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Remobilization of pentavalent antimony and vanadium from a granular iron hydroxide material – A comparative study of different leaching systems

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ABSTRACT

The remobilization of antimony and vanadium from previously loaded commercial granular ferric-hydroxide GEH material (intended for water treatment) was examined by using a sequential extraction procedure and three different leaching systems to evaluate their physicochemical mobility and potential availability under different simulated environmental conditions. A classical batch extraction, an extraction cell (EC) and rotating-coiled columns (RCC) were used as extraction systems.

For each system it could be shown that the content of ion-exchangeable antimony and vanadium in previously loaded material is negligible (<1.5%). The oxyanions were sorbed strongly and could be predominantly remobilized through reducing agents, which means through dissolution of the iron (hydr)oxide matrix.

The major advantages of dynamic systems in comparison to batchwise fractionation technique are the drastically reduced extraction time and the possibility of generating information to the leaching kinetics. It is shown that the efficiency of the three leaching systems is quite different employing Wenzel's sequential fractionation protocol. Only by working with RCC, the iron (hydr)oxide matrix was completely dissolved within four steps resulting in the total mobilization of antimony and vanadium. EC seems to be less suitable for leaching studies of Sb and V sorbed on iron(hydr)oxide. The remobilizable proportion of the several fractions was lower in comparison to batch and RCC and seems to be a result of an agglomeration of the GEH in the EC device.

1. Introduction

GEH (GEH Wasserchemie GmbH & Co. KG, Osnabrück) is a widely used commercial product for water treatment. It is specified as akaganeite. This sorbent can be used for the removal of oxyanions like, arsenate [1–3], antimonate [4,5] and vanadate [6,7] from water. The uptake of these metal(loid)s is influenced by pH value, ionic strength and sorption competitors and can vary up to a value of several hundred milligrams of metal(loid) per gram of akaganeite. A more detailed discussion about the material and the sorption behavior is given by Driehaus et al. [2] and Kolbe et al. [8].

Next to sorption capacities, the bonding strengths between the adsorber and the metal(loid)s play a decisive role for risk assessment by disposal of such a material that had been used for water treatment. As well-known from many studies targeted at arsenic, also the mobility, the bio-availability and the toxicity of antimonate and vanadate depend mainly on their chemical form.

For the assessment of environmental exposure related to trace metals and metalloids, different groups of extractants are commonly used, including water, buffered aqueous salt solutions, and weak or strong acids, reductive or oxidative extractants and complexing agents [9].

Batch sequential extraction procedures are traditionally used for the fractionation of metal(loid)s according to their mobility [10–13]. The 'nominal forms' determined by operational fractionation are employed to estimate the amounts of metal(loid)s in different 'reservoirs' in soil and sediment materials that could be mobilized under changes in chemical properties, especially of soil and sediments [14–17]. The original [13] and modified BCR procedures [18] have received widespread acceptance, especially for metals. However, a five step batch procedure was developed by Wenzel et al. [19] for the leaching of arsenic from iron(hydr)oxide enriched soils. In comparison to the BCR procedure Wenzel's scheme is characterized by two significant differences. While the BCR procedure was designed for the leaching of metals (cations), Wenzel's procedure is specific for the oxyanion arsenate, and therefore it seems to be most suitable for the leaching of antimonate and vanadate. Additionally, a distinction between amorphous and

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crystalline bounded amounts of Sb and V is possible with Wenzel's scheme due to two reducible fractionation steps in comparison to one of BCR procedure.

Therefore Wenzel's scheme (sometimes slightly modified) was preferable applied in various studies, especially for leaching of As (and also of Sb) from soils. Only a few works have been published dealing with the application of leaching procedures to study the remobilization of arsenic sorbed on iron oxides [20–23], whereas there is a number of investigations that concern leaching oxyanions from alkaline solids [24].

Even though batchwise extraction methods have been consolidated as tools for investigation of the environmental behavior of potentially toxic metal(loid)s, the results are debatable since a fixed solid to liquid ratio is used, which leads to adjustment of an equilibrium. Thus, dynamic extraction procedures (both single step and sequential) are preferable. Particularly micro-column-based flow-through systems are exploited for expeditious quantification of the mobilizable pools of metal(loid)s, as well as evaluation of the desorption kinetics as well [9]. Flow-through leaching systems, rotating coiled columns (RCC) [25–27] and extraction cells (EC) [28] were preferably used for investigation of oxyanions, especially arsenic, from soils.

