

## Release of vanadium from LD-slag by exposure to ARD

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**Abstract** In abatement of acid rock drainage (ARD) slag from the Linz-Donawitz steel making process (LD-slag) provides high neutralizing capacity at low cost. A serious drawback for the use of this by-product is its high content of vanadium, which makes it a potential source of toxic vanadium species. The aim of this work was to determine the most common vanadium species, V(IV) and V(V), leached from LD-slag by artificial ARD. Capillary electrophoresis was employed to quantify the species. From the results an initial dominance of V(V) and increasing abundance of V(IV) with increasing artificial ARD L/S ratio was observed.

**Key Words** vanadium, LD-slag, ARD, speciation

### Introduction

Mining generates large amounts of waste materials, like parent bedrock and ore residues. In the case of sulphide minerals, abiotic and microbial weathering, generate acid rock drainage (ARD) (Mata et al. 2002). In the abatement of ARD, alkaline by-products like steel slags provide high neutralizing capacity at low cost. A likely candidate is the by-product from the Linz-Donawitz steel making process (LD-slag), through its high content of alkaline oxides, e.g. CaO 45 %, FeO 24 %, SiO<sub>2</sub> 12 % (Merox 2006). Unfortunately, LD-slag is also rich in elements such as chromium (0.17 %), manganese (2.66 %) and vanadium (2.68 %) (Macsik & Jakobssen 1996).

Vanadium is an essential trace element at levels up to  $\mu\text{g L}^{-1}$  in the environment, but at higher levels vanadium is toxic to many living organisms (Klaassen 2001, Soares et al. 2008). For instance, V(V) is found to affect the development of *Crassostrea gigas* at levels around  $50 \mu\text{g L}^{-1}$  (Fichet & Miramand 1998). In 1990, 23 heifers out of 98 died of acute vanadium poisoning after ingestion of LD-slag used eight months earlier as fertilizer on the pasture land (Frank 1996). In South West Province of South Africa eight cattle were affected within 48 to 72 h after ingestion of grass which previously had been flooded after a vanadium mine dam collapse (McCrinkle et al. 2001). The dam collapse led to elevated vanadium concentrations up to some 10 – 20 times in grass and soil, of which 30 – 50 % was recovered as V(V) (Panichev et al 2006).

Determination of the total content of vanadium in environmental matrices is typically done by ICP-OES/MS or AAS (Macsik & Jakobssen 1996, Mandivana & Panichev 2004, Waligora et al. 2010). However, the speciation of the element should be considered since vanadium appears to have a pH dependent redox chemistry (Okamura et al. 2001). The redox state also appears to affect the toxicity. As reported in Klaassen (2001) toxicity seems to increase at higher redox state. Therefore, in order to better understand the environmental chemistry and toxicity of vanadium speciation techniques must be applied. The present study was undertaken in order to determine the redox state of vanadium leached from LD-slag with artificial ARD. Emphasis was put on the two most toxic vanadium species (V(IV) and V(V)) appearing in resulting solution.

### Materials & Methods

LD-slag (diam < 3 mm) was leached with artificial ARD that consisted of sulfuric acid (analytical grade) diluted with deionized water (18.2 M $\Omega$ ) to pH 2.0. The artificial ARD was chosen to avoid possible interactions between vanadium and elements present in natural ARD. Approximately 10 g LD-slag was used for each leaching, put in 50 ml syringes with glass wool stoppers. The leaching was driven by gravity, at a flow rate of about 8 ml / min. Before the test, the sample was washed with 1000 ml deionized water (18.2 M $\Omega$ ).

The leachate was collected in batches of 50 ml, giving an increasing liquid to solid ratio (L/S) by 5, for each sample. pH was measured within 30 min after sampling (Metrohm 744 pH Meter, Schweiz). For analysis of total vanadium by ICP-MS (Agilent 7500 cx, Japan) 1 ml was withdrawn and acidified (1%, HNO<sub>3</sub>, suprapur). All samples were before analysis stored dark at 4°C. Speciation was made within minutes (replicate I) and after 10 days (replicate II) to study the impact of storing.

Capillary electrophoresis (CE) using on-column complexation with EDTA and UV-determination is probably one of the most user-friendly methods for the determination of V(IV) and V(V) (Chen & Naidu 2002). Absorbance maxima for V(IV)-EDTA and V(V)-EDTA complexes are found at 185 nm and 280 nm. At 280 nm the absorptivity is fivefold for V(V)-EDTA in relation to V(IV)-EDTA, which can be used to distinguish between the two complexes (Jen et al. 1997, Chen & Naidu 2002). For good and consistent separation of the species, the running electrolyte pH is of great importance. At pH 4.0 – 6.0 the migration speed for V(V), as  $[\text{VO}_2(\text{EDTA})]^{3-}$ , is higher than for V(IV), as  $[\text{VO}(\text{EDTA})]^{2-}$ , because of its higher charge (Jen et al. 1997, Chen & Naidu 2002). At pH above and below, protonation/deprotonation will influence the charge and size of the complexes. For instance, formation of the larger  $[\text{VO}_2(\text{HEDTA})]^{2-}$  at pH below 4.0, will shift the migration order (Chen & Naidu 2002).

