Mechanism of Vanadium Leaching during Surface Weathering of Basic Oxygen Furnace Steel Slag Blocks: A Microfocus X-ray Absorption Spectroscopy and Electron Microscopy Study

Andrew J. Hobson, Douglas I. Stewart, Andrew W. Bray, Robert J. G. Mortimer, William M. Mayes, Michael Rogerson, and Ian T. Burke

School of Earth and Environment, and School of Civil Engineering, University of Leeds, Leeds, LS2 9JT, U.K.
School of Animal, Rural and Environmental Sciences, Nottingham Trent University, Brackenhurst Campus, Southwell, Nottinghamshire NG25 0QF, U.K.
School of Environmental Sciences, University of Hull, Hull, HU6 7RX, U.K.

ABSTRACT: Basic oxygen furnace (BOF) steelmaking slag is enriched in potentially toxic V which may become mobilized in high pH leachate during weathering. BOF slag was weathered under aerated and air-excluded conditions for 6 months prior to SEM/EDS and μXANES analysis to determine V host phases and speciation in both primary and secondary phases. Leached blocks show development of an altered region in which free lime and dicalcium silicate phases were absent and Ca–Si–H was precipitated (CaCO₃ was also present under aerated conditions). μXANES analyses show that V was released to solution as V(V) during dicalcium silicate dissolution and some V was incorporated into neo-formed Ca–Si–H. Higher V concentrations were observed in leachate under aerated conditions than in the air-excluded leaching experiment. Aqueous V concentrations were controlled by Ca₃(VO₄)₂ solubility, which demonstrate an inverse relationship between Ca and V concentrations. Under air-excluded conditions Ca concentrations were controlled by dicalcium silicate dissolution and Ca–Si–H precipitation, leading to relatively high Ca and correspondingly low V concentrations. Formation of CaCO₃ under aerated conditions provided a sink for aqueous Ca, allowing higher V concentrations limited by kinetic dissolution rates of dicalcium silicate. Thus, V release may be slowed by the precipitation of secondary phases in the altered region, improving the prospects for slag reuse.

INTRODUCTION

Basic oxygen furnace (BOF) steelmaking is a primary method of steelmaking which accounts for ∼2/3 of worldwide steel production. In a basic oxygen converter low carbon steel is produced by blowing oxygen through molten pig iron and recycled scrap steel to remove carbon. BOF slag is the primary byproduct of BOF steelmaking and is produced when limestone (or dolomite) is added to the molten iron as a fluxing agent to draw out impurities. Because of the large quantities of steel slag produced worldwide (170–250 million metric ton/year) reuse has become increasingly important in order to comply with environmental regulations limiting disposal of wastes. Currently steel slag that cannot be recycled in blast furnaces is primarily reused as aggregate in road surfacing and construction due to its high stability and skid resistance, while other uses include neutralization of acidity in soils or mine wastes and possibly for CO₂ sequestration. Depending on its precise mineralogy, some steel slag may be unsuitable for reuse, particularly in engineering applications. Steel slag may be enriched in phases such as free lime (CaO) and periclase (MgO) which expand on hydration, resulting in significant volume change. In situations where slag cannot be reused, or where supply exceeds after-use demand, slag is generally disposed to landfill.

Steel slag formed during primary steelmaking (i.e., from BOF or electric arc furnace (EAF) processes) typically comprises a mixture of Ca oxides, Fe oxides, and silicates. The precise chemical composition varies by iron source and processing; however, the bulk chemical composition is relatively consistent between locations worldwide (Table 1). Typically BOF slag is dominated by Ca, Fe, and Si, with minor amounts of Mg, Mn, and Al. The mineralogical composition can be complex but typically contains a range of calcium-containing silicate phases (e.g., Larnite, β-Ca₃SiO₄; Merwinite CaMg(SiO₄)₂), calcium and aluminum ferrite phases (e.g., Brownmillerite, Ca₅FeAlO₁₀), Srebrodolskite, Ca₅Fe₂O₅), free Mg and Ca oxides (e.g., lime, CaO; periclase, MgO) and a refractory oxide solid...
solution of Fe–Mg–Mn–Ca– oxides (e.g., Wüstite, FeO).3,11–17
When stored in contact with water, CaO and Ca-silicates in
BOF slag readily react to generate a high pH leachate (typically
pH 10–12.5), for example, via eqs 1 and 2.18,19

$$\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{OH}^- \quad (1)$$

$$\text{Ca}_2\text{SiO}_3 + 2\text{H}_2\text{O} \rightarrow 2\text{Ca}^{2+} + \text{H}_2\text{SiO}_4^{2-} + 2\text{OH}^- \quad (2)$$

