

Removal of vanadium from neutralized acid mine drainage (AMD) by adsorption to saw dust

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Abstract

Treatment of AMD with alkaline waste materials such as LD-slag may cause increased mobilization of potentially toxic metals, particularly those that form oxyanions. Vanadium is one of them and it can reach up to 3 % (weight) in the LD-slag. In this report a multivariate approach was used to study the removal of primarily vanadium from AMD neutralized with LD-slag by adsorption to wood. Two of the most important factors for the adsorption were pH and contact time. Some 90 % removal of vanadium was obtained after a contact time of 7 days when 25 g L⁻¹ saw dust was added to AMD neutralized with LD-slag.

Keywords: vanadium, LD-slag, adsorption, AMD, saw dust

Introduction

At many mine sites formation of acid mine drainage (AMD) may pose severe environmental threats. To reduce the negative impact of generated AMD one strategy is neutralization of the leachate with alkaline oxides/hydroxides/carbonates. Alkaline waste products can be well suited for the process, providing that they have both high neutralizing capacity and low cost (Sartz 2010). One such highly alkaline waste product is the slag from the production of high grade stainless steel by the Linz-Donnawitz process, commonly referred to as LD-slag. The major constituents of the slag are oxides such as CaO (Merox 2006). Addition of LD-slag to AMD increases the pH and decreases the metal content in solution by e.g. sorption or coprecipitation with hydroxides. However, some elements e.g. vanadium and chromium may form oxyanions in solution under such conditions and are hence not removed from the solution. Since the slag contains some 3 % vanadium the release of vanadium may increase (Merox 2006, Mácsik & Jacobsson 2002). It has been found that the final solution after neutralization of AMD with LD-slag may contain up to 1.4 ppm vanadium (Sartz 2010). Primarily, the vanadium was found as V(V) (Sjöberg *et al.* 2010).

Removal of dissolved vanadium has been done by adsorption to saw dust and bark (Kaczala *et al.* 2009, Palma *et al.* 2003). At near neutral conditions 43 % vanadium was removed by saw dust from a solution containing 73 ppb vanadium of unknown redox state and speciation (Kaczala *et al.* 2009). By decreasing the pH to 4, 95 % vanadium was removed (Kaczala *et al.* 2009). When bark was used the adsorption at neutral pH was 29.6 % from a solution containing 1 g L⁻¹ V(V) (Palma *et al.* 2003). As for the saw dust an increased adsorption was obtained if the pH was lowered and at pH 3, 66.8 % was adsorbed (Palma *et al.* 2003).

Vanadium adsorption may depend on many different variables such as ionic strength, amount of adsorbent, initial pH, vanadium redox state, counter ions to VO₃⁻, initial vanadium concentration and contact time. In this report the

adsorption of vanadium to aspen shavings is studied using a multivariate experimental design including six different variables. Finally the results are used to test whether saw dust can be used for removal of vanadium from AMD neutralized with LD-slag and whether it provides sufficient selectivity to be used for recovery of vanadium.

Materials & Methods

Adsorbents

For the multivariate study of vanadium adsorption, air dried shavings (5 x 5 x 0.5 mm) of aspen (*Populus tremula*) was used. Adsorption of vanadium from AMD neutralized with LD-slag was conducted with air dried saw dust (< 2 mm) containing equal amounts of pine (*Pinus sylvestris*), spruce (*Picea abies*) and birch (*Betula sp.*).

Vanadium stock solutions

For the multivariate study three different stock solutions, containing 200 ppm vanadium each, were prepared by dissolving required amounts of VOSO_4 , NaVO_3 and NH_4VO_3 in de-ionized water (18.2 M Ω). Neutralized AMD was prepared by mixing acid generating mine waste (diam. < 2 mm) with 10 % (weight) LD-slag (diam. < 0.56 mm). After mixing, de-ionized water (18.2 M Ω) was added until L/S 10 was reached and the mixture was agitated (end-over-end shaker) for 7 days to reach some 1 ppm vanadium in solution (Sartz 2010).

Analytical techniques

Metals were analyzed with ICP-MS (Agilent 7500 cx). Measured isotopes were ^{23}Na , ^{24}Mg , ^{27}Al , ^{39}K , ^{43}Ca , ^{51}V , ^{53}Cr , ^{55}Mn , ^{57}Fe , ^{59}Co , ^{60}Ni , ^{63}Cu , ^{66}Zn , ^{85}Rb , ^{88}Sr , ^{107}Ag and ^{137}Ba . Before analysis all samples were diluted 100 times with 1 % nitric acid (sub boiled distilled) in de-ionized water (18.2 M Ω) thereby decreasing the interference from $^{35}\text{Cl}^{16}\text{O}^+$ to less than 3 % for samples containing 10 ppb vanadium or more. As internal standard 10 ppb ^{103}Rh was added to the samples prior to analysis. Measurement of pH was done with a Metrohm 744 pH meter.

