

## Treatment of Seepage Water from a Tailings Pond of Uranium Mining: Column Tests with a Novel Schwertmannite Adsorbent

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### Abstract

Based on biotechnologically synthesized schwertmannite (SHM) from iron and sulfate containing lignite mine water, the agglomerated, filter-stable adsorbent ‘SHM-sorpP’ was developed by compacting SHM in a briquette press (Peiffer et al., 2012; Janneck et al., 2014). As investigated by Fukushi et al. (2003), Regenspurg and Peiffer (2005), and Schroth and Parnell (2005), schwertmannite offers excellent adsorption properties towards arsenic.

Building on several laboratory test regarding the suitability of the new adsorbent for the removal of arsenic from water (Peiffer et al. 2012), SHM-sorpP was tested in this study in comparison to the commercially available iron hydroxide adsorbents Ferrosorp®Plus (HeGoBiotec GmbH) and GEH®104 (GEH Wasserchemie & Co KG) with regard to its suitability for the treatment of seepage water from an uranium tailings pond in column tests. The seepage water was characterized by high pH (8.7–8.9) and significant concentrations of arsenate, molybdate, and phosphate. For the tests, a water pretreatment was realized by decreasing its pH to 7 (pH 7 scenario) and pH 5 (pH 5 scenario) with a dosage of hydrochloric acid (33%), respectively.

In the pH 7 scenario (columns with each of the three adsorbents) no molybdate could be adsorbed by Ferrosorp®Plus, GEH®104, and SHM-sorpP. In contrast, all adsorbents were able to immobilize more or less arsenate and phosphate with SHM-sorpP offering the most efficient adsorption. In the pH 5 scenario (columns with SHM-sorpP and Ferrosorp®Plus each), SHM-sorpP again offered the better performance in the tests: in comparison to Ferrosorp®Plus, about 30% more arsenate and phosphate as well as 100% more molybdate could be adsorbed.

Key words: Schwertmannite, Water Treatment, Seepage Water of a Tailings Pond, Uranium Mining

### Introduction

A pilot plant for microbiologically mediated ferrous iron oxidation is operated by the Vattenfall Europe Mining AG and G.E.O.S. company 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) for the treatment of iron and sulphate rich mine water from the Nochten pit.

In the framework of a research project funded by the German Ministry of Education and Research (Peiffer et.al., 2012), two methods for the production of agglomerated adsorbents based on the ‘byproduct’ schwertmannite from the Nochten pilot plant were developed for their utilization in passive water treatment systems. The adsorbent ‘SHM-sorpP’ was obtained by compacting SHM in a briquette press, the adsorbent ‘SHM-sorpX’ by curing with an organic polymer (Janneck et al., 2014).

As investigated by Fukushi et al. (2003), Regenspurg and Peiffer (2005), and Schroth and Parnell (2005), schwertmannite offers excellent adsorption properties towards arsenic. Based on this knowledge, batch and small scaled column tests regarding the suitability of the new SHM adsorbents for the removal of arsenic from water were successfully performed (Peiffer et al., 2012). In continuation to the laboratory tests and with the kind support of Wismut GmbH (Chemnitz, Germany), columns filled with SHM-sorpP and two commercially available iron hydroxide adsorbents, respectively, were operated in the

bypass of a treatment plant for seepage water from an uranium tailings pond. In this pilot test, which was part of the ongoing research project ‘SAWA’ and funded by the Federal Ministry of Education and Research (FKZ 02WQ1309), the adsorption potentials of the new Schwertmannite adsorbent to arsenate as well as the structurally similar oxoanions molybdate and phosphate were investigated under real conditions. This study presents selected results of the pilot test.

**Methods**

Our pilot test could be realized on the location of an active water treatment plant of Wismut GmbH (Chemnitz, Germany) which supported the experiments significantly, especially by the ICP-OES analysis of As and Mo concentrations in influent and effluent water samples. In the water treatment plant (WTP), an alkaline **seepage water** (pH 8.7 -8.9, see table 1 for characteristic components) of an uranium tailings pond in Saxony (Germany) is purified. Officially authorized discharge limit values of the WTP are 0.3 mg As/L and 0.5 mg U/L. Phosphate was analyzed in the laboratory of the Institute for groundwater Management by an UV-VIS spectrometer Lambda 10 (Perkin Elmer). The measurement of pH-values was done on-site by a pH meter 323 and pH probe SenTix41 (WTW).