The release of Ca$^{2+}$ and H$_2$SiO$_4^{2-}$ to solution can lead to
oversaturation with respect to calcium silicate hydrates (Ca–
Si–H, eq 3), and secondary carbonates in the presence of
atmospheric CO$_2$ (eq 4).20 Spinel (e.g., magnetite, eq 5) and
hydroxide phases can also form where di- and trivalent metal
ions are released.20

$$3\text{Ca}^{2+} + 2\text{H}_2\text{SiO}_4^{2-} + 2\text{OH}^- \rightarrow 3\text{CaO}2\text{SiO}_2\text{H}_2\text{O} \quad (3)$$

$$\text{Ca}^{2+} + \text{CO}_2 + 2\text{OH}^- \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \quad (4)$$

$$\text{Fe}^{2+} + 2\text{Fe}^{3+} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 8\text{H}^+ \quad (5)$$

Steel slags usually contain a variety of trace elements from
the primary ore that become concentrated by processing. At
high pH, several potential toxic metals are solubilized and
become mobile in leachate including Al, Fe, and V.18–21 In
recent years V leaching has received significant attention due
to its relative enrichment in BOF slag (0.04–1.48 wt %3,21) and
the potential mobility and toxicity of V(V) species in alkaline
leachates. V is present in steel slag in multiple oxidation states
that phases, making evaluation of V leaching behavior
difficult.23 This uncertainty is compounded by the use of
damaged analysis, or on a Thermo iCAP Qc ion-coupled
mass spectrometer (ThermoFisher Scientific, USA, ICP-OES;
major elements), or on a Thermo iCAP Qc ion-coupled
plasma mass spectrometer (ThermoFisher Scientific, USA,
ICP-MS; minor elements).

Scanning Electron Microscopy. The leached blocks and
an unleached control block were cut in half widthwise under
water using a diamond saw and the resultant ~1 cm$^3$ blocks
were set into epoxy resin. The surface to be examined was then

Previous research has shown that under air-excluded leaching
conditions up to 1.7% of the V in BOF slag was released to
solution.20 This is due to the relatively high reactivity of the V
hosting phase, and the prediction that V(III) and V(IV) can be
oxidized to V(V) during slag weathering.17,20,22 No data are
available concerning leaching of steel slags under aerated
conditions that will be more favorable to V oxidation. Equally,
the role of secondary phase formation in controlling V release is
currently unknown, although the potential for aqueous V to be
incorporated into Ca–Si–H has been noted.20

A thorough understanding of weathering processes in BOF
slag is essential to enable long-term, cost-effective management
and use of steel slag while protecting both the environment and
human health from its potentially hazardous components. This
study used scanning electron microscopy (SEM) and X-ray
absorption near-edge spectroscopy (XANES) to determine the
distribution and speciation of V within BOF steel slag, and to
determine whether leachate equilibrium atmosphere affects V
release during slag leaching. This research provides new insights
into the distribution of V within both unweathered and
weathered BOF slag, and investigates the mechanisms under-
inpinning enhanced V leaching and its fate in neo-formed phases.

### METHODS

Sample Collection and Characterization. Basic oxygen
furnace (BOF) steel slag was collected in May 2013, within 1
week of its deposition, from British Steel’s Yarborough Landfill
(Scunthorpe, UK; LAT 53°35′22.24″ LONG 0°35′41.52″). The
sample consisted of 50–500 g blocks (~100 kg total). Subsamples
were either cut into smaller 8 g blocks (20 mm × 10 mm × 10 mm) using a diamond saw for use in leaching experiments, or ground to <150 μm powder for compositional analysis. Major and minor element composition was
determined using an Olympus X-5000 X-ray fluorescence
(XRF) analyzer. Mineralogical analysis was performed using
50–100 mg samples mounted on silicon slides on a Bruker D8
X-ray diffractometer (XRD) using Cu Kα radiation and
scanning between 2° and 70° 2θ.

