

Uranium Migration in Argillaceous Sediments as Analogue for Transport Processes in the Far Field of Repositories (Heselbach Site, Germany)

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Abstract. Essential goal of investigations at Heselbach site has been, so far, to identify an U-accumulation at the eastern rim of Wackersdorf lignite basin - known from literature - and to check its suitability as natural analogue for transport processes in the overburden of a final repository for radioactive wastes. On the basis of at first four exploration drillings, located along a profile vertically to the basin rim, this task has been completed and a follow-on project has started.

Introduction

Long-term safety of underground repositories for radioactive wastes is based on a multi-barrier concept in which clay materials often play an important role as geological barriers. For performance assessment (PA) of those repositories it is essential to consider the potential mobility of critical radionuclides through relevant rock material under representative long-term conditions. Information on these time scales can only be obtained by studying natural occurrences of radioisotopes and trace elements.

The Heselbach site has been chosen, since its similar geological but different geochemical conditions (near surface, more oxidizing environment) are able to complete the results obtained at the Natural Analogue Site Ruprechtov, Czech Republic. The aim of the Natural Analogue Study in general is to understand and to quantify relevant geochemical and hydraulic processes at the site and to identify the mechanisms leading to transport and immobilisation of uranium, thorium and radium. After detailed characterization of the site, flow and transport models will be applied to describe the migration of these three elements at Heselbach site. Therefore this study intends to contribute to data acquisition and model testing for performance assessment (PA).

Geology

Heselbach site is located at the NE rim of Wackersdorf Tertiary lignite basin (30 km N of Regensburg, Bavaria), within a small E-oriented side-bay of former mining district ‘Wackersdorf Nord’ (Fig.1) (Brasser et al. 1998).

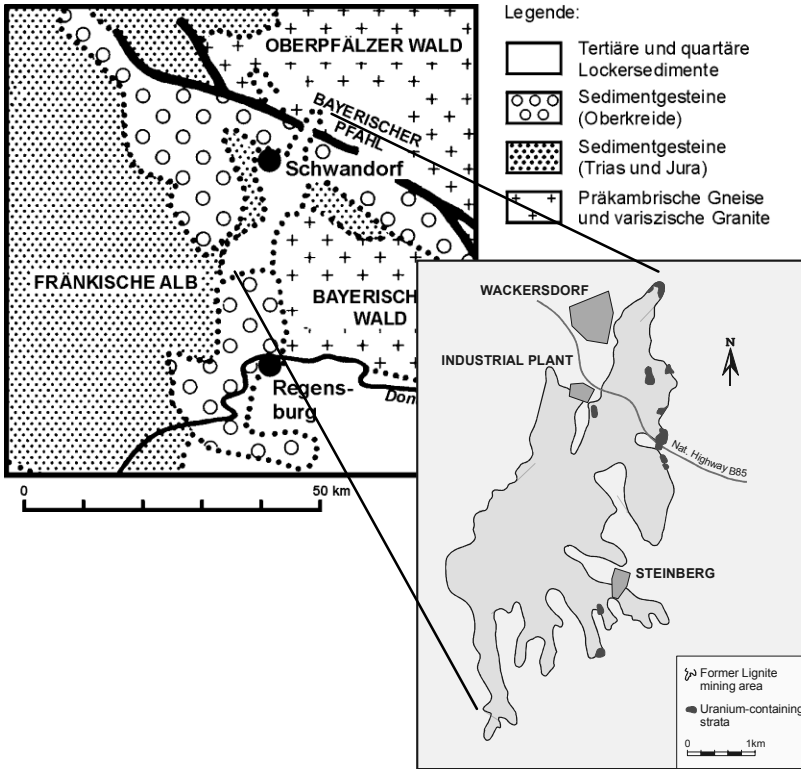


Fig. 1. Outline of geological situation of Oberpfalz region (left) and Wackersdorf lignite basin (right); project area is located at E-rim of basin, directly N of federal highway B85.