Vanadium adsorption, multivariate experimental design

Variables are listed in Table 1 together with the range in which they were studied. To adjust the ionic strength NaClO_4 was used due to its limited ability to form vanadium complexes. According to the design of the solution systems formation of stoichiometric solid phases were avoided.

Table 1 Experimental variables.

Variable	Range
Ionic strength	De-ionized water or 0.1 M NaClO_4
Aspen shavings	25 – 50 g L ⁻¹
Initial pH	3 – 11
Vanadium redox state and counter ions	VOSO_4 , NaVO_3 or NH_4VO_3
Vanadium concentration	1 – 10 ppm
Contact time	3 – 60 min

In a traditional experimental design where at least 3 values of each variable are examined the resulting experimental design contains at least 486 different experiments. By using a multivariate experimental design the number of experiments was decreased to 21 (Table 2). For experimental design and data evaluation the software Modde 9.1 (Umetrics AB) was used. In the evaluation of the model output the level of difference was set to $p < 0.10$.

All experiments were conducted in 100 ml polypropylene (PP) beakers with stirring (magnetic bar at 300 – 450 rpm). Samples were prepared by adding 80 ml of the matrix solution to the beaker according to the composition in Table 2. A volume corresponding to the subsequent addition of vanadium stock solution was removed and discarded. Then the desired amount of aspen shavings was added and the dry shavings were left to moisturize. After approximately 2 minutes the pH was adjusted to be within 0.1 pH units from the desired value with 1 M NaOH and concentrated HClO₄. The system was allowed to equilibrate during approximately 10 minutes. After the pH-adjustment, the required amount of the vanadium stock solution was added. After the desired contact time the pH was noted and a 100 µl sample was withdrawn and analyzed for its vanadium concentration. Adsorption of vanadium to the wood shavings was then calculated by equation 1.

$$Me_{\text{adsorption}}(\%) = \frac{c_0 - c_t}{c_0} \times 100 \quad (1)$$

Where

C₀ = initial metal concentration in solution (ppm)

C_t = metal concentration in solution (ppm) at time t

Adsorption of vanadium from neutralized AMD

After filtration (0.20 µm, PP) of the produced leachate the pH and the metal concentrations were measured. Triplicates of 20 ml each were then transferred to 50 ml test tubes (Sarstedt®, PP) containing 0.5 g dry saw dust (25 g L⁻¹). After agitation (end-over-end shaker) for 2.5 and 7 days a 100 µl sample was withdrawn and analyzed with respect to its metal concentration. Calculation of the metal adsorption was performed using equation 1.

Table 2 Multivariate experimental design.

Exp. no	Matrix	Wood (g L ⁻¹)	pH	Redox species	Concentration (ppm)	Contact time (min)
1	MQ	25	3	VOSO ₄	1	3
2	MQ	25	7	NaVO ₃	5.5	31.5
3	MQ	25	11	NH ₄ VO ₃	10	60
4	MQ	37.5	3	VOSO ₄	5.5	31.5
5	MQ	37.5	7	NaVO ₃	10	60
6	MQ	37.5	7	VOSO ₄	5.5	31.5
7	MQ	37.5	7	VOSO ₄	5.5	31.5
8	MQ	37.5	7	VOSO ₄	5.5	31.5
9	MQ	37.5	11	NH ₄ VO ₃	1	3
10	MQ	50	3	NaVO ₃	1	60
11	MQ	50	7	NH ₄ VO ₃	5.5	3
12	MQ	50	11	VOSO ₄	10	31.5
13	0.1M NaClO ₄	25	3	NH ₄ VO ₃	10	31.5
14	0.1M NaClO ₄	25	7	VOSO ₄	1	60
15	0.1M NaClO ₄	25	11	NaVO ₃	5.5	3
16	0.1M NaClO ₄	37.5	3	NaVO ₃	10	3
17	0.1M NaClO ₄	37.5	7	NH ₄ VO ₃	1	31.5
18	0.1M NaClO ₄	37.5	11	VOSO ₄	5.5	60
19	0.1M NaClO ₄	50	3	NH ₄ VO ₃	5.5	60
20	0.1M NaClO ₄	50	7	VOSO ₄	10	3
21	0.1M NaClO ₄	50	11	NaVO ₃	1	31.5

