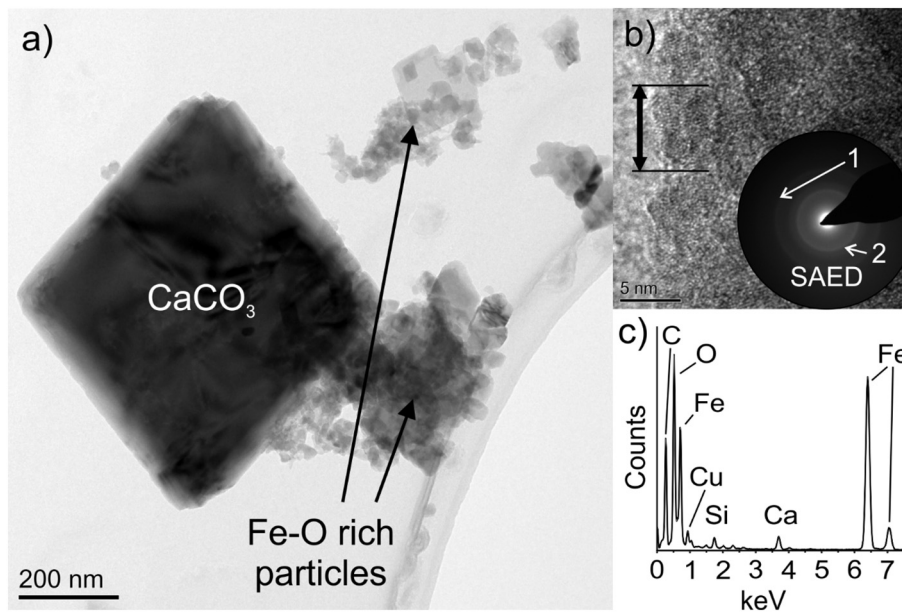
Fig. 5. Solid residue recovered from unamended HB source water neutralisation experiments. A) Low resolution TEM image showing calcite and Fe-O-rich crystals. B) High resolution TEM image and SAED pattern from Fe-O-rich crystals; arrows show extent of crystallite structure and C) EDS spectrum from Fe-O-rich crystallites.

(am) (SI < −2) resulting in conservative behaviour. The conservative behaviour of Si and K throughout the sampled area suggests that dilution of the leachate is minimal in Howden Burn. Therefore, removal mechanisms exist for V, Al and Fe which are independent of dilution and contemporaneous with the decrease in pH and the precipitation of Ca as $CaCO_3$. Fe and Al removal are easily explained via formation of insoluble (oxy)hydroxide phases during pH reduction from pH 12 to 10 (Langmuir, 1997), however, V (present in surface waters as $V^{(V)}$ at high pH) is not predicted to precipitate as (oxy)hydroxides over this pH range (Wanty and Goldhaber, 1992) highlighting the likely role of mineral incorporation and adsorption processes in V removal.

3.2. Mechanism of V removal during leachate neutralisation

The composition of each leachate type used during neutralisation experiments is shown in Table 1. In all leachate systems, pH was buffered to final values between 7.5 and 8.5 (Fig. 3). Mineral-amended HB source water took 10 h to reach a final pH of 7.5, however, unamended HB source water took 20 h to reach the same final pH. Block leachate took 30 h to equilibrate under all three conditions. Unamended synthetic leachate took 45 h to equilibrate and both mineral-amended synthetic leachate systems took ~55 h to equilibrate.

All three leachate neutralisation systems show removal of Ca from solution as well as pH reduction over time (Fig. 4), indicating that ingress of atmospheric CO_2 has led to the precipitation of $CaCO_3$. This was confirmed by low resolution TEM imaging (Fig. 5a) of the solid residue recovered from the unamended HB source water neutralisation experiments, which showed the presence of 100–1000 nm rhomboid crystals with EDS spot analysis spectra that contained Ca, C and O (data not shown). This mineral shape and composition are consistent with the calcium carbonate mineral calcite. The slight increase in Ca concentrations seen in experiments below pH 8.5 (Fig. 4) is due to continued CO_2 ingress, which in this pH range results in the generation of H^+ ions, leading to minor amounts of $CaCO_3$ dissolution. Ca-removal was broadly comparable in the unamended, goethite-amended and kaolinite-amended systems for all three leachate types, with rapid removal as the pH fell from 12 to 11 followed by a slower removal thereafter.

