A Laboratory Assessment of Uranium and Arsenic Removal Efficiency from Schneckenstein Uranium Tailing Leachates Using Scrap Iron

Clement Mbudi, Broder J. Merkel

Department of Hydrogeology, TU Bergakademie Freiberg, Gustav-Zeuner-Straße12, 09599 Freiberg/Germany, E-Mail: Mbudi@mailstud.tu-freiberg.de

The potential of scrap metallic iron to remove uranium and arsenic from Schneckenstein (Saxony, Germany) leachate was assessed using batch and columns reactors. Leachate used in the experiments was either the original collected at the tailing drainage outlet PNP9 or its upgraded version to higher arsenic and/or uranium concentrations. The pH was near neutral to alkaline. The scrap metallic iron range size less than 0.056 mm to 0.125 mm efficiently removes at least 90 % of uranium. The scrap metallic iron removes up to 95 % of both uranium and arsenic particularly at higher concentrations. At lower concentration, arsenic removal is poor. This apparent poor removal efficiency and discrepant behaviour of arsenic observed at lower concentrations might be more related to analytical measurements uncertainty rather than arsenic intrinsic properties.

---

1 Background

1.1 Motivation

Past and current mining activities have been and still considered to be the major source of harmful metals and metalloids in natural waters (AGRICOLA 1556). Metallurgical processing of uranium ores or even acid rain leaching of uranium tailings can dissolve uranium and arsenic containing minerals and hence liberate uranium and arsenic into receiving water bodies.

Uranium and arsenic are of a major concern for proponents in the mining and the environmental industries as well as for the general public due to the world wide awareness of their chemical toxicity. Their long-term stability in the environment is of much preoccupation. Also, considering the recent increase of the uranium price in the world market, it is expected that more uranium ores will be mined. Thus, the likelihood of much release of uranium and arsenic in natural waters is even higher in a foreseeable future. This threat is still real despite the current ecological-based mining practices and stringent environmental regulations that carry the potential of reducing the overall direct, indirect and cumulative environmental impact.

1.2 Uranium Tailings Schneckenstein

The Uranium Tailings Schneckenstein in the Erzgebirge mountain range, Vogtland region of Saxony, Germany, is one of those numerous dumps scattered mainly in the eastern part of the country. Back in 1506, mining in Schneckenstein first concerned minerals of tin and arsenic as well as pyrite. This activity quickly shifted to uranium after the discovery of uranium by Klaproth in the same region in 1789 and later of its strategic radioactivity by Pierre and Marie Curie. The mining in region had its apogee during the Soviets occupation and was terminated in the early 1960s. The Schneckenstein Uranium tailings cover 6 hectares for a total volume of 700,000 m^3. Although most uranium has been removed during the primary ore body processing, still the sandy to silty tailings are estimated to contain 387 and 1794 tons of uranium and arsenic respectively, prone to acid rain leaching. The total leachate has been estimated to 0.04 $L\ s^{-1}$ (MERKEL et al 1998) adding in 400—1500 $\mu g\ L^{-1}$ of dissolved uranium with a yearly load of 70 to 100 kg to receiving water bodies. Currently “do nothing” strategy that mainly relies on natural attenuation through dilution into receiving water bodies seems to be adopted. Besides, a small spontaneous wetland developed at the toe of the main tailings dam is reported to equally lower uranium and arsenic leachates up to 20 % (LANDGRAF et al. 2002).

Over the last decades, such legacy of past poorly managed mining related residual solid waste scattered throughout the world (USA, Canada, Congo DR, Brazil, South Africa, etc) have triggered studies designed to mitigate or remediate the resulting contaminated sites.

1.3 Mechanism of uranium and arsenic Fixation by Zero-Valent Iron (Fe^0)

Among the many passive technologies developed to remove inorganic contaminants in natural waters, reactive barrier filled with metallic iron is seen by many as the most promising. As an in situ fixation technique, a reactive barrier filled with metallic iron has the potential to remove metals from waters and stabilize them in soils (MA et al. 1993). This approach to metals immobilization, however, has a major drawback: the probability of the fixed metal going back into solution. Thus, two factors are worth of consideration (SING et al. 2001):

- the system must be effective under a variety of existing geochemical conditions and
- immobilized metals should be stable and remain nonleachable under varying environmental conditions.

