

How geochemical modelling helps understanding processes in mine water treatment plants – examples from former uranium mining sites in Germany

Anne Weber¹, Andrea Kassahun²

¹ *GFI Grundwasser-Consulting-Institut GmbH Dresden, Meraner Straße 10, 01217 Dresden, Germany, aweber@gfi-dresden.de*

² *Wismut GmbH, Jagdschänkenstraße 29, 09117 Chemnitz, Germany*

Abstract Mine waters from former uranium mining sites in Germany contain high concentrations of metal(loids). They are treated by lime precipitation and adsorption technologies. In this work well-defined lab scale experiments were modelled to elucidate reaction networks and their susceptibility to varying water composition. Both treatment technologies involve mineral precipitation-dissolution, gas exchange, surface complexation at ferrihydrite. It was shown that the formation of alkaline earth uranyl carbonate complexes and the precipitation of liebigite-group minerals determine uranium retention in WISMUT's mine water treatment operations. Sensitivity towards sludge composition and stability of arsenic sorption even at reducing conditions were derived from scenario simulations.

Key words: mine water treatment, geochemical modelling, uranium, arsenic

Introduction

In the course of remediation of the former Eastern German uranium mining sites, WISMUT GmbH operates six water treatment plants (WTPs). More than 25 Mm³ of tailings management facility seepage and mine waters are treated annually to remove site specific contaminants (e.g. uranium, radium, arsenic, iron, manganese). Modified lime precipitation is the prevailing technology, immobilizing contaminants by lime addition and induced precipitation of ferrihydrite Fe(OH)₃.

Evolving changes in mine water composition will influence the efficiency of water treatment with respect to the specific contaminants and require adjustments in the treatment technologies. For that purpose different strategies are pursued, e.g. implementation of treatment trains into geochemical models in order to use them as a prognosis tool and search for alternative treatment technologies. For both approaches lab experiments were conducted by WISMUT GmbH under purposefully defined conditions. These experiments allowed for building geochemical models comprising all system relevant processes with proper parameterization. This paper focusses on modelling the processes in selected lab tests.

Methods

Conduction of lime precipitation batch tests

Three precipitation batch tests FV₁, FV₂, FV₃ were conducted representing conditions in the lime precipitation train of the WTP Ronneburg. Per batch test 1 L of inflow water from the WTP was used and the pH was elevated until 9.6 during five stirring steps lasting 20 min each. Increase of pH was achieved by gas exchange with the atmosphere of the carbonate

oversaturated water and lime water addition in steps three to five. Flocculant (Kemira Superfloc® A110) was added before the final 3 h settling period. Experiments FV2 and FV3 were supplemented with 20 mL high density sludge (HDS) before pH rise corresponding to the WTP treatment. Starting solution of FV3 was enriched with 275 mg/L NaHCO₃ to reflect future increase of carbonate concentrations in the Ronneburg mine water.

Water samples were taken from the starting solution and from the experiments before and after settling of precipitates. They were analysed for pH, pe, O₂, Fe²⁺, anions (IC), elements (ICP-OES, ICP-MS). Composition and metal binding of the precipitating sludge was analysed by sequential extraction procedure according to Graupner et al. (2007). Main reactive minerals in the HDS were derived by analysing the results of sequential extraction resulting in a composition of 39 % ferrihydrite, 14 % calcite, 14 % CaO, 5 % magnesite, ca. 1% MgSO₄, CaSO₄, FeCO₃, MnCO₃. Assessment of saturation indices in HDS pore water additionally indicated the presence of swartzite/bayleyite or calciumuranate (UO₄Ca), uranophane (Ca[UO₂]₂[SiO₃OH]₂:5H₂O).

Conduction of FerroSorp® sorption column test

In a lab scale column test 5 mL bed volume of FerroSorp® Plus (HeGo Biotec GmbH) were fed with in average 6.6 mL/h (maximum 12.5 mL/h) seepage water from the tailings management facility (TMF) Helmsdorf (Kassahun et al. 2016) over a period of 280 days. To optimize surface complexation of target contaminants the pH in the seepage solution was adjusted to 6.0 by 0.5 M HCl. Inflow solution was stored in gas tight bags (Tesseraux) to prevent any degassing, precipitation and pH change during the experiment. . Outflow was collected in Erlenmeyer flasks

Samples were taken from each inflow stock solution and at every weekday from the outflow (mixed sample). Samples were analysed for pH, anions (IC), elements (ICP-OES, ICP-MS). Mineralogical analysis of a similar FerroSorp® AW material from Schöpke (2016) declared a composition of 18 % calcite, 5 % goethite, 2 % hematite and 72 % amorphous phases. The latter was attributed to ferrihydrite according to FerroSorp® Plus product information sheet. The effective porosity (0.4) of the filter bed was calculated from measured water volume in the bed. Total porosity (0.8) was taken from Schöpke (2016).

