

Wiluna uranium project: Long-term fate of uranium and vanadium: Supplementary reactive transport simulations and recommended future investigations.

Henning Prommer, James A Davis and Grant Douglas

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Executive summary

In February 2015 CSIRO was commissioned (i) to critically review a previously performed reactive transport modelling study that predicted the long-term fate of uranium and other groundwater constituents at Toro Energy's proposed Centipede Uranium deposit near Wiluna, Western Australia and (ii) to undertake, based on the previous modelling setup, additional model simulations that specifically quantify the potential impact of the formation of uranyl-carbonate and uranyl-calcium complexes on the overall mobility of uranium. The newly performed model simulations that were conducted as part of the present work also included cases that explore the impact of additional source scenarios in terms of the assumptions made for source composition and in terms of how long leakage of TSF waters might occur. A second objective of the present report was to suggest a series of future studies that will reduce the substantial uncertainties contained in the current model predictions due to the current use of literature-derived rather than site-specific model parameters.

The model simulations were performed with the USGS geochemical model PHREEQCv2 (Parkhurst and Appelo, 1999). For consistency with the earlier modelling work the simulations relied on the previously defined one-dimensional setup (SWAC, 2012), which considers concentration attenuation by longitudinal dispersion while neglecting the impact of transverse mixing and dilution. In the absence of site-specific geochemical characterisation data the model scenarios also relied on the assumption that aerobic aquifer conditions would persist along the entire simulated hypothetical 500m long flowpath, therefore neglecting the substantial concentration attenuation effect that could occur under more geochemically reducing conditions.

The results of the supplementary modelling scenarios illustrate that under the currently made assumptions a number of factors may allow elevated uranium concentrations to migrate further than in the originally defined modelling scenarios. Increases in predicted uranium concentrations were found as a result of considering uranyl-calcium complexes in the simulations and also as a result of modifying source-term assumptions from a slug-type fluid release to a more continuous source release.

The simulation results suggest that future investigations should be aimed at reducing the current uncertainties and to replace current conservative assumptions with better validated assumptions based on site-specific data and research. In terms of the hydrological processes this can be achieved by

- incorporating a greater variety of the currently available and future hydrogeological/hydrological characterisation data to construct a three-dimensional reactive transport model that accounts more accurately for the site's hydrogeological conditions and accounts for concentration attenuation by transverse dispersion/mixing processes and by geochemical processes
- defining further refined source term scenarios to establish more realistic boundary conditions for the three-dimensional reactive transport model.

In terms of geochemical uncertainties, site-specific information on the sorption behaviour of uranium onto sediments and a thorough assessment of whether a sufficiently reducing conditions would trigger redox transformations and thus act as a natural barrier for uranium migration along the predicted flowpath is required.

This could be achieved by

- a refined hydrogeochemical field-site characterisation
- a detailed mineralogical characterization that identifies the mineral inventory
- characterisation of potential TSF solutes

- batch sorption tests for uranium and vanadium with various sediment materials from the aquifers that are potentially affected by leakage from TSF facilities
- developing site-specific surface complexation models that capture the characteristic sorption behavior of the sediments along the major transport pathways
- laboratory-scale column testing of uranium migration with sediments, groundwater and other aqueous solutions that most likely represent the composition of fluids egressing from the proposed TSF facilities. The tests would be aimed at using site-specific material to demonstrate and validate geochemical processes that cause U immobilisation
- controlled field-scale push-pull or forced gradient injection test that verify the attenuating role of Fe-sulfides and other attenuation processes
- assessment of suitable techniques to assist in engineered immobilization of contaminants in tailings solutes and/or in the surrounding aquifer

1 Background and objectives of study

In 2012 Soil Water Consultants (SWC) performed reactive transport simulations for RPS – Aquaterra to predict the long-term fate of uranium and other groundwater constituents at Toro Energy's proposed Centipede Uranium deposit near Wiluna, Western Australia (SWAC, 2012). A series of one-dimensional simulations were carried out with the geochemical transport code PHREEQC (Parkhurst and Appelo, 1999) to investigate time-scales and distances to which uranium and vanadium might migrate. The conceptual model underlying the numerical modelling study assumed a short-term (temporary) release of a limited volume of tailings liquor, followed by continuous flushing with ambient groundwater. The study reported a total of nine different modelling scenarios that sought to predict uranium and vanadium concentrations for up to 10,000 years. The various model scenarios tested in particular the sensitivity of the results with respect to the assumed groundwater flow rates, with respect to the assumed sorption properties, and with respect to the dominant mineralogy along a hypothetical 500m long flowpath. All simulation results suggest that elevated uranium and vanadium concentration will only occur in the immediate vicinity of the source zone.

In 2015 CSIRO was commissioned to critically review the previous modelling study and to undertake, based on the previous modelling setup, additional model simulations that specifically quantify the potential impact of the formation of uranyl-carbonate and uranyl-calcium complexes on the overall mobility of uranium. The need for this investigation has evolved from relatively recent research findings (e.g., Fox et al., 2006, Fox et al., 2012, Dong and Brooks, 2006, Dong and Brooks, 2008, Guillaumont et al., 2003) that have demonstrated that the formation of such complexes has the potential to significantly affect and often to enhance uranium mobility (e.g., Ma et al., 2014). The newly performed model simulations that were conducted as part of the present work were also aimed at exploring the impact of additional source scenarios in terms of the assumptions made for source composition (specifically calcium and carbonate concentrations) and in terms of how long leakage of TSF waters could occur. The main objective of these supplementary simulations was to explore whether the revised model assumptions and data have a strong impact on the previously obtained model predictions and the resulting assessment that naturally prevailing uranium (and vanadium) concentrations would not be strongly elevated by accidental leakage from the proposed TSF facility.

A second objective of the present report was to recommend future studies that will help to successively reduce the substantial uncertainties contained in the current model predictions as a result of using literature-derived rather than site-specific model parameters. Future assessments will need to underpin or replace currently made model assumptions with site-specific data and parameters that can be derived through additional hydrogeological and geochemical characterisation of the aquifer system surrounding the proposed TSF locations and through experimental work with materials from the site. The set of recommendations is based on the review of the previous modelling work, the results from the present model simulations and the experience gained at uranium-affected field-sites.

2 Investigated supplementary model scenarios

The present study consists of six modelling scenarios that were aimed at clarifying the influence of previously unconsidered aspects of the conceptual and numerical model. Table 1 summarises the six scenarios that are discussed in the following sections.