Generally, the minimization of metals mobility and their transfer from solutions to solid surfaces involve a wide range of physical and bio-geochemical processes.

For uranium immobilization by Zero Valent Iron, there is to date no consensus on the responsible mechanism. Mechanisms most taught to control the process are reductive precipitation/Co-precipitation, adsorption or the combination of both. Reduction of U(VI) followed by precipitation of solids compounds such as UO_2 is claimed by most authors as the main mechanism controlling the fixation of uranium by Fe^0 (GU et al. 1998; ABDELOUAS et al. 1999). Others argue that sorption of uranium onto the surfaces of iron corrosion products is the main immobilization mechanism (BOSTICK et al. 1996; FIEDOR et al. 1998; NOUBACTEP et al. 2003).

The behaviour of arsenic in contact with iron corrosion products is also of much debate. Some authors favour the co-precipitation hypothesis of the reduced As (III) from As (V) by Zero-Valent Iron as the main mechanism of arsenic removal from groundwater (MCRAE et al. 1999). For others adsorption of both As (V) and As (III) in iron corrosion products or other pre-existent oxyhdroxides is the mechanism of arsenic removal in ground water, at least in near neutral to alkaline conditions (MALLANS et al. 2002).

Furthermore, many studies have reported evidence of uranium and arsenic respective removal by reactive-Zero Valent Iron passive mitigation technology. Yet some studies also mentioned discrepant behaviour of uranium and arsenic in contact with oxyhydroxides surfaces (SU & PULS 2001).

This paper investigates the removal efficiency of both uranium and arsenic from leachate originating from Schneckenstein Uranium Tailings using cheap scrap metallic iron. Scrap metallic Iron offers the advantage of being cheaper (40—50 Euro/ton) compared to the commercial ZVI (150—400 Euros) (DAHMKE et al. 2000). It also highlights on uranium behaviour under arsenic and iron influence.

2 Experimental Setting

2.1 Materials

2.1.1 Scrap Metallic Iron

The Scrap Metallic Iron used as Fe^0 was obtained from Metallaufbereitung Zwickau (MAZ) known as S69. The S69 contains 92.8 % Fe, 3.5 % C, 2.1 % Si, 0.9 % Mn and 0.7 % Mn (Noubactep et al. 2003). The raw scrap metallic iron (1—10 cm) was crushed and sieved as received without further treatment. The fraction less than 0.56 to 1.25 mm was used in all experiments

2.1.2 Quartz Sand

The quartz sand F32 from Quarzwerke (Frenchen, Germany) with an average grain size of 0,24 mm and a specific theoretical surface area of 102 $cm^2\ g^{-1}$ was used. It contains 99.7 % SiO_2, 0.2 % Al_2O_3, and 0.03 % $Fe_2 0_3$. XRD revealed 98.6±0.26% quartz and 1.4±0.26 % calcite.

2.1.3 Reagents and Solutions

All chemicals and reagents used throughout were of analytical grade and include uranyl nitrate 6-hydrate $UO_2(NO_3)_2.6H_20$ (Chemapol, Germany), Sodium Arsenate $Na_2HAsO_4.7H_20$, HCl 37 % (Baker, Germany). Arsenazo III (1,8-dihydroxynaphthalene-3,6-disulphonic acid-2,7-bis[(azo2)-phenylarsonic acid)] (Riedel-de-Häen, Germany) used as 0.15 % (m/v) aqueous solution, 200 mg of high purity Zn granules (Fluka, Germany), Ascorbic acid and oxalic acid both of Chemapol used as 1 g each in 100 ml water. Doubled distilled water of 0.6 µS cm^{-1} was used throughout as aqueous solvent.

