Dynamical Models for Uranium Leaching – Production and Remediation Cases

Harald Kalka[1], Horst Märten[1,2], Rene Kahnt[3]

[1]Umwelt- und Ingenieurtechnik GmbH Dresden, Germany
E-mail: h.kalka@uit-gmbh.de
[2]Heathgate Resources Pty. Ltd., Australia, E-mail: h.maerten@uit-gmbh.de
[3]WISMUT GmbH, Chemnitz, Germany

Abstract. Leaching is a process of mass transfer between immobile mineral aggregate phases and mobile phases (reactive fluid). For such reactive transport phenomena a dynamical compartment model was developed. It combines solute transport in double porosity media with geochemistry (kinetics as well as thermodynamics described by PHREEQC). Besides several other applications, the model has been used to simulate quite different real-world scenarios related to uranium mining: (i) production case at Beverley mine and (ii) remediation case at Königstein mine.

Introduction: General Model Concept

Geochemical and hydrogeological modeling related to uranium mining cases is the scientific background for forecasts including optimization of plant operation and remediation. This paper describes model simulations of two quite different real-world scenarios:

- Production case: In-situ leaching (ISL) of uranium at Beverly mine, South-Australia ⇒ focused on optimum leaching chemistry and hydrology, interfering leaching effects as well as groundwater restoration after mining
- Remediation case: Flooding of Königstein mine, where ISL has been performed in underground mine works in the past ⇒ focused on most efficient flooding and minimum impact on the environment (adjacent aquifers)

In both examples, *geochemical* and *technological* processes are combined in an intricate manner. Code families for reactive transport alone (Domenico and

Schwartz 1998; PHAST, TACK and other programs) are not adequate to describe such complex systems.

Main Principles

To solve the problem numerically with adequate resolution the system is decomposed in suitable compartments (or boxes). The compartments are coupled by hydraulic and mass flows: *internal* couplings between compartments and *external* couplings to the environment. The structure of the box-system depends on the local conditions incl. availability of relevant data (cf. Fig.1 and Fig.5).

In addition to this global design and flow pattern each compartment can be "equipped" with (i) proper mechanisms of mass transformation (geochemistry) and (ii) technological devices like pumps, pipelines, plant components (like ion-exchange columns for U capture) and reactive materials.

Mathematically, the governing set of differential equations for each compartment i is derived from the principle of material balance:

$$\frac{dm_i}{dt} = \left(\frac{dm_i}{dt}\right)_{trans} + \left(\frac{dm_i}{dt}\right)_{reac} \tag{1}$$

This equation holds for any chemical element/species with mass m = cV, where both concentration c(t) and water volume V(t) are time-dependent. The transport term describes the hydraulic processes (without reactions) and is given by

$$\left(\frac{dm_i}{dt}\right)_{trans} = \sum_j \left(Q_{j\to i}c_j - Q_{i\to j}c_i\right) + Q_i^{in}c^{in} - Q_i^{out}c_i \tag{2}$$

Here, $Q_{i\to j}(t)$ denotes the internal flow from box i to box j; $Q_i^{in}(t)$ and $Q_i^{out}(t)$ represent the external flow *from* or *to* the environment, respectively. Whereas $Q_{i\to j}(t)$ is calculated from hydraulic conditions at time t (using Darcy's Law), the quantities $Q_i^{in}(t)$ and $Q_i^{out}(t)$ are input data ("boundary conditions" taken from the regional model). The water balance equation is a special case of Eq. (2) with c = *const* as the "concentration" of H_2O molecules:

$$\frac{dV_i}{dt} = \sum_j \left(Q_{j\to i} - Q_{i\to j}\right) + Q_i^{in} - Q_i^{out} \tag{3}$$

In case of flooding scenarios, the water amount in a compartment is not constant, but instead changes with time: dV/dt > 0 (cf. remediation case Königstein mine).

The reaction term in Eq. (1) is the key quantity of the model. Its proper specification defines the mass transformations between solid and aqueous phases, i.e., the leaching process inside the compartment i. In this way, this term operates as a source/sink term. If N_{phas} denotes the number of aqueous and solid phases, Eq. (1) splits into N_{phas} differential equations. Examples are given below: First, Eq. (4) and (5) for a single compartment (without transport term), and second, Eq. (11) and (12) for a modified double-porosity model.

