Development of an Adsorbent Comprising Schwertmannite and its Utilization in Mine Water Treatment

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ABSTRACT

Two different kinds of agglomerated and filter stable adsorbents were developed based on bio-technologically synthesized schwertmannite (SHM) from iron and sulfate containing lignite mine water. The adsorbents were obtained by compaction and by mixing SHM with an organic polymer without impairing its adsorption capacity regarding arsenic, respectively.

At first, both types of SHM adsorbents were tested in comparison to the commercially available iron hydroxide adsorbent (Ferrosorp®Plus, HeGoBiotec GmbH) in two batch test series with (1) tap water stocked with 20 mg/L As(V) and As(III), respectively and (2) drainage water from an abandoned uranium mine of the ore mountains (Eastern Germany) which contained about 1 mg As/L. Both types of SHM adsorbents showed higher maximum As(III) and As(V) adsorption capacities (28.0 to 31.1 mg/g adsorbent) than Ferrosorp®Plus (22.7 and 18.0 mg/g adsorbent, respectively).

Thereafter, two column test series were performed directly at the abandoned uranium mine site with the drainage water and a filter bed residence time of 11 to 34 minutes. Due to its slow adsorption kinetic, the effluent limit value of 0.1 mg As/L was exceeded significantly earlier in the Ferrosorp®Plus column than in the columns filled with SHM-adsorbents. The compacted product SHM-sorpP showed a better long time effect due to its 40% higher bulk density.

In dumping experiments with the As loaded SHM adsorbents and alternating rain water (pH 5) and continuous groundwater elution (pH 7), only 0.13 – 0.6% and 0.03% of the adsorbed As were desorbed within 285 days, respectively. Currently, further pilot scale trials are being prepared for testing the SHM agglomerates with various kinds of mine and industrial wastewaters.

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INTRODUCTION

The Vattenfall Europe Mining AG and the G.E.O.S. company are operating in close collaboration a pilot plant for microbial-mediated ferrous iron oxidation in the open pit lignite mine near Nochten (Lusatia, Germany) where schwertmannite (SHM) is synthesized as a byproduct of a worldwide unique water treatment process (Janneck et al, 2010 ; DE 102 21 756 B4). The pilot plant (Figure 1) is operated with iron and sulfate rich mine water from the Nochten pit. In the framework of a recently finished research project founded by the German Ministry of Education and Research (Peiffer et.al., 2012), two methods for the production of an agglomerated adsorbent based on SHM were developed for utilization of water stable agglomerates in passive treatment systems for Arsenic-contaminated mine waters.

MATERIALS AND METHODS

Adsorbents

The SHM-based adsorbents were fabricated a) by compaction (called SHM-sorpP thereafter) and b) by mixing SHM with an organic polymer (called SHM-sorpX thereafter), respectively. The latter was produced by using filter-moist SHM (approximately 48 wt-% water content), a binder amount of 8 wt% (in order to obtain a stable product), a drying step of 6 hours at 85°C and a curing step of 1 hour at 120°C thereafter. The binder-free adsorbent was produced by high-pressure compaction in a briquette press with controllable pressure gradient at the Höcker Polytechnik GmbH, Hilter, Germany (Figure 2). For this purpose, the SHM was dried at 60°C in order to obtain a water content of 10 to 20 wt-%. The moisture of the raw material SHM has an important influence on the briquette quality. SHM does not adhere and will still remain as a dusty powder if the water content is too low, even at sufficient pressure conditions. If the water content is too high, the substance exhibits thixotropic behavior. Details of the briquette fabrication are given in EU patent application EP 2664376A1.