Table 1 Overview of supplementary model scenarios

MODEL SCENARIO	SOURCE TYPE	WATER COMPOSITIONS AND MINERAL ASSEMBLAGE	DATABASE
S1	SWC model scenario 1	PULSE Ambient and source as in SWC report	minteq4.dat + U/V reactions
S2	Modified base case	PULSE Ambient and source as in SWC report Calcite SI = -0.28, equilibrium with CO ₂ (g) removed	minteq4.dat + U/V reactions
S3	Role of updated database	PULSE Ambient and source as in SWC report Calcite SI = -0.28, equilibrium with CO ₂ (g) removed	minteq4.dat + updated U reactions
S4	Role of long-time source	200 years Ambient and source as in SWC report Calcite SI = -0.28, equilibrium with CO ₂ (g) removed	minteq4.dat + updated U reactions
S5	Role of increased alkalinity in the source	200 years Ambient and source as in SWC report Calcite SI = -0.28, equilibrium with CO ₂ (g) removed, alkalinity in the source increased	minteq4.dat + updated U reactions
S6	Role of carnotite	200 years Ambient and source as in SWC report Calcite SI = -0.28, equilibrium with CO ₂ (g) removed, carnotite included with SI set to 0.62	minteq4.dat + updated U reactions
S7	Role of Fe-sulfides	200 years Ambient and source as in SWC report Calcite SI = -0.28, equilibrium with CO ₂ (g) removed, pyrite and present in parts of the flowpath, uraninite allowed to precipitate	minteq4.dat + updated U reactions
S8	2D scenario: Role of Fe-sulfides + heterogeneity/dispersion	200 years Ambient and source as in SWC report Calcite SI = -0.28, equilibrium with CO ₂ (g) removed, pyrite present in parts of the flowpath, uraninite allowed to precipitate	minteq4.dat + updated U reactions

2.1 S1: Base case scenario

As a first step of this modelling study the original PHREEQC input files, as provided by SWC were run as provided and inspected. The unmodified MINTEQC database, as supplied by the USGS with PHREEQC (minteq.v4.dat, translated by David Parkhurst) was used for this base case scenario, which corresponds to the Scenario 1 case in the SWC report. Details of the model input are listed in Table 1 and selected results for this simulation (Cl, pH, Alkalinity, U and V concentrations after 20, 200 and 1000 years) are shown in Figure 1. The results of this scenario show background uranium concentrations of ~1.5 mg/L and a maximum concentration of ~4.4 mg/L at 15m distance after 20 years, corresponding to a ~10-fold decrease compared to the concentration that was assumed within the source zone at the start of the simulation (initial concentration in the first model cell). Simulated uranium concentrations at later times are near the background concentration.

Table 2 PHREEQC/PHT3D input for base case (S1) and other scenario.

	AMBIENT WATER COMPOSITION	SOURCE COMPOSITION
pH	7.08	9.91
pe	13.53	10.7
O(0)	5.3 mg L ⁻¹	6.4 mg L ⁻¹
Ca	550 mg L ⁻¹	1 mg L ⁻¹
Mg	3730 mg L ⁻¹	1 mg L ⁻¹
Na	30500 mg L ⁻¹	22200 mg L ⁻¹
K	2780 mg L ⁻¹	1110 mg L ⁻¹
Cl	48800 mg L ⁻¹	23900 mg L ⁻¹
S(6)	11200 mg L ⁻¹	10300 mg L ⁻¹
F	0.5 mg L ⁻¹	13.6 mg L ⁻¹
Alkalinity	86 mg L ⁻¹ as CaCO ₃	300 mg L ⁻¹ as CaCO ₃
Al	0.005 mg L ⁻¹	0.005 mg L ⁻¹
As	0.0005 mg L ⁻¹	0.161 mg L ⁻¹
Ba	0.049 mg L ⁻¹	0.087 mg L ⁻¹
Cd	0.0002 mg L ⁻¹	0.00001 mg L ⁻¹
Cu	0.038 mg L ⁻¹	0.059 mg L ⁻¹
Pb	0.0005 mg L ⁻¹	0.0001 mg L ⁻¹
Mn	0.086 mg L ⁻¹	0.0001 mg L ⁻¹
Ni	0.013 mg L ⁻¹	0.01 mg L ⁻¹
Se	0.005 mg L ⁻¹	0.01 mg L ⁻¹
Sr	12.3 mg L ⁻¹	0.09 mg L ⁻¹
U	0.365 mg L ⁻¹	38.5 mg L ⁻¹
Zn	0.012 mg L ⁻¹	0.075 mg L ⁻¹
Fe	0.0025 mg L ⁻¹	0.0025 mg L ⁻¹
B	1.37 mg L ⁻¹	0.45 mg L ⁻¹
V	0.005 mg L ⁻¹	6.805 mg L ⁻¹
Calcite (all scenarios)	1 mol L ⁻¹	na
Pyrite (S7 and S8)	0.1 mol L ⁻¹	
Carnotite (S6)	0 mol L ⁻¹	na
Cation exchange capacity (CEC)	0.0011 mol L ⁻¹	na
Hfo_wOH (weak sorption sites)	7.16e-03 mol L ⁻¹	na
Hfo_sOH (weak sorption sites)	1.79 ×10 ⁻⁴	na
TRANSPORT PARAMETERS		
Groundwater flow rate	0.5 m year ⁻¹	
Simulation time	1000 years	
Longitudinal dispersivity	5m	

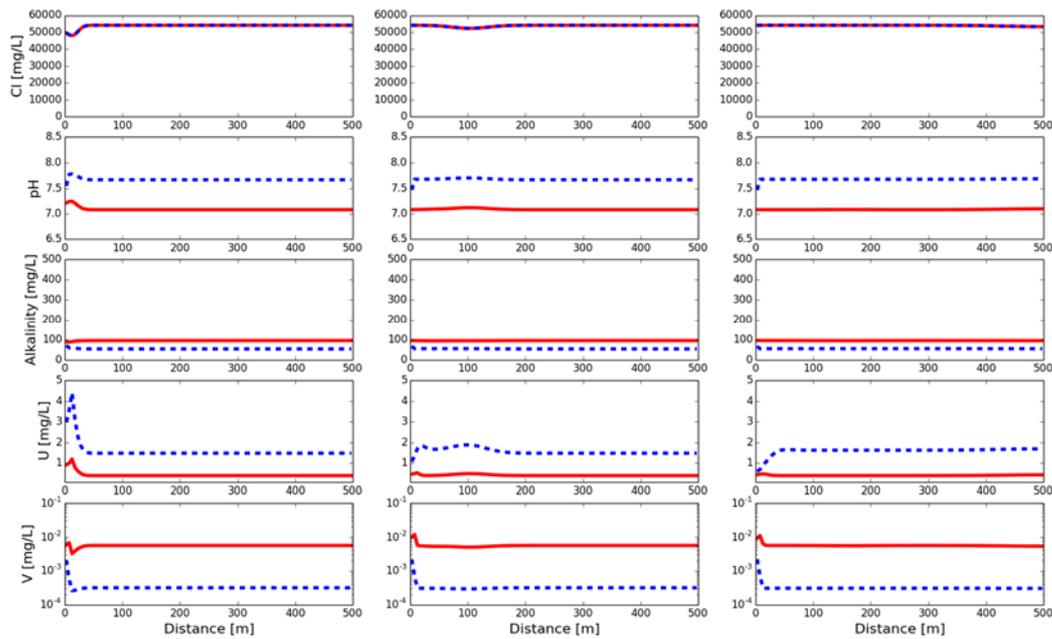


Figure 1 Comparison of selected simulation results for scenarios S1 (SWC scenario 1, blue dashed line) and S2 (modified base case, red solid line) after 20 (left), 200 (centre) and 1000 (right) years simulation time.