2.2 Uranium and arsenic fixation

2.2.1 Batch fixation using glass test tube reaction vessels

In a 1/10 (weight/weight) solid to solution ratio, 25 ml capped glass test tube in duplicate were used to equilibrate 2 g of MAZ scrap metallic ion of grain size varying from 0.056 mm to 1.25 mm with 20 mL of Schneckenstein leachate for 36 hours. This leachate collected at a location coded PNP9 contained in mg L^{-1} 1.4 F^-, 7.5 Cl^-, 3.6 NO_3^-, 210 SO_4^-, 47 Na^+, 2.4 K^+, 45 Ca^{2+}, 13.4 Mg^{2+}, 0.05 Fe, 0.035 Mn, 0.09 Cu, 0.006 As, and 0.691 U. Also, in order to assess the influence of concentration of As on U and As behaviour, As concentration was increased in eight duplicated test tubes by adding 0.001 mM to 0.1 mM. For the latter, the same solid to solution ratio as above was used but with a grain size of 25 % (0.25 mm—0.5 mm) and 75 % (0.5 mm—0.8 mm).

2.2.2 Fixation using glass column reaction vessels

Three columns made of glass, 2.4 cm diameter, 40 cm height, glass wool filter within the top cap, and about 0.5 cm layer of granule silica beads at bottom. All three columns were covered with aluminium foil to minimize photochemical reactions known prone to affect iron containing systems:

- Column 1 contained sieved sand Frechen F32 washed with diluted (1:10) 65 % nitric acid and kept in for 24 hours, rinsed with deionised water and air-dried in laboratory settings.
- Columns 2 and 3 contents: Frechen F32 sand conditioned as in above column 1 but mixed as 90 wt% with 10 wt% crushed and sieved metallic iron from. The metallic iron fractions 0.5 mm—0.8 mm (75 %) and 0.25 mm—0.5 mm (25 %) were used.

The three columns were filled half with deionised water first and then respectively sand/mixture was poured in to minimize preferential flow path. This filling has resulted in an average porosity of 0.3 and a pore water volume of 65 mL. Several pore volumes of deionised water were thereafter pumped in from bottom to top. Meanwhile 25 g of tailings from the bottom part of a 5 m deep uranium tailing material from Schneckenstein was mixed with 250 ml 0.01 M glucose as $C_6H_{12}O_6.H_2O$ using a 500 ml Erlenmeyer placed in a horizontal shaker for 1 hour. Afterwards a 25 ml aliquot from a diluted 1:1000 supernatant of 0.01 M glucose was added in both columns from the top after removing the cap bearing glass wool filter. This step was followed by the pumping of several pore volumes of deionised water first and then by 0.01 M glucose for conditioning and flushing. A tracer test was performed using Cl. Again several volumes of deionised water and then 0.01 M glucose were pumped through the column. An influent solution obtained by upgrading the Schneckenstein leachate to 1/1 (uranium/arsenic) molar ratio with 0.05 mM uranium (11.9 mg L^{-1}) and 0,05 mM arsenic (3.7 mg L^{-1}) was continuously pumped in column 1 and 2. This water was mixed with a 0.001 M glucose solution through a Y connector at the same rate of 0.16 ml min^{-1}. In column 3, only the original Schneckenstein leachate without concentration upgrading was pumped throughout with the same rate.

2.3 Analytical Procedures

Samples collected at all columns designated outlets were filtered with a 0.2 µ filter (Schlecher & Schuell, Germany and Sartorius, Germany), preserved with 1/1 nitric acid and later cooled at 4 Celsius grad. They were analysed for uranium and arsenic.

Uranium was analysed by photometry using arsenazo III method. To 3 mL of water sample, two times 2 ml concentrated HCl and 200 mg Zn granule were added to reduce U (VI) to U (IV). The resulting reaction was followed after completion by adding 250 µl of oxalic-ascorbic acid solution, and 250 µl of arsenazo III. The absorbance was determined using a HACH UV-VIS spectrophotometer at a wavelength of 665 nm using 1 cm glass cells.

The determination of total arsenic was done with an Atomic Absorption Spectrometer Zeiss AAS 4 EA equipped with auto sampler and an arsenic electrodeless discharge lamp (EDL) operated at EDL current of 380 mV, wavelength: 193.7 nm, slit: 0.7 nm. Peak height was used for data processing of low absorbance while peak area for high absorbance. Both spectrometers were calibrated following a five point procedure. pH and Eh were measured with combined glass electrodes (WTW GmbH, Germany).