The new SHM-based adsorbents (Figure 3) for the treatment of arsenic contaminated mine water should be compared to that of a commercially available iron-hydroxide adsorbent like Ferrosorp®Pus (HeGo Biotec GmbH). Table 1 summarizes the characteristic parameters of all three adsorbents.
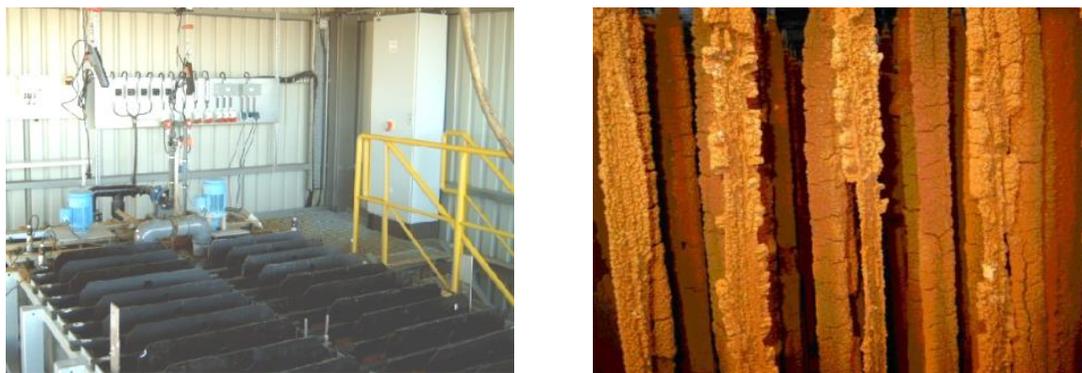
Figure 1 1-2.5 m³/h pilot plant in Tzschelln (left), where schwertmannite is generated as a byproduct of microbial catalysed lignite mine water treatment on special carrier elements (right)

Figure 2 Höcker BrikStar press (left) was used for production of cylindrical briquettes with 5 cm in diameter (right)

Figure 3 SHM-based adsorbents, obtained by mixing with an organic polymer (left) and high pressure compaction, crushing and sieving (right). Grain size: 1-2 mm in both pictures

Table 1 Selected parameters of the SHM-sorpX, SHM-sorpP and Ferrosorp®Plus

Adsorbent		SHM-SorpX	SHM-SorpP	Ferrosorp®Plus
Grain size	[mm]	1-2	1-2	0.63 -2
Grain density ρ_s	[g/cm^3]	2.43	3.06	3.02
Bulk density ρ_d	[g/cm^3]	0.6	1.0	0.60
Filter bed porosity	[%]	75	69	80
Specific surface area (SSA)	[m^2/g]	143.9	64.7	320.8
Micropore surf. area	[m^2/g]	8.7	25	276.6
Micropore volume	[cm^3/g]	0.0031	0.0044	0.0983
Intraparticle porosity*	[%]	0.75	1.29	29.7

*intraparticle porosity = grain density * micropore volume

Table 2 Selected parameters of the As(III) or As(V) enriched tap water used in batch tests and the drainage water of an abandoned uranium mine (Ore Mountains, Germany) used in pilot scale column tests

parameter	pH [-]	TIC	SO₄	Ca	Mg [mg/L]	Fe	Si	As
Tap water	8.15	18.2	31.0	40.2	3.4	<0.1	1.9	(+10/ +20)
Drainage water	7.05	63.1	0.49	49.7	11.8	<0.1	10.0	0.85-1.8

Water

Two kinds of water were used in the study. For the investigation of the principal As adsorption behavior (adsorption capacities and kinetics), batch test series with As-enriched tap water were performed. The suitability of the new SHM adsorbents for practical water mine treatment was studied in two field site column test series at an abandoned uranium mining site (Ore Mountains, Eastern Germany) using drainage water. Table 2 summarizes the parameters of these waters.

Test methods

Batch tests In order to investigate the principal As adsorption behavior (adsorption capacities and kinetics) of the new SHM adsorbents, samples of SHM-SorpX and SHM-SorpP were prewashed to remove residual, superficially-adhered sulfate. The As uptake behavior was investigated in 250 mL glass bottles with screw caps at an initial As(III) and As(V) concentration of 10 and 20 mg/L tap water (quality mentioned in the pre-selection test section) as $Na_2HAsO_4*7H_2O$ p.a. and $NaAsO_2$ p.a., and an adsorbent mass of 0.5 g/L for an overall time of 24 days. Prior to the beginning of the experiments, the solution pH was adjusted to a value of 7.4 +/- 0.1 with diluted HCl. The bottles were gently shaken on a horizontal shaker at T= 22 ± 2°C. During the experiments, no pH buffering was done in order to simulate conditions of water treatment plants. Sampling of pH and As concentration was performed after 1, 3, 6, 11 hours and 1, 2, 4, 6, 10, 14 and 24 days. In order to compare the As(III) and As(V) adsorption capacities of both SHM-adsorbents with the iron hydroxide adsorbent Ferrosorp®Plus, parallel tests with 10 and 20 mg/L As(III) or As(V) and dose of 0,5 g/L of these adsorbents were performed and sampled after 1 hour and 14 days. As(III) experiments were carried out under nitrogen atmosphere in a glove box and the tap water used for the As(III) stock solution was degassed under vacuum.