Simulation software and thermodynamic data base

Geochemical simulations were performed with the chemical reaction code PHREEQC (version 3) by Parkhurst & Appelo (2013). As thermodynamic data base (TDB) ThermoChimie (Giffaut et al. 2014) from the French National Radioactive Waste Management Agency was used (version 9bo). It comprises self-consistent data for a still growing number of elements.

In order to fit for conditions in the experiments, ThermoChimie had to be supplemented. Aqueous zinc species and phases as well as molybdenum phases were implemented from the Wateq4F data base. Uranium phases from Minteq.v4 and LLNL data bases (PHREEQC distribution) were supplemented if not already contained. All further included aqueous spe-

cies and phases are summarized in tab. 1 and 2. Focus was set on the implication of uranyl-calcium/magnesium-carbonato-species which were presumed to possibly determine uranium speciation in the WTPs from previous studies (Lietsch et al. 2015).

Data for surface complexation onto ferrihydrite were taken from the Wateq4F data base (PHREEQC distribution), which base on the model of Dzombak & Morel (1990). Surface complexation data further added to the ThermoChimie TDB are summarized tab. 1. Data for uranyl surface complexation were replaced by the more comprehensive data in Waite et al. (1994).

Table 1 Equilibrium constants of aqueous and surface complexes added to the ThermoChimie data set. *Hfo_s*, *Hfo_w*: strong and weak binding sites onto ferrihydrite according to Dzombak & Morel (1990). a: Data base file distributed with PHREEQC.

Reaction	log(k)	Source
$Mg^{2+} + 3 CO_3^{2-} + UO_2^{2+} = MgUO_2(CO_3)_3^{2-}$	26.11	Lietsch et al. (2015)
$6 MoO_4^{2-} + Al^{3+} + 6 H^+ = AlMo_6O_{21}^{3-} + 3 H_2O$	54.99	Minteq.v4 ^a
$3 H_3(AsO_3) + 6 HS^- + 5 H^+ = As_3S_4(HS)_2^- + 9 H_2O$	72.31	Wateq4F ^a
$H_3(AsO_3) + 2 HS^- + H^+ = AsS(OH)(HS)^- + 2 H_2O$	18.04	Wateq4F ^a
$2 Hfo_wOH + UO_2^{2+} = (Hfo_wO)_2UO_2 + 2 H^+$	-6.28	Waite et al. (1994)
$2 Hfo_sOH + UO_2^{2+} = (Hfo_sO)_2UO_2 + 2 H^+$	-2.57	Waite et al. (1994)
$2 Hfo_wOH + UO_2^{2+} + CO_3^{2-} = (Hfo_wO)_2UO_2CO_3^{2-} + 2 H^+$	-0.42	Waite et al. (1994)
$2 Hfo_sOH + UO_2^{2+} + CO_3^{2-} = (Hfo_sO)_2UO_2CO_3^{2-} + 2 H^+$	3.67	Waite et al. (1994)
$Hfo_wOH + Co^{2+} = Hfo_wOCO^+ + H^+$	-3.01	Minteq.v4 ^a
$Hfo_sOH + Co^{2+} = Hfo_sOCO^+ + H^+$	-0.46	Minteq.v4 ^a
$Hfo_wOMo(OH)_3 = Hfo_wOH + 2 H^+ + MoO_4^{2-} + H_2O$	17.96	Gustafsson (2003)
$Hfo_wOMoO_3^- + H_2O = Hfo_wOH + H^+ + MoO_4^{2-}$	9.50	Dzombak & Morel (1990)
$Hfo_wOHMoO_4^{2-} = Hfo_wOH + MoO_4^{2-}$	2.40	Dzombak & Morel (1990)
$(Hfo_wOH)_3(Hfo_wO)Ra^+ + H^+ = 4 Hfo_wOH + Ra^{2+}$	4.45	Sajih et al. (2014)
$(Hfo_wOH)_2(Hfo_wO)_2Ra^{4+} + H^+ = 4 Hfo_wOH + Ra^{2+} + 2 H^+$	-22.20	Sajih et al. (2014)

Except for speciation calculations the data base was used in a modified version with decoupled redox species for uranium (+3, +4, +5, +6) and iron (+2, +3). All relevant reactions were assumed to be equilibrium reactions at any time of the experiments and temperature was set 20 °C (average lab temperature).