3 Results and Discussion

In all batch and column experiments, the removal efficiency REff is computed as REff= 100* [(C_0-C)/C_0] whereby C_0 stands for starting concentration of the contaminant whilst C is the concentration at the end of the 36 hours equilibration time. In all reported experiments, the initial pH was near neutral to alkaline. When near neutral, the pH increased to 8.5—11 at the end of the experiments. E_H conditions ranged from slightly oxidant to strongly reducing particularly in column 3.

3.1 The Influence of Scrap Metallic Iron Size

The reversed "S" shaped Figure 1 shows that at experimental conditions and assuming analytical related uncertainty kept minimal, uranium removal efficiency is scrap iron size dependent. The fraction 0.056—0.125 mm is the most efficient in removing more or less 90 % of uranium from the leachate while the fraction above 1.25 mm is the least.

This uranium removal trend highlights the role of the adsorbing scrap iron and resulting corrosion products' surface area on the control of the system. It also suggests a predominance of reductive adsorption mechanism over precipitation/co-precipitation as might be expected for a longer equilibration time span of several weeks. The importance of co-precipitation in the fixation of uranium by zero valent iron has been shown by NOUBACTEP et al. (2002) and NOUBACTEP et al. (2003).

Arsenic on the contrary do not exhibit any trend related to scrap metallic iron size. Overall its removal efficiency is poor (less than 40 %) particularly for the fraction size of 0.056—0.5 mm whilst uranium is far much more removed at the same conditions. This apparent discrepant behaviour with respect to scrap iron size as illustrated by Figure 2 do not fit with common knowledge on surface area influence on sorption phenomena. Reasons for this arsenic might be found in either higher uncertainty in its analytical determination or in arsenic intrinsic physico-chemical properties. For the latter, scrap metallic iron and corrosion products under experimental conditions might not to favour low arsenic

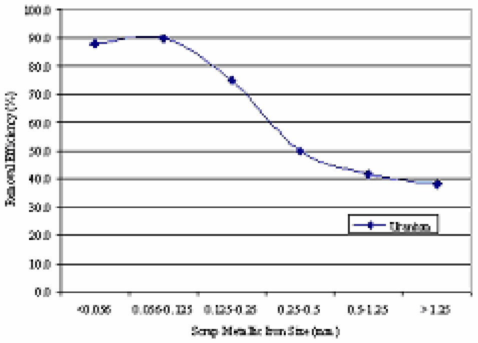

Figure 1: Influence of scrap metallic iron on removal efficiency of uranium from Schneckenstein PNP9 leachate at starting concentration C_0 of 691µg L^{-1}.

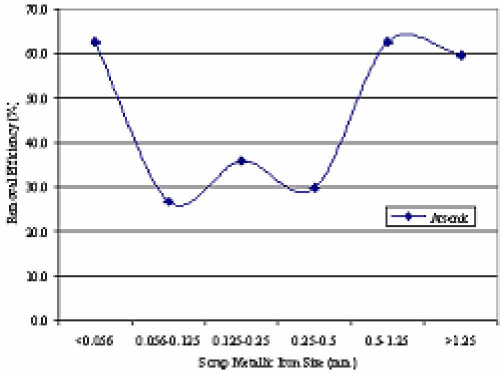

Figure 2: Removal of arsenic from Schneckenstein leachate as a function of scrap metallic iron size (initial arsenic concentration C_0 = 6µg L^{-1}).

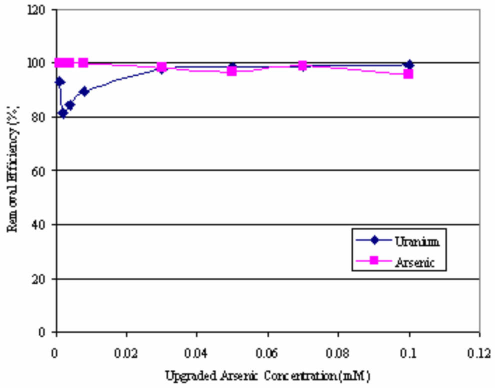

Figure 3: The influence of arsenic concentration on uranium and arsenic removal from upgraded Schneckenstein leachate.

concentrations to competing higher uranium concentrations.