Field site column tests Thanks to the support of WISMUT GmbH, two column test series could be performed directly at an abandoned uranium mining site. From these tests, the suitability of the new SHM adsorbents for passive mine water treatment systems could be investigated. Table 3 contains important data including trial periods, column dimensions and filter bed residence times. In the 1st column series, the column plant was placed directly at the outlet of the abandoned uranium mine (shaft G1), where the drainage contained about two-thirds arsenite (As(III)). Thereafter, the drainage flows through an aeration cascade and two sedimentation ponds and is decontaminated in a passive water treatment system subsequently (operated by the WISMUT GmbH). The residence time of the drainage water between the mine outlet and this treatment system is approximately 7 days, along the way As(III) is completely oxidized to As(V). Based on the results of the previous batch tests, where the SHM adsorbents offered better adsorption properties

for As(V), the column plant was placed directly at the inlet of the passive water treatment system (shaft G4B) for the 2nd column test series. Figure 4 shows the column set-up.

Table 3 Test parameters of the field site column test series

Test series	Location	Trial period	Dimension of the columns	C(As, influent)	Filter bed residence time
1	shaft G1	2012, sept.-dec. & 2013, may –sept.	D = 4 cm, L = 20 cm V_{column} = 251 cm^3	**ca. 1.8 mg/L:** 65% As(III), 28% As(V)	28 - 34 min
2	shaft G4B	2013, oct.- dec.	D = 3 cm, L = 14.5 cm V_{column}= 102 cm^3	**ca. 0.85 mg/L:** 100% As(V)	11 – 16 min

Sampling of each column influent and effluent were done three times a week, and ferrous iron and pH were estimated by a test kit. Arsenic was analysed by AAS (Perkin Elmer) after membrane filtration (0.2 μm Cellulose Acetate) and conservation by 1% HNO_3(c). The development of As-Species from shaft G1 to shaft G4B was investigated during a field campaign according to the method of (Le et al., 2000).

Figure 4 Field site column test design with a prefilter (sand column) and an admission pressure pump (left), the column test plant with effluent containers (middle) and the Plexiglas columns filled with adsorbents (right)

Dumping tests Dumping tests were performed to verify the long-term binding stability of SHM-sorpX and SHM-sorpP for arsenic. Therefore, the As-loaded SHM-adsorbents from the batch tests were tested under two "worst case" scenarios. (1) A rainwater elution scenario should represent a dumping site with an insufficient surface cover and (2) a groundwater elution scenario should simulate a dumping site without basic sealing. For the rainwater scenario, the SHM adsorbents were wetted by synthetic rainwater (pH 5, Ca: 0.6 mg/L, K, Na, NH_4, Mg: 0.3 mg/L, NO_3, SO_4: 2 mg/L, Cl: 0.5 mg/L) for 24 hours every 2 to 4 weeks. A non-contaminated mine water from Ehrenfriedersdorf (Ore Mountains, Eastern Germany) with pH 7.9, EC 445 μS/cm, SO_4: 102 mg/L, HCO_3^-: 47.3 mg/L, Si: 6,5 mg/L, Fe: < 0.1 mg/L and Mn: <0.1 mg/L was used for the groundwater

elution scenario respectively. In all tests, the water to adsorbent ratio was 1:10. The change of the equilibrium water phase and the subsequent As analysis (sample preparation and analytical method as mentioned above) were done every 2-4 weeks (in a total of 15 cycles) for an overall test time of 9.5 month (285 days).

RESULTS

Batch tests

Figure 5 shows the adsorption kinetic of As(III) and As(V) for both SHM-sorpX and SHM-sorpP. The amount of adsorbed As (q_t in mg/g adsorbent) was plotted against the square-root of the shaking time t (in days$^{0.5}$) in order to visualize different adsorption kinetic behaviours. According to (Weber & Morris, 1963), theses q_t-$t^{0.5}$-plots (with $q_t = k^* t^{0.5}$ and the slope/equilibrium rate constant k) show multi-linearity, if not only an external diffusion of the adsorbate (As(III) or As(V)) to the surface of the adsorbents, but also intraparticle diffusion controls the adsorption behaviour. The main part of As adsorption was controlled by external diffusion of As to the adsorbent surfaces and appears within the first two days of the experiments, Intra-particle diffusion of superficially adsorbed As into the meso- or micropores of the SHM adsorbents could be evidenced in minor parts by a second, significantly lower slope of each q_t-$t^{0.5}$ plot. SHM-sorpX shows a faster 'short-time' adsorption behavior for As(III) and As(V) (steeper slopes of the first parts of the q_t-$t^{0.5}$-plots), whereas SHM-sorpP takes over thereafter (during the 'long-time' adsorption, steeper slopes of the second parts of the q_t-$t^{0.5}$-plots), especially in the experiments with As(V). During the contact with water in the batch test, SHM-sorpP seems to form higher intraparticle porosity than SHM-sorpX, which could be very advantageous for a longtime use in filter bed systems. This can be attributed to the curing of the SHM-sorpX product by the binder addition.