Speciation analysis was conducted with CE (Hewlett Packard 3D CE, Germany), equipped with a 40 cm x 50  $\mu\text{m}$  silica capillary (34.5 cm effective length) and UV detection (191 nm and 280 nm). Before analysis the capillary was washed with 1.0 M NaOH for 10 min, MQ-water for 5 min followed with approximately 1 hour of running electrolyte, consisted of 5 mM EDTA (analytical grade) in  $\text{H}_3\text{PO}_4$  (analytical grade) diluted with deionized water (18.2 M $\Omega$ ) to pH  $4.00 \pm 0.05$ . After each sample the capillary was rinsed with electrolyte for 2 min. Sample injection was made for 20 s at 30 mbar pressure with a capillary temperature of 25  $^\circ\text{C}$ . The separation voltage was set at 20 kV negative polarity. To prevent capillary clogging all samples were filtered through 0.40  $\mu\text{m}$  polycarbonate filter before analysis. Species concentrations were calculated from calibration curves after checking with standard addition. The calibration standards were 0.05 mM, 0.1 mM and 0.2 mM which is in the lower linear range according to Jen et al. (1997).

## Results & discussion

The principal acid neutralizing agent in the LD would be CaO, with a reported content up to 45%. In this study, pH drops from 12 to 2 after percolation of 200 ml artificial ARD (L/S 20) (figure 1 (◆)). This corresponds to a content of 2–3 % CaO and indicates a limited available content of acid neutralizing agents. There are several possible reasons for this observation. The three most likely would be a) formation of an easily dissolved surface coating during storage of the slag in combination with b) the kinetics of LD-slag dissolution and c) formation of a dense surface coating. The presence of  $\text{Ca}(\text{OH})_2(\text{s})$  and/or  $\text{CaCO}_3(\text{s})$  as a result of contact with air can not be concluded without measuring solid surface species. However, equilibrium modeling with PHREEQC (Parkhurst & Apello 1999) indicates solution conditions close to saturation with calcium carbonate and sulfate at high pH but only the sulfate at low pH. As a consequence, before practical use of the LD-slag these properties should be more closely examined.

Formation of an easily dissolved surface coating (i.e. non-crystalline  $\text{Ca}(\text{OH})_2 / \text{CaCO}_3$ ) is supported by the rapidly increasing V/Ca ratio at L/S 20 (figure 1 ( $\Delta$ )), which indicates a dissolution of

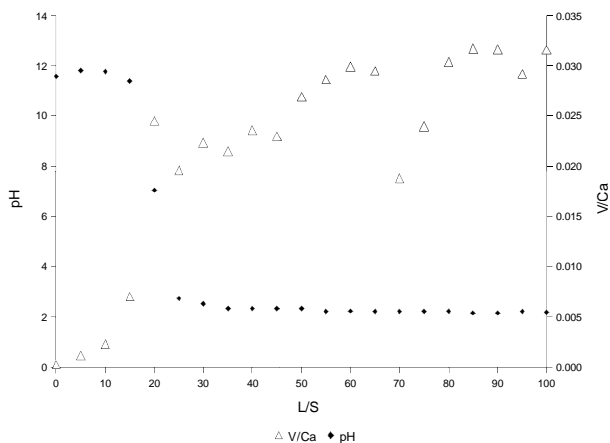
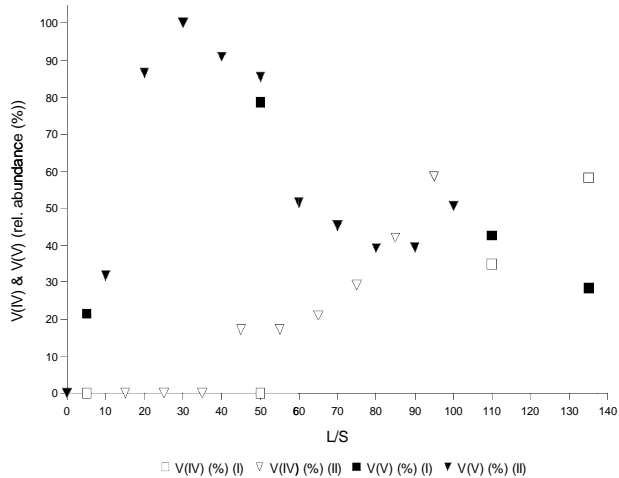


Figure 1 Plot of pH (◆) and V/Ca ratio ( $\Delta$ ), as a function of L/S



**Figure 2** Plot of V(IV) (□, ▽) and V(V) (■, ▼) as a function of L/S

a Ca-phase poor in vanadium up to L/S 20. Thereafter the total vanadium concentration stabilizes at some 3 ppm, which indicates a steady state or equilibrium between the vanadium-bearing phases and the artificial ARD.

Figure 2 shows the relative abundance of V(IV) (□, ▽) and V(V) (■, ▼) as a function of L/S. The conditions indicate an initial leaching of a limited supply of V(V) which is replaced by V(IV) as L/S increases. This could be caused by different vanadium redox species present in the LD-slag, or by the low pH which facilitates the reduction of V(V). The latter seems highly plausible according to figure 2 since storing of samples (replicate II) in the dark at 4 °C for 10 days resulted in the reduction of V(V), up to an L/S of 95. These results also illustrate the need for either an immediate analysis, or to develop a species specific preservation, of the samples in order to maintain the original distribution of species.

Leaching of vanadium from LD-slag has also been confirmed by a field study in progress where the solid is used for abatement of ARD, and in several laboratory studies where LD-slag was used as an amendment in mine waste and as a filter material for ARD.

## Conclusions

Using LD-slag as an alkaline material in abatement of artificial ARD (sulfuric acid pH 2.0), gives an initial high neutralizing capacity with a pH around 12, but is lowered to pH 2 after a L/S of 25. Vanadium is released from the material at an almost constant rate of 3 ppm once the pH drop has occurred. Thus it constitutes a potential environmental threat. Speciation by capillary electrophoresis revealed that the released vanadium initially (high pH) was in the form of V(V). As the neutralizing capacity was depleted and pH dropped to slightly above 2 the abundance of V(IV) started to increase. This indicates a pe-pH dependent redox chemistry and eventually also release of vanadium and that species-specific methods must be used to better understand the properties of the material as well as the element.

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