Geochemistry

The specific chemical simulations inside each compartment – represented by the second term in Eq. (1) – are carried out by using the well-known U.S.G.S.-code PHREEQC (Parkhurst and Appelo 1999), which is implemented as a subroutine. In this way, the model includes the standard procedures:

- aqueous speciation and complexation
- mixing of water flows
- mineral dissolution and precipitation
- acid-base reactions (H^+-transfer)
- oxidation-reduction reactions (e^--transfer)
- reactions due-to addition and dosage of chemicals
- ion exchange

Reactions that are not in thermodynamic equilibrium are represented by kinetic concepts. The latter are defined by the *order* and *rate* of the reaction.

Production Case: In-situ Leach at Beverley Mine

Heathgate Resources Pty Ltd operates the uranium in-situ leaching mine in Beverley, South Australia. It is Australia's first commercial acid ISL mine commissioned in late 2000.

The above dynamic compartment model has been adapted to ISL processing for optimizing wellfield operation and uranium processing under various orebody conditions (minimizing both operational costs and environmental impacts). The simulation includes underground leaching dynamics in conjunction with U recovery and further technological stages in the processing plant (total water/material balance for ISL production cycle).

ISL Production Circuit – Compartment Structure

To describe the leaching dynamics and the corresponding mass transformations for U and other important species like SO_4, Fe, Cl, Ca, Si etc., the technological scheme "ISL cycle" is mapped onto a system of several interconnected compartments as schematically shown in Fig.1.

The acid solution (barren lixiviant) is injected into the underground via a sophisticated system of wells. Uranium is mobilized in the permeable ore body, together with interfering leaching effects and acid consumption. Submersible pumps in extractors pump the uranium-rich solution (pregnant lixiviant) to the surface for processing in the plant abbreviated by "IX" (IX stands for ion exchange applied to capture the U from the lixiviant circulating in a closed loop). The barren lixiviant is refreshed by adding sulfuric acid and oxidizing reagents. The loaded IX resin is further processed to recover U and to produce yellow cake finally.

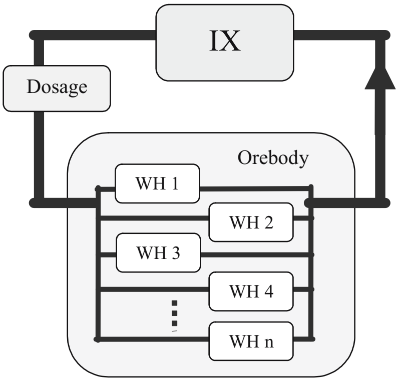

Fig. 1. Simplified compartment structure of the closed ISL cycle.

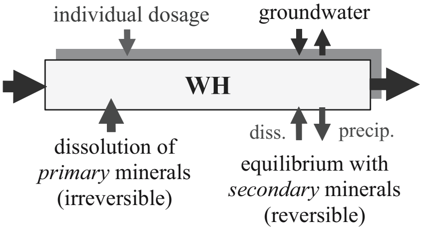

Fig. 2. Mass transfer within a single wellfield (diss. – dissolution, prec. – precipitation).

The subsystem "orebody" simulates the in-situ leaching process in several wellfields (wellhouses WH# with distribution to injection wells and collectors to combine pregnant lixiviant flows from the extractors). As shown in Fig.2, each wellfield represents a separate compartment to calculate the leaching processes involving reactions between minerals and the moving aqueous solution, but also including such effects like groundwater exchange within the aquifer. The dissolution of *primary* minerals is controlled by pH, ORP and salinity of the lixiviant. At the same time, the solution is assumed to be in chemical equilibrium with *secondary* minerals (as the reason for precipitation effects).

Finally, the compartment "IX" represents a network of ion-exchange columns for the sorption of Uranium from the lixiviant (Kalka 2004).