Leaching Experiments. Two 8 g slag blocks were placed in
a 2 L graduated glass screw-top bottle containing 2 L of
deonized water (DIW). Air-excluded (O$_2$ and CO$_2$-free)
conditions were established by purging for 45 min with N$_2$
before the bottle was capped and stored in a Coy anaerobic
pump. Leaching continued for 6 months before the blocks were
removed from the bottles and dried under N$_2$/H$_2$ atmosphere
in the Coy Cabinet. The leachate pH was determined following
removal of the blocks using an Orion DualStar pH/ISE
benchtop meter (Thermo Scientific, USA) with electrodes
collected at pH 4, 7, and 10. Metal concentrations in aqueous
leachate samples (0.2 μm; PTFE filtered) were determined
with an analytical uncertainty of < ± 3% either on a Thermo
iCAP 7400 radial ion-coupled plasma optical emission
spectrometer (ThermoFisher Scientific, USA, ICP-OES;
major elements), or on a Thermo iCAP Qc ion-coupled
plasma mass spectrometer (ThermoFisher Scientific, USA,
ICP-MS; minor elements).

Scanning Electron Microscopy. The leached blocks and
an unleached control block were cut in half widthwise under
water using a diamond saw and the resultant ~1 cm$^3$ blocks
were set into epoxy resin. The surface to be examined was then

Table 1. Chemical Composition of BOF Steel Slags
Including XRF Analysis of the Slag Used in This Study. Data
Is Presented in Nominal Oxide Format

<table>
<thead>
<tr>
<th>major elements</th>
<th>Indiana, USA</th>
<th>Sweden</th>
<th>Taiwan, China</th>
<th>Yarborough UK</th>
</tr>
</thead>
<tbody>
<tr>
<td>oxide wt %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>39</td>
<td>45</td>
<td>39</td>
<td>40 ± 5.4</td>
</tr>
<tr>
<td>FeO</td>
<td>30</td>
<td>22</td>
<td>38</td>
<td>32 ± 9.4</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>12</td>
<td>11</td>
<td>7.8</td>
<td>14 ± 3.4</td>
</tr>
<tr>
<td>MgO</td>
<td>10</td>
<td>9.6</td>
<td>8.6</td>
<td>5.2 ± 1.1</td>
</tr>
<tr>
<td>MnO</td>
<td>2.7</td>
<td>3.1</td>
<td>4.2</td>
<td>4.5 ± 0.8</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>2.2</td>
<td>1.9</td>
<td>1.0</td>
<td>1.2 ± 0.4</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>1.0</td>
<td>0.52</td>
<td>n.d.</td>
<td>1.3 ± 0.4</td>
</tr>
<tr>
<td>V$_2$O$_5$</td>
<td>n.d.</td>
<td>2.6</td>
<td>n.d.</td>
<td>0.81 ± 0.24</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.40</td>
<td>1.4</td>
<td>0.94</td>
<td>0.30 ± 0.13</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>0.20</td>
<td>0.07</td>
<td>n.d.</td>
<td>0.24 ± 0.13</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>0.12</td>
<td>0.05</td>
<td>0.23</td>
<td>0.09</td>
</tr>
<tr>
<td>TOTAL</td>
<td>97.6</td>
<td>97.2</td>
<td>99.6</td>
<td>98.7</td>
</tr>
</tbody>
</table>

*Notation: n.d., not determined; n, number of samples.*
polished using a water-free diamond paste to remove the top 1–2 mm of material potentially exposed to water during cutting. The samples were carbon coated (~10 nm) and backscatter electron images were collected on a FEI Quanta 650 FEGESEM environmental scanning electron microscope (SEM) equipped with an Oxford Instruments INCA 350 energy-dispersive X-ray spectroscopy system that had an 80 mm X-Max silicon drift detector. Energy-dispersive X-ray spectroscopy (EDS) mapping and quantitative point analysis were processed using the Oxford Instruments AZtec acquisition and analysis software (see Supporting Information (SI) section S1 for further details). False color SEM-EDS composite elemental maps were used to identify phases, and phase composition was subsequently determined both near and remote from the leached surface of each slag block by point counting using randomly oriented 20 × 20 μm grids;25 (e.g., SI Figure S1a).