2.2 S2: Modified base case scenario

An inspection of the SWC Scenario 1 model showed that the groundwater composition that was assumed to define the initial concentrations was slightly under-saturated with respect to calcite (saturation index $SI = -0.28$) and therefore equilibration with calcite occurred at the start of the model simulations. To make subsequent model simulations that use a revised reaction database which includes additional calcium and carbonate-uranyl complexes and the comparison among model results more transparent, the base case scenario S1 was modified to force equilibration of the aqueous solution with a SI of -0.28 rather than 0.0 (default). In addition, the previously assumed equilibrium with an atmospheric CO_2 partial pressure of -3.5 (throughout the model simulation) was found to be unjustified as this would correspond to an “open” rather than a closed system. While degassing could indeed occur, it may not decrease the partial pressure to a value as low as -3.5 . Therefore this assumption was omitted in the modified base case scenario and all subsequent simulation scenarios. Selected simulation results (Cl , pH , Alkalinity, U and V concentrations after 20, 200 and 1000 years) in comparison with the results from the original base case scenario (S1, SWC scenario 1) are shown in Figure 1. The comparison shows complete agreement between S1 and S2 for the conservative species chloride (Cl). However, discrepancies exist in the simulated pH of ~ 0.5 units and therefore also in the simulated aqueous uranium and vanadium concentrations. The background aqueous uranium concentration is ~ 0.40 mg/L and the maximum concentration after 20 year simulation time is ~ 0.40 mg/L at a distance of 10m from the source.

2.3 S3: Role of uranyl-carbonate and uranyl-calcium complexes

For this simulation scenario the database employed in the SWC models as well as S1 and S2 was modified to include additional complexation reactions for various uranyl-calcium and uranyl carbonate complexes. Those reactions and the corresponding reaction constants are listed in Table 2. The constants were compiled from the recent literature (e.g., Fox et al., 2006, Fox et al., 2012, Dong and Brooks, 2006, Dong and Brooks, 2008, Guillaumont et al., 2003). The impact of considering the reactions is illustrated in Figure 2, which shows a comparison of selected simulation results between scenarios S2 and S3 after 20, 200 and 1000 years simulation time. Modification of the database has no impact on the background uranium concentration, and in contrast to S1, aqueous uranium concentrations in the background are not impacted by the mineral reactions that occur during the initial equilibration calculations.

Table 3 Additional complexation reactions appended to the minteqv4.dat database for simulation scenarios S3-S5).

COMPLEXATION REACTIONS	LOG K	COMMENT
$11\text{UO}_2^{+2} + 6\text{CO}_3^{-2} + 12\text{H}_2\text{O} = (\text{UO}_2)_{11}(\text{CO}_3)_6(\text{OH})_{12}^{-2} + 12\text{H}^+$	36.43	Modified by JADavis 3/3/2015
$2\text{UO}_2^{+2} + 2\text{H}_2\text{O} = (\text{UO}_2)_2(\text{OH})_2^{+2} + 2\text{H}^+$	-5.62	Modified by JADavis 3/3/2015
$2\text{UO}_2^{+2} + \text{CO}_3^{-2} + 3\text{H}_2\text{O} = (\text{UO}_2)_2(\text{CO}_3)(\text{OH})_3^- + 3\text{H}^+$	-0.855	Modified by JADavis 3/3/2015
$2\text{UO}_2^{+2} + \text{H}_2\text{O} = (\text{UO}_2)_2\text{OH}^{+3} + \text{H}^+$	-2.70	Modified by JADavis 3/3/2015
$3\text{UO}_2^{+2} + 6\text{CO}_3^{-2} = (\text{UO}_2)_3(\text{CO}_3)_6^{-6}$	53.88	Modified by JADavis 3/3/2015
$3\text{UO}_2^{+2} + 4\text{H}_2\text{O} = (\text{UO}_2)_3(\text{OH})_4^{+2} + 4\text{H}^+$	-11.90	Modified by JADavis 3/3/2015
$3\text{UO}_2^{+2} + 5\text{H}_2\text{O} = (\text{UO}_2)_3(\text{OH})_5^+ + 5\text{H}^+$	-15.55	Modified by JADavis 3/3/2015
$3\text{UO}_2^{+2} + 7\text{H}_2\text{O} = (\text{UO}_2)_3(\text{OH})_7^- + 7\text{H}^+$	-32.2	
$3\text{UO}_2^{+2} + \text{CO}_3^{-2} + 3\text{H}_2\text{O} = (\text{UO}_2)_3\text{O}(\text{OH})_2(\text{HCO}_3)^+ + 3\text{H}^+$	0.655	Modified by JADavis 3/3/2015
$4\text{UO}_2^{+2} + 7\text{H}_2\text{O} = (\text{UO}_2)_4(\text{OH})_7^+ + 7\text{H}^+$	-21.90	Modified by JADavis 3/3/2015
$\text{UO}_2^{+2} + 2\text{SO}_4^{-2} = \text{UO}_2(\text{SO}_4)_2^{-2}$	4.41	Modified by JADavis 3/3/2015
$\text{UO}_2^{+2} + \text{Cl}^- = \text{UO}_2\text{Cl}^+$	0.141	
$\text{UO}_2^{+2} + 2\text{Cl}^- = \text{UO}_2\text{Cl}_2$	-1.146	
$\text{UO}_2^{+2} + \text{SO}_4^{-2} = \text{UO}_2\text{SO}_4$	3.15	Modified by JADavis 3/3/2015
$\text{UO}_2^{+2} + \text{H}_2\text{O} = \text{UO}_2\text{OH}^+ + \text{H}^+$	-5.25	Modified by JADavis 3/3/2015
$\text{UO}_2^{+2} + 2\text{H}_2\text{O} = \text{UO}_2(\text{OH})_2 + 2\text{H}^+$	-12.15	Modified by JADavis 3/3/2015
$\text{UO}_2^{+2} + 3\text{H}_2\text{O} = \text{UO}_2(\text{OH})_3^- + 3\text{H}^+$	-20.25	Modified by JADavis 3/3/2015
$\text{UO}_2^{+2} + 4\text{H}_2\text{O} = \text{UO}_2(\text{OH})_4^{-2} + 4\text{H}^+$	-32.20	Modified by JADavis 3/3/2015
$\text{UO}_2^{+2} + \text{CO}_3^{-2} = \text{UO}_2\text{CO}_3$	9.94	
$\text{UO}_2^{+2} + 2\text{CO}_3^{-2} = \text{UO}_2(\text{CO}_3)_2^{-2}$	16.61	
$\text{UO}_2^{+2} + 3\text{CO}_3^{-2} = \text{UO}_2(\text{CO}_3)_3^{-4}$	21.84	
$\text{UO}_2^{+2} + \text{Ca}^{+2} + 3\text{CO}_3^{-2} = \text{CaUO}_2(\text{CO}_3)_3^{-2}$	27.18	
$\text{UO}_2^{+2} + 2\text{Ca}^{+2} + 3\text{CO}_3^{-2} = \text{Ca}_2\text{UO}_2(\text{CO}_3)_3$	30.7	
$\text{UO}_2^{+2} + \text{Mg}^{+2} + 3\text{CO}_3^{-2} = \text{MgUO}_2(\text{CO}_3)_3^{-2}$	25.8	Species added by JADavis 3/3/2015
$\text{U}^{+4} + 4\text{CO}_3^{-2} = \text{U}(\text{CO}_3)_4^{-4}$	35.05	
$\text{U}^{+4} + 5\text{CO}_3^{-2} = \text{U}(\text{CO}_3)_5^{-6}$	33.82	
$\text{U}^{+4} + 2\text{SO}_4^{-2} = \text{U}(\text{SO}_4)_2$	10.5	
$\text{U}^{+4} + \text{Cl}^- = \text{UCl}^{+3}$	1.697	
$\text{U}^{+4} + \text{H}_2\text{O} = \text{UOH}^{+3} + \text{H}^+$	-0.541	
$\text{U}^{+4} + 2\text{H}_2\text{O} = \text{U}(\text{OH})_2^{+2} + 2\text{H}^+$	-1.091	
$\text{U}^{+4} + 3\text{H}_2\text{O} = \text{U}(\text{OH})_3^+ + 3\text{H}^+$	-4.69	
$\text{U}^{+4} + 4\text{H}_2\text{O} = \text{U}(\text{OH})_4 + 4\text{H}^+$	-9.98	
$\text{U}^{+4} + \text{SO}_4^{-2} = \text{USO}_4^{+2}$	6.6	
Mineral equilibrium with Carnotite $\text{KUO}_2\text{VO}_4 + 4\text{H}^+ = \text{K}^+ + \text{UO}_2^{+2} + \text{VO}_2^+ + 2\text{H}_2\text{O}$	0.23	