The aim of this study was to investigate the leaching behavior of antimony and vanadium sorbed to the commercial GEH material, and to compare two dynamic leaching systems as well as classical batch leaching applying Wenzel's sequential extraction protocol. The results are also meant to serve as a provisional risk assessment regarding the dumping of loaded iron(hydr)oxides.

2. Materials and methods

2.1. Chemicals and materials

All chemicals used were pure grade. The solutions for leaching protocol $(NH_4)_2SO_4$ (0.05 M Merck), $(NH_4)H_2PO_4$ (0.05 M, Merck), $(NH_4)_2C_2O_4{\cdot}H_2O$, 0.2 M, Merck) and $C_6H_8O_6$ (0.1 M, Roth) were prepared by dissolving the appropriate salts in de-ionized water (Direct-QTM 5 system; Millipore). The stock solutions were prepared by dissolving $K[Sb(OH)_6]$ (Riedel de Häen) in de-ionized water and V_2O_5 (Merck) in NH_4OH (10%, Merck) with subsequent neutralization using HCl (1 M, Merck).

The loaded granular ferric hydroxide material under study was prepared by shaking each 15 g GEH (GEH Wasserchemie GmbH & Co. KG, Osnabrück, Germany) with a grain size of 0.3–2 mm and 40 mL of antimonate and vanadate (each 1 g L^{-1}), respectively. Afterwards the loaded materials were filtrated, air-dried at 105 °C and ground to a particle size <100 μm. The concentration of Sb and V in the loaded GEH materials was determined by energy dispersive X-ray fluorescence spectrometry (X-LAB 2000, SPECTRO A.I.), after homogenizing and subsequent pelleting with stearine wax (Hoechst wax for XRF-analysis) as binder in a ratio 80:20 (m/m) resulting in concentrations of 2100 mg kg^{-1} and 3100 mg kg^{-1} of antimony and vanadium, respectively.

2.2. Leaching protocols

Wenzel's leaching protocol [19] was applied for batch, RCC and EC procedures (see Sections 2.2.1–2.2.4 for modifications). Briefly, the following five extraction steps in the original scheme for 1 g solid sample are:

1st step (non-specifically sorbed): 0.05 M $(NH_4)_2SO_4$, 25 mL;
2nd step (specifically sorbed): 0.05 M $(NH_4)H_2PO_4$, 25 mL;
3rd step (amorphous Fe oxides bound): 0.2 M $(NH_4)_2C_2O_4{\cdot}H_2O$, pH 3.25, 25 mL, in the dark;
4th step (crystalline Fe oxide bound): 0.2 M $(NH_4)_2C_2O_4{\cdot}H_2O$ + 0.1 M L-ascorbic acid, 25 mL, 96 °C;
5th step (residual): HNO_3/H_2O_2 microwave assisted digestion, 50 mL.

2.2.1. Batch leaching

The amount of the sample was reduced to 300 mg to adapt the procedure to the dynamic leaching systems (EC and RCC) where this amount was used too. In the 1st step the material was shaken with 25 mL 0.05 M $(NH_4)_2SO_4$ for 4 h at 150 rpm in the overhead shaker. After centrifugation (3000 rpm, room temperature), the supernatant was decanted and the residual was washed with 12.5 mL of the same reagent for 1 min. The washing agent was added to the eluent. Such a washing procedure was accomplished for each further step.

In the 2nd step the procedure was repeated with 30 mL of 0.05 M $(NH_4)H_2PO_4$ for 16 h. After this, the residue was shaken in a 3rd step for 4 h using 12.5 mL 0.2 M $(NH_4)_2C_2O_4{\cdot}H_2O$, followed by boiling the resulting suspension after adding of 12.5 mL 0.2 M $(NH_4)_2C_2O_4{\cdot}H_2O$ + 0.1 M L-ascorbic acid at 96 °C for 30 min (4th step). At least (5th step) the residue was totally dissolved with 4 mL HNO_3 (60%, v/v) and 1 mL H_2O_2 (30%, v/v) microwave assisted (Microwave, Perkin Elmer).