The actual research area comprises mainly three essential geological units which are also represented by core material received from drilling of four wells (Fig.2):

- Burgsandstein (middle Keuper - ‚Keuper Sandstone’) as underlying strata, resp. eastern surrounding of lignite basin,
- Remaining relicts of Tertiary lignite seams after termination of open-pit coal mining as well as
- Inner dump of former mining district ‘Wackersdorf Nord’ with raised material of different origin up to former level of land surface.

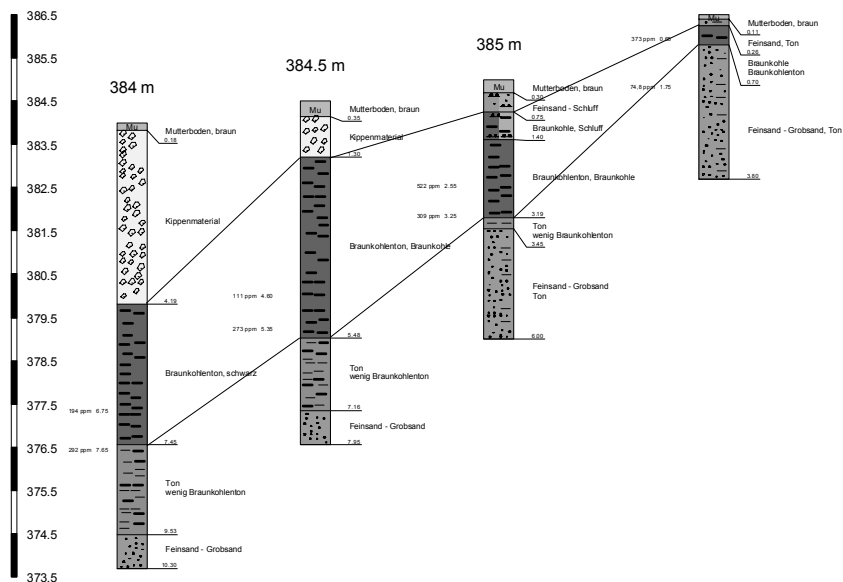


Fig. 2. Geological correlation of exploration drillings at Heselsbach site (B3 - B2 - B1 - B4, from left to right); assumed groundwater flow is from right to left.

Hydrogeology

Investigations of groundwater chemistry for characterization of hydrochemical milieu comprised 'normal' lab-analytics, on-site measurements of T, EC, pH and Eh as well as on-site spectrophotometric determination of Fe^{2+} , Fe_{tot} , SO_4^{2-} and S^{2-} .

Results from these on-site measurements already illustrate the different hydrochemical milieu with respect to Ruprechtov site. Along with comparable total mineralization at both sites, groundwaters from Heselsbach site clearly show lower pH- and positive Eh- values.

Altogether, groundwaters from Heselsbach site are from Ca- SO_4 -Cl-type. TIC-concentrations correspond with a partial pressure of CO_2 which is just slightly above partial pressure of CO_2 in atmosphere. At pH-values around 5, the predominant percentage is represented by H_2CO_3 , as well as solved CO_2 . Main components are plotted in a (modified) Piper-diagram (Fig.3).

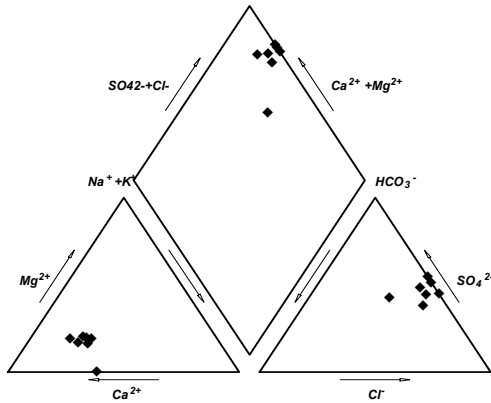


Fig. 3. Plot of groundwater-analyses (B1 - B4; main components) in a modified Piper-diagram

Radiometry

All 4 exploration drillings are characterized by two horizons of U-accumulation, the upper one coming across the lignite seam itself, the lower one across the transition zone between lignite and underlying clays. Differentiation between both horizons is decreasing with increasing depth (Fig.4).