Analytical Approach for a Single Wellfield

At a first stage of modeling, the leaching dynamics is studied within a simple analytical model for a single wellfield. A wellfield consists of a network of 28 injection and 14 extraction wells with a complex flow pattern. Just this complexity gives rise to an effective description (averaging over different ore grades and hydraulic parameters within an ideally mixed reservoir). The uranium leaching process is understood as a combination of dissolution and flushing. Mathematically, it can be described by

$$\frac{dm_{ore}}{dt} = -\lambda m_{ore} \qquad \text{with} \qquad m_{ore}(0) = m_0 \tag{4}$$

$$\frac{dm}{dt} = \lambda m_{ore} - qm \qquad \text{with} \qquad m(0) = 0 \tag{5}$$

where m_{ore} and $m(t) = c(t)V_P$ refer to the uranium in the orebody and in the aqueous phase, respectively; V_P is the pore water volume. The "initial mass" $m_0 = c_0V_P$

at t = 0 represents the available pre-mining reserve in the orebody. λ symbolizes the dissolution rate, whereas q is the flushing rate (inverse residence time or pore-volume exchange rate). Integrating both equations one gets the uranium concentration in the lixiviant

$$c(t) = c_0 \frac{\lambda}{\lambda - q} \left[e^{-qt} - e^{-\lambda t} \right] \tag{6}$$

Finally, leaching at a flow rate Q per wellfield yields the time dependent mass flow j(t) = Q·c(t) as

$$j(t) = m_0 \frac{\lambda q}{\lambda - q} \left[e^{-qt} - e^{-\lambda t} \right] \qquad \text{with} \qquad \int_0^\infty j(t)dt = m_0 \tag{7}$$

This model includes 3 parameters

“Initial” concentration: $c_0 = m_0 / V_P$ (8)

Flushing rate: $q = Q / V_P$ (9)

Dissolution rate: $\lambda = a \cdot e^{b\,(2-\mathrm{pH})}$ (10)

Here, the dissolution rate of the main uranium-silicate mineral *coffinite* is assumed to be pH-dependent with $a \approx 0.5 \cdot 10^{-7}\ s^{-1}$ and $b \approx 3.2$.

For example, the wellfields WH8 and WH9 are characterized by an area of about 10 000 m^2 at an effective aquifer thickness of about 10 m; the porosity is $n \approx 0.3$. Accordingly, the estimate yields:

WH8:	$V_P = 30\,000\ m^3$	$m_0 \approx 170$ t U_3O_8
WH9:	$V_P = 35\,000\ m^3$	$m_0 \approx 225$ t U_3O_8

The initial mass m_0 was taken from geologic exploration data that show higher ore grade in WH9. The leaching was performed at an average flow rate of $Q = 200\ m^3/h$, whereas the leaching pH was 1.6 and 1.7, respectively. Using these data one gets the two parameter sets

WH8:	$c_0 = 5.7$ g/L	$q = 0.160\ d^{-1}$	$\lambda = 0.016\ d^{-1}$
WH9:	$c_0 = 6.4$ g/L	$q = 0.136\ d^{-1}$	$\lambda = 0.011\ d^{-1}$

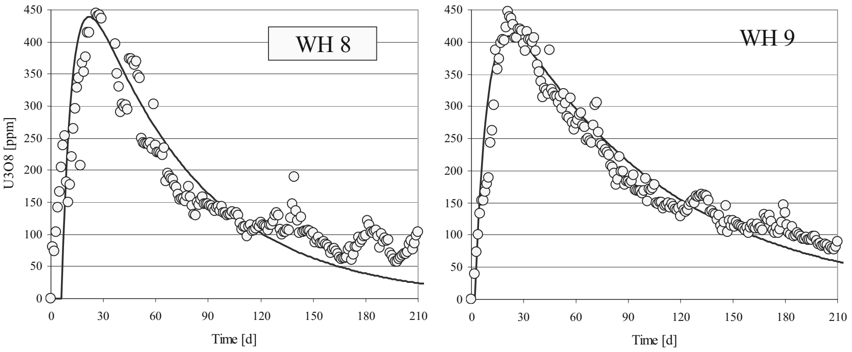

Fig. 3. Measured and calculated uranium concentration in the lixiviant for two wellfields.

The uranium extraction curves based on Eq. (6) are shown in Fig. 3. Despite the simplicity of the analytical model there is a good agreement with the observed data. Deviations from the measured data after more than 6 months are due to additional technological measures (like shut-off's of wells and addition of infill wells) to optimize leaching performance for maximum recovery.