2.2.2. Leaching using extraction cell (EC)

Dried, homogeneous GEH (300 mg) was placed for leaching in the flow-through sample container with an inner volume of 2.8 mL, which was described in detail by Buanuam et al. [29]. The extraction unit was connected to the extractant reservoir and the fraction collector vials using Tygon® tubing. A peristaltic pump (Minipuls 3, Abimed-Gilson) was used to pump the extractants (steps 1–4) at a flow rate of 3 mL min^{-1} through the device containing the sample at room temperature. The resulting leachates passing through a membrane filter were collected as a sub-fraction of each 15 mL. The number of sub-fractions varies from four (step 1) to ten (steps 2–4). This means liquid-to-solid ratios (related to the initial mass) of 200 (step 1) and of 500 (steps 2–4) were achieved. Because of technical conditions, step 4 had to be executed without any heating.

After drying, the residual was completely dissolved by microwave digestion (5th step) as in the batch procedure.

2.2.3. Rotating coiled column (RCC)

A RCC system Spring 3 (Institute of Analytical Instrumentation of St. Petersburg, Russia) was used. Briefly, the solid sample is retained as a stationary phase in vertical one-layer coiled polytetrafluoroethylene (PTFE) column vertical (1.5 mm inner diameter; 20 mL inner volume) fixed on one axis of a planetary centrifuge. The leaching solutions are pumped through the column via a peristaltic pump at room temperature. The fractionation of metal(loid)s is performed when the spiral column rotates around its axis (750 rpm) and simultaneously revolves around the central axis of the unit with the aid of a planetary gear (with identical rpm). Before commencing the leaching procedure, the column was filled with de-ionized water. Afterwards the aqueous slurry of the GEH material (300 mg) was filled for leaching in the PTFE column. Then, while the column was rotated, aqueous solutions of different reagents (steps 1–4), used as the mobile phase, were continuously delivered to the column at a flow rate of 2 mL min^{-1}. The leachate was collected on the outlet of the column in sub-fraction of 15 mL each. The number of sub-fractions was identical to what was used in the EC technique.

A microwave digestion was not necessary, because material was entirely dissolved after the fourth step. The collected sub-fractions of the effluent were directly analyzed without filtration.

2.3. Analytical procedure

All sub-fractions and the dissolved residuals were analyzed after appropriate dilution by ICP-atomic emission spectrometry (CIROS, Spectro A.I.) at the emission lines of Sb (206.833 nm) and V (292.464 nm).

Matrix adapted calibration solutions were used by appropriate addition to the leaching solutions, 0.05 M $(NH_4)_2SO_4$, 0.05 M $(NH_4)H_2PO_4$, 0.2 M $(NH_4)_2C_2O_4\cdot H_2O$, 0.2 M $(NH_4)_2C_2O_4\cdot H_2O$ + 0.1 M L-ascorbic acid and nitric acid.

3. Results and discussion

3.1. Batch leaching

The pre-loaded GEH material was leached sequentially in the established batch mode first. Although batch leaching is not an appropriate technique for dynamic processes, it was used for comparison of the results with the applied RCC and EC leaching approaches.

It was found that the concentration in the solution resulting in the 1st fractionation step ($(NH_4)_2SO_4$), which resolves the non-specifically sorbed anions by ion exchange, is negligible for Sb and V as shown in Table 1. Such low remobilization by $(NH_4)_2SO_4$ might be caused by the high affinity to iron(hydr)oxides as reported for Sb by Wilson et al. [30]. This finding indicates that both Sb and V are not nonspecifically sorbed at the surfaces of the particles.

Within the following 2nd fractionation step the “specifically sorbed” anions are mobilized by phosphate solution, e.g. by ligand exchange; 1.4% of antimony and no vanadium can be leached with phosphate solution.