*Table 1 Concentration (C) range of characteristic parameters of the seepage water used as influent water for the pilot test*

parameter	TOC	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Fe <sup>2+</sup>	As	Mo	PO <sub>4</sub> <sup>3-</sup>	U
C(mg/L)	10-22	≈ 1000	≈ 1900	≈ 30	≈ 50	<0,01	1-1.3	1-1.3	3-5	7-10

By use of a total of ten columns (figure 1, each 3 cm in diameter and 15 cm in length, total column volume V= 106 cm<sup>3</sup>), the new **adsorbent SHM-sorpP** was investigated in comparison to the commercially available **iron hydroxide adsorbents Ferrosorp®Plus** (HeGoBiotec GmbH) and **GEH®104** (GEH Wasserchemie & Co KG) with regard to their suitability for the treatment of the seepage water described above. SHM-sorpP was produced by a briquette press. As shown in table 2, the three adsorbents differ considerably in their bulk densities and therewith their filter bed porosities.

*Table 2 Filter bed parameters of adsorbents used in the pilot test (grain size 0.63-2mm)*

adsorbent		SHM-sorpP	GEH®104	Ferrosorp®Plus
bulk density $\rho_d$	(g/cm <sup>3</sup> )	0.78	1.15	0.47
grain density $\rho_s$	(g/cm <sup>3</sup> )	2.81	2.96	3.02
filter bed porosity $n$	(%)	72	61	84
filter bed volume $BV = n \cdot V$	(cm <sup>3</sup> )	76	65	89
adsorbent weight/ column $m$	(g)	99	157	59



**Figure 1** Adsorbent SHM-sorpP



**Figure 2** Columns of the pilot test



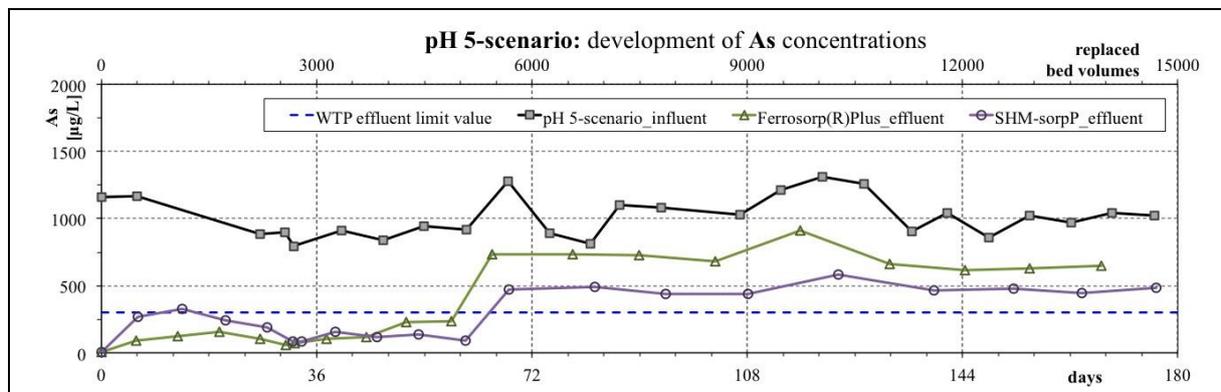
**Figure 3** Pilot test setup: influent 200L-influent barrels, columns, peristaltic pump and effluent canisters

In two pilot test scenarios, a pretreatment of the seepage water was realized by decreasing its pH by hydrochloric acid (33%) dosage to pH 7 (**'pH 7 scenario'**, each two columns with SHM-sorpP, Ferrosorp®Plus and GEH®104 in series) and pH 5 (**'pH 5 scenario'**, each two columns with SHM-sorpP and Ferrosorp®Plus in series). The flow rate  $Q$  was set to 7.7 to 8.1 l/d, resulting in a filter bed residence time of 16 to 20 min and 93 to 121 replaced bed volumes (RVB) of the filter bed per day.

