Impact of organic carbon in the release of vanadium from LD-slag

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Abstract Remediation of acid rock drainage (ARD) can be performed with alkaline materials, either as water treatment or as reactive covers. To decrease the cost alkaline waste materials such as steel slag can be used. One such material is the slag from the Linz-Donawitz steel making process (LD-slag). However, a major disadvantage with LD-slag is its high content and potential release of toxic vanadium. If LD-slag is used in reactive covers it is commonly covered with soil to protect people and animals from the highly alkaline material. In such cases it is important to consider any impact of soil organic matter on the LD-slag in terms of stability and element mobilization. This report focuses on the release of vanadium from LD-slag in close contact with a natural carbon source at different degrees of water saturation during the first year of contact. When aspen (*Populus tremula*) wood shavings was used and the mixture were kept at field capacity the release of vanadium after 50 weeks reached more than 10 % of the LD-slag's total vanadium content, while pH was changed from 10.5 to 8.6. If the mixture of LD-slag and wood shavings was water saturated, mimicking water logging, the release of vanadium after 50 weeks was less than 0.5 % of the total content and only a minor change in pH was observed, from 12.1 to 11.8.

Key Words Vanadium, Organic carbon, Wood shavings, LD-slag

Introduction

There is today in Sweden more than 200 known historical mine sites that releases heavy and toxic metals in such extent that remediation of the sites are necessary (SEPA 2011). In most cases the heavy and toxic metals are released in acid rock drainage (ARD) from the deposit, resulting from abiotic and microbial activity on the ore residue (Mata *et al.* 2002). Since most of those mining areas have been abandoned for more than one hundred years there is no existing company responsible for the environmental damage that the ARD causes. Instead the local municipality are the authorities that are dealing with the problems. Much research has been made about treatment of ARD and the most cost effective method seems to be addition of alkaline waste materials due to their low cost and good buffering capacity (Sartz 2010). One such material is the residue from the Linz-Donawitz steel making process called LD-slag. The content of alkaline oxides reaches some 80 % and CaO, FeO and SiO are the dominating species (SSAB Merox 2006). However, by using LD-slag there is a potential risk of releasing vanadium to the environment since the content of this element in the slag is some 3 % (Macsik & Jakobssen 1996).

If alkaline LD-slag is used for ARD treatment it may be applied as a cover on the waste heap to increase the pH of the percolating water or as filters down stream to increase the pH of the ARD. To protect people and animals from getting in contact with the highly alkaline material soil can be added on top of the covered heap. In such cases it is very important to consider any impact of soil organic matter on the LD-slag in terms of stability and element mobilization. It has been found that alkaline incineration ash facilitates the alkaline degradation of cellulose results in a multitude of components including isosaccharininc acid (ISA) which is a powerful complexing agent for many metals (log K 50—55) (Svensson *et al.* 2007). Thus, an increased release of metals from the ash was found. The amounts of produced ISA from softwood sawdust in a NaOH/KOH/$Ca(OH)_2$ solution was found to be approximately 3 g/L after 1 year of degradation (Pavasars *et al.* 2003).

In this report we focus on the release of vanadium from LD-slag in close contact with organic carbon in the form of aspen wood shavings at different degrees of water saturation during the first year of contact.

Materials & Methods

Before use the LD-slag was gently crushed and sieved and a size fraction of 0.25 to 0.56 mm was collected for the experiments. Material less than 0.25 mm was discarded and larger material was recrushed. Wood shavings, of approximately 5x5 mm, were used as received from the planer. To obtain good contact between the wood shavings and the LD-slag some 2.5 gram of each material were put in layers in 50 ml polypropylene test tubes (Sarstedt®). Water saturated samples were prepared by adding de-ionized water (18.2 MΩ) to the 50 ml mark on the test tube after which the samples were stored with the lid on. Samples at field capacity were prepared by adding 50 ml de-ionized water (18.2 MΩ) to the 50 ml mark on the test tube and then draining excess water through a nylon mesh (100 µm). To maintain the water content at a stable level the field capacity samples were stored open in a humidor. All samples were stored dark and at room temperature. Sampling was conducted by adding de-ionized water (18.2 MΩ) to the 50 ml mark shaking the test tubes for about 30 seconds and collecting the water after it had drained through a nylon mesh. Within 30 minutes after sampling the pH of the samples were measured (Metrohm 744 pH Meter). Samples for vanadium analysis were acidified with HNO_3 (final concentration 1 %) and analysed by ICP-MS (Agilent 7500 cx). To estimate the total amount of vanadium in the batch of LD-slag, microwave assisted acid digestion was performed on fine grained LD-slag with concentrated HNO_3 (L/S 100) for 60 minutes at 18 °C in sealed Teflon bombs (CEM Mars5).