This is in contrast to the values for arsenic, which were found for the same material to be about 20% (unpublished results), and for iron oxide impregnated brick sand to be about 10% [22]. In the literature, an identical behavior was reported for soils (10% to 20% [19,26,31]). Arsenic was mobilized in this fraction; antimony was comparably less mobile (less than 10%) [31,32]. This is in good agreement with our results. The differences in the remobilization of As in comparison to Sb by $(NH_4)H_2PO_4$ can be explained in respect to the chemical structures of the different species. Arsenate and phosphate have similar pK_a values (As(V): 2.2, 6.9 and 11.5; P(V): 2.2, 7.2 and 12.3) [35] and tetrahedral structures (Fig. 1). Although antimonate has a similar pK_{a1} value (2.6) [35], it differs in its structure [33,34] compared to arsenate and phosphate. In aqueous solution antimonate has an octahedral structure. We assume that this may be the reason for the different behavior of $H_2SbO_4^-$ in comparison to $H_2PO_4^-$ and $H_2AsO_4^-$. The chemistry of vanadium is even more variable. As illustrated in its Eh-pH diagram [24,38,39] under oxic conditions the vanadium(V) species is $H_2VO_4^-$ (pH 7–pH 5.8), which also has a tetragonal structure (Fig. 1). The pK_{a1} value is 3.8 [36] and from the free energies [37] one can calculate the pK_{a2} (8.1) and pK_{a3} (13.3) values. However, a mobilization by ion exchange with phosphate seems again not to take place in the case of vanadate.

In the 3rd step oxalate was used to remobilize the metalloids from the amorphous iron oxide. The eluent power was enhanced in the 4th step by adding ascorbic acid and increasing of the desorption temperature to 96 °C to leach the crystalline bounded metalloids as well. As shown, most of Sb (84% of XRF value) was remobilized under reducing conditions (3rd and 4th steps) from the amorphous and crystalline iron oxides. This is even more than the Sb amounts leached from soils under reducing conditions as reported in the literature, for example 7.1–46% [40] and 30–50% [41], which points to the presence of other sparingly soluble Sb compounds in soils which is in contrast to the uniform matrix of our material. Moreover, as regards use of the Wenzel leaching scheme, we had assessed in a previous study considerably variable mobilization rates for antimony (25–80%) from different soils in these two fractions [31]. By comparison with data for soils, it must also be considered that when extracting soil samples in the 1st and 2nd steps (leachable and the freely exchangeable fractions), substantial amounts of Sb (and V) are mobilized. This is caused by the variability of the mineral matrix components in soils in comparison to the much simpler composition of this material.

We found that more than 95% of vanadium was mobilized under reducing conditions. About 19% of antimony and 12% of vanadium of the total amount (XRF values) remained in the residual fraction.

The total concentrations of Sb and V obtained by adding up all fractions (including residue) are in good agreement with the total concentration determined by X-ray fluorescence spectrometry. The recoveries were within the mean ($n = 3$) 104% for antimony and 111% for vanadium, which is quite good for such a multi-step procedure.

3.2. Extraction cell (EC)

As stated above, batchwise extraction methods inherently are based upon the establishment of a single equilibrium between solid and liquid phases and do not involve the fast removal of desorbed compounds from the surface of the matrix. Therefore, EC as a flow-through approach, which was successfully tested in fractionation studies, was conducted to investigate the remobilization of Sb and V.

Again, neither antimony nor vanadium could be leached in the 1st and 2nd steps. Even in the 3rd and 4th steps the efficiency in mobilization of these two elements from loaded GEH under reducing conditions is decreased in relation to batch extraction substantially, despite higher liquid to solid ratios – see Table 1. Only about 35% of Sb and about 45% of V were remobilized in the oxalate and oxalate/ascorbic acid fractions, and a high portion of both elements remains in the residual fraction.

This indicates that the equilibrium state is not attained in the 3rd and 4th steps under the flow conditions in the EC (100 min total contact time in the 3rd and 4th steps). One reason for this could be that the leaching in the 4th step was done at room temperature employing EC due to technical reasons in contrast to the enhanced temperature of 96 °C using the batch technique.

