

## Thermodynamic Characterization of Dissolved Uranium Species in Flooded Uranium Mines and Tailing Management Facilities

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**Abstract** For the effective treatment of uranium-containing mine waters, an identification of predominant uranium species is of great interest. Therefore, species distributions are modeled with the hydrogeochemical software PhreeqC. Modeling results depend extensively on the used thermodynamic data. When considering calcium uranyl carbonates, one of them appears predominant at neutral pH values. However, this complex does not occur at low pH. These facts influence mine water treatment processes.

**Keywords** mine water, uranium speciation, alkaline earth uranyl carbonate, modeling

### Introduction

Since the closure of uranium mines in the early 1990s, their remediation is an important task in the German federal states of Saxony and Thuringia. It is done by Wismut GmbH within one of the largest environmental remediation programs in Europe. One of the main aspects of remediation is the treatment of mine waters, like pit water, drainage water, pore water and dump leachate. Typical contaminants in such waters are uranium, radium, arsenic and other trace elements. In order to protect ground water and surface water around old uranium mine sites from pollution, the mine waters should be treated in mine water treatment plants. Most of the plants operated by Wismut use precipitation processes for the effective removal of uranium. Predominant uranium species influence the sorption and precipitation behavior due to their varying charge states. Therefore the speciation has great impact on the procedure and effectiveness of water treatment processes.

In order to identify typical uranium species in mine waters, hydrogeochemical modeling is performed. For this purpose the hydrogeochemical software PhreeqC (Parkhurst and Appelo 1999) with different thermodynamic data is used. Databases included in PhreeqC do not contain thermodynamic data of calcium/magnesium uranyl carbonate complexes. However, these species occur predominant at neutral pH values, if they are added to the database. Hence, the results of hydrogeochemical modeling are strongly dependent on the used thermodynamic data and especially on the consideration of calcium/magnesium uranyl carbonate complexes.

Mine water samples with dissolved uranium species are analyzed at an external research institute on their uranium speciation. The comparison of analyzed and modeled uranium species distribution provides information about the plausibility of the performed modeling.

Results of this ongoing research are not only of particular interest for Wismut GmbH, but can also contribute to the current and upcoming water treatment tasks in other uranium mining regions.

### Influence of thermodynamic data on uranium species distribution

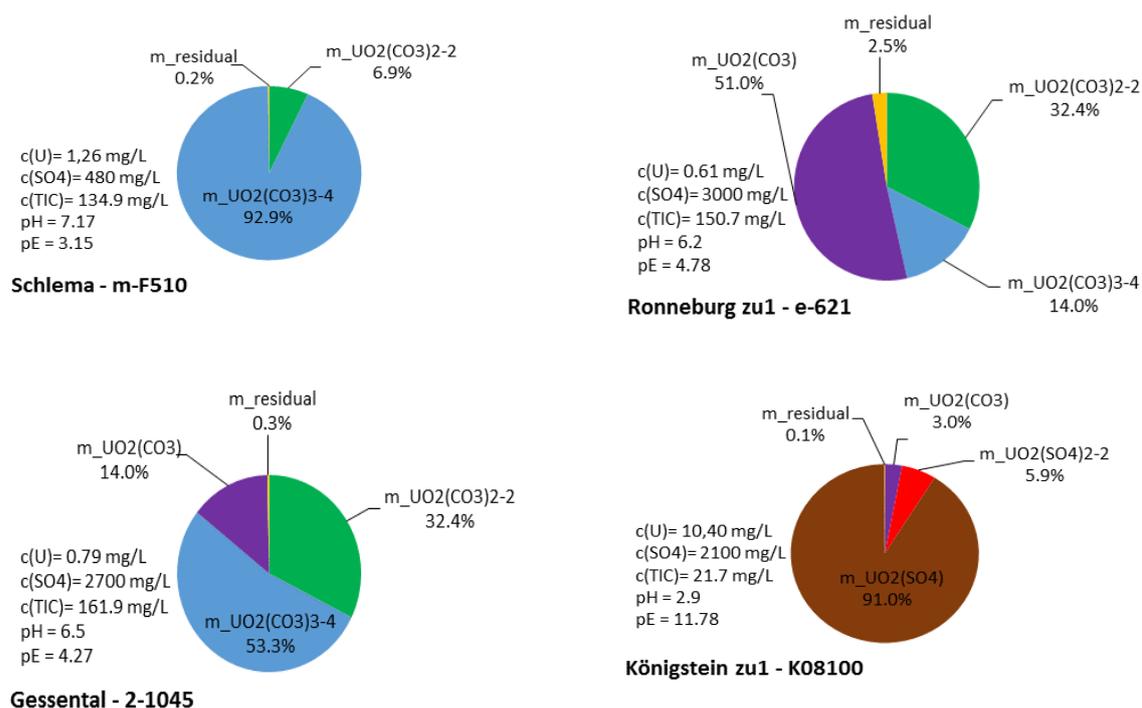
As mentioned above, hydrogeochemical modeling on analyses of relevant water samples is carried out with PhreeqC. Thermodynamic parameters are provided by the detailed database *sit.dat*, which is selected to characterize uranium species distributions in mine water samples.