Numerical Model Calculations for ISL Cycle Operation

The compartment model for the ISL cycle shown in Fig.1 combines the geochemistry (leaching) with the process chemistry (U-removal in ion-exchange columns) in a consistent way. The dynamics is simulated by discretization of the process into small time steps in the order of $\Delta t \approx 10$ h and assuming a quasi-equilibrium (calculated with PHREEQC) at each time step.

The dissolution kinetics for coffinite $USiO_4$ and other *primary* silicate minerals was assumed as first-order with a pH-dependent rate similar to Eq. (10). The dissolution of silicate minerals leads to interfering leaching, which influence the concentration of Si, Al, Fe, K, Mg, Ca etc. in the lixiviant, superposed by dilution effects due to wellfield start-up's (thus, keeping those concentrations quite constant). Additionally, chemical equilibrium with *secondary* minerals like gypsum, hydroxides, amorphous silica was taken into account. For example, adsorptive capacities of precipitated amorphous/colloidal silica SiO_2 are important for U(VI)-compounds.

In conclusion, the model calculations yield the time dependent dependence of pH, ORP and major ion concentrations (U, SO_4, Cl, Fe, Ca, Na, Al, Mg, K, Si). Fig. 4 shows the results for WH8 and WH9 as an example.

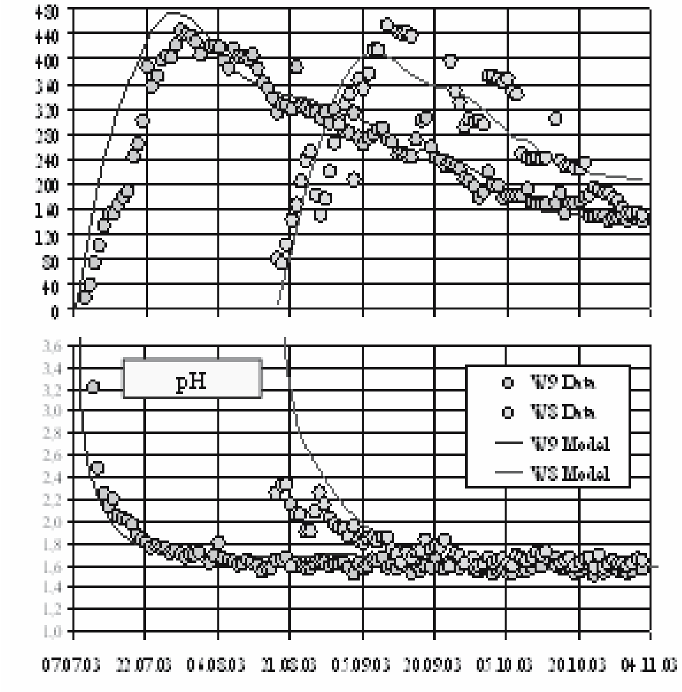

Fig. 4. Time-dependence of U_3O_8 and pH in the lixiviant of WH8 and WH9 – prediction and reality

Remediation Case: Flooding of Königstein Uranium Mine

The sedimentary uranium deposit of Königstein is located in the south-east of Saxony. Mining commenced in 1967. In 1984, ISL in the mineworks replaced conventional mining entirely. After an intermediate phase between 1991 and 2000, mainly for remediation works in the underground, flooding started in January 2001 (Schreyer et al. 2002).

Simulations of deep-mine flooding is a special task quite different from common hydrogeologic modeling because: (i) there are open mine voids in combination with porous media and fracture networks, (ii) the system is extremely dynamic (several cm per day rise of flooding level), (iii) the hydraulic changes cause drastic changes in geochemistry due to increased rock-water contact, and (iv) technological operations are included (pumping from a control tunnel system).

In conclusion: The description of flooding dynamics calls for a special site-specific compartment model (Kalka et al. 2002).

Compartment Structure

The compartment structure of the Königstein mine is schematically shown in Fig. 5. It consists of 18 mine-works compartments and 7 compartments of sandstone pillar between former mine-works and control tunnel, where flooding water is collected via a drainage system and pumped to the surface for treatment.