Compared to S2 the simulated peak concentrations are substantially increased at all representative times, i.e., after 20, 200 and 1000 years (Figure 2). Simulated maximum concentrations after 20 years increase from ~ 1.2 mg/L to ~ 7.8 mg/L. This increase reflects the newly included aqueous uranyl complexes that can now form in this simulation. The total aqueous uranium concentration (red solid line) is similar to the sum of the concentrations of the uranyl complexes $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$, $\text{CaUO}_2(\text{CO}_3)_3$, $\text{MgUO}_2(\text{CO}_3)_3$, $\text{UO}_2(\text{CO}_3)_2$, UO_2CO_3 (green circles, Figure 2). The formation of these aqueous complexes effectively reduces the affinity for uranyl sorption reactions, which would otherwise occur between uranyl (UO_2) and the sorption sites. A comparison of sorbed uranium concentrations for the two cases (S2 and S3) shows that in S2 substantially more uranium is sorbed under natural, undisturbed conditions while in the case of S3 the affinity for sorption is also lower under natural conditions (Figure 3).

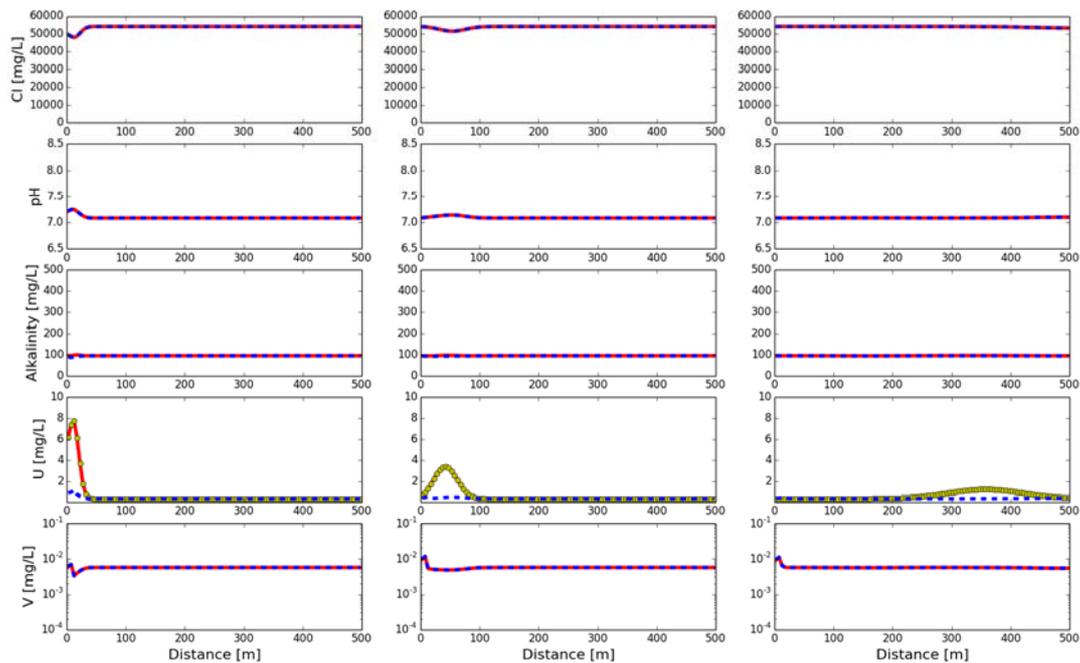


Figure 2 Comparison of selected simulation results for scenarios S2 (modified base case, blue dashed lines) and S3 (updated reaction database, red solid line) after 20 (left), 200 (centre) and 1000 (right) years simulation time. Yellow circles indicate the sum of the concentrations of the newly added uranyl complexes.

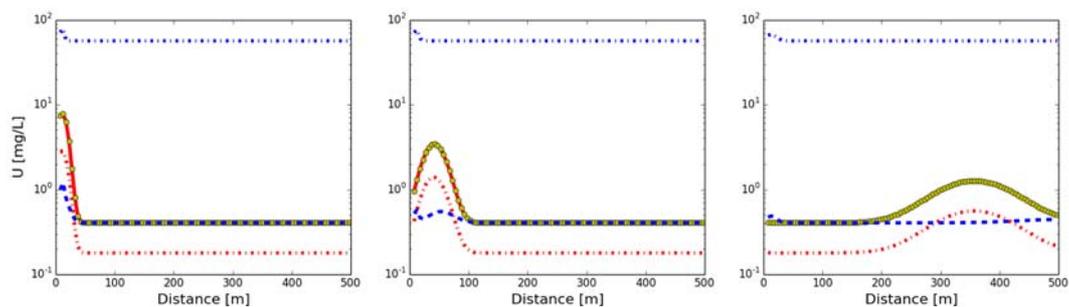


Figure 3 Comparison of aqueous and sorbed uranium concentrations for scenarios S2 (blue) and S3 (red) after 20 (left), 200 (centre) and 1000 (right) years simulation time. Total aqueous uranium concentrations are indicated by the solid red line (S3) and the dashed blue line (S2). Yellow circles indicate the sum of the concentrations of the newly added uranyl complexes in S3. The dash-dotted lines indicate sorbed uranium concentrations for S2 (blue) and S3 (red).

2.4 S4: Role of a non-instantaneous source

Scenarios S1-S3 were based on the previously established conceptual model that assumes a single pulsed-release of TSF-impacted water. Scenario S4 simulates the impact of a longer-lasting alkaline source, reflecting persistent water-sediment interactions (leaching) and, for example, additional leaching of uranium from the TSF fines. For simplicity it was assumed that the source would be active for 200 years, followed by a period of 800 years during which flushing with unimpacted aquifer groundwater occurs. A comparison of the results with the results of S2 is shown in Figure 4. The simulated chloride concentrations profiles illustrate the impact of the modified conceptual model with simulated chloride concentrations for S4 changing more strongly compared to the scenarios S1-S3 that assume a pulse-type release as in this case the role of dilution by longitudinal dispersion is reduced. Correspondingly, the concentration profiles representing the simulated alkalinity and pH also show more pronounced changes. In contrast to the previous scenarios where the highest concentrations occurred in the early part of the simulation (shown in the 20 year plots), maximum uranium concentrations (~ 40 mg/L) are now attained after 200 years before flushing with ambient groundwater starts and therefore dilution can occur at the front and the tail of the uranium plume.