Table 4 contains the As(III) and As(V) adsorption capacities for SHM-sorpX, SHM-sorpP and Ferrosorp®Plus after 1 hour and 14 days, respectively. Whereas the As(III) adsorption to both SHM adsorbents was slightly lower than that of Ferrosorp®Plus after 1 hour, SHM-sorpP and SHM-sorpX had adsorbed more As(III) than the iron hydroxide adsorbent after 14 days. In contrast to this, the As(V) adsorption to SHM-sorpP and SHM-sorpX was always significantly higher than that of the iron hydroxide adsorbent, even after 1 hour. This could be referred to a more positive surface charge of the SHM because of a proton release during its hydrolysis.
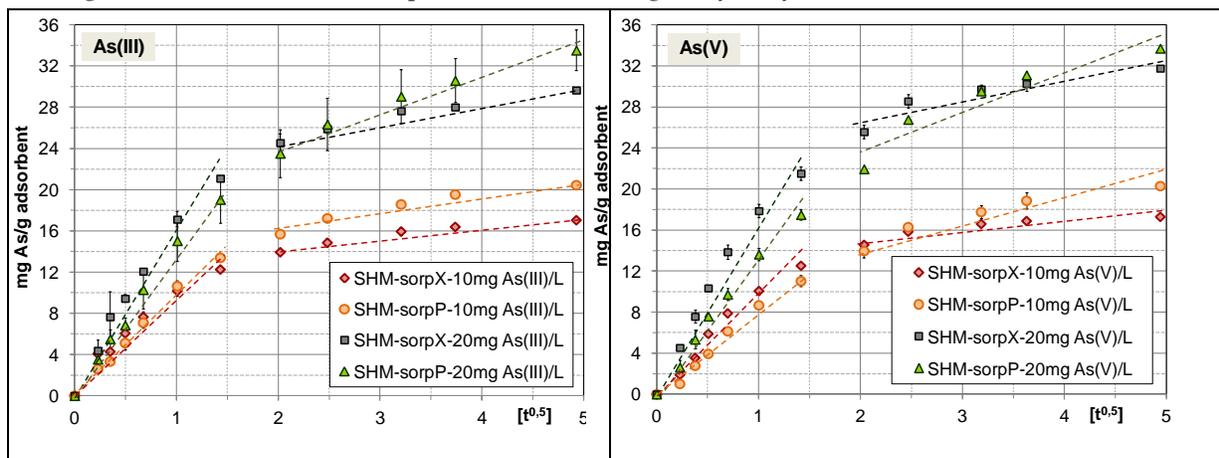
Figure 5 As adsorption kinetics of SHM-adsorbents, 0.5 g ads./L, pH$_{start}$: 7.4±0.1, no pH buffering during the tests

Field site column tests

In both test series, a significantly better performance could be demonstrated for the newly developed SHM adsorbents compared to Ferrosorp®Plus (Figure 6). Thereby, the higher bulk density of SHM-sorpP proved to be a major advantage. This allows 40% higher amounts of adsorbent in the filter beds and so their lifetimes can be increased greatly. In addition, it seems that the 'open' (in contrast to product SHM-sorpX not glued) surface structure allows a slight kinetic sorption (intraparticle diffusion), whereby initially superficial adsorbed arsenic is carried deeper into the granule structure and the surface adsorption area can receive new arsenic. The second series of experiments has been shown that the new SHM-adsorbents due to their, already in the laboratory tests (Tab.1) proven, better As (V) – adsorption kinetics have another big advantage compared to the adsorbent Ferrosorp®Plus. This enables much shorter residence times in the filter bed and the water flow rate could be increased significantly. Due to the beginning of the frost period, the test series 2 was completed by December 2013.