Results & Discussion

Depending on the experimental setup, 0 – 40 % vanadium was adsorbed to the aspen shavings (Table 3). In general, adsorption was highest at pH below 7. Above pH 7 only minor amounts were adsorbed. At all studied pH an increased adsorption was observed if the contact time was increased. After processing the data in Modde 9.1 to generate a model for prediction, adsorption data in experiments number 1 and 3 were excluded, since the measured adsorption was more than 10 % above or below the predicted range (Table 3). After excluding outlying data the fitness of the model was 92 % and the predictability was 68 % (Figure 1). Mainly four variables had significant impact on the vanadium adsorption i) pH, ii) amount of aspen shavings, iii) initial vanadium concentration and iv) contact time. Increased pH and vanadium concentration decreased the adsorption with the later probably being an effect of insufficient contact time. Increased amount of aspen shavings also decreased the adsorption, but the narrow range in concentrations may increase the uncertainty for this variable. However, it has been shown that addition of more than 50 g L⁻¹ saw dust do not increase the adsorption (Kaczala *et al.* 2009). Contact time acted opposite to the other three variables and increased contact time increased the adsorption. For the adsorption of V(V) to aspen shavings there was no significant difference (p 0.10)

whether sodium or ammonium was the counter ion. Vanadium in the form of V(IV) had a slightly positive impact on the adsorption and compared with NaVO_3 , the adsorption of V(IV) was significantly higher ($p = 0.10$). Compared with NH_4VO_3 there was no difference in adsorption why it was concluded that the initial redox state was of minor importance in the adsorption process. Ionic strength had no significant impact on the adsorption but lower ionic strength seemed to enhance the adsorption.

Since the results from the initial study indicated a limited adsorption of vanadium at high pH during the first 60 minutes of contact the software was used to predict whether a higher adsorption could be obtained with extended contact time. After re-processing the data allowing for increased contact time the model predicted some 80 % vanadium adsorption after 7 hrs from a solution containing 3 ppm vanadium at pH 10. A high ionic strength did not affect the adsorption and some 30 g L⁻¹ aspen shavings were required. The result was tested by addition of saw dust to AMD neutralized with LD-slag (pH 9.4) containing some 1 ppm vanadium and other elements that eventually affects the adsorption process (Table 4).

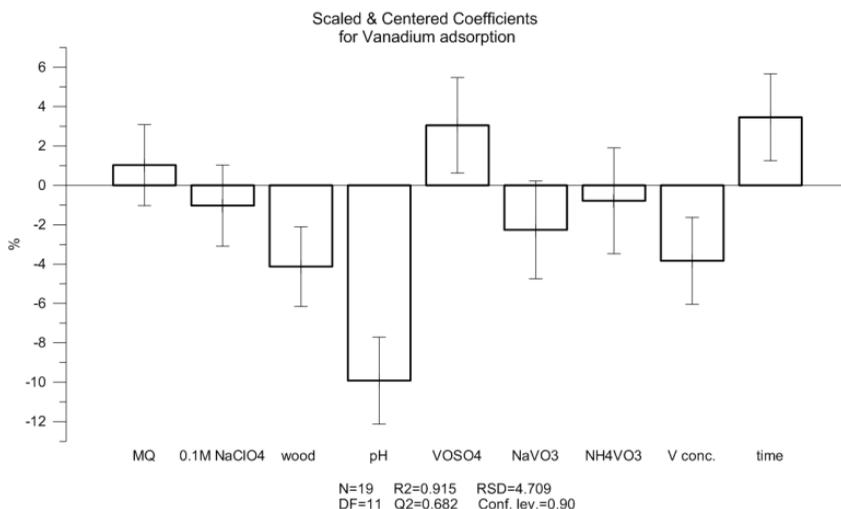


Figure 1 Effect of studied factors on the adsorption of vanadium to wood aspen shavings.

Table 3 *Experimental and predicted data.*

Exp. no	Vanadium adsorption (%)	Predicted vanadium adsorption			Final pH	Predicted final pH		
		Lower (%)	Mean (%)	Upper (%)		Lower	Mean	Upper
1	(12)	32	42	53	3.01	2.00	2.71	3.42
2	25	16	22	29	6.42	6.37	6.94	7.52
3	(28)	-2	10	22	10.5	9.79	10.56	11.34
4	38	30	36	42	3.18	2.05	2.54	3.02
5	17	8	16	24	6.61	6.12	6.77	7.42
6	21	19	23	27	6.00	5.83	6.21	6.59
7	29	19	23	27	5.70	5.83	6.21	6.59
8	22	19	23	27	6.24	5.83	6.21	6.59
9	0	-2	6	13	10.93	9.96	10.67	11.39
10	30	26	34	42	3.02	2.20	2.97	3.75
11	10	2	8	15	6.56	6.30	6.95	7.60
12	0	-8	-1	6	10.45	9.18	9.82	10.47
13	24	22	30	38	3.24	2.37	3.08	3.79
14	40	29	36	44	5.36	5.18	5.88	6.58
15	2	-5	2	10	10.86	9.76	10.47	11.19
16	16	11	18	26	3.25	2.36	3.08	3.79
17	26	16	22	27	6.52	6.05	6.62	7.20
18	6	5	12	19	9.89	8.87	9.50	10.13
19	29	21	29	36	3.04	2.07	2.78	3.49
20	10	-2	6	13	5.23	5.31	6.01	6.71
21	2	-6	1	8	10.15	9.46	10.17	10.89