Modest V removal is also observed in all three leachate systems as pH fell from pH 12 to 11 (Fig. 4). Subsequently, V concentrations

remained relatively stable in all the unamended systems. TEM analysis of solid residues from the unamended Howden Burn source water experiment found distinct 100–300 nm Fe and O rich particles were also
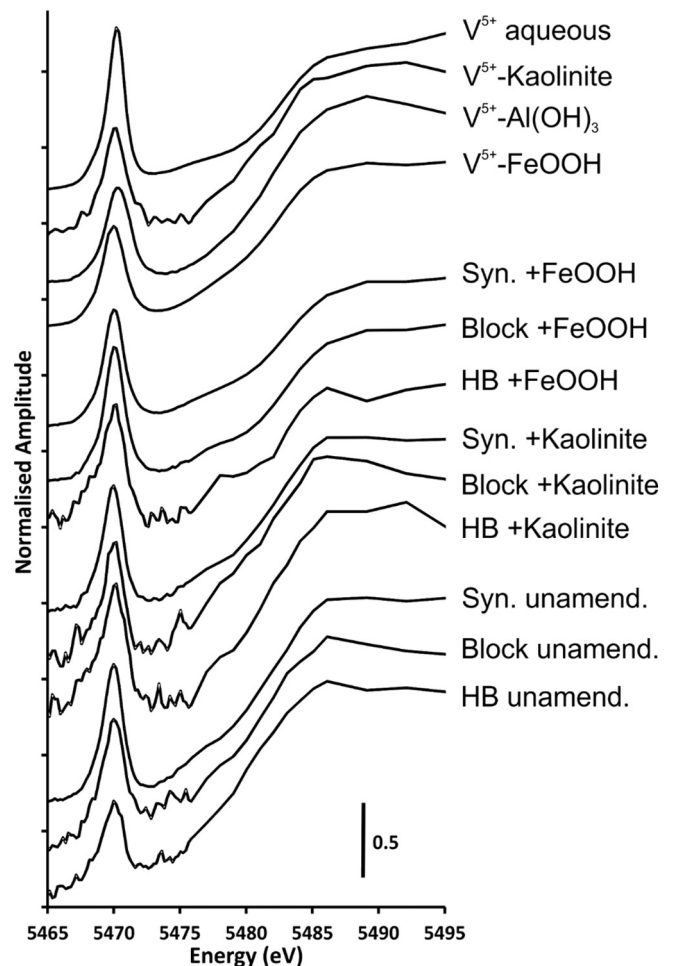

Fig. 6. V K-edge XANES spectra collected from precipitates recovered from the leachate experiments after aerobic neutralisation and from V^{5+} containing standards.
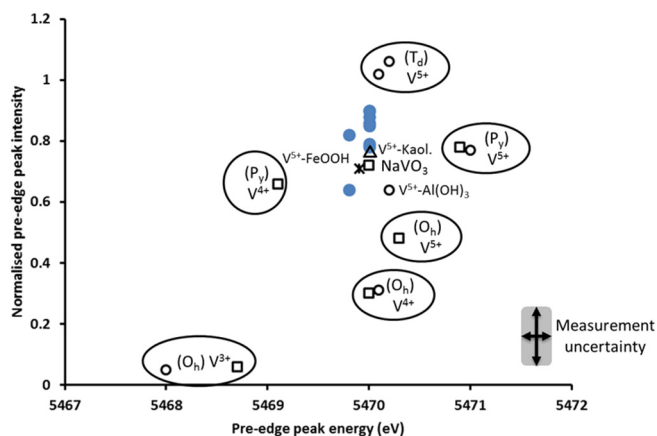
Fig. 7. Plot of pre-edge intensity vs. pre-edge peak energy derived from V K-edge XANES spectra. Symbols: (●) refers to the experimental samples; (*, Δ) Vanadate adsorption standards; (○) standards from Burke et al. (2013); (□) standards taken from Bronkema and Bell (2007); Chaurand et al. (2007b). (T$_d$), (P$_y$) and (O$_h$) refers to tetrahedral, square pyramidal and octahedral co-ordination respectively.

