# THE ROLE OF COLLOIDS IN URANIUM TRANSPORT: A COMPARISON OF NUCLEAR WASTE REPOSITORIES AND ABANDONED URANIUM MINES

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## Abstract

The formation of colloids containing U(IV) or U(VI) was studied by experiments simulating geochemical processes under anoxic and oxic conditions. It is concluded that both transport-facilitating effects of colloids on “immobile” radiotoxic contaminants such as U(IV) and transport-impeding effects on “mobile” radiotoxic contaminants such as U(VI) may play a part in the surroundings of nuclear waste repositories and abandoned uranium mines.

## Introduction

It is widely recognized that colloids can influence the migration of toxic and radiotoxic elements such as uranium. There are transport-facilitating and transport-impeding effects on contaminant transport caused by colloids.

One of the major scenarios assumed in performance assessment for nuclear waste repositories is contaminant transport through anoxic aquifers. In this case, colloids are usually considered to facilitate the transport of highly insoluble compounds. However, colloids may behave differently in abandoned uranium mines where oxic conditions play a role and the uranium can be readily soluble. Here, colloids may have the potential to impede the transport of the dissolved uranium and to mitigate the environmental hazard.

In this paper we want to analyze in greater detail the influence of colloids on uranium transport under the different geochemical conditions in nuclear waste repositories and abandoned uranium mines.

## Uranium solubility and colloids

Classic approaches of determining solubility constants are dissolution experiments (condition of undersaturation) or precipitation experiments in combination with phase separation by ultrafiltration, ultracentrifugation etc. (condition of oversaturation). We measured the solubility of amorphous uranium dioxide $UO_2 \cdot xH_2O(am)$ by applying a novel type of precipitation experiment which avoids the precarious phase separation step: Coulometric titration combined with laser-induced breakdown detection (LIBD; Opel et al., 2007). For the given reaction, $UO_2 \cdot xH_2O + 4\,H^+ = U^{4+} + (2+x)\,H_2O$, a solubility product of

$$\log K_{sp}^{0} = -54.30 \pm 1.0$$

was found by this approach. Figure 1 shows the solubility of tetravalent uranium as a function of the proton concentration $[H^+]$ based on this solubility product.

Under oxidizing conditions, uranium occurs as $UO_2^{2+}$ complexes, the precipitation of which is normally prevented due to the formation of highly soluble carbonato complexes (Guillaumont et al., 2003) or calcium-uranyl carbonato complexes (Bernhard et al., 2001). As an example, Figure 2 gives the results of a thermodynamic calculation for the solubility of U(VI) in a simplified oxic, carbonate-containing groundwater. The assumed water composition is given in the figure caption. The first members of the paragenetic sequence of mineral formation (printed in bold) are regarded as the minerals determining the solubility of freshly precipitated uranium(VI).

A minimum solubility of about $10^{-8}$ mol/L and $10^{-5}$ mol/L is indicated by the two figures for U(IV) and U(VI), respectively. Thus, the tetravalent U is normally regarded as “sparingly soluble” and being deposited onto conduit walls (immobile), whereas the hexavalent U is considered as “readily soluble” and being dissolved (mobile).

Nevertheless, this picture may be counteracted by the influence of colloids. The sparingly soluble U(IV) may form intrinsic colloids or be deposited on carrier colloids and if the colloids are mobile, the tetravalent uranium may get a certain degree of mobility. On the other hand, the readily soluble U(VI) may be adsorbed by colloids, and if the colloids possess only little mobility, the hexavalent uranium may lose its mobility by adsorption, colloid aggregation and aggregate sedimentation, colloid filtration or colloid adsorption onto the conduit walls. The colloids may cause “natural attenuation” in this case.

## Colloids in nuclear waste repositories

Nuclear waste repositories consist of a "multi-barrier system" (see e.g. Toulhoat, 2002). The transport of radionuclides starts after the degradation of the spent fuel containers (first barrier), i.e. typically after several hundred years or later (Grambow et al., 1996). The chemical conditions are normally reducing after this time period. Thus, the uranium should be tetravalent and "immobile" then. However, this immobility might be counteracted by mobilization via the colloid mechanism. Clay mineral particles from the weathering of rock material, nanoparticles of precipitated secondary minerals (e.g. aluminosilicates, siderite, green rust) or organic nanoparticles are possible carrier colloids for the tetravalent uranium.