Table 2 Equilibrium constants of phases added to the ThermoChimie data set. Thermodynamic data taken from Alwan and Williams (1980) and Gorman-Lewis et al. (2008) for grimselite.

Phase	Reaction	log(k)
Andersonite	$Na_2CaUO_2(CO_3)_3 \cdot 6 H_2O = 2 Na^+ + Ca^{2+} + UO_2^{2+} + 3 CO_3^{2-} + 6 H_2O$	-37.5
Bayleyite	$Mg_2UO_2(CO_3)_3 \cdot 18 H_2O = 2 Mg^{2+} + UO_2^{2+} + 3 CO_3^{2-} + 18 H_2O$	-36.40
Liebigite	$Ca_2UO_2(CO_3)_3 \cdot 10 H_2O = 2 Ca^{2+} + UO_2^{2+} + 3 CO_3^{2-} + 10 H_2O$	-37.20
Swartzite	$CaMgUO_2(CO_3)_3 \cdot 12 H_2O = Ca^{2+} + Mg^{2+} + UO_2^{2+} + 3 CO_3^{2-} + 12 H_2O$	-37.92
Grimselite	$NaK_3UO_2(CO_3)_3 \cdot H_2O = Na^+ + 3 K^+ + UO_2^{2+} + 3 CO_3^{2-} + H_2O$	-37.1

Modelling metal(loid) immobilisation in lime precipitation batch tests

To reproduce metal(loid) retention in the precipitation batch tests, the following processes were implemented in PHREEQC models:

- equilibrium with HDS reactive phases and oxygen, carbon dioxide in the atmosphere,
- complete oxidation of ferrous to ferric iron and precipitation of ferrihydrite,
- addition of lime water as $\text{Ca}(\text{OH})_2$ and precipitation of calcite,
- precipitation of gypsum, carbonates, oxides to model matrix elements,
- surface complexation at ferrihydrite from HDS and at precipitated ferrihydrite,
- precipitation of uranium and cobalt carbonate phases.

Analysed dissolved concentrations of start solutions and after settling of precipitates are shown in fig. 1 together with the modelled concentrations in the supernatant water. Not shown are pH-values which increased from 6.6...7.0 to 9.3 during the experiment and could be reproduced by the model adequately. Generally, modelled concentrations were in good agreement with measured ones, except for manganese. Its, however, low concentrations of 0.1...0.2 mg/L were underestimated by the model.

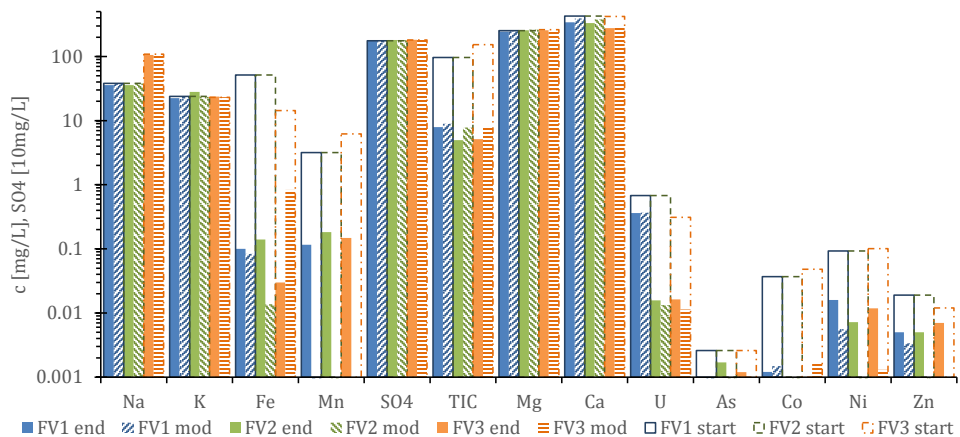


Figure 1 Dissolved concentrations for pH, matrix elements and contaminants in three precipitation batch tests: measured starting and end concentrations and modelled end concentrations (mod).