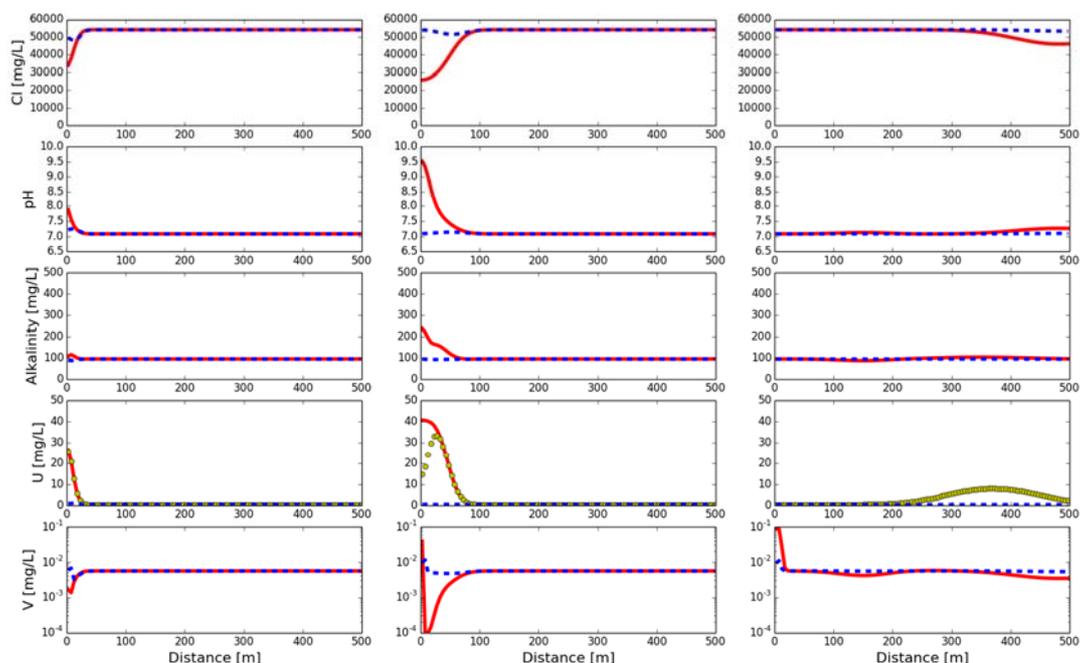


Figure 4 Comparison of selected simulation results for scenarios S2 (modified base case, blue dashed lines) and S4 (updated database + source active over 200 years, red solid line) after 20 (left), 200 (centre) and 1000 (right) years simulation time. Yellow circles indicate the sum of the concentrations of the newly added uranyl complexes.

2.5 S5: Role of increased alkalinity levels

Scenarios S1-S4 assumed alkalinities (as CaCO_3) of 86 mg/L and 300 mg/L for background tailings liquor, respectively. Model scenario S5 investigates the role of increased alkalinity. As it was expected that the simulation results would depend on the prevailing alkalinity this scenario quantifies the impact of a 10-fold increase of the alkalinity (3000 mg/L instead of 300 mg/L as CaCO_3) within the tailings liquor fluids. The impact of this change on the simulated alkalinity and pH profiles, with the most pronounced changes occurring for the concentration snapshot after 200 years simulation time is shown in Figure 5. However, no

substantial impact occurs for the mobility of uranium, with simulated aqueous uranium concentrations resembling those obtained in the scenario S4.

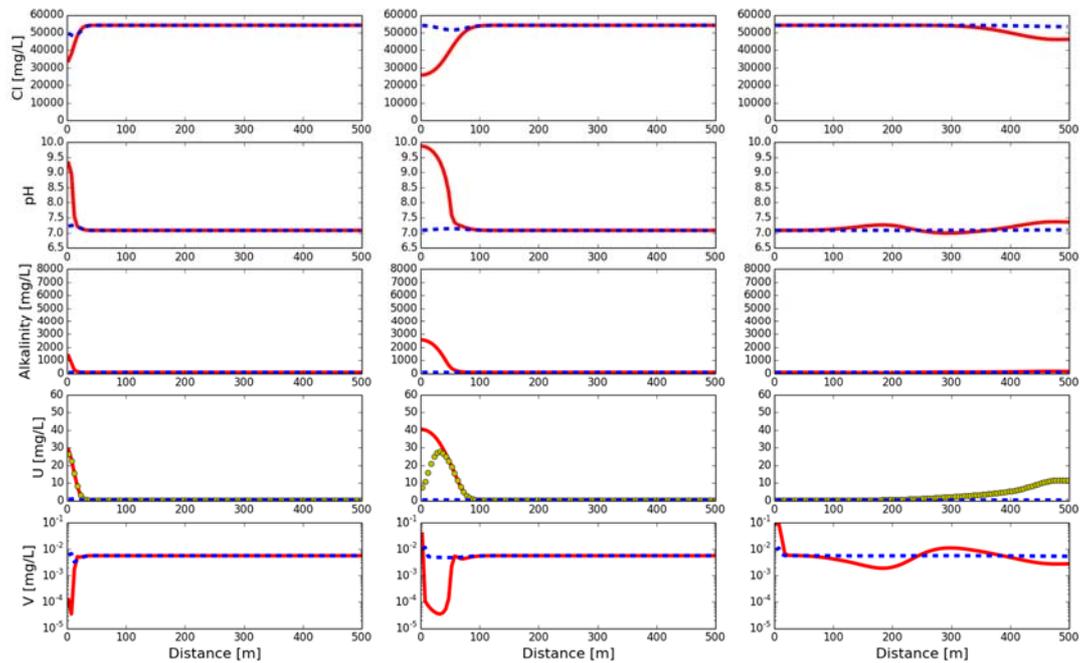


Figure 5 Comparison of selected simulation results for scenarios S2 (modified base case, blue dashed lines) and S5 (updated database + source active over 200 years + increased alkalinity in the source, red solid line) after 20 (left), 200 (centre) and 1000 (right) years simulation time. Yellow circles indicate the sum of the concentrations of the newly added uranyl complexes.

2.6 S6: Role of equilibrium with carnotite

A speciation calculation for the ambient groundwater indicate that the aqueous solution is relatively close to being in equilibrium with carnotite ($\text{K}_2\text{U}_2\text{O}_7$), with a saturation index (SI) of 0.62 (slightly oversaturated). This final scenario investigates therefore the potential role that carnotite could have as a solubility control for uranium. Therefore this scenario assumes a mineral equilibrium with carnotite, whereby the target saturation index was set to 0.62, corresponding to the background conditions of the aquifer. All other model assumptions were adopted from S4. The simulation results show that while uranium concentrations are further elevated after a 200 year simulation time (compared to S4 and S5), there is a substantial reduction of the concentrations at further distances where elevated uranium concentrations were observed in scenarios S4 and S4, showing the mitigating effect that carnotite precipitation might have on controlling the mobility of uranium.

Figure 6 Comparison of selected simulation results for scenarios S2 (modified base case, blue dashed lines) and S6 (updated database + source active over 200 years + carnotite equilibrium, red solid line) after 20 (left), 200 (centre)

and 1000 (right) years simulation time. Yellow circles indicate the sum of the concentrations of the newly added uranyl complexes.

