Impact of an Organic Carbon Source on the Leaching of Vanadium from LD-Slag

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Abstract
Highly alkaline solid wastes, e.g. ashes and slags, pose environmental threats similar to those from ARD, but from other toxic elements. Thus, strategies have to be developed to deal with such materials in a rational way. Both dry covers and storing under water have been suggested. The leaching rate of vanadium from LD-slag was studied in controlled laboratory systems as a function of water saturation and the presence of a carbon source. Leaching in the absence of an external carbon source would be an abiotic process, whereas heterotrophic mobilization could be significant in systems with an organic carbon source. The study shows that storing under water results in leaching rates that are independent of the presence of organic carbon. In systems at water field capacity, however, and with wood chips as an external carbon source, the leaching rate is several orders of magnitude higher than in the absence of a carbon source. The leaching rate is highly influenced by the heterotrophic activity, leading to decreasing pH and an enhanced release of vanadium in particular, as well as the generation of low molecular weight (polyhydroxy) carboxylic acids from the degradation of the wood.

Key Words: vanadium, LD-slag, organic carbon

Introduction

Environmental impact from highly alkaline solid waste materials such as steel slag, incineration ashes or residues from lime production have received relatively little attention compared to refuse generating acidic leachates. However, large amounts are produced every year and from steel production in Sweden alone, the amount of slag can be counted in 1000s of tonnes. Environmental impact from those alkaline residues is not only correlated to the potential increase of pH in surrounding soil/water but also to the release of toxic elements such as vanadium, chromium and molybdenum which all include oxyanions with high solubility at alkaline pH. In the slag obtained from production of high grade stainless steel by the Linz-Donawitz process the amount of vanadium and chromium are close to some 3 and 0.2 % respectively (Macsik and Jakobssen 1996). However, large variations occur due to the heterogeneity of the raw iron used in the process, resulting in variations in the quality of the slag, such as alkalinity and metal content.

The high content of alkaline CaO and MgO (some 50 % (SSAB Merox 2006)) has made it an interesting option as amendment for acid refuse such as mine waste and recently as a raw material for critical elements such as vanadium. During storage, chemical processes change the LD-slag due to reactions with carbon dioxide and water, which converts the original metal oxides to metal carbonates and hydroxides. Therefore, the material is best described as an oxide/hydroxide/carbonate solid mixture. Unfortunately, the physical properties make the steel slag very resistant to dissolution and since there is no cheap method for recovering vanadium from the slag most of the slag is stored in waste piles near the smelter, often uncovered and exposed to wind and rain erosion or covered by soil to establish a plant cover. Regardless of whether the waste is covered or not, the naturally occurring microbial community will affect the material despite the high pH (Willscher and Bosecker 2003). The contact with high molecular weight organic carbon compounds also results in the production of strong metal complexing agents like isosaccharinic acid (ISA) by alkaline hydrolysis of wood (Klinke *et al*. 2002; Svensson *et al*. 2007). This production can be as high as 3 g l^{-1} when softwood sawdust is undergoing alkaline hydrolysis (Pavasars *et al*. 2003).

In this study, we focused on the behaviour of the weathered LD-slag in close contact with organic carbon in the form of aspen shavings (*Populus tremula*) both under water saturation and during water field capacity in terms of release of vanadium and production of potential vanadium complexing agents such as organic acids.

Materials & Methods

To estimate the total content of vanadium in weathered LD-slag, acid digestion was performed by the following process. To create a homogeneous fraction of LD-slag, a 100 g portion of slag was gently crushed and sieved through a 560 µm mesh. By discarding all material finer than 250 µm the influence of static electricity during sample preparation was minimized. From the 250-560 µm fraction a 20 g sub-sample was mechanically milled with a electric mill (IKA A11 Basic) until > 90 % passed through a 125 µm sieve. Sub-samples of 50 mg from the obtained fraction was then dissolved in sub boiled nitric acid (liquid to solid ratio 100) by microwave assisted acid digestion for 60 min at 1200 W and 180 ^{o}C (CEM MarsV). After cooling for 30 minutes the samples were diluted with de-ionized water (18.2 MΩ) to a final volume of 50 ml and allowed to settle for 24 hrs. Prior to element analysis by ICP-MS (Agilent 7500cx) 10 ppb Rh was added as internal standard.