Measured concentrations of uranium, arsenic, cobalt, zinc, nickel, cadmium could be reproduced applying the surface complexation model without any modification. For uranium and cobalt only additional mineral precipitation reflected measured concentrations. Phases were carefully selected by their saturation index in the solution. Minerals from the liebigite group (swartzite and bayleyite) could match uranium concentrations in the experiments final supernatant best, which coincided with speciation modelling results for the HDS pore water. By addition of spaeocobaltite (CoCO_3) precipitation, supernatant cobalt concentrations could be described well.

In fig. 2 the mass balance of metal(loid)s in the models of the three experiments show the importance of surface complexation at $\text{Fe}(\text{OH})_3$ for metal(loid) treatment in the WTP. In FV1 (no HDS added), immobilisation is lower, especially for uranium, according to the measurements. On the other hand, increase of TIC in the initial solution (FV3) does not significantly change the original (FV2) metal(loid) immobilisation. Scenario calculations with changed initial surface site composition (data not shown), however, identified surface site composition being a sensitive parameter with respect to whether uranium and cobalt are sorbed or not.

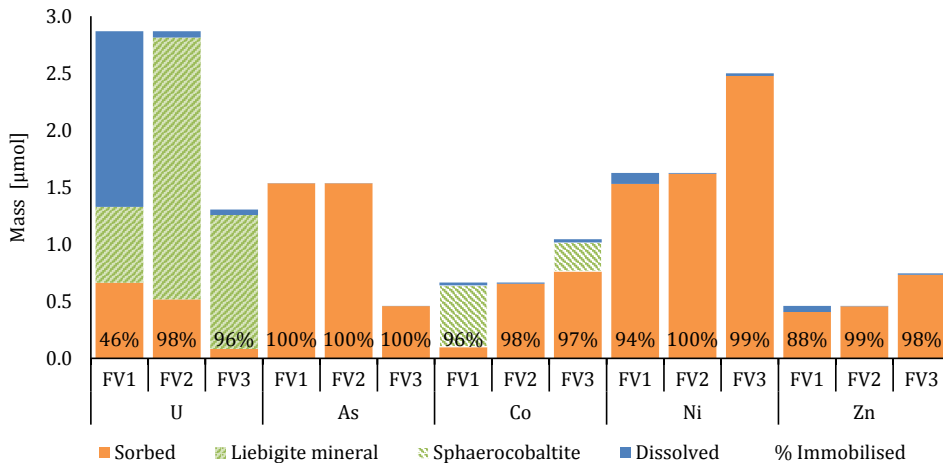


Figure 2 Modelled metal(loid)s mass balances and percentage of immobilisation in precipitation batch tests.

Modelling metal(loid) immobilisation in FerroSorp® sorption columns

Before modelling the FerroSorp® column experiments, possible mineral precipitation or dissolution reactions within the columns were identified by equilibrium calculations of feed and outflow solutions. Thereby, transition of mineral equilibria within the columns was indicated for CaCO_3 -phases, phosphates (e.g. anapaite, chloroapatite), liebigite like minerals (tab. 2), ferrihydrite and magnesite. EDX analysis of the FerroSorp® material before and after the experiment further revealed significant changes in its main composition with an increase of Fe, P and a decrease of Ca content (data not shown).

Modelling the column experiments in PHREEQC was done by first taking into account milieu determining processes and subsequently adapting less sensitive settings to reflect immobilisation of trace elements, in detail:

- one dimensional transport of inflow solution with measured varying composition and flow rate through a porous medium,
- degassing of CO_2 and kinetic dissolution of calcite to reflect pH of ~ 7 within the FerroSorp® bed,

- equilibrium with and surface complexation at ferrihydrite $\text{Fe}(\text{OH})_3$,
- precipitation of liebigite and chloroapatite.

Fig. 3 shows measured and modelled concentrations of four selected elements. Concentration of molybdenum appeared to be sensitive with respect to pH, which is determined by TIC. This was used to adapt pH in the model to 6.8...7.1 within the FerroSorp® bed (no direct pH measurement in the adsorber bed was preformed).