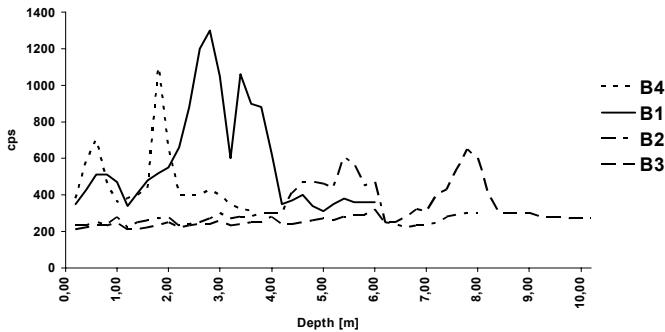


Fig. 4. Measurement of gamma-radiation along sediments of exploration drillings B1 - B4 with help of a portable differential-spectrometer.

Two samples per borehole with high gamma-activity have also been analysed for alpha-activity. Results of both, gamma- and alpha-measurements are compared in Fig.5 and indicate a rather good correlation.

In Fig.6, activities of relevant isotopes of the U-decay chain are plotted. Fig.7 shows activity ratios of $^{230}\text{Th}/^{238}\text{U}$ versus $^{234}\text{U}/^{238}\text{U}$. Except one sample from lower horizon of B1 all samples are characterized by $^{230}\text{Th}/^{238}\text{U}$ -ratios which are <1 .

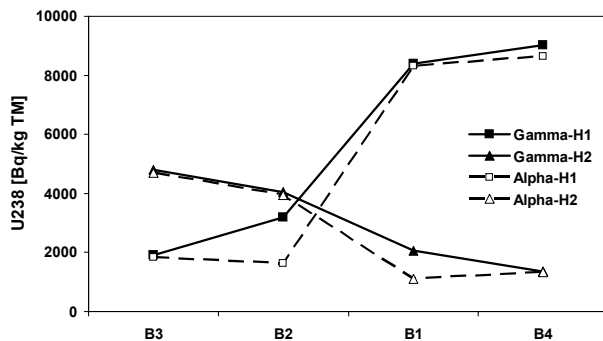


Fig. 5. Distribution of ^{235}U -activity along profile B3 - B2 - B1 - B4 (H1 = upper horizon, H2 = lower horizon).

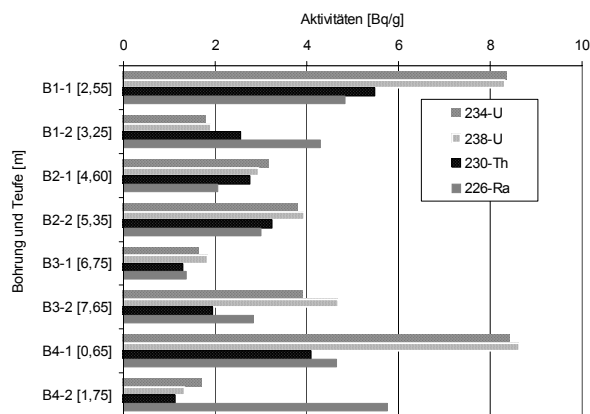


Fig. 6. Activities of isotopes of U-decay chain (sediment samples from B1 - B4).