To describe the geochemical mass transformations (leaching and flushing) each compartment is decomposed into two subspaces: (i) "pore space" P containing the highly contaminated pore fluid and (ii) a "free space" F of water in mine voids. As shown in Fig. 6 the boxes are connected only via the percolating mine water in the open voids of space F. On the other hand, the production (and storage) of mass occurs in the pore space, whereas the stagnant water is in contact with the rock and secondary minerals. P and F are coupled by density driven forces.

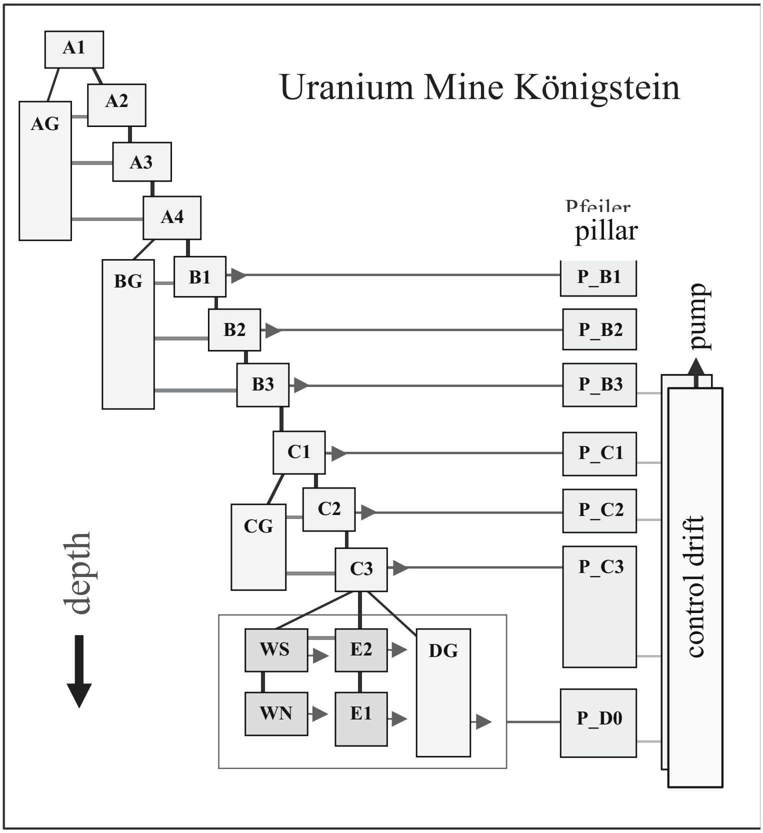

Fig. 5. Compartment structure of the Königstein mine.

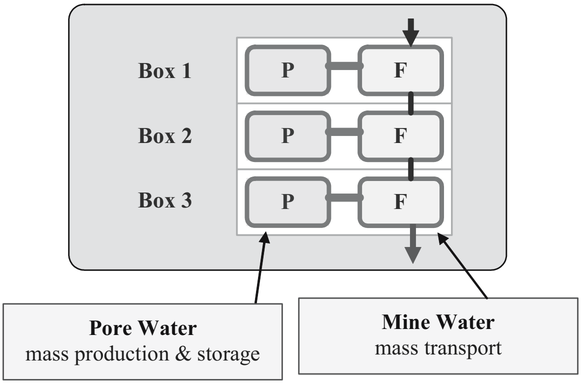

Fig. 6. Interplay between stagnant pore water and mobile mine water (leaching process).

Model Calculations

The model is based on a set of differential equations for the mass changes in both P and F in a given compartment i:

$$\frac{dm_i^F}{dt} = \left(\frac{dm_i}{dt}\right)_{trans} + \left|Q_i^{exch}\right| (c_i^P - c_i^F) + m_i^{sekm}\ \delta\,(t - t_i) \tag{11}$$

$$\frac{dm_i^P}{dt} = -\left|Q_i^{exch}\right| (c_i^P - c_i^F) \tag{12}$$

Here, the contaminant source consists of two parts: a *long-term* source which describes the transport of contaminants from P to F (leaching process) and a *short-term* source which describes the dissolution of secondary minerals/salts once the open voids get contact with flooding water. The leaching is density-driven with

$$Q_i^{exch} = \Lambda\ (\rho_i^P - \rho_i^F)/\rho_0 \tag{13}$$

and $\rho_0 = 10^3$ kg/m^3. The value of the exchange parameter $\Lambda \approx 1\,500$ m^3/h was adjusted to previous flooding history. The high contamination in the sandstone pores is a relic of the former block-leaching mining with sulphuric acid.