Based on this finding, the leaching process was time-resolved monitored by sampling of 10 sub-fractions (of each 15 mL) in the 3rd and 4th steps using EC (Fig. 2). The resulting extractograms, i.e. plots of concentration of the elements extracted vs. sub-fraction number, show distinct differences in their pattern. Contrary to the usual shape of the plots (dropping the intensities with the number of fractions), a steady leaching of both Sb and V was obtained in the 3rd fraction. This indicates that very unfavorable conditions exist in this system for remobilization of both elements. In the 4th step by adding ascorbic acid to $(NH_4)_2C_2O_4\cdot H_2O$ – to enhance the reductive power – the common pattern of the extractograms for V is in evidence. However, the pattern for Sb also indicated the insufficient reaction condition in the system. It could come also to formation of agglomerates, whereby intensive exchange between solid and solution would be obstructed, as discussed later on.

One can also see by the relative high remobilization rates in the 8–10 sub-fractions that the leaching is incomplete for V and Sb, and also a high residue of iron(hyd)oxides was not dissolved.

3.3. Rotating-coiled columns (RCC)

The results obtained by leaching loaded GEH samples employing RCC are also given in Table 1. As already seen above, the concentrations in ion exchangeable fractions (steps 1 and 2) are

Table 1
Extractable amounts of antimony and vanadium in mg kg^{-1} for the several leaching systems. Results are declared as the mean of three replicates ± standard deviation.

Element	System	1st step	2nd step (mg kg^{-1})	3rd step (mg kg^{-1})	4th step (mg kg^{-1})	Residual (mg kg^{-1})	Sum (mg kg^{-1})	XRF (mg kg^{-1})	Recovery (%)
Sb	Batch	<LOD[a]	29.5 ± 6.3	695 ± 117	1070 ± 60	391 ± 98	2180 ± 282	2100	104
	EC	<LOD[a]	<LOD[a]	190 ± 78	520 ± 112	1511 ± 41	2220 ± 230		106
	RCC	<LOD[a]	16.1 ± 4.3	972 ± 101	1160 ± 172	No residue	2150 ± 288		103
V	Batch	<LOD[b]	<LOD[b]	1490 ± 75	1590 ± 91	371 ± 80	3460 ± 246	3100	112
	EC	<LOD[b]	<LOD[b]	418 ± 104	968 ± 66	1660 ± 276	3040 ± 445		98.1
	RCC	<LOD[b]	<LOD[b]	1680 ± 167	1210 ± 100	No residue	2892 ± 266		93.3

[a] LOD of Sb: 0.08 mg L^{-1} using solution.
[b] LOD of V: 0.1 mg L^{-1} using solution.

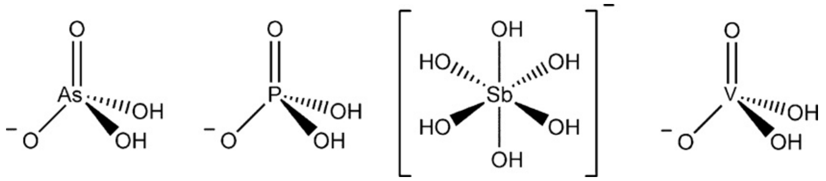

Fig. 1. Chemical structures of arsenate, phosphate, antimonate and vanadate at pH 7.

very low to non-detectable. These findings are confirmed once again with the RCC technique. However, Sb and V were very effectively remobilized in the 3rd and 4th steps applying the RCC. Using RCC technique we also could not work at elevated temperatures in step 4 due to technical reasons. Fortunately, the GEH material was completely dissolved in the 4th step, even at room temperature. This behavior is due to the intensive interactions using the RCC technique. The iron hydroxide particles are held in suspension due to the planetary forces of the RCC and no agglomeration of the samples occurs. Consequently, a maximum of surface area for leachant interaction and minimal contact of solids with barriers are realized. The equilibrium between solid and liquid phases can be adjusted very fast with constant renewal of the solvent at the solid surface. Additionally, one have to consider that repeated extractions – using in sum the identical solid to liquid ratio – result in a higher cumulative extraction yield. This results in the dissolution of the whole material, which can be expected for akaganeite under reducing conditions. The reduction of Fe^{3+} to Fe^{2+} leads to the dissolution of the sorption material.

This result is remarkable, since with the batch procedure in this process step, increased temperatures are used and a higher reaction time is given. It is also in contrast to the results obtained by employing EC.