Bernhard et al. (1996 , 2001) introduced and validated the formation of  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ . Since then, ternary complexes of alkaline earth uranyl carbonates ( $\text{M}_x\text{UO}_2(\text{CO}_3)_3^{(2x-4)}$ -complexes) have been investigated by different authors. Dong & Brooks (2006) measured and calculated thermodynamic parameters not only for calcium and magnesium, but also for strontium and barium uranyl carbonates. However, thermodynamic data of  $\text{M}_x\text{UO}_2(\text{CO}_3)_3^{(2x-4)}$ -complexes has not been included in PhreeqC databases yet. Therefore, reaction equations and log-K values have to be added manually (Merkel 2011).

### Modeling without ternary complexes of alkaline earth uranyl carbonates

In this investigation, modeling will be carried out without  $\text{M}_x\text{UO}_2(\text{CO}_3)_3^{(2x-4)}$ -complexes at first, and including them in a next step. Thus, a comparison between the results of modeling before and after addition of  $\text{M}_x\text{UO}_2(\text{CO}_3)_3^{(2x-4)}$ -complexes will be possible.

Initially, the unaltered database sit.dat is used, which already contains a wide range of uranium species, so that a general characterization of mine waters is possible. fig. 1 shows the uranium species distribution in waters of different mine sites. In order to describe characteristics of the respective water, environmental parameters are specified along with the pie charts. These mine waters differ in uranium concentration, but the focus is also on sulfate/carbonate content and pH value.



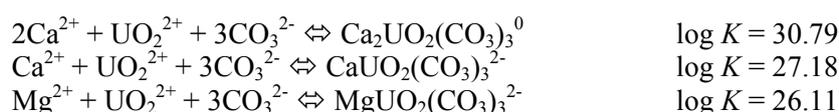
**Fig. 1** Uranium species distribution of four different mine waters; modeled with PhreeqC and the unaltered database sit.dat

Due to different water characteristics, uranium species distributions vary as well. Mine water samples, which are characterized by a pH value around 7, are dominated by uranyl carbonates. However, fractions of  $\text{UO}_2(\text{CO}_3)_3^{4-}$ ,  $\text{UO}_2(\text{CO}_3)_2^{2-}$ , and  $\text{UO}_2\text{CO}_3^0$  differ. In contrast, the water from mine site Königstein is dominated by  $\text{UO}_2\text{SO}_4^0$ . Uranyl carbonates are less important in that case.

Bachmaf et al. (2008) describe the pH dependence of uranium species distributions in the presence of sulfate and carbonate. Hence,  $\text{UO}_2(\text{CO}_3)_3^{4-}$ ,  $\text{UO}_2(\text{CO}_3)_2^{2-}$  and  $\text{UO}_2\text{CO}_3^0$  occur at neutral pH values, whereas between pH 7 and pH 5 the zero-valent species predominates compared to the anionic species. Below pH 5, no uranyl carbonates occur, as carbonates transform into  $\text{CO}_2$  at low pH values. In sulfate-containing waters,  $\text{UO}_2\text{SO}_4^0$  reaches considerable dominance at low pH values. Above pH 6 uranyl sulfates can be neglected. Based on that knowledge, species distributions of the modeling results in Fig. 1 can be explained to a certain extent. First, there is a shifting dominance from  $\text{UO}_2(\text{CO}_3)_3^{4-}$  to  $\text{UO}_2\text{CO}_3^0$  with decreasing pH value (around pH 7). Second, dominating fraction in mine water of Konigstein is  $\text{UO}_2\text{SO}_4^0$ , due to the low pH value and high sulfate content. Nevertheless, the uranium species distribution will change significantly after the addition of  $\text{M}_x\text{UO}_2(\text{CO}_3)_3^{(2x-4)}$ -complexes to the thermodynamic database. This aspect will be discussed in the following subsection.

### Modeling including calcium and magnesium uranyl carbonates

For the modeling of uranium species distributions, the addition of thermodynamic data concerning the anionic and zero-valent species of calcium, magnesium, strontium and barium to the thermodynamic database has to be considered. Formation of strontium and barium uranyl carbonates was of minor importance in pretests and is therefore neglected. The following reaction equations and log-K values are added to the PhreeqC Inputfile (according to Dong & Brooks 2006):

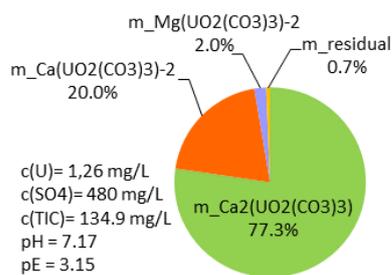


Bernhard et al. (2001) declared these species to be of great relevance for uranium-containing mine waters with high calcium/magnesium and carbonate content at neutral to alkaline pH value.