present. High resolution imaging (Fig. 5b) showed these to be aggregates of 5–10 nm spherical crystallites, which were identified as two-line ferrihydrite by selected area electron diffraction. At high pH the dominant Fe species in aqueous solution is Fe(OH)$_4^-$ (Langmuir, 1997) but this will transform to Fe(OH)$_3^0$ and precipitate as insoluble hydroxides as the pH is reduced (Eq. (4)).

$$Fe(OH)_4^-(aq) \rightarrow Fe(OH)_3(s) + OH^- \qquad (4)$$
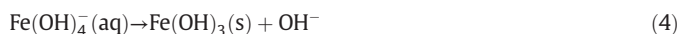
Fe hydroxides are known to contain abundant surface sites that are able to sorb V$^{(V)}$ (Peacock and Sherman, 2004), which may, therefore, contribute to the V removal observed. Any Al present in solution (as Al(OH)$_4^-$) is also predicted to precipitate from solution as pH is lowered (Eq. (5)), however, neoformed Al hydroxides do not provide surfaces for efficient V sorption (Burke et al., 2013).

$$Al(OH)_4^-(aq) \rightarrow Al(OH)_3(s) + OH^- \qquad (5)$$
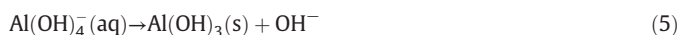
Despite the known affinity of V for Fe hydroxide surfaces, this was probably not the only V removal mechanism in Howden Burn, as V removal is also seen in the synthetic leachate system which does not contain any aqueous Fe. Therefore it is probable that a small amount of V can be incorporated into neoformed CaCO$_3$ at high pH. Currently no data is available concerning incorporation of HVO$_4^{2-}$ to CaCO$_3$ although studies by Goh et al. (2010) and Hua et al. (2007) have shown that similar tetrahedral anions (e.g. arsenate, chromate) may be sparingly

incorporated into the trigonal carbonate site. V was not detected in SEM-EDS analysis of CaCO$_3$ rinds formed on weathered BOF slag blocks (Hobson et al., 2017), however, the low concentrations incorporated into carbonates would likely be orders of magnitude below EDS detection limits (0.1–0.5 wt%).

All XANES spectra from the leachate neutralisation experiment solids indicated the presence of V in the precipitates. Experimental samples displayed a prominent pre-edge peak at 5470 eV (±0.25 eV), the normalised intensity of which varied between 0.64 and 0.90. The position of the main absorption edge (E$_{1/2}$; the point at which absorption reaches 50% of normalised absorption) varied between 5477 and 5482 eV (Fig. 6). Comparison with standard spectra suggested that V was present in all samples in the V$^{(V)}$ oxidation state. Analysis of pre-edge peak intensity and energy position following the method of Chaurand et al. (2007b) shows that V speciation in the products from the neutralisation reactions plot close to data collected from standard materials containing vanadate adsorbed to clay and hydroxide surfaces (Fig. 7; Bronkema and Bell (2007); Goh et al. (2010); Tanaka et al. (1988)). The pre-edge peak is formed during electron transitions from the 1s to hybridised 3d/4p orbitals. The extent to which this hybridisation occurs is a function of speciation and coordination environment with the effect being most pronounced for V$^{(V)}$ in tetrahedral coordination. EXAFS analysis of vanadate has revealed that in sorption environments the VO$_4$ tetrahedral become distorted, reducing the effect of hybridisation and resulting in a correspondingly less intense pre-edge peak (Bronkema and Bell, 2007; Tanaka et al., 1988). A similar molecular distortion (and reduced pre-edge peak intensity) is noted for vanadate in some polyvanadate species such as sodium metavanadate (NaVO$_3$) (Bronkema and Bell, 2007). Incorporation of vanadate to the trigonal site in calcite is also very likely to cause a similar distortion. Therefore, detailed analysis shows the V K-edge XANES data for the leachate neutralisation samples are consistent with either vanadate incorporation to neoformed calcite precipitates, or adsorption to precipitated Fe hydroxides, during neutralisation.