Considering, however, the output of a related experiment shown in Figure 3, it is more likely that uncertainty in the analytical determination of arsenic is the main reason of the discrepancy. The starting arsenic concentration was in fact only 6µg L^{-1} whilst the AAS detection limit was 1µg L^{-1}.

3.2 The influence of arsenic concentration (batch system)

Figure 3 shows the influence of arsenic upgrade from 0.001 mM to 0.1mM (0.075—7.5 mg L^{-1}) on both uranium and total arsenic removals using scrap metallic fractional size made of 0.25—0.5 mm (25%) and 0.5—0.8 mm(75%). From around 0.04 mM of added arsenic, more than 95% of both uranium and arsenic are removed from solution contrary to what can be observed from Figures 1 and 2. Figure 3 suggests that at higher concentrations, the addition of arsenic above arsenic solubility limit breaks the system overall equilibrium. Thus, the system becomes prone to not only precipitation of arsenic alone but also co-precipitation of both uranium and arsenic starting around 0.04 mM uranium (9.5 mg L^{-1}) and arsenic (3 mg L^{-1}). Although such higher concentrations of uranium and arsenic have not been reported so far for the site, still the tailings have the potential to it (MERKEL et al. 1998; NAAMOUN 2002, GOTTSCHALK 1979). Also, preliminary results of ongoing leaching experiment of the tailings under both anoxic and oxic conditions suggest the possibility of higher uranium and arsenic concentrations. Whether such higher concentrations can be observed or not in situ is much related on factors that include the tailings buffering capacity of the acidic rain, the prevalence of run off or infiltration, the tailings porosity, and water-tailings contact time.

3.3 The influence of uranium and arsenic concentrations (dynamic system)

Figure 4 portrays the quasi efficient removal of uranium by zero valent iron and corrosion products whilst arsenic presents a discrepant and unpredictable behaviour.

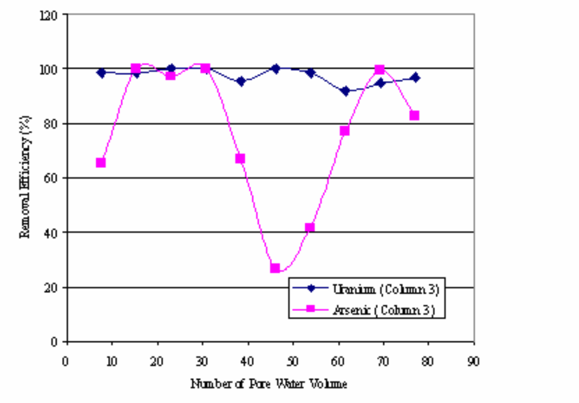

Figure 4: Uranium and arsenic removal from Schneckenstein leachate in a dynamic system.

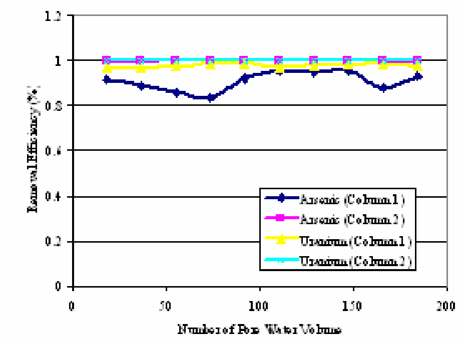

Figure 5: The influence of upgraded uranium and arsenic on their removal efficiency from Schneckenstein tailings.

For a total of about 77 pore water volume (5000 mL) eluted, more than 85 % of uranium was removed. The observed arsenic removal efficiency varies from as low as 20 % to more than 90 %. Reasons evoked above for the batch system to explain this unpredictable arsenic behaviour also applies in dynamic system under consideration.

Thus, under both batch and dynamic column experimental conditions, arsenic apparent inefficient removal seems much more likely related to analytical measurement uncertainties. As for the batch system, it might also be related to preference of uranium over arsenic by of adsorbing scrap metallic iron and corrosion product surfaces. Hence, zero valent iron might be inefficient to remove low concentration arsenic in a complex mine water matrix such as Schneckenstein leachate particularly when competing uranium is present in higher concentration.