μX-ray Absorption Spectroscopy. Using the polished blocks described above, μX-ray analysis near edge structure (μXANES; ~2 μm resolution) spectra were collected at the V K-edge (5465 eV) on beamline I18, Diamond Light Source, UK in February 2016. Standard spectra were collected from a range of laboratory chemicals and aqueous solutions (1000 ppm). Multiple μXANES spectra were averaged to improve signal-to-noise ratio, normalized, and plotted using Athena v0.9.2426 (see SI section S2 for detailed methodology).

Figure 1. Slag surface structure after 6 months weathering under aerated conditions; backscatter electron image and false color EDS element maps.
**RESULTS**

**Slag Composition.** The elemental composition of the slag was dominated by Ca, Fe, and Si, with Mn and Mg as minor constituents; the V concentration was 0.45 ± 0.13 wt % (Table 1; SI Table S1). XRD analysis showed that the slag contained Larnite (dicalcium silicate; $\beta$-Ca$_2$SiO$_4$), brownmillerite (dicalcium aluminoferrite; Ca$_2$(Al, Fe)$_2$O$_5$), free lime (CaO), and wüstite (refractory oxide; FeO) (SI Figure S4).

**SEM Microanalysis.** SEM analysis showed that the center of slag blocks consists of an interlocking crystalline matrix (Figure 1). EDS mapping showed that each subregion within the matrix had relatively uniform composition and four different chemically discrete phases were identified. Quantitative EDS spot analyses (e.g., SI Figure S1b; SI Table S2) was used to further characterize these phases. The first phase had an average molar Ca/Si ratio of 2.2 ± 0.1, corresponding to the dicalcium silicate phase identified by XRD; this phase also contained P, V, and trace Fe. The composition of the second phase was dominated by Ca, Al, and Fe suggesting that it is the dicalcium aluminoferrite phase identified by XRD; this phase also contained Mn, Ti, Mg, Cr, and V. EDS spot analysis indicated that the third phase was principally CaO, but this free lime phase was also substituted with Mn and Fe. The fourth phase contained FeO, MnO, MgO, and CaO, suggesting it is a refractory oxide solid solution (e.g., a phase indistinguishable from Wüstite by XRD). The proportion of each phase in the slag (by volume) is shown in Table 2. Vanadium was present in only the dicalcium silicate (0.44 ± 0.23 wt %) and the dicalcium aluminoferrite phase (1.14 ± 0.14 wt %) and not detectable in the free lime and Wüstite phases.

SEM imaging of experimental blocks showed the presence of a compositionally distinct altered region at the block surface that was absent in unweathered samples (Figure 1; SI Figure S5). EDS analysis showed that this region was depleted in both Ca and Si. High resolution imaging showed that dicalcium silicate is depleted and free lime is absent, but the refractory oxide and dicalcium aluminoferrite phases appear largely unaltered (Table 2). A low density Ca and Si containing phase (Ca/Si ratio of 2.1 ± 0.4) is observed in this region, the composition of which is consistent with calcium silicate hydrate phases (Ca–Si–H; SI Figure S6). Occasional blade-like morphology is consistent with Ca–Si–H(II), which has an imperfect Jennite-like structure and a Ca/Si ratio in the range 1.5–2.2. This Ca–Si–H phase also contained V (0.70 ± 0.57 wt % SI Table S2), Fe and P (SI Figure S1f). The thickness of this altered region was 38 ± 11 (n = 92) and 45 ± 14 μm (n = 76) in the aerated and air-excluded tests, respectively, and this difference is statistically significant (Mann–Whitney U, p = 0.001). Blocks from the aerated experiment had an additional continuous 10–30 μm layer outside the altered region, which consisted of blocky crystals that contained principally Ca, C, and O with trace P consistent with precipitation of CaCO$_3$ (Figure 1, SI Figure S1g).

**Leachate Composition.** The pH values and the concentration of key elements in the leachate after 6 months are shown in Table 3. Both leachates were dominated by Ca and Si.

The pH values of the leachate from the aerated and air-excluded systems were 8.0 and 11.9, and V concentrations were 859 μg L$^{-1}$ and 493 μg L$^{-1}$, respectively.