The model predicts the hydraulic processes (rise of water level and pillar drainage) as well as the time dependence of geochemistry and water composition (pH and 13 elements) at different locations in the mine. For example, Fig.7 shows the sulfate and uranium concentrations in the drainage water behind the pillar. For illustration, on a 1.5 GHz PC the running time is 8 h for a total time span of 8 years; the “subroutine” PHREEQC is called about half million times.

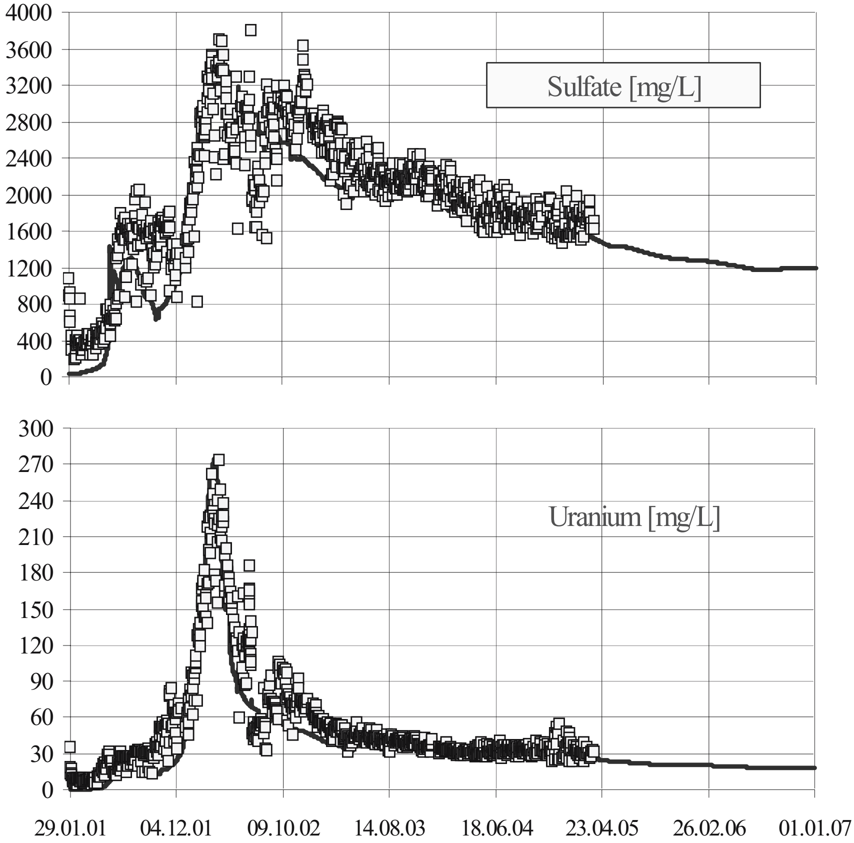

Fig. 7. Sulfate and uranium concentration in the drainage water behind the pillar (available data and forecast).

Conclusions

Modeling of uranium chemistry in heterogeneous aquatic systems including technological processes (drainage, pumping, treatment, reactive materials) requires the adequate combination of hydrogeology, geochemistry, reaction kinetics as well as process chemistry. To solve the non-standard task for the two application cases discussed in this paper, individual models with a quite different (multi-dimensional) compartment structure were developed. The compartment model describes mass transport *within* and *between* the compartments as well as chemical equilibrium and nonequilibrium processes (e.g. dissolution kinetics) performed by the use of PHREEQC. In particular, the dual-porosity model has been implemented into model compartments.

After model construction and calibration, the software tools are extensively used for forecast and simulation of various production (ISL) and flooding scenarios. In this way, models of such type are useful to

- Evaluate the dynamics of mine water / flood water chemistry in complex environments
- Select optimized strategies for leaching (ISL) and remediation (flooding)
- Interpret laboratory and pilot experiments
- Systemize chemical and hydraulic field data
- Derive a guidance for process monitoring

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