As per batch experiments, up to 12000 mL of Schneckenstein PNP 9 drainage leachate upgraded to 0.05 mM U (11,9 mg L^{-1}) and equal molar amount of arsenic (3.75 mg L^{-1}) were pumped respectively in column 1 and 2 under experimental conditions described above. The idea behind the experimental set up was to evaluate natural attenuation potential for column 1 and the efficiency of zero valent iron in removing both uranium and arsenic for column 2.

The Schneckenstein uranium tailings seem to possess a good natural attenuation capacity as seems to suggest Figure 5. Above 80 % removal efficiency for both columns 1 and 2 that do respectively not contain and contain scrap metallic iron. Microbial activity in column 1 in particular may be the main control of this unexpected uranium and arsenic fixation in a only sandy column. Column 2 containing scrap metallic removes both uranium and iron at more than 95 %. This latter observation correlates well with similar batch experiment. Thus at higher concentrations of uranium and arsenic, uranium and arsenic combined removal is most likely controlled by precipitation and/or co-preciptation by scrap metallic iron corrosion products or/and both elements sparely soluble solid phases. This finding on uranium and arsenic behaviour at higher concentration connects with MALLANTS et al. (2002) and MCRAE et al. (1999) similar observations. MALLANTS et al. (1999) reported 99 % uranium removal when initial concentrations ranged between 2.4 and 24 mg L^{-1}. MCRAE et al (1999) described decreased arsenic concentration from 1 to less than 0.018 mg L^{-1} in a two hour period. They also reported on removal of as much as 15 mg L^{-1} total arsenic in groundwater from industrial and mine sites.

4 Conclusion

Cheap scrap metallic iron can be a good reactive barrier filling material for the removal of uranium and arsenic from drainage leachate produced by Schneckenstein uranium tailings. The material is particularly more efficient for higher concentrations (hundreds of µg L^{-1} to mg L^{-1}) of both uranium and arsenic where reductive precipitation or co-precipitation of newly formed and soluble minerals predominate. At lower concentration, particularly for arsenic, the material seems to show limitations. Whether this apparent limitation that seems to lead to the perception of discrepant behaviour of uranium and arsenic is related to analytical measurements uncertainty of arsenic or to differences in their intrinsic physico-chemical properties need to be clarified. To this end, further laboratory experiment for uranium and arsenic removal using Schneckenstein leachate with naturally lower concentrations of few hundreds of µg L^{-1} should be carried out. Better, up scaling the laboratory observations in situ through a pilot scale application with or without addition of carbon source such as glucose only can confirm apparent arsenic discrepant behaviour or the site natural attenuation potential.

Overall, a full scale application of scrap metallic iron reactive barrier as a supplement to the spontaneous natural wetland at the toe of the main tailing dam would be more cost effective compared to commercial Zero Valent Iron. This move could significantly reduce the yearly uranium and arsenic load into receiving water bodies.

5 Acknowledgements

We thank QuarzWerke GmbH for graciously donating and shipping 50 kg of quartz sand Frechen F32 of very good quality. Metallaufbereitung Zwickau (MAZ) Freiberg Branch is also acknowledged for providing scrap metallic iron. Thanks are also extended to Prof. Dr.Ing. Habil G. Schubert of the department of “Aufbereitungstechnik und Recycling”at the Technische Universität Bergakademie Freiberg for appraising and providing the right equipment to reduce the raw scrap metallic iron into the desired sizes.

6 References

AGRICOLA G. (1556): De Re Metallica. 1St edition.

BOSTICK D., JARABEK I., SLOVER A., FIEDOR N., FARREL J., HELFERICH R. (1996): Zero-Valent Iron and Metal Oxides for Removal of Soluble Regulated Metals in Contaminated Groundwater at a DOE Site. – U.S. Department of Energy K/TSO-35p; Oak Ridge, TN, pp 1—64.