**μXANES Analysis.** Representative XANES spectra for each V-bearing phase in experimental samples and standards are shown in Figure 2a. Vanadium K-edge μXANES spectra (n = 49) collected from all phases present have a prominent pre-edge peak at 5470 eV (±0.25 eV). Normalized intensity (±0.10) of the pre-edge peak for spectra collected from V-bearing phases range from 0.36 to 1.00 in dicalcium silicate, 0.17 to 1.00 in dicalcium aluminoferrite, and 0.61 to 0.94 in the Ca–Si–H (Figure 2b). The main absorption edge ($E_{1/2}$, the point at which absorption reaches 50% of normalized absorption) varied from $579.0$ to $582.3$ eV in dicalcium silicate, $578.9$ to $582.3$ eV in dicalcium aluminoferrite and from $580.1$ to $582.2$ eV in Ca–Si–H (Figure 2b).

**DISCUSSION**

**Reactivity of Phases during Weathering.** The development of a compositionally distinct region at the surface of the blocks shows alteration of slag phases has taken place during the six-month leaching experiments. SEM imaging and EDS analyses show depletion of dicalcium silicate and complete dissolution of free lime phases in this altered region, hence these must be considered the reactive phases during slag weathering (eqs 1 and 2). The Fe-rich phases (dicalcium aluminoferrite and refractory oxide) showed no evidence of alteration over the time period of the experiments. The thickness of the altered region was significantly greater in air-excluded samples than aerated equivalents, indicating that the presence or absence of air is a significant factor contributing to

Table 2. Point Counting Analysis of Phase Distribution (% by Volume) in the Unweathered Slag and the Altered Surface Regions

<table>
<thead>
<tr>
<th>phases</th>
<th>unweathered slag</th>
<th>altered region aerated conditions</th>
<th>altered region air-excluded conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$_2$SiO$_4$</td>
<td>57 ± 3</td>
<td>n. d.</td>
<td>n. d.</td>
</tr>
<tr>
<td>Ca–Si–H</td>
<td>n.d.</td>
<td>64 ± 3</td>
<td>63 ± 3</td>
</tr>
<tr>
<td>wüstite</td>
<td>21 ± 3</td>
<td>20 ± 3</td>
<td>20 ± 3</td>
</tr>
<tr>
<td>Ca$_2$(Fe,Al)$_2$O$_5$</td>
<td>13 ± 3</td>
<td>10 ± 3</td>
<td>14 ± 3</td>
</tr>
<tr>
<td>lime</td>
<td>8 ± 2</td>
<td>n.d.</td>
<td>n. d.</td>
</tr>
<tr>
<td>Ca–Si–H/Fe–O</td>
<td>n.d.</td>
<td>6 ± 2</td>
<td>4 ± 2</td>
</tr>
<tr>
<td>total counts</td>
<td>1012</td>
<td>920</td>
<td>848</td>
</tr>
</tbody>
</table>

*Where present, the CaCO$_3$ layer was excluded from this analysis. n.d., not detected.*

Table 3. Leachate Composition Determined after Six Months in the Aerated and Air-Excluded Slag Leaching Experiments

<table>
<thead>
<tr>
<th></th>
<th>Aerated</th>
<th>Air-excluded</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.0</td>
<td>11.9</td>
</tr>
<tr>
<td>Major Ions (mg L$^{-1}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>23.5</td>
<td>85.2</td>
</tr>
<tr>
<td>Si</td>
<td>23.4</td>
<td>29.5</td>
</tr>
<tr>
<td>Mg</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>K</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td>Na</td>
<td>1.7</td>
<td>2.4</td>
</tr>
<tr>
<td>Minor Ions (μg L$^{-1}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>&lt;2</td>
<td>390</td>
</tr>
<tr>
<td>Cr</td>
<td>6.5</td>
<td>9.6</td>
</tr>
<tr>
<td>Fe</td>
<td>122.7</td>
<td>251.3</td>
</tr>
<tr>
<td>Li</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Mn</td>
<td>8.5</td>
<td>13.1</td>
</tr>
<tr>
<td>V</td>
<td>859.1</td>
<td>492.8</td>
</tr>
</tbody>
</table>

The pH values of the leachate from the aerated and air-excluded systems were 8.0 and 11.9, and V concentrations were 859 μg L$^{-1}$ and 493 μg L$^{-1}$, respectively.
the rate and overall extent of altered region formation on short time-scales.