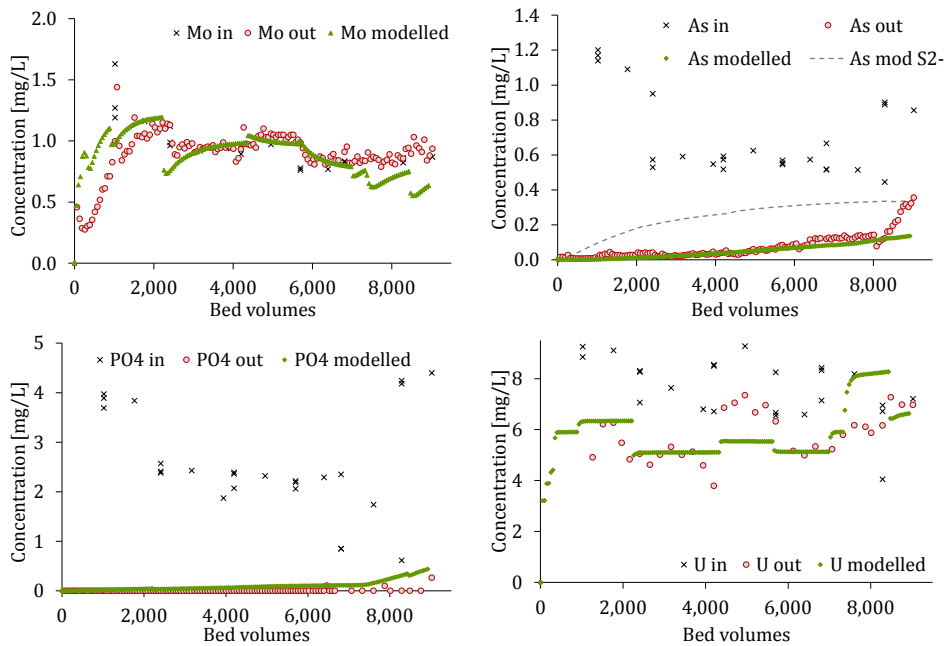


Figure 3 Measured and modelled concentration of target contaminants in a FerroSorp® column test with seepage water from the tailings management facility Helmsdorf. As mod S2-: Additional results from scenario run with 0.5 mg/L S2-in feed solution.

Arsenic immobilisation strongly depends on pH and was only slightly influenced by its redox speciation confirming comparable sorption of the charge neutral arsenite complex (H_3AsO_3) and negatively charged arsenates ($\text{H}(\text{AsO}_4)^{2-}$, $\text{H}_2(\text{AsO}_4)^{-}$) onto ferrihydrite (Jain et al. 1999). Nevertheless, scenario calculations revealed a strong inhibiting effect of dissolved sulphide (fig. 3), which coincides with observations of high arsenic concentrations during periods of microbial sulphate reduction in parallel experiments.

Comparable to the modelling of the lime precipitation tests, uranium effluent concentrations could only be reproduced by the model allowing precipitation of liebigite. Likewise, for phosphate modelled and analysed concentrations match when chloroapatite precipitation is allowed. Surface complexation of uranium only negligibly contributes to its retardation. Liebigite precipitation keeps uranium concentrations at about 5 mg/L according to calcium

availability and pH. However, the newly planned Helmsdorf mine water treatment plant uses ion exchange for uranium retention prior to FerroSorp® adsorption and interactions of uranium with FerroSorp® are secondarily in that case.

Conclusions

Lime induced ferric iron precipitation and sorption at granulated ferric iron hydroxide are current treatment technologies for mine waters from former uranium mining sites in Eastern Germany. Geochemical modelling of lab experiments simulating treatment processes was shown to identify underlying reactions and thus constitutes a useful tool to optimize treatment technologies. Mineral dissolution-precipitation, gas exchange and surface complexation according to Dzombak & Morel well described the behaviour of arsenic, uranium, zinc, nickel, cobalt, molybdenum and other water constituents in water treatment operations. Due to the competitive character of sorption processes, the complete implementation of the reaction network was essential for correct model simulations. This applied especially for the complete carbonate and phosphate reactions.

At site specific conditions uranium forms aquatic alkaline earth carbonate complexes and is marginally subject to surface complexation. Measured uranium concentrations in the experiments could only be modelled by incorporation of minerals from the liebigite-group. Further investigations need to focus on mineralogical detection of these uranium minerals.

Modelling of lime precipitation revealed that the composition of the recirculated sludge was a sensitive parameter for metal(loid) immobilisation. For sorption at granulated ferric hydroxide, the stability of the immobilization process even at reducing conditions for As-III was shown. However sulphate reducing conditions should be avoided as formation of As-S-complexes hinders sorption of arsenic to granulated ferric hydroxide.

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