In order to understand these results better, the leaching behavior was time-resolved plotted. The extractograms in Fig. 3 demonstrate that both in the 3rd and 4th steps of Wenzel's scheme Sb and V are well mobilized. In the 9th sub-fraction of the 4th step, in which the GEH material is visually totally dissolved, <1% vanadium and <2% antimony were detectable. The content of Sb and V in the 10th to 12th sub-fractions was <1% indicating memories in the tube (to obtain 100% recovery) and the need to rinse the system carefully. As a side note, the mixing and carry-over effects by the solid material inside the column when changing the eluent are also visible by the increase in concentration from the 1st to 2nd sub-fractions.

In addition, clear differences between antimony and vanadium are shown in the extractograms. Vanadate is significantly more leachable than antimonate by both eluents in the 3rd and 4th steps. This becomes clear by the substantially stronger rise of the mobilization rate of the vanadium at the beginning of each extraction step and in the faster fade-out phase. Likewise it shows an increased mobilization rate of V (54%) in comparison to Sb (46%) in the 3rd step.

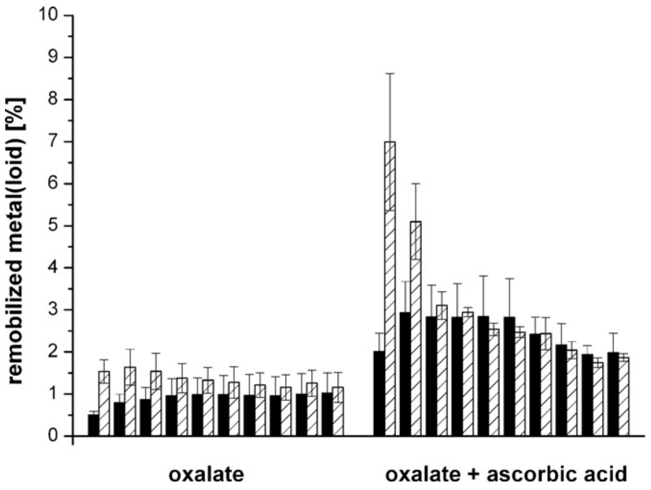

Fig. 2. Kinetics of the EC leaching. Black bars: Sb; striped bars: V (each bar: 15 mL of solution).

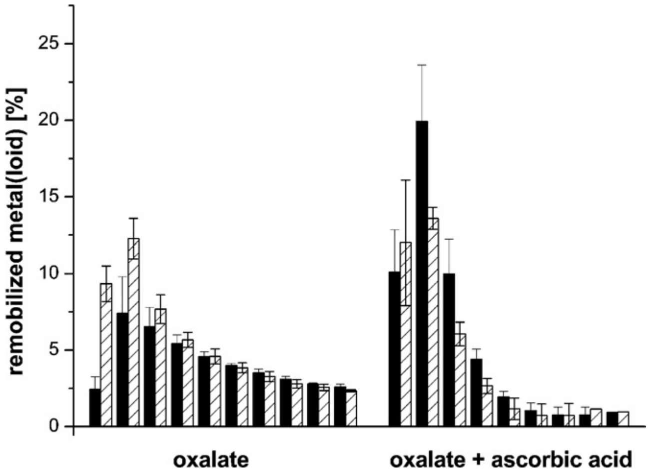

Fig. 3. Kinetics of the RCC leaching. Black bars: Sb; striped bars: V (each bar: 15 mL of solution).

Table 2
Leaching parameters of the several systems.

	Batch	EC	RCC
GEH amounts (mg)	300	300	300
Flow of the eluent (mL min^{-1})	–	3	2
Volume of sub-fraction (mL)	–	15	15
Total volume (steps 1–4) (mL)	100	510	510
Time duration (steps 1–4) (min)	1500	200	255
Total recoveries (Sb/V) (%)	104/111	106/98	103/93
Residual fraction (Sb/V) (%)	19/12	72/53	0/0

3.4. Comparison of the tested protocols

As is clearly recognizable, the RCC technique is best suited to studying the remobilization of Sb and V from GEH in comparison to batch and EC techniques (see Table 2). Because of the planetary forces, the GEH solid material is in abeyance and has a maximum of surface to leachant interaction, minimal contact of solids with barriers and no agglomeration of the solid material. The GEH is surrounded completely by the leaching reagent. Thus fast desorption/dissolution by continuous replacement with renewed eluent can be realized. The considerably reduced expenditure of time and the avoidance of working at higher temperatures are additional advantages using RCC compared with the commonly applied batch technique.

