Assessment of uranium retention in wetlands: Characterisation of bonding strength, considerations regarding reductive precipitation

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Abstract

Data from uranium exploration indicate that uranium is frequently accumulated in wetlands in areas where uranium-rich rocks occur. This observation suggests that in wetlands, it might be possible to extract uranium from solutions as well as to immobilise uranium in organic-rich surficial wetland sediments. The objective of this project is to evaluate whether and how natural and constructed wetlands can be useful in removing uranium from mine water discharges at the former East German uranium mining district. Based on literature studies a main target was to investigate various abiotic and biotic processes in wetlands that act to immobilise uranium.

The major criterion for long term immobilisation of uranium in wetlands is the reduction of soluble U(VI) ions to fairly insoluble U(IV) species. Data on the required redox potential and the involved microbiological processes for uranium reduction are not unequivocal. Within this project predominant redox conditions in wetland sediments from East Germany were assessed through geochemical investigations, for example on the accumulation of iron monosulphide, pyrite and elemental sulphur. The association of uranium with different soil fractions was characterised by sequential extractions. On laboratory scale, uranium adsorption and reduction processes were investigated using artificial wetland substrates.

Current results showed that only a few of the investigated natural wetlands had a major influence on the transport of uranium to areas downstream. Thus, geochemical associations will give some indication of the parameters influencing the efficiency of uranium retention. These results

together with previous studies outlined from a literature survey, will enable relevant processes to be evaluated. The objective is to give recommendations on the construction of artificial wetlands for uranium remediation.

1   Introduction

Uranium bearing groundwater and seepage water is a well-known phenomenon in the environment of former uranium mining districts. These toxic discharges will be flushed out over long periods at low concentrations, therefore making water treatment expensive by means of conventional technologies. Alternatively, passive systems (e.g. permeable reactive barriers (PRB) and wetlands) for the removal of uranium from the water phase offer crucial advantages regarding costs and maintenance expenses. The term "wetland" is used for natural and artificial wet areas like bogs, swamps, fens, which are comparable to man-made reed beds for water purification. Various physical, chemical, and enzymatic processes (adsorption, reduction, precipitation) are capable of extracting uranium from the aqueous phase.

In natural aquatic systems uranium is stable as U(IV) or U(VI), depending on redox conditions. Under reducing conditions uranium exists as mainly insoluble U(IV) mineral phases. In contrast, oxidised hexavalent U(VI) species are highly soluble. They are transported as soluble uranyl ion (UO_2^{2+}), usually complexed with major anions like carbonates and phosphates. Reduction from U(VI) to U(IV) causes uranium precipitation as stable secondary minerals, which are not necessarily re-solubilised if oxidative conditions re-occur. Therefore, the main target mechanism for long term fixation of uranium in wetlands is reduction.

A literature survey indicates that uranium is frequently accumulated in wetlands in areas where uranium-rich rocks occur [e.g. IDIZ et al. 1986, OWEN & OTTON 1995]. This suggests that it is possible to effectively remove uranium from solutions in wetlands as well as to sustainably immobilise uranium in organic-rich surficial wetland sediments [BARNES & COCHRAN 1993]. Attempts to reproduce this phenomenon of accumulation in pilot plants (small constructed wetlands) were carried out in the USA, Australia [AKBER et al. 1992, NOLLER et al. 1994], and since 1995 also in Germany [GERTH et al. 2001].

This study aims to increase our understanding of the process of uranium fixation in natural wetlands by (1) characterising hydrogeological parameters (pH, E_H) in wetlands at the former uranium mining district of Wismut GmbH (East Germany), (2) collecting sediment samples at relevant sites

and characterising them with hydrogeochemical methods, and (3) discussing the results on the basis of findings from laboratory experiments and literature data. It is expected that the results of this study will go some way towards improving current treatment system design, and therefore efficacy of artificial wetlands for uranium remediation.