To investigate the release of vanadium from LD-slag in contact with water, leaching by a sequential batch technique was used. By this technique the LD-slag was successively subjected to an increased liquid to solid ratio. Four samples were collected daily except during weekends and some 90 % of the aqueous phase was decanted at each occurrence. Initially the liquid to solid ratio was increased in steps of 100 and after 4 samplings the step size was changed to 10.

As a source of organic carbon and macro nutrients, shavings of aspen (*Populus tremula*) with a size of approximately 5x5 mm were used as received from the planer. To obtain good contact between the slag and the wood, 2.5 grams of each material was stratified in 50 ml Sarstedt® test tubes. To obtain the desired water content, de-ionized water was added to the 50 ml mark of the test tubes. For the water saturated samples, the lids were tightened. For the field capacity samples, a 100 µm mesh was used instead of the lid and the excess water drained through the mesh. Both treatments where carried out in triplicates. Sampling was carried out once a week for the first 7 weeks, then roughly once a month after 6 months up to 1 year. Prior to sampling, de-ionized water was added to the 50 ml mark, the lids were tighten and the samples were gently shaken for approximately 15 seconds after which the water was drained through a 100 µm nylon mesh and collected. Fresh de-ionized water was then added to obtain the desired water content. Between sampling occasions all samples were stored in a humidor to maintain a constant water vapour pressure.

Within 10 minutes after sampling, pH was analyzed to minimize any changes caused by storage. After filtration (0.20 µm) metal analysis was performed by ICP-MS, quantification of total carbon (TC) with a Shimadzu TOC-VPH and organic acids by capillary electrophoresis according to the method described by Dahlén *et al*. (2000).

Results & Discussion

After microwave assisted acid digestion, the amount of acid soluble vanadium was found to be 17 mg g^{-1} (n=2, SD 0.02). Since the method is rather ineffective in dissolving silicates any vanadium incorporated in ordered silicates will not be dissolved nor analysed. Differences in the vanadium content in this study and in cited literature is therefore probably caused by differences in the digestion technique/equipment or by different composition of the LD-slag.

When LD-slag was subjected to sequential batch leaching with de-ionized water for 45 days the pH changed from an initial pH of 12 to a final pH of 10.6 (Figure 1A). Due to the pH-pattern it was concluded

that the weathered LD-slag consisted of an outer surface (skin) of Ca-hydroxides since equilibrium pH for $Ca(OH)_2$ is 12.6 at 20 °C. With increasing leaching time the pH of the aqueous phase stabilized around 10.6 indicating that more insoluble species such as $CaCO_3$ (equilibrium pH 10.5) controlled the pH, probably together with original CaO. This was supported by the measured alkalinity that was twice as high for the initial sample compared with the final sample.

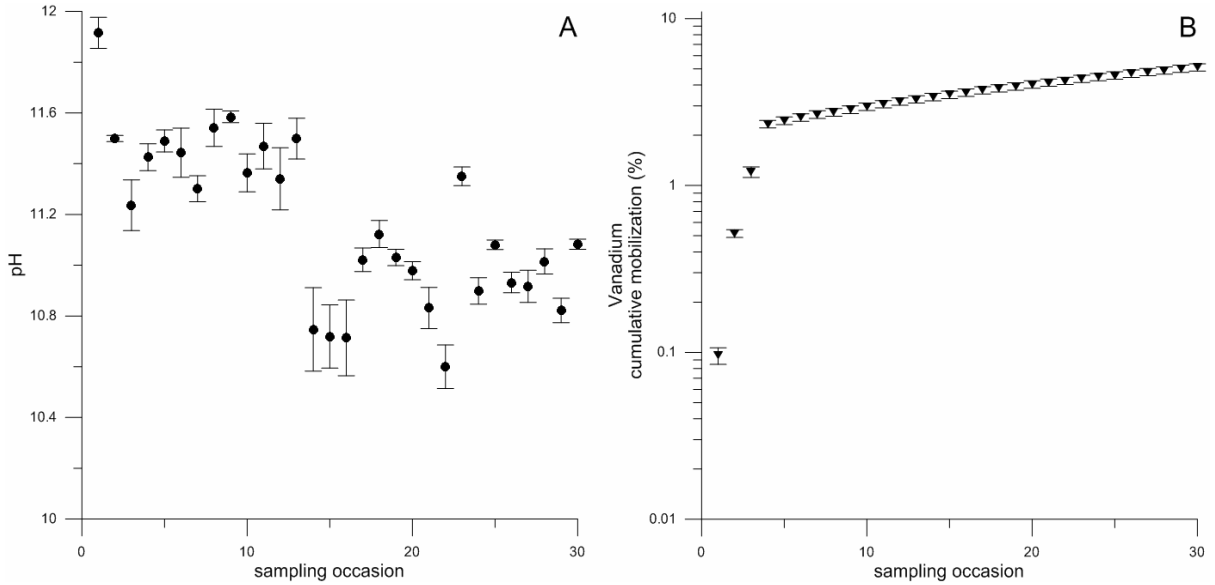

Figure 1A and B. Change in pH and cumulative mobilization of vanadium (% of acid leachable) during sequential batch leaching with de-ionized water of weathered LD-slag.

