Introduction

G.E.O.S Ingenieurgesellschaft mbH developed an innovative treatment technology for mine water from lignite mines. This technology was tested in a pilot plant (Janneck et al. 2010). In contrast to conventional lignite mine water treatment the new technology needs lower quantities of neutralizing agents and produces good drainable residues. By means of microbial catalyzed ferrous iron oxidation and subsequent Fe(III)-hydrolysis the pH in the water falls to approximately pH 3, whereupon the secondary mineral Schwertmannite (SHM) (Fe₈O₈(OH)₆SO₄) is precipitated. The transfer of the technology into mine water treatment practice requires initially an utilization concept for the residue Schwertmannite.

Schwertmannite, which was found in Acid Mine drainage (Bigham et al. 1996) and well known as effective arsenic sink/absorber (see Schroth and Parnell, 2005, Acero et al., 2006 und Regenspurg et al. 2004). In water with higher acid binding capacity it will be transformed into ferric hydroxide. Ferric hydroxide provides a high specific surface for adsorption of contaminants (e.g. Cornell & Schwertmann 2003). Besides, at Schwertmannite conversion (see equation 1) 12 times less acid will be generated than at dissolution of synthetically produced ferric hydroxide (equation 2).

\[
0.125 \text{Fe}_8\text{O}_8\text{(OH)}_6\text{SO}_4 + 1.25 \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 0.125 \text{SO}_4^{2-} + 0.25 \text{H}^+ \quad (1)
\]

\[
\text{FeCl}_3 + 3 \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 3 \text{Cl}^- + 3 \text{H}^+ \quad (2)
\]

Figure 1 Biotechnologically produced Schwertmannite sample.
are listed. The influent flow is characterized by high HCO₃⁻ concentrations, whereby the simultaneously existing uranium is predominantly available in form of poor absorbable UO₂(CO₃)₂²⁻ complexes. Therefore the water for the pilot test plant was taken after the decarbonising step of the WTP. Then the water was to a large extent decarbonised, charged with BaCl₂ for radium precipitation and had a pH of approx. 3.

**Design of the pilot plant**
The pilot plant is shown in Figures 2 and 3. In the reaction tank simultaneously SHM suspension and lime milk were filled. After this flocculation/precipitation and sludge removal by baffle plate thickener took place. For some tests lignite filter ash (LFA)-suspension was used as alternative neutralization agent. The test of the technology was carried out in form of test runs over a duration of one to two weeks in continuous operation with a flow rate of 1 m³/hr. The pilot plant was operated in bypass to the water treatment plant. Samples were taken two to three times per day from influent flow and discharge of the pilot plant.

**Results**

**Optimisation of the Schwertmannite dosing (PTR’s #0, #2 and #5)**
To proof the efficiency of the SHM dosing at first a blind test without SHM was carried out (PTR #0). This test demonstrates that the influent concentration of arsenic (0.68 – 0.97 mg/L) and uranium (1.70 – 1.74 mg/L) couldn’t be reduced to the normal discharge values of the water treatment plant (0.1 mg As/L and 0.2 mg U/L, for reason of reliability this „normal“ discharge values are lower as the legal effluent limits mentioned in the abstract. The results of the test runs were compared with

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**Table 1** Average values of the influent flow into WBA Schlema-Alberoda (sampling point mF-510, sampling November 2010).

<table>
<thead>
<tr>
<th>pH</th>
<th>Eₗ (mV)</th>
<th>SO₄ (mg/L)</th>
<th>HCO₃⁻ (mg/L)</th>
<th>Fe (mg/L)</th>
<th>Mn (mg/L)</th>
<th>U (mg/L)</th>
<th>As (mg/L)</th>
<th>²²⁶Ra (mBq/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.9</td>
<td>204</td>
<td>717</td>
<td>608</td>
<td>4.24</td>
<td>2.63</td>
<td>1.90</td>
<td>0.92</td>
<td>1793</td>
</tr>
</tbody>
</table>
these normal discharge values.) by oxidation of Fe(II) (approx. 5.5 mg/L), which is contained in the mine water, and its subsequent precipitation as iron hydroxide. In the pilot test discharge arsenic concentrations of 0.19 – 0.24 mg/L and uranium concentrations of 0.48 – 0.55 mg/L were analysed.