2   Wetland projects dealing with uranium

Geochemical processes which control the mobilisation and dissemination of uranium in the aquatic environment are outlined in numerous international research studies. In contrast, the general use of artificial wetlands was discussed only in a limited number of studies, which deal typically with the treatment of acid mine drainage. According to our knowledge, information on uranium immobilisation in artificial wetlands is published to a limited extent [e.g. SHINNERS 1996, DUSHENKOV 1997, VESELIC et al. 2002]. Generally, the majority of the published projects dealing with the topic "uranium accumulation in wetlands" focus on investigations of natural wetlands and/or wetland substrate, mainly in the context of geological deposits [e.g. OWEN & OTTON 1995] or repository research for spent fuel. The data show that uranium immobilisation in wetlands does work in principle, both with organic and inorganic wetland substrates. However, only assumptions are provided on the processes for uranium retention, since the relevant mechanisms were not investigated in more detail. Approximately a dozen projects concentrate on the construction of artificial wetlands for the treatment of complex metal loaded mine waters, including uranium. In brief, the long-term use of artificial wetlands for uranium retention has so far failed due to other factors such as high ammonia concentrations [VESELIC et al. 2002], or seriously decreasing efficacy of treatment due to unknown causes within few months. The processes which control the immobilisation of uranium are still not clear, particularly since this was not the focus of most of the studies performed.

3   Uranium accumulation in wetlands

The process of uranium accumulation in wetlands can be considered as analogous with that of ore enrichment in sedimentary type uranium deposits. In such deposits, U(VI) minerals like carnotite and tyuyamunite form, and U(IV) oxide minerals such as pitchblende ($UO_2:2UO_3$) and coffinite ($UO_2:SiO_2$) occur in the less oxidised areas. As uranium (IV) minerals are

relatively insoluble under reduced conditions, reductive precipitation of uranium minerals in wetland substrates could be a possible mechanism for eliminating uranium from mine water discharges, and for long-term fixing of the pollutant under anaerobic conditions. For effective uranium immobilisation the maintenance of reducing conditions within the wetland sediment is a matter of concern. Hence microbial mediated reduction of uranyl ions (U(VI)) may be very important [LOVLEY et al. 1991]. Regarding the necessary redox conditions for uranium reduction, contradictory statements can be found in literature. ABDELOUAS et al. [1998] describe uranium reduction parallel to manganese reduction. FRANCIS et al. [1994] assume manganese and iron reduction whereas DUFF et al. [1999] consider the beginning of uranium reduction noticable after mangenese and iron reduction. It remains to be determined whether chemical reduction of uranium is the significant immobilisation mechanism in natural uranium accumulating wetlands, and if so can this be applied as a model for designing artificial wetlands.

Adsorption by plants or inorganic substrates is also a significant mechanism for uranium retention in wetlands [e.g. DUFF et al. 1999]. Initial fixation of uranium may be due to adsorption, rather than due to reductive precipitation of uranium minerals [ZIELINSKI et al. 1987]. PAYNE et al. [1998] discuss the importance of factors such as pH, kinetics, organic components and solute concentrations for sorption. Although uranium sorption on wetland sediments may be very strong, it is not an irreversible process, so release of uranium must be expected.

4   Data assessment at natural wetlands

In the context of a doctoral thesis several uranium accumulating wetlands were sampled. They formed naturally in the reclamation area of the former East German uranium mining district of Wismut GmbH. More than 20 locations with natural wetlands within the vicinity of the former mining area Ronneburg were explored altogether. Ten of these wetlands were chosen for hydrogeochemical investigations. Analyses and laboratory tests of soil and water samples were used to evaluate the remediation potential of these wetlands for uranium. In summary, uranium is not enriched in the soil horizons of the investigated wetlands, compared to soil samples from the surrounding area. The observations and analyses indicate that no suitable environmental conditions could develop or had developed for removing uranium quantitatively from solution and fixing it in the wetland setting.

In the vicinities of the former uranium milling site at Seelingstaedt and Zwickau however, three organic-rich wetlands were explored, in which uranium had clearly accumulated since the beginning of the milling process approximately 40 to 50 years ago. At these three locations in Thuringia and Saxonia, hydrogeological surveying and sampling was performed to characterise the hydrogeochemistry and redox conditions of the sediment and water phases in detail. Furthermore, the wetland's influence on the groundwater was evaluated by means of quantifying uranium immobilisation.