3.3. Additional effect of minerals on V removal during neutralisation

The observed trends in Ca-removal were largely unaffected by the addition of either kaolinite or goethite during neutralisation (Fig. 4). V removal in the kaolinite-amended systems follows a similar pattern of removal to the unamended systems between pH 12 and 11 followed by a stabilisation in V concentrations. In the kaolinite-amended block leachate system, initial V removal lowered V concentrations from ~550 to ~490 ppb. The kaolinite-amended HB source water experiments showed a similar trend to unamended equivalents (fall from 35 to 25 ppb) but had a large amount of scatter. V concentrations fell from 2500 to ~2000 ppm in the kaolinite-amended synthetic leachate then increased slightly to ~2100 ppm between pH 9.5 and 8.5.
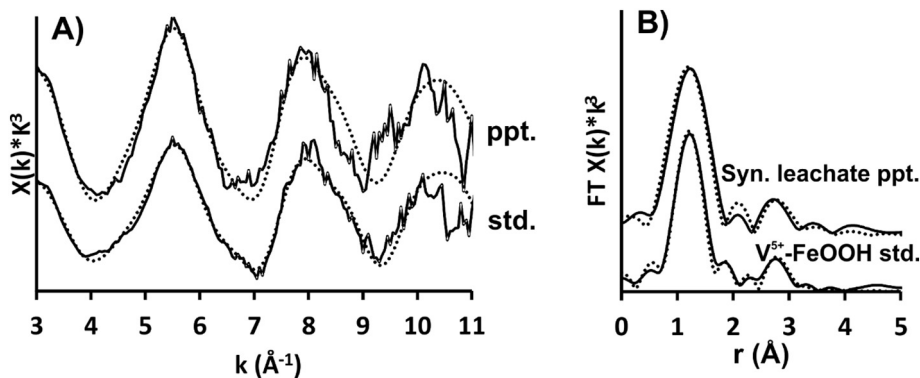
Fig. 8. A) V K-edge EXAFS spectra collected from precipitates formed in the goethite-amended synthetic leachate experiment after aerobic neutralisation; and the vanadate – FeOOH sorption standard at pH 8; and B) corresponding Fourier transformations. Dashed lines represented best fits to the data calculated in Artemis (Demeter v0.9.47) using the parameters given in Table 2.

Table 2
V K-edge EXAFS fits, where N is the Occupancy (±25%; only whole number fits used), r is the interatomic distance, σ2 is the Debye–Waller Factor and reduced χ^2 and R are the goodness of fit parameters. Uncertainties in the last digit(s) shown in parentheses.

Experiment Description	Pathway	N	r (Å)	σ^2 (Å^2)	χ^2; R
1. Syn. Leachate + FeOOH ppt @pH 8.	V-O	4	1.69(2)	0.004(3)	215; 0.0170
$\delta e0 = -6(3)$	V-Fe	2	3.33(6)	0.004(7)	
$S^2_0 = 0.7(2)$	MS VO$_4$[a]	4	2.97(4)	0.007(6)	
2. FeOOH-vanadate std. @pH 8.	V-O	4	1.67(1)	0.003(2)	161; 0.0178
$\delta e0 = -10(2)$	V-Fe	2	3.31(3)	0.006(4)	
$S^2_0 = 0.5(1)$	MS VO$_4$[a]	4	2.91(4)	0.005(4)	

[a] MS VO$_4$ = multiple scattering pathways within the VO$_4$ tetrahedral.

Final equilibrated pH values of between 7.5 and 8.5 were measured in all kaolinite-amended leachate systems which is well above the point of zero charge (PZC) of most clay minerals, including kaolinite (PZC < 3.7; Hu et al. (2003); Kosmulski, 2011). Therefore, at all leachate pH values, kaolinite is negatively charged and does not readily interact with anions in solution. As such, it is likely that in kaolinite-amended systems, the observed decrease in V concentrations is due to incorporation into neoformed CaCO$_3$ as previously discussed, rather than sorption to either AlOH or SiOH sites on kaolinite surfaces.

V uptake is significantly enhanced under goethite-amended conditions. In the goethite-amended HB source water experiments, V was completely removed within the initial drop of pH from 12 to 11.5, however, these flasks had a higher solid: solution ratio of goethite (1.0 g L^{-1}) than the goethite-amended block leachate and goethite-amended synthetic leachate systems (0.2 g L^{-1}). In these latter two systems, initial V removal at pH 12 was very rapid (~500 to ~400 ppb and ~2500 to ~1600 ppb in goethite-amended block and synthetic systems respectively). This was followed by a steady decrease in V concentration throughout the remainder of the experiments to a minimum of ~300 ppb in the goethite-amended block leachate and ~1200 ppb in the goethite-amended synthetic leachate. The PZC of goethite is significantly higher than that of kaolinite (pH 7–9.5; Kosmulski (2016)) and so as leachate pH evolves towards these values, progressively stronger interactions with anions such as vanadate will take place. Therefore, whilst vanadate adsorption to iron oxides can occur across the range of leachate pH values observed in the experiments (12–7.5; Langmuir (1997)), it is expected to be significantly enhanced below pH 10.