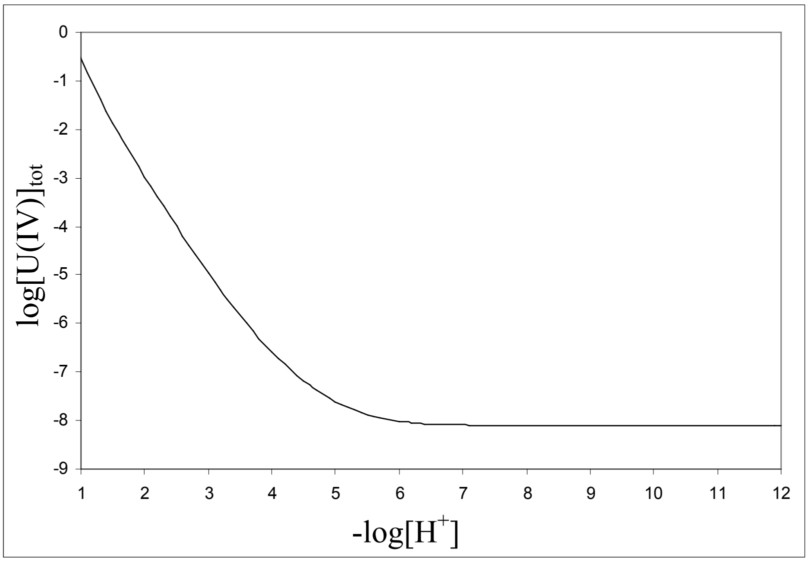

**Figure 1. Solubility of amorphous hydrous $UO_2$ as a function of $[H^+]$ based on the solubility product determined by Opel et al. (2005) and the hydrolysis constants recommended by Neck and Kim (2001).**

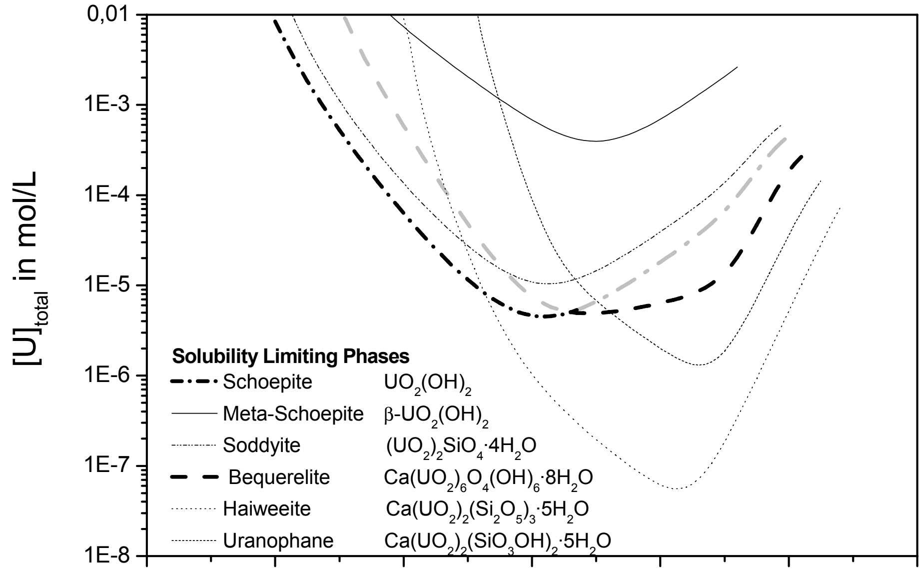

**Figure 2. Uranium(VI) solubility as a function of pH in a simulated natural oxic water (5.4 mg/L $Na^+$, 1.5 mg/L $K^+$, 37.7 mg/L $Ca^{2+}$, 2.7 mg/L $Mg^{2+}$, 1.5 mg/L $NO_3^-$, 12.7 mg/L $Cl^-$, 64.7 mg/L $SO_4^{2-}$, 1.6 mg/L Si in equilibrium with atmospheric $p$CO$_2$ ($10^{-3.5}$ atm)). Computed with EQ3/6 (Wolery, 1992) based on NEA TDB (Guillaumont, 2003), with the $Ca_2UO_2(CO_3)_3$(aq) complex (Bernhard et al., 2001) added (minimum solubility of the first members of the paragenetic sequence of mineral formation printed in bold).**