* Numbers between brackets represent excluded data

After 2.5 days 85 % vanadium was adsorbed from the solution together with 23 % copper and 13 % chromium (Table 5). If the contact time was extended to 7 days 90 % vanadium was adsorbed but the selectivity decreased since 33 % copper, 27% chromium and 30% silver were also adsorbed (Table 5). This indicates that saw dust is an efficient and partially selective adsorbent that can be used for adsorption of vanadium even from complex metal mixtures. Recovery of vanadium may then be done via combustion and electrostatic separation of vanadium from the flue gases. Due to the high calorific value of saw dust, the method may be economically feasible.

Table 4 Composition of neutralized AMD before and after contact with saw dust (n=3)

	Neutralized AMD	2.5 days contact with 25 g L ⁻¹ saw dust	7 days contact with 25 g L ⁻¹ saw dust
pH	9.38 (0.05)	[6.8 – 7.0]	[6.8 – 7.0]
Ca (ppm)	838 (12.7)	1036 (62.5)	863 (35.7)
Mg (ppm)	4.49 (0.46)	12.1 (1.18)	10.3 (0.52)
K (ppm)	3.52 (0.42)	8.56 (0.57)	7.45 (0.55)
Fe (ppm)	3.52 (0.22)	4.82 (0.40)	4.37 (0.31)
Na (ppm)	1.46 (0.12)	3.73 (0.23)	3.50 (0.30)
V (ppm)	1.06 (0.12)	0.16 (0.02)	0.10 (0.02)
Sr (ppm)	0.25 (0.00)	0.41 (0.02)	0.33 (0.01)
Cu (ppb)	56.5 (3.74)	43.6 (1.00)	38.1 (6.13)
Ba (ppb)	27.1 (5.00)	334 (16.6)	230 (32.4)
Rb (ppb)	25.2 (1.31)	44.2 (3.15)	37.1 (2.58)
Al (ppb)	14.4 (1.33)	305 (77.6)	278 (58.7)
Cr (ppb)	11.2 (1.29)	9.81 (1.12)	8.20 (1.10)
Ni (ppb)	7.81 (0.48)	24.4 (4.82)	21.7 (3.78)
Zn (ppb)	2.92 (0.65)	454 (31.9)	373 (12.5)
Mn (ppb)	1.69 (0.19)	3351 (179)	2747 (114)
Co (ppb)	1.10 (0.10)	3.34 (0.20)	2.85 (0.15)
Ag (ppb)	0.73 (0.27)	0.78 (0.26)	0.51 (0.06)

* Numbers between brackets represent standard deviation

** Numbers between squared brackets represent predicted values

The adsorption process is unclear and needs further study, however it is likely due to i) electrostatic adsorption to a net-positive surface on the wood, ii) direct adsorption of cationic vanadium species onto negative sites on the wood or iii) binding via adsorbed divalent cations such as calcium or magnesium giving a positive charge on the wood surface.

Table 5 Removal of V, Cu, Cr and Ag from neutralized AMD with saw dust. (n=3)

	2.5 days contact with 25 g L ⁻¹ saw dust	7 days contact with 25 g L ⁻¹ saw dust
V (%)	85	90
Cu (%)	23	33
Cr (%)	13	27
Ag (%)	-7	30

Conclusions

Aspen shavings are an effective adsorbent for vanadium. At short contact time the adsorption is most effective at acidic pH. Multivariate data analysis predicts the adsorption to be as much as 80 % even at alkaline pH if only the contact time is increased to at least 7 hrs. When the prediction was tested with an alkaline solution (pH 9.4) and 25 g L⁻¹ saw dust, 85 % vanadium was adsorbed after 2.5

days of contact. After 7 days the adsorption had increased to some 90 %. The results indicate that saw dust can be used as a cheap adsorbent for removal of vanadium from alkaline solutions even at rather high vanadium concentrations. Since the selectivity for vanadium was good saw dust may be used for recovery of vanadium from vanadium containing leachates. However, more research is needed to investigate the adsorption mechanisms and minimize the release of other elements from the saw dust.

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