2.7 S7: Impact of Fe-sulfides on U mobility

All previous scenarios assumed that the geochemical conditions in the flowpath remain fully oxidised. However, under geochemically reducing conditions uranium would persist as U(IV) and dissolved concentrations are then limited by the solubility of U-bearing minerals such as uraninite. Geochemically reducing zones may persist where labile electron donors such as dissolved or sediment-bound organic carbon (DOC/SOM) consume electron donors such as oxygen and sulfate or where minerals have been reduced in the past. In the model the impact of a geochemically reducing zone was investigated by assuming the presence of pyrite along the flowpath between $x = 200$ and $x = 500$ m. In addition, uraninite was allowed to precipitate. Sorption and ion exchange capacities were eliminated in the reducing zone. The presence of pyrite consumes dissolved oxygen and triggers the precipitation of uraninite as a result of the shift in redox conditions. Spectroscopic evidence for the predicted U(VI) reduction in the presence of Fe-sulfides has been reported, for example, by Wersin et al., 1994).

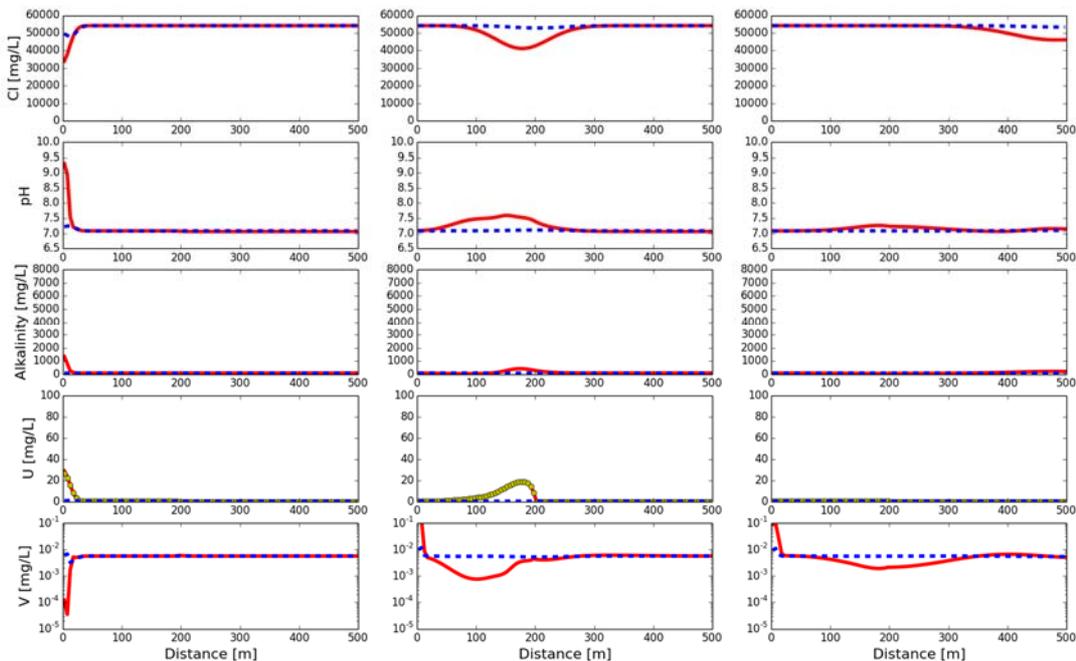


Figure 7 Comparison of selected simulation results for scenarios S2 (modified base case, blue dashed lines) and S7 (updated database + source active over 200 years + pyrite between $x = 200$ and $x = 500$ m, red solid line) after 20 (left), 200 (centre) and 1000 (right) years simulation time. Yellow circles indicate the sum of the concentrations of the newly added uranyl complexes.

2.8 S8: Impact of Fe-sulfides on U mobility in a 2D flow domain.

The previous case (S7) was further investigated to illustrate the impact of localised reducing zones on U mobility. The simulations were performed with PHT3D (Prommer et al., 2003), a MODFLOW/MT3DMS-based three-dimensional reactive transport model that incorporates PHREEQC to compute geochemical reactions. PHT3D has previously been applied to simulate uranium transport (e.g., Greskowiak et al., 2010, 2011; Ma et al., 2010, 2014a,b, Sengor et al., 2015). For simplicity the 2D setup involves a parallel flow-field in a hydrogeologically homogeneous aquifer, with the prevailing flow velocities assumed to be identical to the PHREEQC-based scenarios S1-S7. The water compositions and mineral assemblages were adopted from S7. Similar to S4-S7 it was assumed that the source was active for 200 years before flushing with ambient water occurred. The width of the source was assumed to be limited to 10m, i.e., 10% of the width of the model. Similar to the S1-S7 a longitudinal dispersivity of 5m was assumed, while transverse lateral dispersivity was estimated to be 0.5 m. In contrast to previous scenarios transverse mixing can contribute to the attenuation of concentrations. Pyrite was assumed to be present in three discrete zones. Figure 8 shows selected simulation results (concentration snapshots as 2D contours) after 100, 200, 500 and 1000 years simulation time. The results illustrates the significant impact of the presence of Fe-sulfides on the mobility of uranium as uraninite precipitates where transitions from more oxidising conditions towards more reducing conditions (as indicated by the absence of dissolved oxygen and negative pe zones) occur.