Results & Discussion

When LD-slag was leached with de-ionized water for 45 days at a liquid to solid ratio of 10 the resulting change in pH of the solution was from an initial pH of approximately 12 to a final pH of approximately 11 (figure 1). The initial pH was probably controlled by hydroxides in the weathered surface of the LD-slag and the final pH controlled by oxides present in the unaffected core of the LD-slag. This hypothesis was supported by the initial alkalinity of 10.4 (SD 0.41) meqv/l that was more than twice as high as the final alkalinity of 4.53 (SD 0.25) meqv/l.

If organic carbon in form of aspen wood shavings was added to the LD-slag the change in pH was from 12.1 to 11.6 with the minimum reached within 10 weeks when the mixture was saturated with water (figure 2). Then a slight increase to approximately 12 was observed (figure 2). If the amount of water was decreased to the mixtures field capacity an initial pH of 10.5 was obtained (figure 2). During incubation the pH decreased continuously and after 1 year of incubation it had reached 8.6 (figure 2). As for the water leaching of LD-slag the alkalinity was measured. However, no significant change was observed over time and the alkalinity for the saturated and the field capacity samples was 16.6 meqv/l and 2.16 meqv/l respectively. This indicates that the addition of aspen wood shavings contributes to the alkalinity at water saturation probably due to retention or release of alkaline species e.g. CO_3^{2-} together with the slower diffusion rate of gases i.e. CO_2 in water. At field capacity aspen wood shavings enhances the diffusion rate of gases since more air may enter the mixture thus lowering the alkalinity since buffering CO_2 easily enters the aqueous phase. Thus, the decrease in pH is probably related to the release of organic acids from microorganisms present in the samples (Karlsson *et al.* 2011).

Leaching with de-ionized water for 30 days resulted in an increasing cumulative release of vanadium reaching approximately 5 % of the acid leachable amount (figure 1). During the first year of incubation, the release of vanadium from LD-slag in contact with aspen wood shavings also showed an increasing cumulative release (figure 3). From the water saturated samples approximately 0.5 % vanadium was released after 1 year of incubation (figure 3). It may be a result of adsorption of vanadium to the aspen wood shavings since it is possible for vanadium to adsorb to sawdust (Kaczala *et al.* 2009). At water field capacity the release of vanadium reached approximately 10 % after 1 year of incubation (figure 3). To study

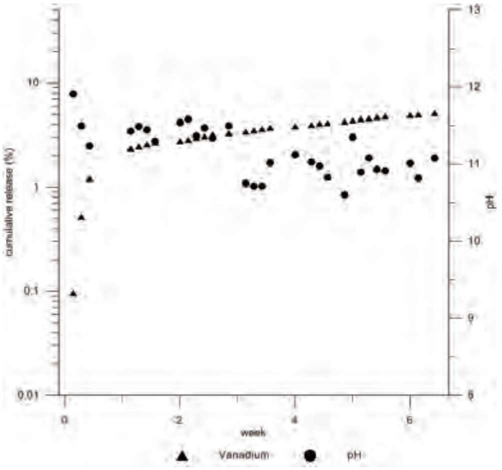

Figure 1 *Change in pH and release of vanadium over time during de-ionized water leaching of LD-slag.*

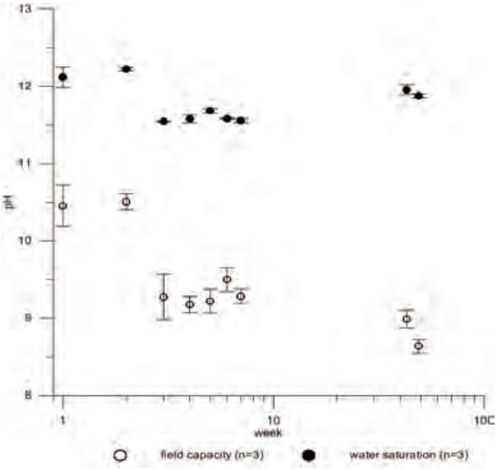

Figure 2 *Change in pH over time at water saturation and field capacity in the presence of aspen wood.*