Table 4 As(III)- and As(V)- capacities estimated in batch tests with 0.5 g adsorbent/L and 20 mg As/L, pH_{Start}= 7,4±0,1 after 1 hour and 14 days (rather maximal adsorption capacities)

Adsorbent	after 1 hour		after 14 days	
	mg As(III)/g ($pH_{equilibrium}$)	mg As(V)/g ($pH_{equilibrium}$)	mg AsIII)/g ($pH_{equilibrium}$)	mg As(V)/g ($pH_{equilibrium}$)
SHM-sorpX	**4.4**±1.0 (pH 6.8)	**4.5**±0.7 (pH 6.9)	**28.0**±0.7 (pH 6.8)	**30.3**±0.2 (pH 6.8)
SHM-sorpP	**3.5**±0.4 (pH 7.0)	**2.6**±0.01 (pH 7.0)	**30.6**±2,1 (pH 6.6)	**31.1**±0.7 (pH 6.9)
Ferrosorp®Plus	**4.8**±0.1 (pH 7.6)	**1.6**±0.3 (pH 7.3)	**22.7**±0.4 (pH 8.2)	**18.0**±0.2 (pH 7.9)

Table 5 and 6 contain a summary of the characteristic parameters and the filter-bed volumes which could be exchanged up to the exceedance of the effluent limit concentration of 0.1 mg As/L. Because of the higher residence time in the 1st test series, the calculated, integral As loading of the adsorbents were in the same range. However, it should be considered, that the filter bed system with SHM-sorpP contained a 40% higher adsorbent mass. In the 2nd test series, the As loading of Ferrosorp®Plus was remarkably lower, and demonstrated its worse adsorption kinetic again.
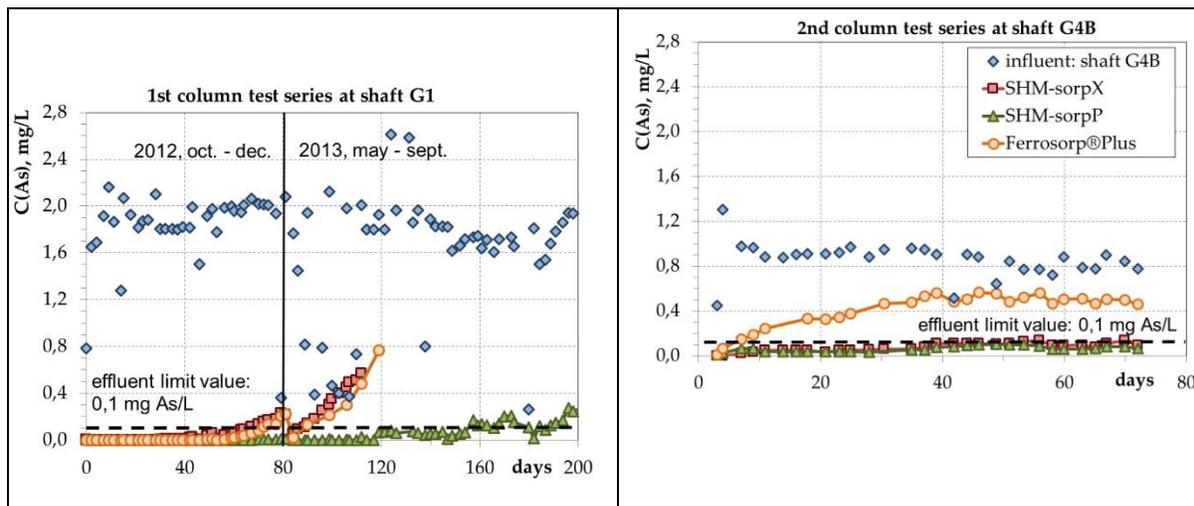
Figure 6 Development of As-concentrations in the column effluents of the 1st (left) and 2nd test series

Table 5 Summary of the 1st column test series at shaft G1

Adsorbent (mass)	Filter bed residence time	Filter bed volumes treated $C(As)_{effl}$ >0.1 mg/L	Total through put / test time at $C(As)_{effl}$ >0.1 mg/L	Calculated As adsorp. capacity at $C(As)_{effl}$ >0.1 mg/L
Ferrosorp®Plus (153 g)	34 min	2,784	501 L/ 72 d	6.1 mg As/g Ads.
SHM-sorpX (177 g)	32 min	3,633	654 L/ 90 d	6.1 mg As/g Ads.
SHM-sorpP (304 g)	28 min	6,389	1214 L/ 157 d	6.9 mg As/g Ads.