4.1   Uranium distribution

From wetland soil and pore water analyses, depth profiles of the uranium distribution in three wetlands were determined and enrichment factors were calculated. In each case, the uranium outflow concentration is lower than the inflow concentration. Uranium contents of the wetland substrates were enriched up to 2000 times compared to pore water values. However, there is no obvious connection between uranium concentration and analysed organic carbon content (C_{org}), or redox potentials (E_H) measured in soils and pore waters. In two of the locations, the measured potential (E_H) suggests chemical reduction and precipitation. However, the highest soil uranium concentrations were found in horizons in which the measured redox potential does not permit reduction of uranium. Paradoxically, most uranium is also fixed in the wetland in which neither anaerobic nor anoxic conditions were present at the time of sampling. These contradictory observations could be explained in two ways: (1) the electrochemical E_H measurements are not reliable (see below), or (2) uranium was not immobilised in reduced form. In order to confine the environment conditions, extractions of inorganic sulphur (TRIS) were performed (see below). The results show that only small amounts of reduced sulphur were fixed in the wetland soils. That may indicate that microbiological sulphate reduction was not a dominant process in these wetlands. In order to reveal the main uranium immobilising mechanism (e.g. sorption or reduction), sequential extractions were carried out at sediment samples of the 22 investigated horizons, following the protocol of MILLER et al. [1986]. The data illustrate the association of uranium to particular soil fractions. The association of sulphur species and heavy metals in the individual extraction solutions are also investigated.

Regarding the vertical distribution of uranium in the investigated profiles, it is noticeable that the highest uranium concentrations occur in the upper 20 cm of the wetland soils independent of C_{org} content or macro-

scopic composition. Below that topmost horizont a decrease with up to 75 to 90 % is found, even though one wetland consists of homogeneous *Sphagnum spp.* moss up to 50 cm depth. That leads to the assumption that, between water and wetland soil, a contact zone of intensive exchange is limited to horizons close to the surface. The observed uranium enrichment may result from the implied flow pattern, seepage flowing through the uppermost decimetres of the wetland sediments. Similar observations at mining stockpile leachates were published by EGER et al. [1980], regarding the retention of nickel and copper in wetland sediments.

4.2   Hydrochemistry

With regard to assessed E_H values (electrochemical E_H measurements) and pH values, thermodynamic uranium reduction should have taken place in most of the investigated horizons. Equilibrium computations (PhreeqC) based on horizon-wise pore water analyses imply a supersaturation of oxidised and reduced uranium minerals for individual horizons. Further investigations with REM (scanning electron microscope + microprobe) and XPS (X-ray photoelectron spectroscopy), however, could not reveal positive findings, so with these methods uranium could not be proven to be present in any of the samples. The reason therefore may be that either the instrumental detection limit for uranium was not exceeded and/or the uranium precipitates were too small to be detected by means of REM. It may be possible that the precipitation of uranium minerals was kinetically impossible.

Correlation of uranium concentrations with pH values and possible sorptive ligands do not imply a dominant uranium association with special ligands.

4.3   Sulphur extraction (TRIS)

The mine water discharges flowing into the wetlands show high to very high sulphate concentrations. The redox conditions during sedimentation can be deduced from the proportions of different sulphur species. When compared to direct E_H measurement with redox electrodes, this indirect determination allows for the difficulties of electrochemical potential methods to be circumvented (e.g. duration of equilibrating). As a result of E_H measurements (combined glass electrodes, WTW Co., Germany),both in situ as well as freshly centrifuged pore water, it can be concluded that the determined redox potentials at the investigated wetlands do not correlate with C_{org} content, mineral phases, or redox couples in solution. It is therefore

assumed that, despite 20 minutes measuring period, in these environments no relevant E_H values are available from electrochemical potential measurements. This problem was also described by SCHULTE-EBBERT & HOFMANN [2000] after long-term redox measurements in anaerobic environments, as equilibrium still had not established after 60 hours of measuring time.