The pre treatment of SHM in PTR #2 (Figure 4) appears to effect a more efficient arsenic and uranium removal than dosing of unbuffered SHM (Figure 5). However, it must be kept in mind, that pre tratment of SHM requires additional lime milk addition. Therewith, in the reaction tank more calcium is available for calcium-uranate precipitation; but it results in higher sludge volumes. In PTR #5 the normal arsenic discharge values of the water treatment plant were mostly met. By suspending dry SHM in PTR #6 instead of filter-moist SHM higher contaminant removal couldn’t be reached. During the runs PTR #1 - #6 the minimum SHM dose for keeping the normal arsenic and uranium discharge values was determined to be approx. 20 – 25 mg SHM-Fe/L.

Table 2 Overview over the SURFTRAP test runs.

<table>
<thead>
<tr>
<th># PTR</th>
<th>Duration (d)</th>
<th>Average flow rate (m³/h)</th>
<th>SHM-sample</th>
<th>SHM-quality</th>
<th>SHM-Dosing (mg Fe/L)</th>
<th>Neutralisation agent/ additional agents</th>
</tr>
</thead>
<tbody>
<tr>
<td>#0</td>
<td>1.2</td>
<td>1.0</td>
<td>none</td>
<td>none</td>
<td>0</td>
<td>Lime milk</td>
</tr>
<tr>
<td>#1</td>
<td>2.2</td>
<td>0.8</td>
<td>S2-013</td>
<td>pre treated</td>
<td>48</td>
<td>Lime milk</td>
</tr>
<tr>
<td>#2</td>
<td>3.3</td>
<td>0.9</td>
<td>S2-013</td>
<td>pre treated</td>
<td>25</td>
<td>Lime milk</td>
</tr>
<tr>
<td>#3</td>
<td>4.0</td>
<td>0.9</td>
<td>S2-013</td>
<td>filter-moist</td>
<td>21</td>
<td>Lime milk</td>
</tr>
<tr>
<td>#4</td>
<td>2.3</td>
<td>0.9</td>
<td>S2-015</td>
<td>filter-moist</td>
<td>0.5 - 36</td>
<td>Lime milk</td>
</tr>
<tr>
<td>#5</td>
<td>7.1</td>
<td>0.8</td>
<td>S2-015</td>
<td>filter-moist</td>
<td>16</td>
<td>Lime milk</td>
</tr>
<tr>
<td>#6</td>
<td>8.0</td>
<td>0.9</td>
<td>S2-001</td>
<td>dry powder</td>
<td>18</td>
<td>Lime milk</td>
</tr>
<tr>
<td>#7</td>
<td>9.0</td>
<td>1.0</td>
<td>S2-013</td>
<td>filter-moist</td>
<td>25</td>
<td>LFA 5%</td>
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<tr>
<td>#8a</td>
<td>6.0</td>
<td>1.1</td>
<td>S2-015</td>
<td>filter-moist</td>
<td>19</td>
<td>LFA 2%</td>
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<tr>
<td>#8b</td>
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<td>1.0</td>
<td>S2-015</td>
<td>filter-moist</td>
<td>16</td>
<td>LFA 5%</td>
</tr>
<tr>
<td>#9</td>
<td>6.0</td>
<td>1.0</td>
<td>S2-015</td>
<td>filter-moist</td>
<td>27</td>
<td>lime milk/ KMnO4</td>
</tr>
</tbody>
</table>

1) Pre treatment of SHM with lime milk 2-3% and 1-day reaction time for SHM conversion to ferric hydroxide.

Figure 4 Development of arsenic (left) and uranium (right) concentrations in pilot test run #2 (SHM pre-transformed).

Figure 5 Development of arsenic (left) and uranium (right) concentrations in pilot test run #5 (SHM original).
Use of lignite filter ash (LFA) as neutralisation agent (PTR’s #7 and #8)

Because of positive results from laboratory tests in run #7 a 5% LFA-suspension was used for influent water neutralisation instead of lime milk. As shown in Figure 6 the arsenic discharge value exceeded the value of 0.1 mg/L in the second third of the test run. LFA dosing disturbances in the first and last third of the test resulted in discontinuous pH buffering correlating with higher arsenic discharge values. Uranium removal was significant lower than in PTR’s #1 - #6.

In PTR #8a and #8b the effect of 2 percent and 5 percent LFA suspension were compared with each other, and its part in the As, U and $^{226}$Ra removal (Figure 7) was analysed. During PTR #8 less arsenic was immobilised (average value 0.42 mg As/L) than in preceding runs, but the SHM dosing was comparatively low too (16 – 19 mg SHM-Fe/L).

