

Site characterisation of the potential Natural Analogue Site Heselbach in Bavaria/Germany

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Abstract. The U-enrichment at Heselbach/Bavaria was checked to be a suitable Natural Analogue for transport processes in the far field of an underground repository. For that reason investigations at Heselbach were carried out to identify mobilization and immobilization processes of uranium and thorium in lignite and clay sediments. Geology, hydrology and radiochemistry were studied in order to get detailed information on these topics. Subsequent to the experimental investigations a uranium transport model has been developed.

Introduction

With regard to long-term performance assessment (PA) for radioactive waste repositories Natural Analogues (NA) have been investigated for several decades to improve the understanding of the behaviour of radioactive elements in the natural environment. In NA-studies the potential mobility of radionuclides could be obtained by studying the natural occurrence of these critical elements on time scales which are relevant for underground repositories (~ 1 Ma). Next to the quantification of relevant transport processes NA-studies could be further used to identify natural immobilization processes.

U-enrichments are often formed where oxygenated or carbonate-enriched ground- or surface waters with highly soluble uranyl-carbonate complexes encounter organic-rich sediments (Culbert and Leighton 1978). Main mechanisms which could induce immobilization of uranium in such an environment are adsorption, ion exchange, reduction and/or (co)-precipitation processes. Negatively charged substances like humic acids or clay minerals do have a strong affinity for the positively charged uranyl-ion (Shanbhag and Choppin 1981) and may appear as adsorbents. In environments with high rates of evaporation U(VI)-minerals like

autunite $[\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2]$ or carnotite $[\text{K}_2(\text{UO}_2)(\text{VO}_4)_2]$ may precipitate. The embedding of uranium in new mineral formations like Fe-(Mn)-oxyhydroxides could be a further possibility to generate a natural uranium accumulation (Payne et al. 1996). Reduction of U(VI) to U(IV) by organic matter, Fe^{2+} minerals like pyrite or Markasit, H_2S , CH_4 and/or sulfate reducing bacteria are another common enrichment process which produces insoluble U(IV)-minerals such as uraninite $[\text{UO}_2]$ or coffinite $[\text{UO}_2\text{SiO}_4]$.

To find out what are the dominating immobilization processes at Heselbach site a sequential extraction procedure, EXAFS-analyses, and U(VI)/U(IV) separation were performed. Hydrological investigations including aqueous chemistry and flow regime studies as well as radiometric analyses complete the site characterization and enable the development of a U-transport model for this location.

Site location and description

The Heselbach U-enrichment in Bavaria, Germany is located 30 km N from Regensburg and 30 km S from Weiden. The research area comprises 0.3 km^2 and is located at the E-margin of the former Wackersdorfer lignite-mining district. In Fig. 1 the geology of the tertiary river system with research area and drilling locations is plotted.

At the outer rim of the basin structure, relicts of the tertiary (miocene) lignite

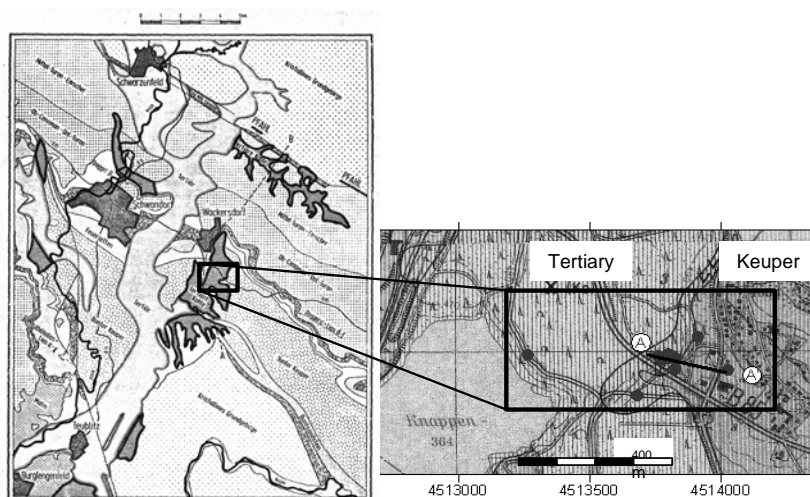


Fig. 1. Geological situation of the tertiary Ur-Naab basin with research area (a) and location of exploration drillings and cross section A-A' at the rim of the tertiary side bay (b).