Secondary Phase Formation Ca–Si–H and CaCO₃.
Dissolution of dicalcium silicate in the slag blocks released Ca and Si to solutions, which results in precipitation of a Ca–Si–H phase (eq 3) in place of dicalcium silicate in the altered region under both aerated and air-excluded conditions. Low elemental totals from EDS spot analyses (SI Table S2) of Ca–Si–H phases represent areas with high volumes of carbon-rich resin (as carbon is not determined in EDS analysis). This indicates that Ca–Si–H has a porous structure which will allow diffusion of water and ions through the altered region. Thus, it is likely that dicalcium silicate dissolution switched from initially solubility limited to a diffusion limited process as the altered region developed (i.e., the rate of removal of Ca and Si from the slag surface controls rate of weathering). Therefore, formation of Ca–Si–H may have an armoring effect on slag, slowing the rate of dicalcium silicate weathering. Pseudomorphs of lime were also found in the altered region, containing Ca, Si, Fe, Mn, and O (SI Figure S1). This may represent a distinct Fe(Mn)-substituted Ca–Si–H phase or coprecipitated Ca–Si–H and Fe(Mn) spinel phases. Formation of CaCO₃ is only observed in aerated experiments, as it requires the ingassing of atmospheric CO₂ to allow aqueous Ca to precipitate. Such ingassing consumes OH⁻, which reduces the pH (eq 4) and significantly lowers the Ca concentration in the aerated leachate.

Si was used to track elemental mass balance during the replacement of dicalcium silicate by an approximately equal volume of Ca–Si–H (Table 2). Comparing the mean Si concentration found within the dicalcium silicate phase (13.2 ± 0.7 wt %; SI Table S2) with that found within the Ca–Si–H phase (4.7 ± 2.2 wt %) indicates that only 36 ± 22% of the Si present in the original dicalcium silicate phase was retained in the Ca–Si–H Layer. A mass balance using Ca concentrations produces a similar result (33 ± 18%; SI Table S2). Thus, during weathering of dicalcium silicate in these experiments, very approximately one-third of the weathered Si (and Ca) was retained as Ca–Si–H and two-thirds was released as ions to solution. The Si found in the 2 L solution at the end of the experiments (47 and 59 mg; Table 3) equates to approximately 4.5 or 5.6% of the total Si present in the original 2 × 8 g blocks in the aerated and air-excluded experiments, respectively (i.e., the slag contained 6.5 ± 1.6 wt % Si; SI Table S1). If the Si found in solution is assumed to represent two-thirds of the original dicalcium silicate that was weathered, then as much as 6.7 or 8.4% of the dicalcium silicate in the blocks was involved in the weathering reaction. The volume of the alteration layer calculated from thickness measurements (38 mm, aerated; 45 mm, air-excluded) equates to only 1.9 or 2.3% of the total block volume (2000 mm³). This considerable discrepancy indicates that the reaction must have involved weathering of dicalcium silicate via the internal porosity (BOF slag has high porosity of 4–6%) and along fractures.

V Speciation, Behavior, and Controls on Solubility.
The position of the main absorption edge (E₁/₂) and the normalized pre-edge peak intensity determined from V K-edge XANES spectra can be used to define V oxidation state. Spectra collected from the BOF slag samples indicate that V is present as either V(IV) or V(V) (Figure 2b). Vanadium is present throughout the dicalcium silicate phase as V(V) in tetrahedral co-ordination with just one spectrum displaying characteristics of V(IV); however, this was taken from a region of high V concentration and may not be representative of the bulk phase. In the dicalcium aluminoferrie phase V is present as both V(IV) in octahedral co-ordination and V(V) in
tetrahedral co-ordination. Both oxidation states can be
accommodated in dicalcium aluminoferrite because it contains
octahedral Fe(III) sites into which V(IV) can readily substitute
(due to similar size and charge) and tetrahedral Al sites into
which V(V) substitutes.\textsuperscript{33} No V(III) was detected within the
slag.