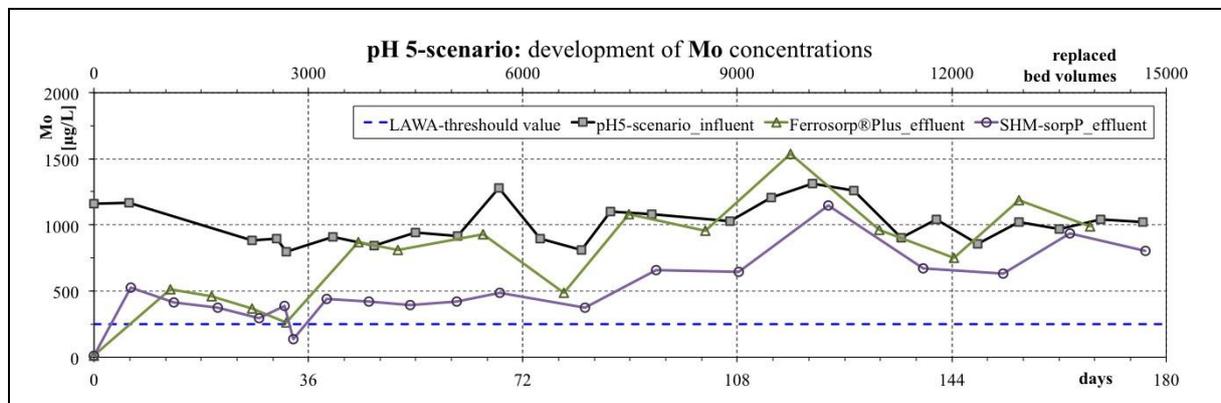
**Results**

Figures 4 and 5 show the breakthrough of As and Mo in the column effluents of the pH 5 scenario. SHM-sorpP retained both oxoanions significantly better than Ferrosorp®Plus. The As discharge limit of the WTP (0.3 mg/L) was exceeded after 60 days (about 5000 RVB) and 66 days (about 5500 RBV) for Ferrosorp®Plus and SHM-sorpP, respectively. At the end of the pilot test (after 176 days), about 10% of the influent As concentration could still be immobilized in the column filled with Ferrosorp®Plus, but only 3% of influent Mo. SHM-sorpP still adsorbed about 30 % of the influent As concentration and about 22% of the influent Mo concentration at this time. The breakthrough behaviour of PO<sub>4</sub> (data not shown) was similar to As (about 10% and 28 % of the influent PO<sub>4</sub> were retained in the Ferrosorp®Plus and the SHM-sorpP column at day 176, respectively).

In the pH 7 scenario no molybdate could be adsorbed by Ferrosorp®Plus, GEH®104, and SHM-sorpP (data not shown). In contrast, all products were able to immobilize more or less arsenic (figure 6) and phosphate (data not shown). SHM-sorpP offers again the most efficient adsorption for As and PO<sub>4</sub>. The As discharge limit value of the WTP was exceeded after 28 days (about 2800 RBV), 37 days (about 3700 RBV) and 40 days (about 4000 RBV) in the columns with Ferrosorp®Plus, SHM-sorpP, and GEH®104, respectively. At the end of the pH 7 scenario (after 81 days), about 10% of the influent As concentration could still be immobilized in the columns filled with Ferrosorp®Plus and SHM-sorpP. GEH®104 retained still about 22% of influent As. At a first glance, this might be the best As retention ability. However, the significant higher weight of GEH®104 in the column (see table 2) has to be kept in mind.



**Figure 4** Development of As concentrations in the first of each two columns filled with SHM-sorpP and Ferrosorp®Plus and seepage water pretreatment by lowering its pH from pH 8.8 to about pH 5 (pH 5 scenario: s)



**Figure 5** Development of Mo concentrations in the first of each two columns filled with SHM-sorpP and Ferrosorp®Plus and seepage water pretreatment by lowering its pH from pH 8.8 to about pH 5 (pH 5 scenario)