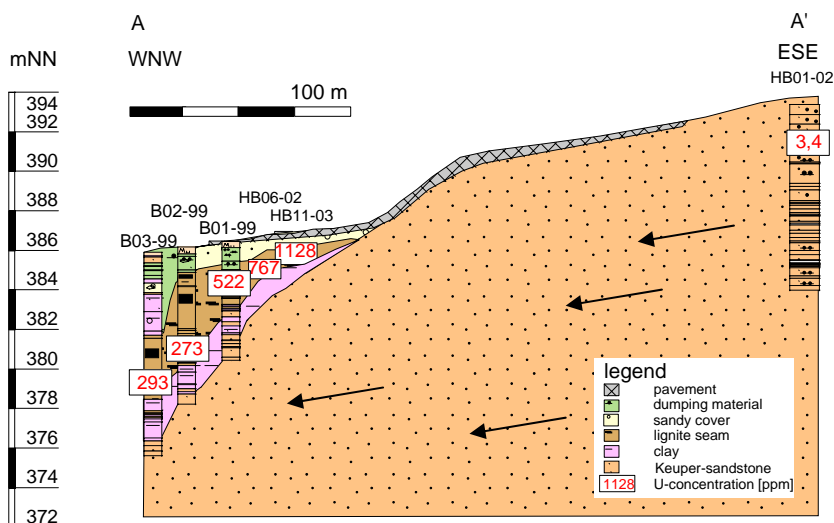


Fig. 2. Cross section A-A' of the tertiary rim with specification of the uranium content in sediment samples. The main groundwater flow is oriented from east to west.

seams remained in which uranium is distributed up to 1200 ppm over a distance of approximately 150 m.

The Keuper sandstone (km, Burgsandstein) does build the eastern limitation and the underlying strata of the tertiary basin. The sediments of the basin itself are composed of a clay horizon at the basis, followed by a clayey lignite seam which is covered by a sand-silt layer on top. The spatial distribution of the sediments at the rim of the basin structure is demonstrated in the cross section A-A' (Fig. 2).

Field and laboratory methods

Hydrology and Hydrochemistry

To characterize the flow regime at Heselbach site hydraulic conductivities of the important hydrostratigraphic units were measured in situ by slug & bail and back-fill tests using the Bower and Rice method calculation.

The determination of the flow velocity in the lignite layer was performed with a tracer test which took place from January to July 2004. A saturated NaCl solution was poured into the injection borehole and detected every 15 min. as electrical conductivity in the nearby observation borehole.

Parameters measured in the field include pH, temperature and electrical conductivity as well as the spectrophotometric determination of $\text{Fe}^{2+}/\text{Fe}_{(\text{tot})}$ and $\text{SO}_4^{2-}/$

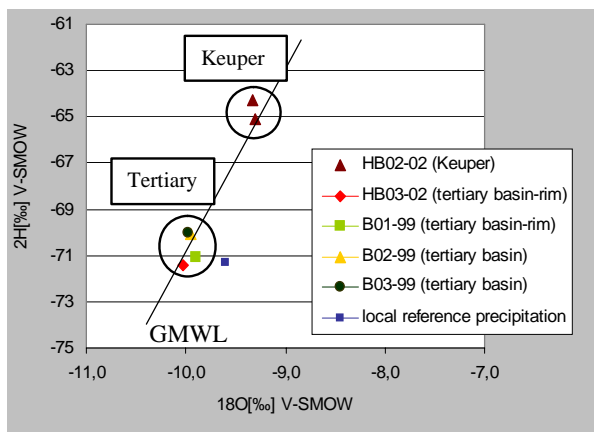


Fig. 3. Stable isotope composition of groundwater and local reference samples (database ISOHIS, IAEA).