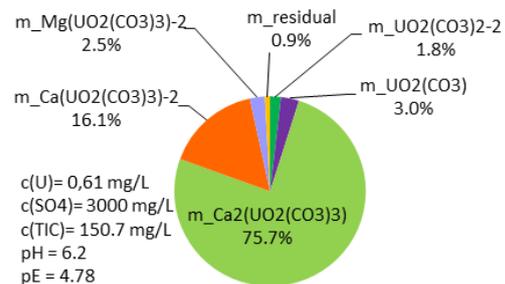
Based on the same analytical data like fig.1, fig.2 shows now the uranium species distributions under consideration of relevant calcium and magnesium uranyl carbonate complexes.

That results in a significant change in the dominating species at near neutral pH values in comparison to fig. 1. Predominant species is now  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$  with a fraction of more than 75 %.  $\text{CaUO}_2(\text{CO}_3)_3^{2-}$  reaches 15 to 20 %, whereas other species are of minor importance. However, uranium species distribution of waters from the mine site Konigstein is still dominated by  $\text{UO}_2\text{SO}_4^0$ . Apparently,  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$  has little influence on the species distribution in Konigstein waters, due to the low pH value.

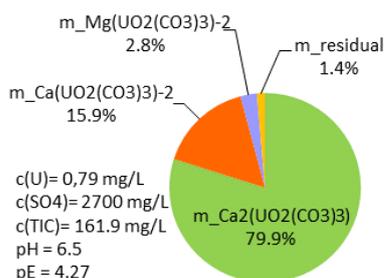
Nair et al. (2013) describe the occurrence of calcium/magnesium uranyl carbonates at different pH values. These species occur only above pH 7. At around pH 8 and higher they are dominating species and other uranyl species can be neglected. Calcium uranyl carbonates show higher concentrations than magnesium uranyl carbonates. Due to that aspects, the difference in uranium speciation between Konigstein and the other mine sites can be explained. As the water from Konigstein has a pH value around 3, carbonates are transformed to  $\text{CO}_2$ . The other samples show a dominance of  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$  already at pH 7, which means a slight deviation from Nair et al. (2013). Also the fraction of  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$  predominates more than expected. Nevertheless, the influence of pH value on uranium species distribution is demonstrated.



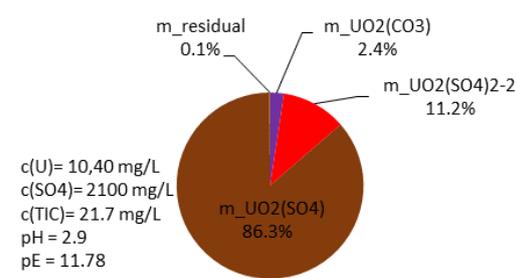
Schlema zu - m-F510



Ronneburg zu1 - e-621



Gessental - 2-1045



Königstein zu1 - K08100

Fig. 2 Uranium species distribution of four different mine waters; modeled with PhreeqC and the database *sit.dat* with addition of calcium/magnesium uranyl carbonate complexes  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ ,  $\text{CaUO}_2(\text{CO}_3)_3^{2-}$  and  $\text{MgUO}_2(\text{CO}_3)_3^{2-}$

### Variation of pH value in mine waters

Based on the knowledge about pH dependence of  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ -occurrence, pH variation tests were carried out. Samples with neutral pH value were treated with acid, so that the pH value decreased. Environmental parameters were analyzed before and after treatment, and uranium species distributions were modeled concerning the analyses.

Result is a shifting from  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ -predominance to a state, where this species does not occur. Tests were continued until pH 5.5. As observed in the mine water from Königstein, at lower pH values  $\text{UO}_2\text{SO}_4^0$  has a larger fraction. Furthermore, examined pH variation showed a predominance of  $\text{UO}_2\text{CO}_3^0$  in this water at pH 5.5. In summary, uranium species distribution at lower pH values is independent from  $\text{M}_x\text{UO}_2(\text{CO}_3)_3^{(2x-4)}$ -complexes, but highly dependent from the characterization of the mine waters.

### Comparison to lab analyses

In order to compare analyzed and modeled uranium species distribution, samples are analyzed at Helmholtz Centre Dresden-Rossendorf concerning dissolved uranium speciation. The comparison provides information about the plausibility of the performed modeling. Unfortunately, the investigations on that topic are not yet completed, but will be discussed in future.

### Findings and results

For a complete characterization of the uranium species distribution in mine waters, an addition of thermodynamic data concerning the alkaline earth uranyl carbonates to the used database in the software PhreeqC is of great significance. At neutral pH values the

$\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ -complex dominates in mine waters, which are characterized by relevant contents of calcium and carbonates. At low pH values,  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$  does not occur, so that uranyl carbonates and uranyl sulfates are predominant.

The knowledge of the uranium species distribution is important for the selection of treatment processes. Some procedures can be influenced by the characteristics of predominant species, e.g. ion exchange. It makes a great difference in the efficiency of an ion exchange module, if the uranium species is anionic or zero-valent. Similar effects can be of importance for the precipitation behavior of uranium and pretreatment processes. Ongoing investigations will focus on the assumption, that with decreasing pH value, zero-valent  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$  is replaced by anionic uranyl carbonates.

For improving uranium precipitation or implement ion exchange in mine water treatment, further knowledge about uranium speciation is required. In this context, uranium speciation analyses from the external institute Helmholtz Centre Dresden-Rossendorf are of great interest.

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