## Colloids in abandoned uranium mines

### 1. Oxic waters

Flooding a mine starts with filling-up the so-called groundwater "depression funnel". The most critical phase for the environment occurs when the floodwater reaches the level of first connections to unprotected surface waters or underground drinking water resources, i.e. the level of first natural or artificial spillways to the unprotected environment. This phase is also called the "first flush" of the mine (Younger, 2002); it is reached after several months to several years. In the upper zones of a mine there are oxic waters. The uranium is hexavalent here, i.e. it should be "mobile". However, this may be counteracted by immobilization via adsorption onto colloids plus colloid aggregation, sedimentation, filtration etc. An example of U(VI) scavenging by colloids is given in Figure 3. It demonstrates the scavenging and immobilization of U(VI) by ferrihydrite-rich colloids during the flooding of a uranium mine. The flooding of a mine can be regarded as the dilution and neutralization of acid mine water due to the inflow of surface water and shallow groundwater. In Figure 3 we simulated the flooding of the uranium mine at Königstein in Germany (Bain et al., 2001) on a 100-liter scale by mixing acid water from the deeper area of this mine with water from an overlying aquifer. In this figure the pH increased as a function of the mixing ratio, i.e. the volume of the mixture divided by the initial floodwater volume. The proportion of colloidal Fe and Al rises with progressive Fe and Al hydrolysis and Fe(II) oxidation, the latter shown by the falling [Fe(II)]/[Fe$_T$] ratio. Figure 4 presents a SEM micrograph of the nanoparticles produced by this mixing experiment.

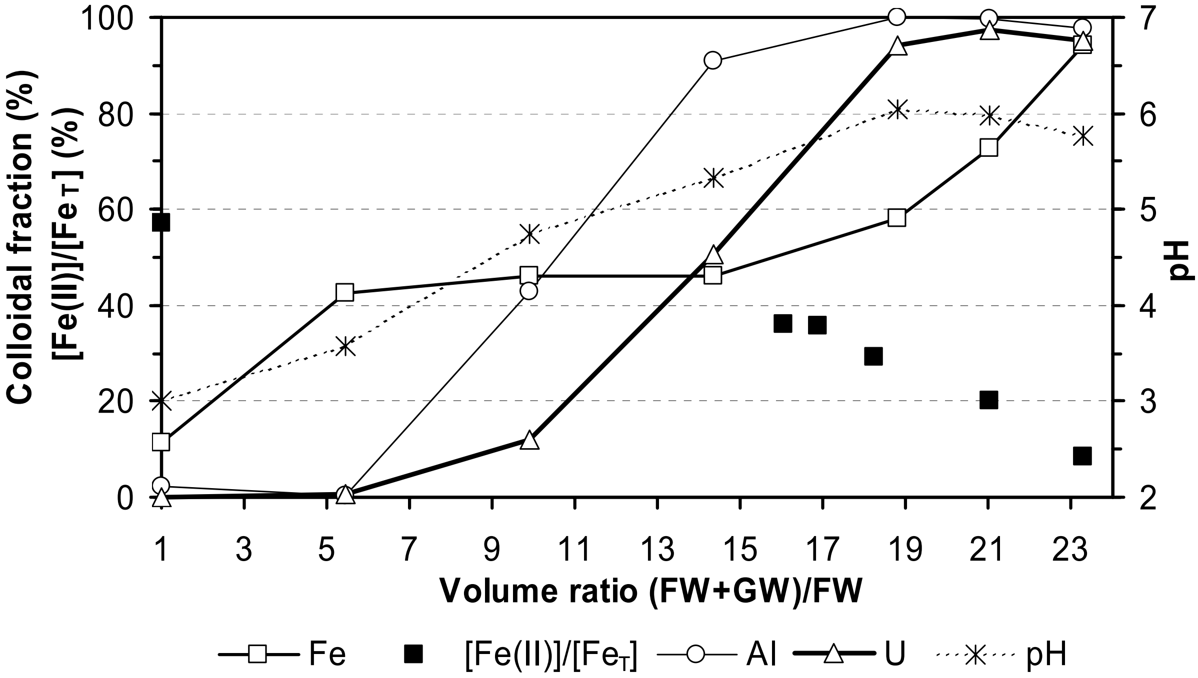

**Figure 3. Result of a mine flooding simulation experiment lasting 120 hours. Percentage of colloidal Fe, Al, U (based on 3kD ultra-filtration), fraction of ferrous to total iron concentration [Fe(II)]/[Fe$_T$] (left ordinate), and pH (right ordinate) as functions of the mixing ratio. Floodwater (FW) from the Königstein mine, Germany (pH 2.85) and near-neutral groundwater (GW) from an aquifer above the mine served as reaction partners.**

The chemical composition of these colloids was: 372.5 mg/g Fe, 55.7 mg/g Al, 13.9 mg/g Si, 24.2 mg/g S, 20.6 mg/g U, 0.54 mg/g Ca and 0.74 mg/g Zn. A particle size of about 100 nm was found. The zeta potential of the nanoparticles was only +5 to +10 mV, therefore they had a high tendency to aggregate and sediment. Up to 98% of the uranium present in the mixture was bound to the colloids at the final pH of about 6.