Comparing the results obtained by using EC with the other two techniques, it becomes clear that its employment to study the remobilization of Sb and V from the GEH material is less suitable (contrary to results obtained by leaching of soils and sediment, as demonstrated in the literature). An explanation would be the formation of agglomerates of the GEH particles (forming preferential flow paths through the cell), which is avoided using RCC (with application of the centrifugal forces). These bulky agglomerates inhibit an optimal distribution of the leaching reagent and lead to reduced interactions between the particles and the leaching solutions.

As can be seen from Table 2, the dynamic systems are much faster. However, the total recovery is similar for all procedures tested and remains within a usual range for such a multi-step procedure.

4. Conclusion

In comparing different leaching systems the question arises, how the results obtained in the laboratory experiments can be used for risk assessment in the environment. In this study a distinction between ion exchange reactions and the reducing steps has to be done. For the exchange reactions (steps 1 and 2) all approaches give similar results – almost no mobilization of antimonate and vanadate appears. For that reason the advantages or disadvantages of the leaching system are difficult to discuss. However, significant differences are observed in the next steps. The EC seems to underestimate the leaching behavior under reducing conditions. The decreased mobilization by using EC seems to be caused by forming agglomerates of the GEH particles, which inhibit an optimal distribution.

In our opinion the best approach is the RCC system. Due to constant renewal of the solvent in the dynamic systems, the reduction is enhanced compared to batch leaching and results in higher mobilization rates. Thus, RCC technique seems to be best suitable for a simulation of long term processes (however without giving a time span). The expected complete dissolution of the matrix material is a strong indication for this.

The content of amorphous and crystalline bounded Sb and V was nearly 1:1 which corresponds to the adsorber analysis resulting by ^{57}Fe-Mössbauer spectroscopy in a ratio of approximately 59% amorphous ferrihydrite and 41% akaganeite (crystalline) [42].

Finally, the risk potential of the antimony and vanadium loaded sorption materials under oxic conditions has been evaluated as low. Remobilization is only possible with strong reducing agents by dissolving the material itself.