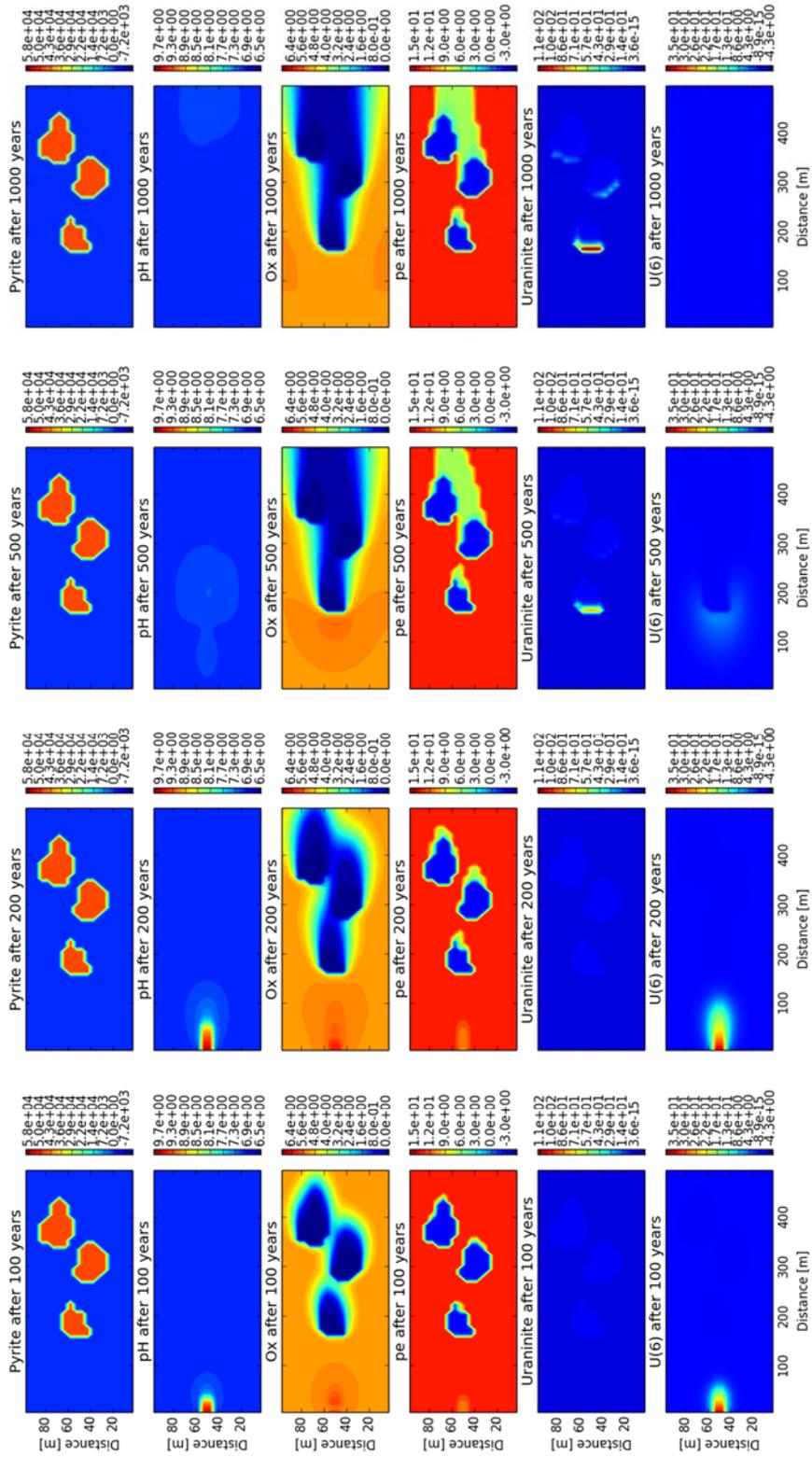


Figure 8 Selected simulation results for S8 after 100, 200, 500 and 1000 years.

3 Implications of simulation results

The results of the supplementary modelling scenarios illustrate that a number of factors may allow elevated uranium concentration to migrate further than in the originally defined modelling scenarios. The two most important factors are (i) the inclusion of the previously unconsidered uranyl-calcium complexes and (ii) the modified source-term assumption. However, the simulations also show that the speciation calculations with the revised database imply that far less uranium than previously predicted is hosted on mineral sorption sites and therefore the risk of mobilising uranium through geochemical changes is reduced. It is important to note that the scenario that included mineral equilibrium with carnotite (S6) showed that carnotite precipitation could possibly prevent that aqueous concentration increase to the predicted high concentrations that were obtained in the preceding scenarios S4 and S5. Also scenarios S7 and S8 show that the localised presence of Fe-sulfides along the flow path would provide an efficient natural barrier for the migration of uranium.

Overall the range of the revised modelling scenarios indicate that future investigations should be aimed at reducing predictive uncertainty. This could be achieved by

- a refined hydrogeochemical field-site characterisation
- a detailed mineralogical characterization that identifies the mineral inventory at potentially affected sites. This could in particular include the identification of geochemically reducing conditions
- batch sorption tests for uranium and vanadium with various sediment materials from the aquifers that are potentially affected by leakage from TSF facilities
- developing site-specific surface complexation models that capture the characteristic sorption behavior of the sediments along the major transport pathways, and
- laboratory-scale column testing of uranium migration with sediments, groundwater and other aqueous solutions that most likely represent the composition of fluids egressing from the proposed TSF facilities.

Such investigations will improve the understanding of the geochemical processes that will influence the behaviour of contaminants contained within accidental releases from the TSF with distance and time. In addition, dispersion and, also diffusion over the anticipated long time-scales, will contribute to the attenuation of any undesired geochemical changes. Modelling of physical transport processes relies on:

- an understanding of the regional groundwater flow system
- a local-scale hydrogeological characterisation of the site
- hydrological data to understand recharge and evaporation rates
- monitoring of groundwater levels
- construction and calibration of a local-scale (>> potential plume) flow model

4 Recommendations for reducing the uncertainty of current reactive transport predictions

The following recommendations are presented in the context of a brief, general guide to developing a better conceptual and quantitative understanding of the reactive transport processes, in particular for uranium, at the Toro Energy's Wiluna sites.

4.1 Hydrogeochemical characterisation

A thorough understanding of the ambient hydrogeochemical conditions upstream and downstream of planned TSF facilities is crucial for reducing the uncertainty of the predictions of the potential fate of uranium (and vanadium) and will support the design of any required preventative measures and / or later remediation activities aimed at mitigating inadvertent uranium release. In the present case, the characterisation will also document the naturally high uranium concentrations within the local environment. Understanding the redox chemistry of the groundwater and sediments will underpin a better understanding of uranium mobility, given that uranium would be likely to be effectively immobilised under reducing conditions. Reducing geochemical conditions downstream of the TSF-facilities, such as created by naturally abundant sediment organic matter liberated during mining and uranium extraction and also within the aquifer would generally promote the reduction of uranyl and subsequent precipitation of uranium as U(IV).

4.1.1 GROUNDWATER CHEMISTRY

Groundwater sampling, including depth-resolved sampling of hydrochemical parameters is required to reliably define the current and potentially future 'ambient' conditions. The interpretation of the measured aqueous chemistry and of spatial patterns (e.g., changes with depth) assists with the identification of the mineral assemblage that currently control or influence the groundwater composition and of minerals or mineral formation or dissolution reactions that may be induced during an inadvertent egress of TSF-derived waters.

4.1.2 SEDIMENT CHARACTERISATION

Both mineralogical and geochemical characterisation of the aquifer material should be performed to support the development of a conceptual model of the major water-sediment reactions that control the groundwater chemistry and therefore also many of the important parameters that control uranium sorption. The mineralogical composition of the samples may be determined with quantitative X-ray diffraction (XRD) whilst the major element composition of the sample may be quantified as element oxide by fusion X-ray fluorescence (XRF) and trace elements by pressed powder XRF analysis. Sample electrical conductivity (EC), pH, acid neutralisation capacity (ANC), acid-digestible metal and total organic carbon (TOC) contents, cation exchange capacity (CEC), and ammonium oxalate-extractable elements may also be determined.

4.2 Laboratory investigations

4.2.1 SORPTION EXPERIMENTS WITH SITE SEDIMENTS

Dedicated sorption experiments with sediments collected from the site will provide the most critical information to improve current model predictions and to reduce uncertainty. These experiments would involve the variation of a range of parameters. Experiments may include:

- Adsorption isotherms for UO_2 at discrete pHs, e.g., at pH 6.5, 7.5, 8.5 and 9.5;
- Variable pH experiments at a fixed, representative UO_2 concentration
- Assessment of competitive sorption effects
- Assessment of ionic strength effects

These experiments can be performed as a series of batch sorption experiments either for representative sediment composite materials or separately for a range of different lithologies. Sorption experiments with the high ionic strength groundwater from the Wiluna site will provide far more robust information than literature sorption data that have been derived under very different geochemical conditions.

4.2.2 SITE-SPECIFIC SURFACE COMPLEXATION MODEL

The results of laboratory batch sorption experiments can be analysed through an inverse geochemical modelling approach (Davis et al., 2004, Hyun et al., 2014, Turner et al., 2014) and used to construct a sorption model that reproduces uranyl sorption behaviour within the range of the tested geochemical conditions. Such a surface complexation model can be developed with standard geochemical modelling software such as PHREEQC in combination with a parameter estimation tool such as PEST (Doherty, 2010). The coupling of those two tools allows for optimisation of

- the reaction constants (log K_s) of the sorption reactions
- the number of sorption sites (sorption site density) per volume of aquifer

The surface complexation model derived from this procedure would replace the standard Dzombak and Morel (1990) surface complexation model that was used for the SWC and the current model predictions. The Dzombak and Morel database was originally developed for sorption to pure ferrihydrite and not for natural mineral assemblages. A surface complexation model that is developed from experiments with sediment material from the investigated site provides a far more realistic quantification of uranium mobility.