Spectra from the neo-formed Ca–Si–H phase generally
show tetrahedral V(V) with only one exception of V(IV). Ca–
Si–H phases, such as dicalcium silicate, contain tetrahedral Si
sites which can easily accommodate the tetrahedral vanadate
ions, but the phases do not contain any octahedral anion sites.\textsuperscript{34}
The presence of V(V) in Ca–Si–H suggests that some of
the vanadate released to solution by dicalcium silicate dissolution
has been reincorporated into Ca–Si–H.

XANES spectra collected from BOF slag show little, if any
depletion of V(IV) in the altered region. Also, the small
quantities of V(IV) that have been observed in the dicalcium
silicate phase are unlikely to be sufficient to significantly contribute to V release. Hence, the results do not support oxidation of V(IV) to V(V) as a mechanism contributing to enhanced vanadate leaching under aerated conditions, a scenario which would require significant dissolution of dicalcium aluminoferrite (the principal host phase for V(IV)), which is not observed. Thus, over time scales measured in months, it is proposed that essentially all V released to solution must originate from the dicalcium silicate phase as V(V), which is predicted to be soluble as aqueous vanadate species at the measured solution pH.\textsuperscript{35,36}

Dissolution of 6–8\% of the dicalcium silicate present in the
original 8 g blocks would produce a calculated maximum V
concentration in solution of approximately 12 mg L\textsuperscript{−1}. However, total V present in solution is less than 10\% of that value. The Ca–Si–H phase has taken up some of the V released, but due to the relatively poorly ordered nature of Ca–Si–H\textsuperscript{37} this uptake is expected to be unselective, with V incorporation approximately stoichiometric with the V/Si ratio at the time of formation. However, the proportion of Si released by dicalcium silicate dissolution that remains in solution was proportionally much greater than V (≈65\% vs <10\%; see Discussion above). Also aqueous V concentrations were much higher in the aerated test, despite evidence that total dicalcium silicate dissolution was probably ~20\% lower in this test. Therefore, aqueous V concentrations are not well explained by uptake to the Ca–Si–H phase alone. Previous modeling of V solubility in BOF leachates has highlighted the role of calcium vanadate phases in controlling V concentration,\textsuperscript{3,8,20,38,39} with \( \text{Ca}_3(\text{VO}_4)_2 \) (log \( K_{\text{sp}} = -17.97 \)) identified as the relevant phase at high pH.

\[ 3\text{Ca}^{2+} + 2\text{VO}_4^{3−} \rightleftharpoons \text{Ca}_3(\text{VO}_4)_2 \]  \hspace{1cm} (6)

Therefore, the maximum possible aqueous V concentration
will be inversely proportional to the aqueous Ca\textsuperscript{2+}
concentration. The variation in V seen under different experimental conditions (Figure 3) can be explained by the different phases that control the aqueous Ca\textsuperscript{2+} concentration. Under air-excluded conditions, equilibrium with Ca–Si–H phases will permit relatively high aqueous Ca\textsuperscript{2+} concentrations to develop, which result in vanadate concentrations either at or very close to the solubility limit of \( \text{Ca}_3(\text{VO}_4)_2 \) which limits the concentration of vanadate in solution. Under aerated conditions the presence of atmospheric CO\textsubscript{2} leads to the formation of CaCO\textsubscript{3}, providing an additional sink for aqueous Ca. Under these conditions, much higher V concentrations are found in solution, which in our experiments were still under-saturated with respect to \( \text{Ca}_3(\text{VO}_4)_2 \). As there is still dicalcium silicate available in the blocks, this indicates that the leachate composition is limited by kinetic effects related to slower dissolution of dicalcium silicate, partially protected by Ca–Si–H in the altered region. In addition, calcium pyrovanadate (\( \text{Ca}_2\text{V}_2\text{O}_7 \)) solubility (log \( K_{\text{sp}} = -12.0 \)) and surface complexation reactions involving sorption to solids have been suggested as important in controlling V concentrations at pH < 9.5.\textsuperscript{8,38} In the aerated tests, however, where pH was 8.0, V concentrations were broadly consistent with \( \text{Ca}_3(\text{VO}_4)_2 \) solubility limits, and the data presented do not indicate that other phases or surface sorption processes were important in these tests.