In Fig.8 selected results, only from lignite samples (upper horizon), are shown. It is assumed that groundwater discharge takes place in the lignite horizon. Ratios of $^{234}\text{U}/^{238}\text{U}$ -activity show minor variations around 1. This corresponds to ratios measured in groundwater samples from B1 - B4. The ratio of $^{230}\text{Th}/^{238}\text{U}$ -activity is lowest in borehole B4 (0,47), generally increasing with flow direction. Since data are significantly minor 1, an U-deposition has to be assumed for all lignitic sediments. Increase of $^{230}\text{Th}/^{238}\text{U}$ -activity ratio with groundwater flow direction might be attributed to a decrease of the U-precipitation rate. This assumption is supported by generally high U-concentrations in boreholes B4 and B1 and a decrease of U-concentrations in groundwater with flow direction. At present, no sufficient explanation for strong variance of ratios of $^{230}\text{Th}/^{238}\text{U}$ -activity in underlying clay layers can be given. This open question will hopefully be solved with help of additional drillings and samples in the current follow-on project.

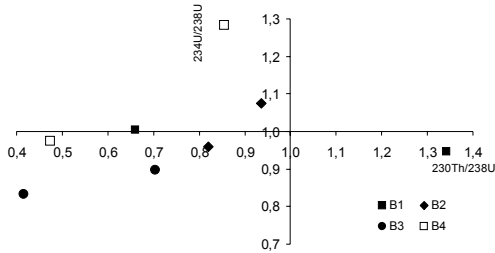


Fig. 7. Ratios of $^{230}\text{Th}/^{238}\text{U}$ - versus $^{234}\text{U}/^{238}\text{U}$ -activities (all analysed samples from boreholes B1 - B4).

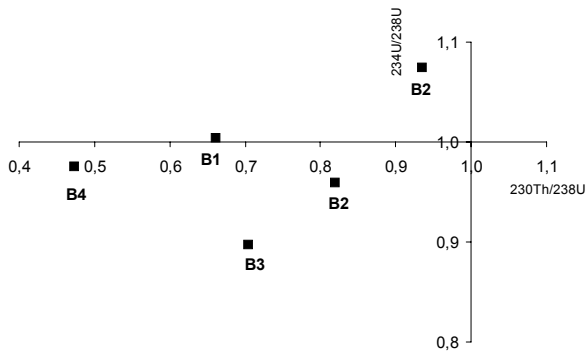


Fig. 8. Ratios of $^{230}\text{Th}/^{238}\text{U}$ - versus $^{234}\text{U}/^{238}\text{U}$ -activities (samples from lignite horizons only).

The ratios of isotope activities from U-decay chain measured in groundwater samples are plotted in Fig.9. Ratios of $^{234}\text{U}/^{238}\text{U}$ -activity in groundwater samples from boreholes B2 and B3 are close to ,1' (with regard to margins of error). This might indicate that chemical and transportation processes run off relatively fast and, in consequence, no influence of α -recoil effects on distribution of isotopes in groundwater can be detected. Since ratios of $^{234}\text{U}/^{238}\text{U}$ -activity are close to ,1' also in sediments a reversible exchange of mobile and non-mobile uranium might occur. Explanation of low ratios of measured $^{234}\text{U}/^{238}\text{U}$ -activity needs expansion of investigation area and number of samples which is one of the targets of the follow-on project. Low ratios of $^{230}\text{Th}/^{238}\text{U}$ -activity are likely be caused by low solubility of Th.

Geochemical modelling

First geochemical modelling has been performed with PHREEQC-code and Wateq 4.0 database, not taking into consideration the uranylphosphate-complexes

$\text{UO}_2(\text{HPO}_4)_2^{2-}$ and UO_2HPO_4 respectively. With regard to present geochemical conditions uranium should exist as hexavalent ion. Measured redox-values vary between 300 and 550 mV, pH-values between 4,7 and 5,4 in most groundwaters.