DAHMKE A., EBERT M., KÖBER R., SCHÄRFER (2000): Konstruktion und Optimierung von passiven Geochemischen Barrieren zur in situ Sicherung CKW-kontaminiert Aquifere. – Unpublished BMBF Report, Mai, 229 pp.

MALLANTS D., DIELS L., BASTIAENS L., VOS J., MOORS H., WANG L., MAES N., VANDENHOVE H. (2002): Removal of Uranium and Arsenic from Groundwater using six different Reactive Materials: assessment of Removal Efficiency. – In: MERKEL B., PLANER-FRIEDRICH B., WOLKERSDORFER C. (Eds.) Uranium in the Aquatic Environment. – Proc. of the Intern. Conference Uranium Mining and Hydrogeology III and the Intern. Mine Water Association Symposium Freiberg, Germany, September 15-21, Springer, Berlin.

FIEDOR N., BOSTICK D., JARABEK J., FARREL J. (1998): Undestanding the Mechanism of Uranium Removal from Groundwater by Zero-Valent Iron using X-ray Photoelectron Spectroscopy. – Environ. Sci & Technol., **32**: 1466—1473.

GOTTSCHALK S. (1997): Hydrogeologische Untersuchungen am Uran-Tailing Schneckenstein. – Unpublished Diplomarbeit (MSc Thesis), Technische Universität Bergakademie Freiberg.

LANDGRAF A., PLANER-FRIEDRICH B., MERKEL B. (2002) Natural Attenuation in a Wetland under Unfavourable conditions-Uranium Tailings Schneckenstein/Germany. – In: MERKEL B., PLANER-FRIEDRICH B., WOLKERSDORFER C. (Eds.) Uranium in the Aquatic Environment. – Proc. of the Intern. Conference Uranium Mining and Hydrogeology III and the Intern. Mine Water Association Symposium Freiberg, Germany, September 15-21, Springer, Berlin.

MA Q.Y., TRAINA S.J., LOGAN T.J., RYAN J.A. (1993): In situ Pb immobilization by apatite. – Environ. Sci. Technol., **27**: 1803—1810.

MCRAE C.W.T., BLOWES D.W., PTACEK C.J. (1999): In Situ Removal of Arsenic from Groundwater Using Permeable Reactive Barrier: A Laboratory Study. – Sudbury' 99 "Mining and the Environment II" Conference, September 13-17, Sudbury, Ontario, pp 601—609.

MERKEL B., PREUßER R., NAAMOUN T., GOTTSCHALK S., KUTSCHKE S. (1998): Natural Leaching of Uranium from the Schneckenstein Uranium Mine Tailing. – In: MERKEL B., HELLING C. (Eds.) Uranium Mining and Hydrogeology II. – Proceedings of the International Conference and Workshop, Freiberg, Germany, Verlag Sven Von Loga, Köln.

NAAMOUN T. (2002): Hydrogeochemical and Radiochemical Investigation of the Uranium Tailings Schneckenstein. – Unpublished Dissertation, Technische Universität Bergakademie Freiberg.

NOUBACTEP C., MEINRATH G., VOLKE P., PETER H.J., DIETRICH P., MERKEL B. (2002): Mechanism of Uranium Fixation by Zero Valent Iron: The Importance of Co-precipitation. – In: MERKEL B., PLANER-FRIEDRICH B., WOLKERSDORFER C. (Eds.) Uranium in the Aquatic Environment. – Proc. of the Intern. Conference Uranium Mining and Hydrogeology III and the Intern. Mine Water Association Symposium Freiberg, Germany, September 15-21, Springer, Berlin.

Noubactep C., Meinrath G., Dietrich P., Merkel B. (2003): Mitigating Uranium in Groundwater: Prospects and Limitations. – Environ. Sci. Technol., **37**: 4304—4308.

SING S.P., MA L.Q., HARRIS W.G. (2001): Heavy Metal Interactions with Phosphatic Clay: Sorption and Desorption Behavior. – J. Environ. Qual., Vol. **30**: November-December.

SU C., PULS R. (2001): Arsenate and arsenite Removal by Zero valent Iron: Kinetics, Redox and transformation, and implication for in situ groundwater remediation. – Environ. Sci. & Technol., **35**: 1487—1492.