XANES spectra obtained from all experimental samples indicate the presence of V$^{(V)}$ which is soluble at high pH as the vanadate ion (HVO$_4^{2-}$, Wehrli and Stumm (1989)). Due to generally very low V concentrations in samples, usable EXAFS data was only collected for the sample recovered from the goethite-amended, synthetic leachate neutralisation experiment. This spectrum was compared to data collected from the 1 wt% V-goethite standard (Fig. 8). Both samples were best-fit with a similar coordination model consisting of 4 V-O single scattering pathways at 1.7 Å and 2 V-Fe single scattering pathways at 3.3 Å (Table 2), consistent with V sorption to goethite surfaces via bidentate inner-sphere complexation (Peacock and Sherman, 2004).

These experimental results (and field data) indicate a system in which V$^{(V)}$ is released to leachate as HVO$_4^{2-}$, followed by limited incorporation to neoformed CaCO$_3$ at high pH following in-gassing of atmospheric CO$_2$. Whilst the concentration of V incorporated into carbonates is very low, the large volumes of CaCO$_3$ precipitated at legacy sites suggest that this is the most important mechanism of V removal during the initial stages of leachate neutralisation. Subsequently, increasing sorption of V to any Fe-(oxy)hydroxide (FeOOH) surfaces present also contributes to removal of HVO$_4^{2-}$ from the leachate, especially at pH values <10.

3.4. Implications for affected environments

V concentrations in emerging leachate in Howden Burn regularly exceed chronic toxicity screening values (19 ppb; Buchman (2008)) and laboratory based leaching tests have demonstrated the potential for V

to accumulate in steel slag leachates at concentrations well in excess of acute toxicity screening values (280 ppb; Buchman (2008), Hobson et al., 2017; Stewart et al., 2018). Incorporation into neoformed CaCO$_3$ phases and adsorption to iron oxides removes V from the leachate during aerobic neutralisation. These processes are expected to reduce the transport of V in affected rivers but also lead to accumulation of toxic V$^{(V)}$ in river sediments downstream. Indeed, environmentally significant V concentrations of >42 ppm (Dutch Target Value; Buchman (2008)) were observed in sediments collected from the Howden Burn stream bed.

Overall, it appears that despite the reduction in V concentrations distal to the source, the combination of high metal loadings in both leachate and sediment, high pH leachate and carbonate smothering have had a deleterious effect the local ecosystem. Therefore, treatment of leachate to reduce alkalinity (and metal concentrations) within a short distance of the source is recommended. Previous studies have demonstrated the efficacy of wetland treatment (Mayes et al., 2006) or cascade systems (Gomes et al., 2017) in neutralisation of leachate and sequestering metals from solution.

4. Conclusions

Concentrations on V in slag leachate are frequently sufficiently high to be an environmental concern at the Howden Burn source, however, V is removed downstream by a mechanism contemporaneous with CaCO$_3$ precipitation. V was present in the V$^{(V)}$ oxidation state (the most toxic form) in all solids recovered from neutralisation experiments indicating its mobilisation in leachate as the vanadate (HVO$_4^{2-}$) oxyanion (which is the predicted speciation at high pH). Leachate neutralisation experiments indicated that V is initially attenuated downstream due to incorporation into neoformed CaCO$_3$. Whilst V incorporation is limited, mass balance suggests that this mechanism is responsible for the majority of V removal at high pH due to the rapid rate of CaCO$_3$ precipitation and the large volumes produced. Subsequently, adsorption of vanadate to Fe (oxy)hydroxides provides the most important sink for V due to formation of strong inner-sphere complexes as solution pH drops. Additional sites for adsorption may be provided by precipitation of Al or Fe (oxy)hydroxides (e.g. ferrihydrite) as solution pH falls. Removal of V from solution may lead to a corresponding enrichment in sediments and future remediation schemes should look to balance efficient removal of V from leachates with safe management of any impacted sediments.

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