**Implications for Slag Weathering, Use, and Storage.**

Heap leaching of BOF slag by rainfall inevitably occurs during
storage in large land-based repositories, and is often actively
promoted to reduce the free lime content of BOF slag to permit its beneficial reuse. During the early stages of heap leaching free lime will be relatively abundant due to the high solid/solution ratios present (8–10 kg L\textsuperscript{−1}). Aqueous CO\textsubscript{2} species in the rainwater (from contact with atmosphere) will precipitate rapidly as it enters the waste, so Ca concentrations will be controlled largely by \( \text{Ca(OH)}_2 \) equilibrium, producing highly alkaline, Ca-rich, leachates with corresponding low V concentrations (Figure 3). However, the concentration of other trace metals solubilized at high pH (e.g., Al, Fe; Table 1) will potentially be maximized by these conditions.

In contrast, most lab-based leaching tests are performed at much lower solid/solution ratios (e.g., 0.01–0.1 kg L\textsuperscript{−1}; this study).\textsuperscript{26} In such leaching tests the free lime phase can be exhausted. Thus, under air-excluded conditions, the Ca concentrations are controlled primarily by the balance of kinetic processes involving dicalcium silicate dissolution and equilibrium processes involving Ca–Si–H precipitation. Typically this produces order of magnitude lower Ca concentrations than found in \( \text{Ca(OH)}_2 \) equilibrated water and correspondingly higher V concentrations due to the inverse
relationship between V and Ca concentrations implied by Ca$_3$(VO$_4$)$_2$ solubility limit. Further, aerated leaching tests are often conducted to investigate the leaching end-point when the slag reaches equilibrium with CO$_2$ species in the influent rainwater, although this will only occur on extremely long time sales in real waste heaps. Under aerated conditions, Ca concentrations are controlled by equilibrium with secondary CaCO$_3$ precipitates that typically have low solubility (e.g., calcite Log K$_{sp} = -8.44$ 40) producing solutions with relatively low Ca concentrations. In this situation, much higher V concentrations are predicted (Figure 3).

One important implication is that these results may represent the sequence of slag leaching expected over time: first CaO/ Ca(OH)$_2$ dominated systems with low V concentrations; then calcium silicate/Ca–Si–H dominated systems with higher V concentrations; and finally CaCO$_3$ dominated systems with the potential for very high V concentrations. However, pH decrease is associated with depletion of reactive V-containing calcium silicate phases (or, more accurately, the availability of these phases for dissolution as particle surfaces become protected by reaction products). Therefore, in a heap leaching situation in which the pore water is continually replaced, V release is kinetically limited and V concentrations are very unlikely to reach the solubility limit of calcium vanadate.

Release of V may also be influenced by the stability of secondary phases incorporating V (i.e., Ca–Si–H) as well as long-term (>6 month) stability of V incorporated into the less reactive dicalcium aluminoferrite phase. It has been suggested that in general these phases become increasingly soluble if the pH of their environment falls over time. A comparison of real site leachates also indicates that the heap weathering process can be very slow. Steel slags deposited in the UK and USA all produce high pH leachates that are largely dominated by Ca(OH)$_2$ derived alkalinity and hence have low V concentrations (Figure 3). Monitoring of leachates from BOF slag deposited at Consett U.K. has shown only modestly reduced alkalinity and Ca concentrations over 36 years since closure, leading to only slightly elevated V concentrations (compared to younger systems). Nevertheless, it should be noted that V concentrations in site leachates often exceed chronic toxicity thresholds (19 µg L$^{-1}$) and that this work indicates that a reducing trend in alkalinity and Ca concentrations over time may not necessarily correspond to a reducing trend in V concentrations.

Overall, the presence of an altered region, and additional CaCO$_3$ precipitate has positive implications for slag after-uses (e.g., as an aggregate) as the presence of an alteration rim may limit (or significantly slow) further dissolution, preventing significant alkalinity generation or metal leaching. On the other hand, calculations of the CO$_2$ capture potential of BOF slag (often based on the reactivity of crushed powder samples or theoretical maximums based on whole mass conversion) may overestimate both the total extent and the rates of carbonation observed in real-life situations.

**REFERENCES**

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