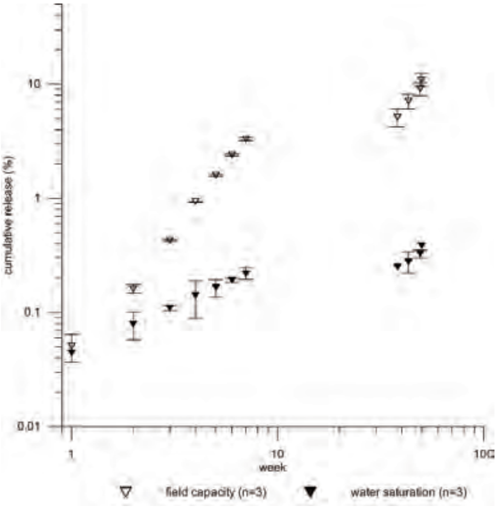

Figure 3 *Cumulative release of vanadium in water saturated samples and samples at field capacity.*

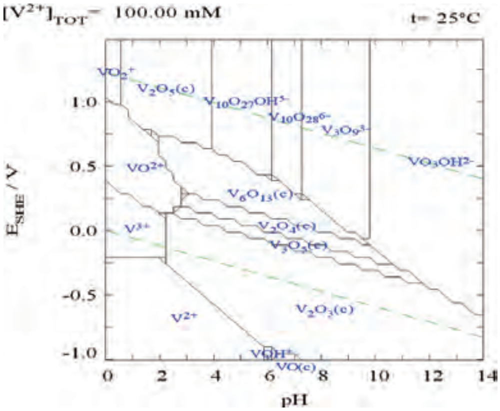

Figure 4 *Pourbaix-diagram of vanadium at different pH and Eh.*

whether time affected the release of vanadium from LD-slag, all samples were left to stand undisturbed for 31 weeks after sampling week 7. Then samples were collected once a month during the following 3 months. As seen in figure 3 the release of vanadium did not increase with increasing time between sampling. However, in both saturated and field capacity samples the release of vanadium will depend on the redox potential. And as seen in figure 4, at all pH above 3, vanadium may precipitate as solid species if the redox potential decreases, which may well be the case in the samples saturated with water.

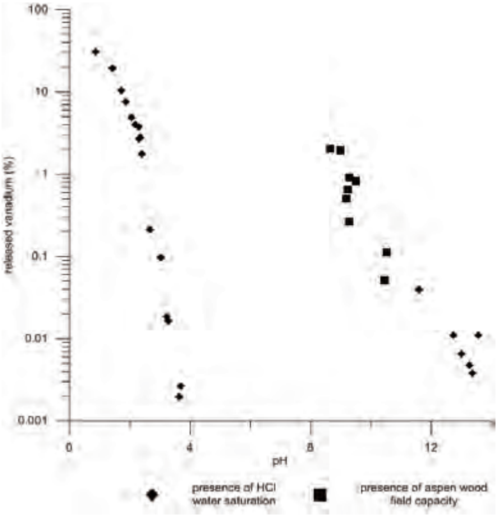

Figure 5 *Release of vanadium from LD-slag at different pH in presence of HCl or aspen wood at field capacity.*

To examine whether organic carbon enhanced the release of vanadium, LD-slag was leached in HCl at different pH to examine the pH-dependent release of vanadium. By plotting the released amount of vanadium versus the solution-pH figure 5 was obtained. With HCl present a release of more than 0.1 % vanadium was obtained at pH lower than 3. At pH around 12 a slight increase was observed but less than 0.05 % of the content was released. If aspen wood shavings were present and the water content was held at field capacity the release of vanadium reached approximately 2 % at pH between 8 and 9 and never fell below 0.05 %. This indicates that the release of vanadium from LD-slag is enhanced if organic carbon sources such as aspen wood shavings are present at pH above neutral. From the data in figure 4 it estimated that the possible vanadium-species was $V_3O_9^{3-}$ in the presence of aspen wood shavings at field capacity due to the estimated higher Eh. The lack of vanadium in the presence of HCl may be caused by precipitation of different crystalline vanadium-polymers due to lower Eh at water saturation.

Conclusions

Addition of organic carbon in the form of aspen wood shavings enhances the release of vanadium from LD-slag when the water content is held at field capacity. If the water content increases and water saturation is reached the release of vanadium decreases with a factor up to 20. This indicates that addition of soil as protective cover on top of LD-slag may cause severe release of vanadium from the slag in a short amount of time but also, depending on the water content, act as a temporary sink for vanadium.

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