Since vanadium is mainly incorporated in the material as Ca-V compounds the cumulative mobilization of vanadium also provided information about the surface composition. With a surface mainly consisting of $Ca(OH)_2$ and low in vanadium, the initial release of the element should be low. By removing the weathered surface during the sequential batch leaching the vanadium concentrations is expected to increase due to the different stoichiometric proportions in the non-weathered LD-slag. This was supported by the cumulative mobilization plotted in figure 1B.

When organic carbon in the form of aspen wood shavings was mixed with LD-slag at water saturated conditions, the pH behaved as when no organic carbon was available i.e. pH values around 11.5 to 12 was obtained (Figure 2A) and the wood did not contribute to any neutralizing effect. But the release of vanadium decreased approximately 10 times (Figure 2B). This could be explained by adsorption of vanadium to the wood shavings which had previously been reported by Kaczala *et al.* (2009). When the water content was held at field capacity the pH was initially below 10.6 and it decreased significantly during the first weeks of incubation to below 8.8 (Figure 3A). Compared with the saturated samples the release of vanadium was 20-fold at water field capacity (Figure 3B). The distinct drop in pH in the samples at water field capacity can be explained by the production of low molecular weight organic acids from heterotrophic microorganisms. Such acids together with strong complexing agents, formed during alkaline hydrolysis of the wood, e.g. ISA can also explain the increased mobilization of vanadium. Either by acidolysis or by complexolysis of the vanadium bearing phase.

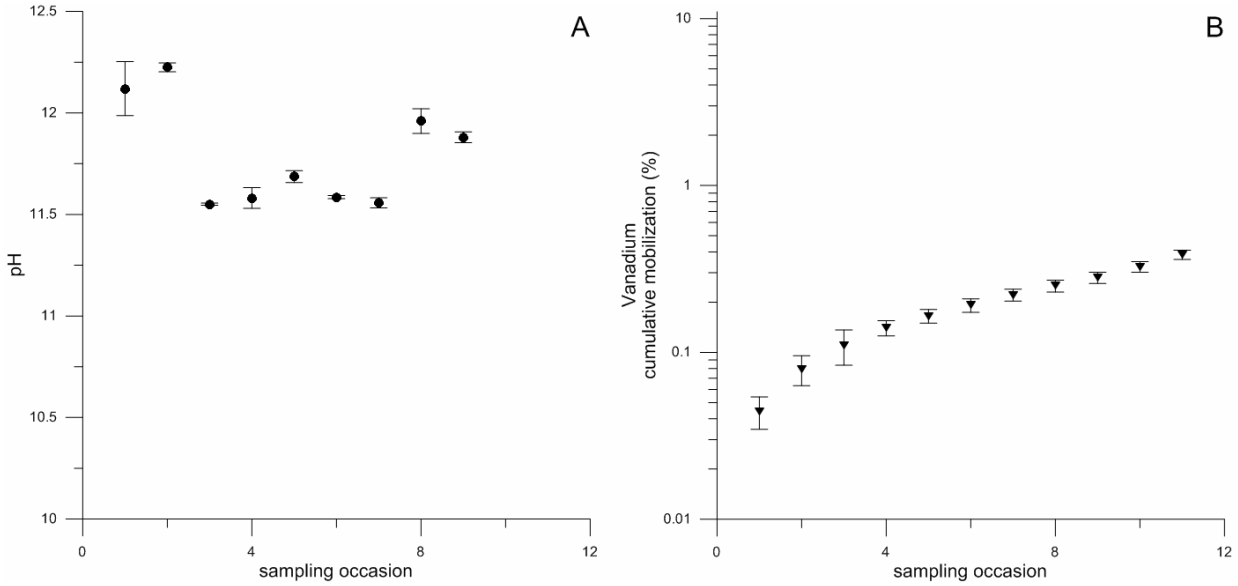

Figure 2A and B. Change in pH and cumulative mobilization of vanadium (% of acid leachable) during incubation with aspen wood shavings at water saturation.