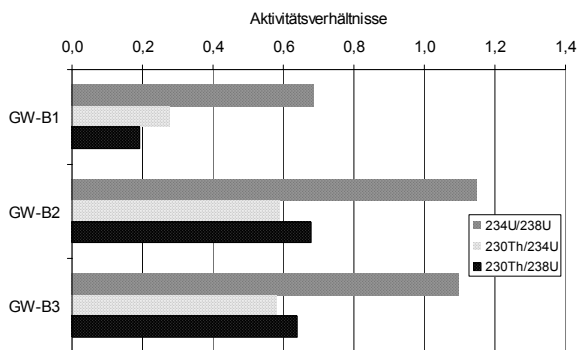


Fig. 9. Ratios of isotope activities (different isotopes from U-decay chain) in water samples (GW = groundwater)

Calculations of U-speciation have been carried out for a pH-range from 4,5 - 6. Additionally phosphate- und TIC-concentrations have been varied from 0,01 - 0,2 mg P/l and 0,1 - 2,5 mg C/l respectively (Noseck et al. 2000, 2002). First results showed that the mobile U-phase is defined mostly by free UO_2^{2+} - cation and UO_2HPO_4 -complex, the last one becoming more important at higher pH-values.

Calculations with U-concentrations in range observed at the site indicate that - even at highest values (4 $\mu\text{g/l}$) - no saturation of U(VI)-minerals is to be expected. Similarly, a variation of redox-values up to 100 mV doesn't result in saturation of U-minerals. Again, this can be taken as indication for U-retention mainly originated by sorption.

Conclusions

So far, results from geochemical, mineralogical and radiometric investigations at Heselbach-site yield in following conclusions:

Within two distinct horizons (upper lignitic and underlying clay layer) U-accumulations up to 640 ppm could be detected. Activity-ratios in lignite clearly indicate U-enrichment processes. U-concentrations in groundwater amount to appr. $3 \cdot 10^{-9}$ mol/l. Decreasing U-concentrations (sediment as well as groundwater samples) with groundwater flow direction imply U-retention mainly by sorption processes. Similarly, geochemical modelling indicates U-minerals to be far from saturation. In-situ - distribution-coefficients (calculated from ratio of non-mobile to mobile U-concentrations) amount to more than $100 \text{ m}^3/\text{kg}$ and are explicitly higher than typical values for U-sorption on clay minerals or iron oxides.

It is still an open question, how or to what extent geochemical conditions at Heselbach site have been influenced by long lasting open-pit mining. Possibly

groundwater lowering has caused oxidation of sulfidic minerals in deeper horizons. The recovery of groundwater level after termination of mining, in consequence, could have originated lower pH-values. Groundwater chemistry might also be influenced by dumping material used for recultivation of mining district.

Based on current knowledge a first hypothetical model for U-transport at Heselbach site has been set up which is sketched in Fig.10. Due to overall geological and hydrogeological situation only Keuper sandstone (Burgsandstein) has to be considered as U-source.

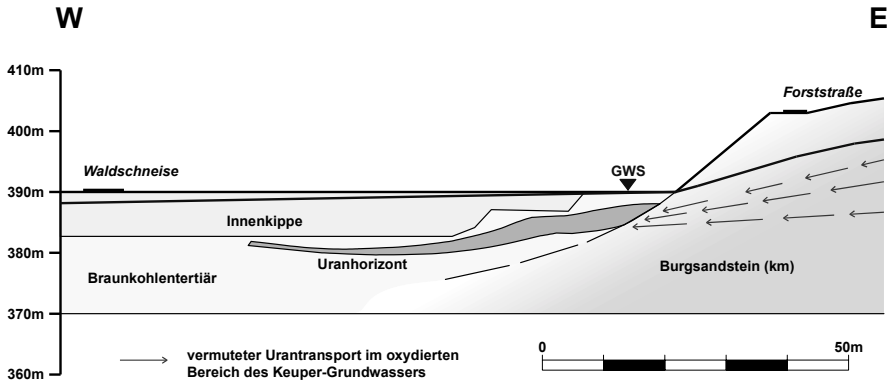


Fig. 10. Sketch of geologic-hydrogeological situation at Heselbach site; arrows indicate groundwater flow and direction of U-transport.

Potential retention processes for uranium are represented by sorption on iron oxides, organic matter and clay material as well as U-co-precipitation processes. An extended follow-on project has started with 10 new boreholes, so far, and new samples for a more detailed investigation of the site.

Acknowledgement

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