S^{2-} concentrations. Redox values of the groundwater in the lignite layer were detected with an in situ data logger.

For groundwater chemistry investigations several sets of water samples were taken into the lab. Samples for natural isotope analyses (^{18}O , ^2H and ^3H) allow the estimation of groundwater ages and the identification of seasonal mixture processes. Samples for analyzing major anions and cations as well as U and Th were filtered $< 0.45 \mu\text{m}$, acidified with nitric acid and refrigerated. These elements were measured by ICP-OES or ICP-MS. Dissolved carbon concentrations (TC, TIC) were analyzed by IR-spectroscopy from a sealed original sample. DOC-samples were filtered $< 0.1 \mu\text{m}$ and acidified with phosphoric acid (50%). A further sample set was stabilized with chloroform to inhibit bacterial growth during transportation and used for detection of ammonium and phosphate by spectral photometry.

Sediment Analyses

All redox sensitive sediment samples were stored in sealed tins under anaerobic conditions until further processing took place in a glove box. A five step sequential extraction procedure after Percival 1990 has been carried out to get information about the distribution of the uranium phases in the sediments.

Selected uranium decay chain isotopes of sediment samples with elevated U-concentrations were determined by alpha-spectrometry. EXAFS-analyses from two selected samples and U(IV)/U(VI)-separation using ion exchange columns (Ervanne and Suksi 1996) provide information of the uranium-valence-state.

Table 1. Tritium concentrations of groundwater (2003)- and local reference (2000) samples.

sediment stratigraphy		Keuper	Tertiary	Tertiary	Tertiary	Tertiary
location/ drilling	local reference	HB02-02	HB03-02	B01-99	B02-99	B03-99
^3H [TU]	9.1 ± 1.6	9.5 ± 0.5	21.7 ± 1.0	19.8 ± 0.9	19.3 ± 0.9	21.9 ± 1.0

^a database ISOHIS (IAEA)

Results and discussion

Groundwater flow regime

Measurements of the hydrological parameters identified a horizontal hydraulic conductivity of $1.54 \cdot 10^{-5}$ m/s for the Keuper sandstone and $2.90 \cdot 10^{-9}$ m/s for the clayey lignite. The very low calculated flow velocity of just 0.01–0.40 m/a in the clayey lignite seam could be confirmed by a tracer test. Even after 6 months the tracer was not detectable in just a distance of 1.1 m from the input borehole indicating nearly stagnant conditions in the tertiary basin.

Correspondingly to those findings two different groups of groundwater could be identified by natural isotope analyses (Fig. 3). Drillings at the rim of the tertiary basin show a near-surface influence, evident by mixture processes with actual rain water.

The ^3H -concentrations of about 20 TU in groundwater samples of the tertiary basin (table 1) indicate a groundwater age of more than 25 years and a rather long groundwater retention time within these layers.

Groundwater chemistry

On-site measurements of Heselbach groundwater show a pH-value around 5 and an Eh-value of 0.1V in the lignite seam. The Fe^{2+} -concentrations vary between 0.02–0.64 mg/l in the tertiary basin groundwater and do increase with the distance of the basin rim and filter depth. This effect demonstrates the susceptibility of the chemical milieu at Heselbach and manifests the oxygen influence in subsurface drillings at the basin rim.

In general groundwater samples from the tertiary basin are from $\text{Ca-SO}_4\text{-Cl}$ -type. U-concentrations vary from 1 to 10 $\mu\text{g/l}$, DOC-values are < 10 mg/l.