More detailed analyses by extended X-ray absorption fine structure (EXAFS) spectroscopy with synchrotron radiation and by attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy revealed that the uranyl can be bound by both a binary inner-sphere uranyl surface complex and an outer-sphere uranyl carbonato species to the ferrihydrite colloids. The ratio of these two uranium(VI) adsorption species depends on the concentration of U(VI) and carbonate (Ulrich et al., 2006; Rossberg et al., 2007).

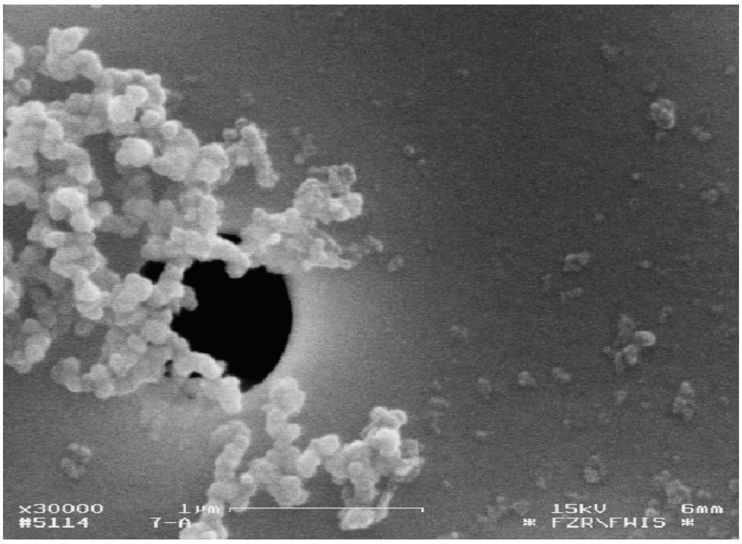

**Figure 4. SEM micrograph of colloids from the mixing experiment and their aggregates on a 1 µm Nuclepore filter membrane.**

**2. Anoxic waters**

The deep water of flooded mines is usually reducing, hence, uranium is expected to be tetravalent and it should be "immobile" in such waters. However, this might be counteracted by mobilization via the colloid mechanism. Carrier colloids that transport the U(IV) might consist of clay minerals from weathering, secondary minerals from precipitation, or organic substances. Even the formation of intrinsic $UO_2 \cdot xH_2O$(am) colloids (colloids without carriers) cannot be ruled out. Not much is known about colloids in reduced waters. Investigations into the field of colloid-borne uranium transport under reducing conditions are underway in our laboratory.

## Conclusions

It is concluded that colloids may have transport-facilitating effects on "immobile" radiotoxic contaminants such as U(IV) and transport-impeding effects on "mobile" radiotoxic contaminants such as U(VI). The key factors determining the impact of colloids on contaminant transport are the contaminant concentration difference between the source of contamination and the geological environment as well as the timescale that needs to be taken into consideration.

Very high contaminant (uranium) concentration differences and very long periods of time must be considered for nuclear waste repositories. Here, the point in time at which the colloid-borne uranium may reach the unprotected environment depends on the moment of spent fuel container failure, the water flow velocity, the concentration and mobility of potential carrier colloids and the reversibility/irreversibility of the binding of the uranium onto the colloids. Impeding effects of colloids on radionuclide transport, even though existing, have long been neglected for nuclear waste repositories.

On the other hand, lower uranium concentration differences between the source of contamination (the mine) and the geological environment and timescales much shorter than those typical of nuclear waste repositories are involved in performance assessment of abandoned uranium mines. For abandoned mines, too, stimulating effects of colloids on contaminant transport are important.

However, for the upper zones of abandoned mines impeding influences of colloids on U(VI) transport are to be considered because they contribute to "natural attenuation" of the environmental hazard during the flooding phase of a mine. Unfortunately, there is a lack of knowledge about the stability and long-term reliability of this colloid-induced U immobilization.

Nevertheless, even if this immobilization proves to be largely temporary, it still causes "attenuation" since it flattens the U release peak of a mine's "first flush". In the lower zone of a mine the uranium is expected to be tetravalent. It is usually regarded as immobile here. However, mobilization by colloids due to binding of U(IV) onto carrier colloids (and possibly the formation of intrinsic U colloids) is possible. Only little knowledge exists about the nature of colloids in reduced natural waters.

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