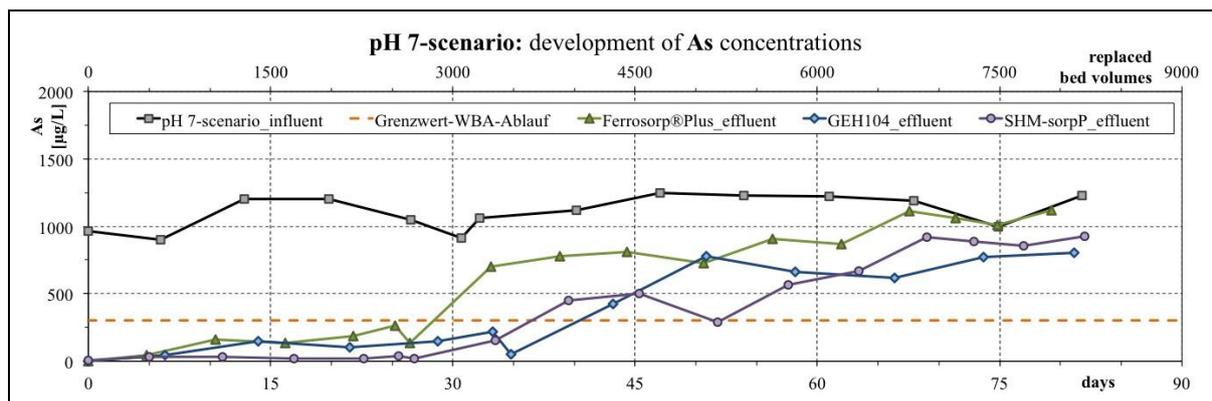


Figure 6 Development of As concentrations in the first of each two columns filled with SHM-sorpP and Ferrosorp®Plus and seepage water pretreatment by lowering its pH from pH 8.8 to about pH 7 (pH 7 scenario)

In order to make the oxoanion adsorption behaviour of the three investigated adsorbents comparable, the adsorbent loadings were calculated in mg/cm<sup>3</sup> by use of their bulk densities from table 2. The results are summarized in table 3, proving the excellent suitability of SHM-sorpP for passive filter bed systems in practice. A better adsorbent loading requires less replacements of the filter bed fillings.

Table 3 Cumulative loading of the investigated adsorbents with arsenate (As), molybdate (Mo) and phosphate (PO<sub>4</sub>) after 81 days (pH 7 scenario) and 176 days (pH 5 scenario), where influent concentrations were almost reached in the effluents of the first column of a double series. Adsorbent loadings in mg/cm<sup>3</sup> were calculated by adsorbent bulk densities from table 2.

scenario adsorbent	pH 7: oxoanion retention (mg/cm <sup>3</sup> )			pH 5: oxoanion retention (mg/cm <sup>3</sup> )		
	As	Mo	PO <sub>4</sub>	As	Mo	PO <sub>4</sub>
Ferosorp®Plus	3.0	<0.1	7.9	5.1	2.2	11.8
SHM-sorpP	4.9	<0.1	14.3	7.4	5.5	21.1
GEH®104	3.8	0.4	10.6	not investigated		

### Conclusions

In order to compare the adsorption ability of the new Schwertmannite-based adsorbent ‘SHM-sorpP’ and the commercially available iron hydroxide adsorbents Ferrosorp®Plus and GEH®104 with regard to the oxoanions arsenate, molybdate and phosphate under real conditions, a pilot test with two pH scenarios (pH 7 and pH 5) was performed. This the pilot test was friendly supported by Wismut GmbH via providing basic seepage water from a tailings pond of uranium mining (pH 8.7-8.9), the test facility and oxoanion analysis.

In the pH 5 scenario, the retention of the oxoanions As, Mo, and PO<sub>4</sub> was significantly better than in the pH 7 scenario, whereas SHM-sorpP offers the best adsorption ability for all three oxoanions. However, a pretreatment of the seepage water by lowering the pH with hydrochloric acid is a significant cost factor. A cost comparison resulted in a compensation of the additional hydrochloric acid costs (pH 5: 0.20 € versus pH 7: 0.05 € per m<sup>3</sup> seepage water) already by the better retention of arsenate.

For a practical application, clogging of the filter bed systems by secondary precipitates or CO<sub>2</sub> should be prevented by further pretreatment of the seepage water in a column packed with gravel (pH 7 scenario) and by stripping of CO<sub>2</sub> (pH 5 scenario), respectively.

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