In order to determine the prevailing redox conditions in uranium containing wetlands from the former East German uranium mining districts more reliably, total reduced inorganic sulphur (TRIS) speciation in sediments from the wetlands were performed, and the association of sulphide sulphur and reduced heavy metal phases was investigated. The extraction method was developed after CANFIELD [1989], FOSSING & JØRGENSEN [1989] and HSIEH & YANG [1989] and was performed at the Centre for Environmental Research (UfZ) Magdeburg.

In summary, based on data from the sulphur extractions it can be concluded that conditions for sulphate reduction have not yet been established in the wetlands; this is important as uranium reduction occurs under similar conditions [LOVLEY & PHILLIPS 1992, BARNES & COCHRAN 1993, DUFF et al. 1999]. This observation along with the temporal variability of redox processes lead us to further conclude that uranium reduction has not been substantial in this environment so far.

5   Uranium co-precipitation with iron oxides

The mechanism of uranium uptake from aqueous phases by secondary iron minerals (oxides, hydroxides - iron corrosion products) was investigated with laboratory experiments. For this purpose, aqueous uranium solutions were allowed to react with a scrap iron (metallic iron - Fe^0). NOUBACTEP et al. [2002, 2003] had shown that under these conditions, aqueous uranium is fixed through co-precipitation with iron corrosion products. In this study, co-precipitation experiments were conducted for five months with 200 mg/L U and 16 g/L Fe^0. In some experiments, the co-precipitation was favoured by adding a pyrite mineral (FeS_2) to the system (system "Fe^0 + FeS_2"). Since FeS_2-addition considerably retards the process of co-precipitation of uranium [NOUBACTEP et al. 2003] with the corrosion products, it is expected that the crystallinity of the corrosion products will be sufficient for uranium detection by means of spectroscopic (XRD, XPS) and microscopic (REM) techniques.

First results show that XRD was not able to detect uranium in the mass of corrosion products, although calculations showed that corrosion prod-

ucts contained up to about 50 wt.-% uranium. These results suggest that uranium could be present in more complex natural samples, but may not be detectable by simple techniques.

6   Preliminary conclusions and further work

Based on field and laboratory investigations the following statements are possible:

- Adapted from preliminary computations, some pore water horizons of the investigated wetlands are, with regard to uranium, thermodynamically supersaturated.
- The wetland with lowest C_{org} content exhibits the smallest uranium enrichment. However, the highest uranium concentrations do not coincide with the horizons with the highest C_{org} contents. There is no evidence for correlation of C_{org} with uranium content in the investigated profiles. This may indicate that organic carbon does not play a crucial role for uranium retention. From sequential extractions (analysis data expected) it will be revealed to what extent uranium is associated with the organic soil fraction. Further investigations on differences in the organic substrates are planned.
- Uranium is mainly enriched in the upper 20 cm of the investigated wetland substrates. Possible causes (e.g. flow preferences, uranium enrichment by plant biomass, microbial settlement) are to be evaluated.
- Direct redox measurements in the investigated locations are not interpretable and supply paradox values compared to other physicochemical and mineralogical parameters obtained. Thus the redox environment is better characterised by combining results from inorganic sulphur extraction, sequential extraction and X-ray diffraction data (analyses data expected).
- In the wetland horizon, in which most uranium is fixed, uranium reduction is an enrichment process which can be excluded (O_2 content and indirectly determined redox environment). Physicochemical processes are more probable for the retention of uranium in peat horizons [e.g. IDIZ et al. 1986]. Additional statements will be possible from expected analyses data.
- From laboratory experiments on uranium removal (co-precipitation) through iron materials and subsequent remobilisation experiments it could be concluded that the uranium uptake from solutions in iron rich environments is reversible to some extent. Therefore, from iron rich dis-

charges a sustainable geochemical isolation of uranium in wetlands cannot be guaranteed.

7   Acknowledgments

8   References

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