Table 6 Summary of the 2nd column test series at shaft G4B

Adsorbent (mass)	Filter bed residence time	Filter bed volumes treated $C(As)_{effl}$ >0.1 mg/L	Total through put / test time at $C(As)_{effl}$ >0.1 mg/L	Calculated As adsorp. capacity at $C(As)_{effl}$ >0.1 mg/L
Ferrosorp®Plus (73 g)	15.6 min	549	44 L/ 7 d	0.5 mg As/g Ads.
SHM-sorpX (66 g)	13.2 min	4,418	353 L/ 39 d	4.7 mg As/g Ads.
SHM-sorpP (118 g)	11.4 min	5,966	418 L/ 49 d	2.9 mg As/g Ads.

After the end of both column test series, the As-loaded SHM adsorbents were also analyzed by aqua regia digestion for their arsenic content in the inlet and outlet areas of the columns (Table 7). The results show, that the As adsorption capacities of the SHM adsorbents have not been fully exhausted compared to the values reached in the batch tests. If a series connection of two columns

will be used, As adsorption capacity up to 20 mg As/g should be achievable in the entire first column.

Table 7 As content of the SHM adsorbents after the end of the column tests

Column	SHM-sorpP		SHM-sorpX	
	inlet area	outlet area	inlet area	outlet area
Series 1	20.3 mg As /g	5.1 mg As/g	16.4 mg As/g	4.2 mg As/g
Series 2	8.4 mg As/g	1.7 mg As/g	13.4 mg As/g	2.8 mg As/g

Dumping tests

Sequential elution tests with groundwater and synthetic rainwater were performed with As loaded SHM adsorbents from the As(III) adsorption kinetic tests. Between 0.13% and 0.6% of the adsorbed As were desorbed by a total of 15 cycles of alternating wetting with rainwater and subsequent drying (Table 8). Leaching of As by continuous elution with groundwater for 285 days was not significant (0.03 % of the initial value). After one elution cycle, the concentration limit of 2.5 mg/L of dumping class DKIII (German DepVerwV, 2005) was not exceeded in any case of dumping. This assessment demonstrates that dumping of As-contaminated SHM adsorbents would be tolerable according to German dumping classes even under worst case conditions like a dumping site without an intact surface or bottom sealing and no additional treatment of the SHM adsorbents for immobilisation purpose is necessary.

Table 8 Desorption of As from SHM-adsorbents

Adsorbent	SHM-sorpX	SHM-sorpP	SHM-sorpX	SHM-sorpP
C(As, adsorbed)	32.8 mg/g	31.5 mg/g	32.8 mg/g	31.5 mg/g
Elution procedure	**Alternating rainwater elution (pH 5)**		**Continuous groundwater elution (pH 7)**	
Total As eluated (15 cycles)	0.13 %	0.60%	0.03 %	0.03%
C(As, eluated, 1st cycle)	1.41 mg/L	1.87 mg/L	1.57 mg/L	0.72 mg/L

CONCLUSION

Schwertmannite, biotechnologically synthesized in a pilot plant for lignite mine water treatment, was used for the production of two filter stable adsorbents (grain size 1-2mm) in order to use them in passive treatment systems for As contaminated mine waters. The adsorbents were obtained by compaction and by mixing SHM with an organic polymer, respectively.

In batch tests series with both SHM-adsorbents and a commercially-available iron hydroxide adsorbent (Ferrosorp®Plus, HeGo Biotec GmbH) as well as tap water enriched with 20 mg/L As(III) or As(V), 28.0 to 31.1 mg As/g SHM-adsorbents and 22.7 to 18.0 mg As/g Ferrosorp®Plus were estimated after 24 days equilibrium time, respectively. Thereafter, two column test series were performed directly at an abandoned uranium mining site with drainage water. Because of its worse adsorption kinetic, the effluent limit value of 0.1 mg As/L was exceeded in the Ferrosorp®Plus column significantly earlier than in the columns filled with SHM-adsorbents. Thereby, the

compacted product SHM-sorpP showed a better long time effect due to its 40% higher bulk density. In dumping tests with As loaded SHM adsorbents and alternating rain water (pH 5) and continuous groundwater elution (pH 7) elution, only 0.13 – 0.6% and 0.03% of the adsorbed As were desorbed into 285 days, respectively.

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