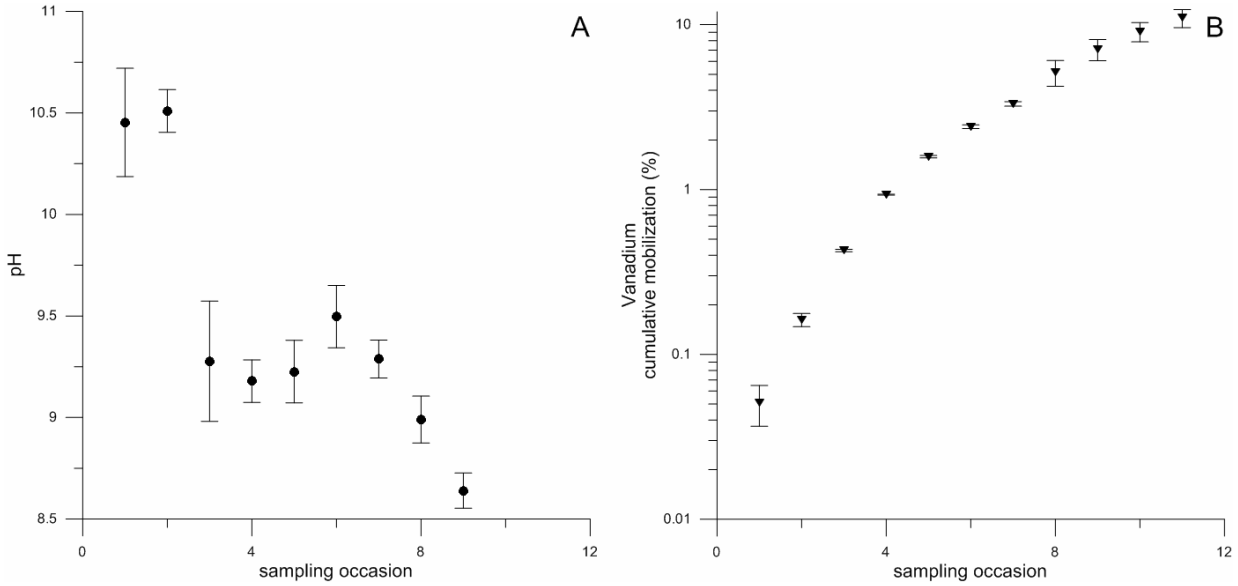

Figure 3A and B. Change in pH and cumulative mobilization of vanadium (% of acid leachable) during incubation with aspen wood shavings at water field capacity.

In a system where the amount of TC is controlled by hydrolysis of the wood, the concentration should remain essentially constant over time once the kinetics of the process are established and the system has reached steady state. With the high amount of alkaline material and high pH this was expected to be the case. Initially the TC was approximately 600 mg l^{-1} both in the saturated and in the field capacity samples and approximately 50 mg l^{-1} in the reference sample. However, the concentrations in the saturated and in the field capacity samples did not behave as expected, but slowly approached the concentration of the reference sample (Figure 4). This may be a consequence of the changed composition of the LD-slag surface due to washout of the highly alkaline species formed by weathering processes, resulting in a decrease in the alkaline hydrolysis.

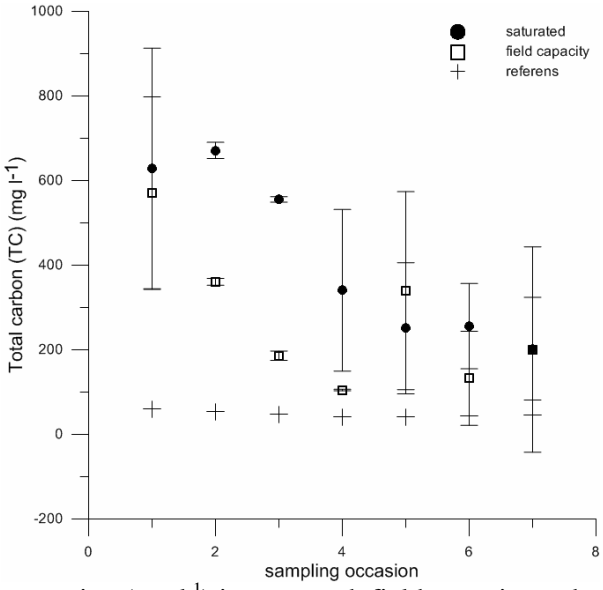

Figure 4. TC-concentration (mg l^{-1}) in saturated, field capacity and reference samples.