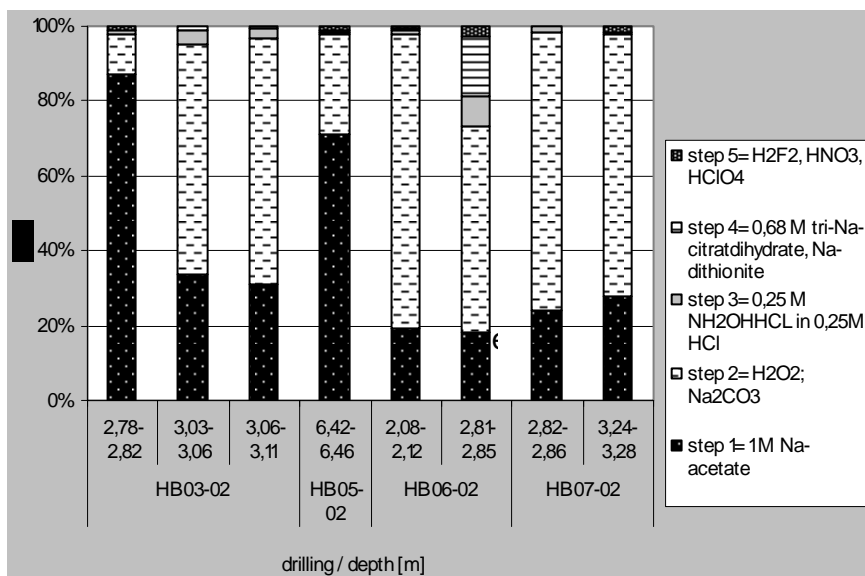


Fig. 4. Uranium distribution [%] of sequential extracted sediment samples

Uranium fixation and remobilization

Sequential extraction examinations determine that > 90 % of the U is bound to the adsorbed (1 M Na-acetat) and the organic (H_2O_2 , Na_2CO_3) fraction (Fig. 4).

Furthermore EXAFS-measurements demonstrate that uranium does occur in the U(VI)-valence-state with covalent bonds to oxygen atoms, most likely as UO_2^{2-} (Dardenne and Denecke 2004). This result corresponds to the U(IV)/U(VI) separation analysis, which identified 99 % of the present U as U(VI) (Suksi 2004).

In addition to the experimental investigations saturation indices were calculated using the PHREEQC-code. The WATEQ4F database was used without the contested uranium-phosphate complexes $\text{UO}_2(\text{HPO}_4)_{\text{aq}}$ and $\text{UO}_2(\text{HPO}_4)_2^{2-}$ (Duerden 1992). Organic compounds and colloids have not been taken into account. The calculations indicate that U(IV)-minerals like uraninite [$\text{UO}_2(\text{c})$] and coffinite [USiO_4] as well as the U(IV)/U(VI)-mineral U_4O_9 could be theoretically originate at Eh-values $\leq 0.1\text{V}$. U(VI)-minerals are not existent at any redox-value.

Altogether the uranium fixation at Heselbach site could be interpreted as an U(VI)-organic phase like Uranylhumate and/or as an Uranyl-sorption process on Fe-(Mn)-oxyhydroxides or clay minerals. Top concentrations of $130\text{ }\mu\text{g/l}$ uranium in groundwater samples of borehole HB03-02 are due to the increased hydrogen carbonate concentration, which is caused by recent paving work (calcareous gravel). The observed actual remobilisation of part of the uranium is a further hint that rather fast adsorption processes play an important role at Heselbach site.