Likewise the uranium removal (average 1.21 mg/L) was lower than in PTR’s #1 - #6; but uranium removal was higher by dosing 2 percent LFA suspension than by 5 percent LFA solution. In Figure 7 furthermore the $^{226}$Ra removal is shown. About one third of radium could be removed from the influent water; no significant difference between the 2 percent and 5 percent LFA suspension could be found. The normal limit discharge values of the WTP for radium (400 g/L) couldn’t be met by solely dosing of LFA suspension. The LFA suspension demand was dependent on its concentration.

In PTR #8a demand of 110 g/L of 2 percent LFA solution was determined. Use of 5 percent LFA solution resulted in a demand of 130 g LFA/L. So the 2 percent suspension can be better (failure-free) dispensed as well as is more efficient. The pH-buffering effect of the LFA suspension is predominantly caused by the solution of the calcium IMWA 2011 Aachen, Germany”Mine Water – Managing the Challenges” Rüde, Freund & Wolkersdorfer (Editors)
and potassium phases during the longer reaction time in the preparation tank because the residence time of the process water in the pilot test plant is very short. If the equilibrium pH of the mineral phases (approx. pH 12) is reached in the preparation tank, than OH⁻-ions can be released no longer. This can explain that in the reaction tank no higher releases of OH⁻-ions can be found by addition of higher concentrated LFA solutions.

**Effect of KMnO₄-dosing on arsenic removal (PTR #9)**

More than 80% of the arsenic in the influent water of the WTP is existent in form of reduced As(III) species (Figure 8) because of the slightly reducing conditions. The lower arsenic concentration of 0.194 mg/L at the discharge of the pilot plant can be caused by arsenic adsorption to SHM and/or its conversion products. Because a XAFS analysis of sludge from PTR #5 showed the existence of pentavalent arsenic species in the residues, it is assumed, that during the process As(III)-oxidation with subsequent As(V)-adsorption take place. Therefore in PTR #9 KMnO₄ should be used to oxidize the characteristic residual arsenic content of the discharge water (0.1 - 0.2 mg/L) which is predominantly available as poor absorbable As(III) species (see Figure 8). As shown in Figure 9, the arsenic and uranium discharge values from the pilot plant were by KMnO₄ addition significantly less than the normal discharge values of the WTP.

**Conclusions**

Within the BMBF research project SURFTRAP a pilot scale test for removal of contaminants from mine water of an abandoned uranium mine was performed in a bypass of the water treatment plant Schlema-Alberoda of Wismut GmbH, where the conventional treatment reagent FeCl₃ was replaced by the residue Schwertmannite. The contribution of Schwertmannite to arsenic and uranium removal from mine water could be proved in several test runs. To comply with the normal arsenic and uranium discharge values of the WTP (approx. 0.1 mg As/L and 0.2 mg U/L) 20 – 25 mg Schwertmannite-iron per litre process water must be added. This is approximately twice the FeCl₃ amount used in the water treatment plant. In spite of higher dosage of SHM the residual sludge volumes are comparable to sludge from conventional treatment using FeCl₃ because SHM sludge shows better thickening behaviour.

The advantage of replacing FeCl₃ by Schwertmannite doesn’t only consist in lower reagent (residue) costs but in the lower lime milk demand required for neutralisation of the Schwertmannite hydrolysis (see equations 1 and 2). So the current lime milk dosage in the WTP (approx. 30 g CaO/m³ mine water) could be reduced by substitution of FeCl₃ by approximately 25%.

Additionally to the use of Schwertmannite in the test runs #7 and #8 a 2 percent and a 5 percent lignite filter ash solution instead of lime milk were tested for neutralisation of the process water. The lower concentrated lignite filter ash suspension was the most efficient solution and could be likewise dosed best. Besides, by use of ash about one third of the radium in the process water could be removed. So, the current BaCl₂ dose in the WTP

**Figure 8** Speciation of arsenic in the influent and the effluent of the pilot plant.

**Figure 9** Development of arsenic and uranium concentrations in pilot test run #9 (using KMnO₄ as oxidizer).
(25 g/m³) could be reduced by one third. However, the use of ash results in significantly higher sludge volumes. In the last test run it could be shown, that the remaining arsenic concentrations in the process water can be efficiently oxidized by addition of KMnO₄. Thus the arsenic and uranium concentration could be reduced to values much lower than the normal discharge values of the water treatment plant. Studies on the binding strength of As in the sludge and the need for sludge conditioning for disposal are still under investigation.

Acknowledgements
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References
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