For samples that were kept at field capacity, the analysis of organic acids revealed that acetic acid occurred in all samples at all times at a rather high proportion (Table 1). The second most common acid was adipic acid which occurred up to week 4 (Table 1). Unfortunately, the matrix conditions in the analysis did not allow for a complete separation of ISA from adipic acid, as evidenced by the UV/Vis spectrum found in this peak of the electropherogram. At week 4, there was also a larger diversity of organic acids. Although all acids were found in the samples at different sampling occasions the two dominating acids, acetic and adipic acid, were always present at concentrations that were at least 10 times higher than the other acids. Due to the lack of or low abundance of anaerobic fermentation acids such as butyric, lactic and valeric acid, there are reasons to believe that the systems remained essentially aerobic during the incubation, thus enhancing the release of elements such as vanadium due to the high redox potential. Initially, the total concentration of organic acids was approximately 13 mg l^{-1} (Figure 5). This concentration decreased with time reaching a minimum of approximately 0.2 mg l^{-1} after 5 weeks of incubation after which a slight increase to approx 1 mg l^{-1} was observed (Figure 5). Moreover, microbial consumption of the organic acids was likely to have occurred, why the amount of acids produced probably was underestimated. Underestimation of the amount of organic acids may also be caused by formation of metal complexes stronger than the Ca-complex used for the qualitative and quantitative in the method described by Dahlén *et al.* (2000). Since the total concentration of organic acids was correlated with the TC (c.f. Figure 4 and 5), with concentrations decreasing with time, the produced organic acids could be a result of microbial degradation of products from the alkaline hydrolysis of the aspen wood.

Table 1. Occurrence (%) of organic acids during incubation of LD-slag and aspen wood at field capacity.

	week 1	week 2	week 3	week 4	week 5	week 6	week 7
acetic	78	61	14	14	58	66	67
adipic	16	28	35	74			
butyric		1		2			
citric				2		11	11
formic			3	2			
fumaric			2				
glutaric			42				
L-tartaric		1		1		3	3
maleic	5	7			13		
malonic			1	2	14	11	10
oxalic	0.3	1	2				
propionic		1	2	2	8	5	6
succinic	1	1	0.3	1	7	4	4
valeric				1			

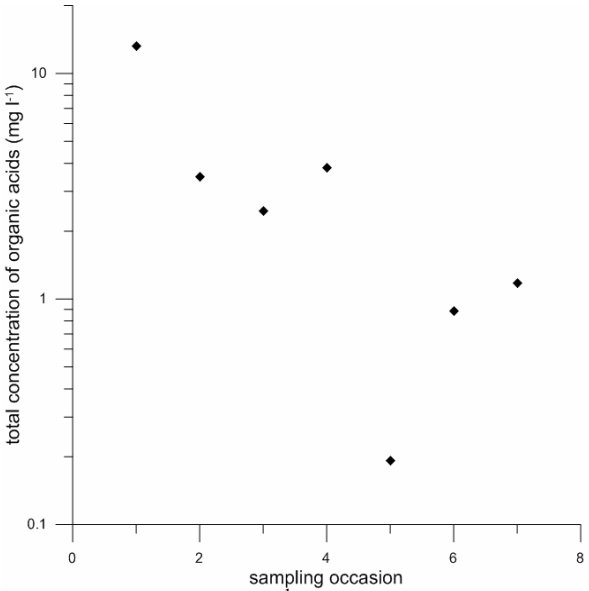

Figure 5. Total concentration of organic acids (mg l^{-1}) in incubated samples of LD-slag and aspen wood at field capacity.

Conclusions

Upon contact with aspen wood, the release of vanadium from LD-slag was highly dependent on conditions such as water content. By changing the water content, it was possible to increase or decrease the release of vanadium to the aqueous phase. At water saturation the total amount of released vanadium was less than 0.5 % after one year of contact compared with more than 10 % released after one year at field capacity. The release of vanadium was probably enhanced by the formation of organic complexing agents, either excreted from the microorganisms or produced by alkaline hydrolysis of the aspen wood. This result indicates that covering of highly alkaline waste materials containing vanadium with organic matter should be avoided due to the possible increased release of toxic elements in the longer time perspective. It also raises the question of whether the addition of organic carbon should be avoided if alkaline waste products are used as amendments for acid forming?? refuse such as sulphidic mine waste.

Acknowledgement

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