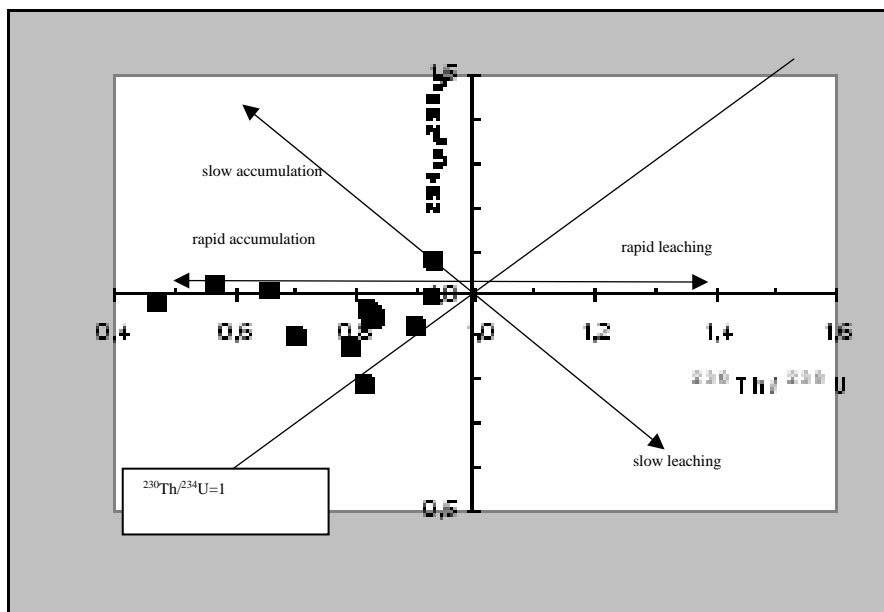


Fig. 5. Activity Ratios from sediments of the clayey lignite seam plotted in a Thiel-diagram

Radiometry

$^{234}\text{U}/^{238}\text{U}$ versus $^{230}\text{Th}/^{234}\text{U}$ activity ratios of sediment samples of the clayey lignite seam are plotted in Fig.5. Nearly all samples are accumulated in the lower left quadrant and show a significant disequilibrium state indicating a rather rapid uranium accumulation process.

In the Keuper sediments $^{234}\text{U}/^{238}\text{U}$ activity ratios vary between 0.75-0.89. These low activity ratios lead to the assumption that α -recoil processes worked over a long time period inducing the observed ^{234}U -depletion before sudden changes of the chemical milieu caused oxidation and U-transportation. Age calculations of the U-enrichment with the $^{234}\text{U}/^{230}\text{Th}$ dating method indicate at least a uranium input during the last 200,000 y.

Conclusions and Uranium transport model

The site characterization of Heselbach/Bavaria, Germany can be summarized by following conclusions:

1. U is accumulated up to 1200 ppm in a depth of 0.5-8 m in the tertiary clayey lignite seam and the underlying clay sediment.

2. Hydraulic investigations ascertained nearly stagnating groundwater with a very low flow velocity in the U-bearing sediments of the tertiary basin.
3. U exists as U(VI); the formation of Uranylhumate, adsorption of uranyl on Fe-(Mn)-oxyhydroxids and clay minerals or embedding are the dominating U-immobilization processes at Heselbach site.
4. U-series-disequilibrium analyses of tertiary lignite samples show rapid accumulation processes during the last 200,000 y.
5. Recent U-remobilization caused by anthropogenic elevation of the hydrogen carbonate concentration demonstrates the disposability of part of U.

Based on the presented results the sketched U-transport model was developed (Fig. 6). Meltwater intrusions during the Quaternary might have changed the chemical milieu and induced a sudden U-oxidation and remobilization from the Keuper sandstone. Increased water levels during that period filled the tertiary basin structure periodically and generated the U-enrichment in the tertiary sediments.

Acknowledgement

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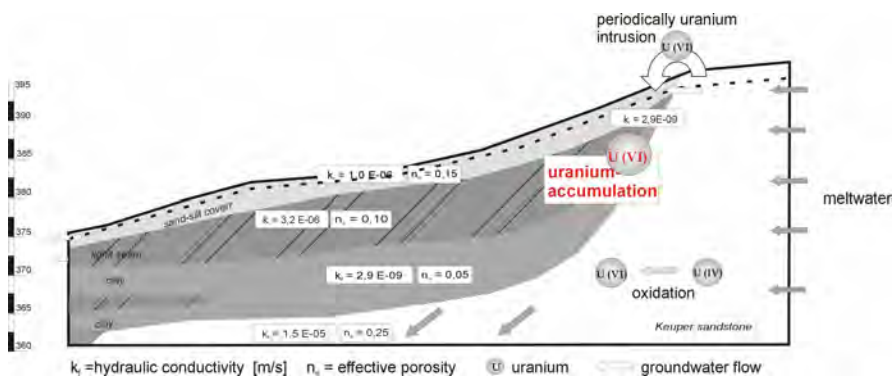


Fig. 6. Geological-hydrological U-transport model for Heselbach site

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