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References

[1] E.A. Deliyanni, D.N. Bakoyannakis, A.I. Zouboulis, A. Matis, Chemosphere 50 (2003) 155–163.
[2] W. Driehaus, M. Jekel, U. Hildebrandt, Water SRT 47 (1998) 30–35.
[3] X.H. Guan, J. Wang, C.C. Chusuei, J. Hazard. Mater. 156 (2008) 178–185.
[4] X. Martinez-Lladó, J. de Pablo, J. Giménez, C. Ayora, V. Marti, M. Rovira, Solvent Extr. Ion Exch. 26 (2008) 289–300.
[5] A.K. Leuz, H. Mönch, C.A. Johnson, Environ. Sci. Technol. 40 (2006) 7277–7282.
[6] D.P.T. Blackmore, J. Ellis, P.J. Riley, Water Res. 30 (1996) 2512–2516.
[7] A. Naeem, P. Westerhoff, S. Mustafa, Water Res. 41 (2007) 1596–1602.
[8] F. Kolbe, H. Weiss, P. Morgenstern, R. Wennrich, W. Lorenz, K. Schurk, H. Stanjek, B. Daus, J. Colloid Interface Sci. 357 (2011) 460–465.
[9] P.S. Fedotov, W. Koerdel, M. Miro, W.J.G.M. Peijnenburg, R. Wennrich, P.M. Huang, Crit. Rev. Environ. Sci. Technol., in press.
[10] W. Calmano, U. Foerstner, Sci. Total Environ. 28 (1983) 77–90.
[11] U. Foerstner, Int. J. Environ. Anal Chem. 51 (1993) 5–23.
[12] A. Tessier, P.G.C. Campbell, M. Bisson, Anal. Chem. 51 (1979) 844–851.
[13] A.M. Ure, P. Quevauviller, H. Muntau, B. Griepink, Int. J. Environ. Anal. Chem. 51 (1993) 135–151.
[14] J.R. Bacon, C.M. Davidson, Analyst 133 (2008) 25–46.
[15] A. Hass, P. Fine, Crit. Rev. Environ. Sci. Technol. 40 (2010) 365–399.
[16] J. Hlavay, T. Prohaska, M. Weisz, W. Wenzel, G.J. Stingeder, Pure Appl. Chem. 76 (2004) 415–442.
[17] K.L. Linge, Crit. Rev. Environ. Sci. Technol. 38 (2008) 165–196.
[18] G. Rauret, J.F. Lopez-Sanchez, A. Sahuquillo, R. Rubio, C. Davidson, A. Ure, P. Quevauviller, J. Environ. Monit. 1 (1999) 57–61.
[19] W.W. Wenzel, N. Kirchbaumer, T. Prohaska, G. Stingeder, E. Lombi, D.C. Adriano, Anal. Chim. Acta 436 (2001) 309–323.
[20] A. Ghosh, A.E. Saez, W. Ela, Sci. Total Environ. 363 (2006) 46–59.
[21] I. Haase, U. Förstner, Acta Hydrochim. Hydrobiol. 23 (1995) 53–60.
[22] F.M. Islam, M.M. Rahman, S. Ahamed, Fate of Arsenic in the Environment, 2003, pp. 181–192. ISBN 984-32-0507-3.
[23] J. Shan, E. Saez, W.P. Ela, J. Environ. Eng. – ASCE 136 (2010) 238–245.
[24] G. Cornelis, C.A. Johnson, T. Van Gerven, C. Vandercasteele, Appl. Geochem. 23 (2008) 955–976.
[25] P.S. Fedotov, A.G. Zavarzina, B. Spivalov, R. Wennrich, J. Mattusch, K. Tietze, V.V. Demin, J. Environ. Monitor. 4 (2002) 318–324.
[26] P.S. Fedotov, W.J. Fitz, R. Wennrich, P. Morgenstern, W.W. Wenzel, Anal. Chim. Acta 538 (2005) 93–98.
[27] M. Schreiber, M. Otto, P.S. Fedotov, R. Wennrich, Chemosphere 61 (2005) 107–115.
[28] J. Buanuam, R. Wennrich, J. Hazard. Mater. 184 (2010) 849–854.
[29] J. Buanuam, K. Tiptanasup, J. Shiowatana, M. Miró, E.H. Hansen, J. Environ. Monit. 8 (2006) 1248–1254.
[30] S.C. Wilson, P.V. Lockwood, P.M. Ashley, M. Tighe, Environ. Pollut. 158 (2010) 1169–1181.
[31] K. Müller, B. Daus, P. Morgenstern, R. Wennrich, Water Air Soil Pollut. 183 (2007) 427–436.
[32] V. Etler, M. Mihaljevic, O. Sebek, Z. Nechutny, Chemosphere 68 (2007) 455–463.
[33] M. Filella, N. Belzile, Y.W. Chen, Earth Sci. Rev. 59 (2002) 265–285.
[34] M. Filella, P.M. May, Geochim. Cosmochim. Acta 67 (21) (2003) 4013–4031.
[35] A.F. Hollemann, E. Wiberg, Lehrbuch der anorganischen Chemie. de Gruyter 91–100., Auflage, Berlin, New York, 1985.
[36] L. Pettersson, B. Hedman, A.M. Nenner, I. Andersson, Acta Chem. Scand. A 39 (1985) 499–506.
[37] K. Post, R.G. Robins, Electrochim. Acta 21 (1976) 401–405.
[38] J.D. Hem, Geochim. Cosmochim. Acta 41 (1977) 527–538.
[39] C.L. Peacock, D.M. Sherman, Geochim. Cosmochim. Acta 68 (2004) 1723–1733.
[40] H. Hou, T. Takamatsu, M.K. Koshikawa, M. Hosomi, Eur. J. Soil Sci. 57 (2006) 214–227.
[41] M. Tighe, P. Lockwood, Commun. Soil Sci. Plant Anal. 38 (2007) 1487–1501.
[42] S. Kleinert, E.M. Muehe, N.R. Posth, U. Dippon, B. Daus, A. Kappler, Environ. Sci. Technol., doi:10.1021/es201522n, in press.