4.2.3 U AND V MIGRATION FLOW-THROUGH COLUMN EXPERIMENTS WITH SITE SEDIMENTS

The site-specific surface complexation model developed through the batch experiment may be verified and refined under well-controlled flow-through conditions with sediments collected at the field site. This type of experiment often provides the most important source of data to test models under well-controlled uniform flow conditions, i.e., geochemical processes can be identified and quantified in the absence of uncertainties induced by hydrogeological and geochemical heterogeneities. A laboratory-scale column setup allows to collect a large number of samples to resolve temporal and spatial concentration gradients, which is generally required to obtain a robust process understanding where complex water-sediment interactions occur.

4.2.4 FIELD-SCALE PUSH-PULL EXPERIMENT

Natural or forced gradient tracer injection experiments and their model-based interpretation (see, e.g., Ma et al., 2014) assure that the laboratory-derived process understanding, as expressed in the conceptual and

numerical models, holds under field-scale conditions. However, such tests involve a significant logistical effort once a large number of monitoring boreholes are sampled. Therefore, push-pull tests (see, e.g., Fox et al., 2012) that involve the injection, storage and recovery of a tracer-spiked controlled volume of water can provide an efficient alternative strategy to test field-scale uranium transport behaviour under variable geochemical conditions.

4.3 Long-term leaching tests

The new model variants (S4-S6) illustrate the impact of a source that persists beyond a short pulse-type release of TSF-derived water. A persisting source might occur where recharge to the TSF would allow to replenish egressing water and solutes. Longer-term flow-through columns tests tailings material would be aimed at quantifying temporal changes in leaching characteristics. These tests would also serve as baseline for testing in situ immobilisation techniques that would prevent off-site migration of solutes even where water flux across the tailings material occurs.

4.4 Reactive transport modelling

Reactive transport modelling is recommended as a means of integrating and interpreting the data collected during laboratory- and field-scale experiments. This step is important for identifying or confirming conceptual models of reactive transport processes and to narrow the range of parameters. Process-based models that incorporate laboratory-derived sorption characteristics have previously shown to describe observed uranium migration patterns with sufficient accuracy (e.g., Ma et al., 2014a,b). Predictive models might be performed using multi-dimensional reactive transport models (Prommer et al., 2003, Turner et al., 2014). Compared to the one-dimensional PHREEQC simulations (as in the present study) this allows to simultaneously account for mixing and dilution processes that often contribute substantially to the attenuation of geochemical changes. Advanced modelling approaches may also take the impact of parameter uncertainty into account and provide probabilities, for example of uranyl concentrations exceeding a certain level as a specified distance and time rather than the result of a single deterministic scenario.

5 Proposed program to test feasibility of U, V and radionuclide in situ immobilisation

5.1 Literature review

A comprehensive literature review should be conducted to identify and document prior and emerging research and industry practices for the capture and immobilisation of U, V and radionuclides (such as Tokunaga et al. 2009) in alkaline leach operations. Where relevant, this information will be used to develop potential in situ immobilisation strategies for Toro Energy's proposed Centipede Uranium deposit.

5.2 Laboratory-scale testing

Where the potential for the mobility of U and V is identified in modelling simulations, laboratory-scale testing to evaluate remediation scenarios would be undertaken using samples of representative host lithologies, ore, tailings and associated solutes, some of which would be potentially derived from pilot-scale testing. Testing would initially be undertaken in batch, and then in column mode to make a detailed assessment of the performance of methods to capture and immobilise, U, V and radionuclides within the TSF and also downstream in the event of leakage. Part of this work would also be used to inform model predictions of the fate of contaminants during and following the closure of mining operations at Toro Energy's proposed Centipede Uranium deposit.

References

- Davis, J.A., Meece, D.E., Kohler, M., Curtis, G.P. (2004). Approaches to surface complexation modeling of Uranium(VI) adsorption on aquifer sediments. *Geochimica et Cosmochimica Acta* 68, 3621-3641.
- Doherty, J. (2010). PEST, Model-independent parameter estimation—User manual (5th ed., with slight additions): Brisbane, Australia, Watermark Numerical Computing.
- Dong, W., and S. C. Brooks (2006), Determination of the formation constants of ternary complexes of uranyl and carbonate with alkaline earth metals (Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+}) using anion exchange method, *Environ. Sci. Technol.*, 40(15), 4689–4695.
- Dong, W., and Brooks, S.C. (2008). Formation of aqueous $MgUO_2(CO_3)_3^{2-}$ complex and uranium anion exchange mechanism onto an exchange resin, *Environ. Sci. Technol.*, 42(6), 1979–1983.
- Fox, P.M, Davis, J.A. and Zachara, J.M. (2006). The effect of calcium on aqueous uranium(VI) speciation and adsorption to ferrihydrite and quartz. *Geochimica et Cosmochimica Acta* 70 (6), 1379-1387, 10.1016/j.gca.2005.11.027
- Fox, P.M., Davis, J.A., Hay, M.B., Conrad, M.E., Campbell, K.M., Williams, K.H. and Long, P.E. (2012). Rate-limited U(VI) desorption during a small-scale tracer test in a heterogeneous uranium-contaminated aquifer. *Water Resour. Res.*, 48, W05512, doi:10.1029/2011WR011472
- Greskowiak, J., Hay, M. B., Prommer, H., Liu, C., Post, V.E.A., Ma, R., Davis, J.A., Zheng, C. and Zachara, J.M. (2011). Simulating adsorption of U(VI) under transient groundwater flow and hydrochemistry: Physical versus chemical nonequilibrium model, *Water Resour. Res.*, 47, W08501, doi:10.1029/2010WR010118.
- Guillaumont, R., Fanghanel, T. Neck, V., Fuger, J., Palmer, D.A., Grenthe, I. and Rand, M.H. (2003). Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium, and Technetium, Elsevier, Amsterdam.
- Dzombak, D.A and Morel, F.M.M. (1990). *Surface Complexation Modeling: Hydrous Ferric Oxide*, Wiley-Interscience, New York, 393 pp.
- Hyun, S.P., Fox, P.M., Davis, J.A., Campbell, K.M., Hayes, K.F., and Long, P.E. (2009). Surface complexation modeling of U(VI) adsorption by aquifer sediments from a former mill tailings site at Rifle, Colorado." *Environmental Science & Technology* 43(24), 9368-9373.
- Ma, R., Liu, C., Greskowiak, J., Prommer, H., Zachara, J. and Zheng, C. (2014a). Influence of calcite on uranium(VI) reactive transport in the groundwater-river mixing zone. *J. Contam. Hydrol.* 156, 27-37.
- Ma, R., Zheng, C., Liu, C., Greskowiak, J. Prommer, H., and Zachara, J.M. (2014b). Assessment of controlling processes for field-scale uranium reactive transport under highly transient flow conditions. *Water Resources Research* 50, 1006-1024.
- Turner, J., Byrne, J., Davis, J., Douglas, G., Kaviani, N., Kent, D., Park, J., Prommer, H., Shackleton, M., Trefry, M., Wendling, L., (2014). Report on Ranger Minesite Pit #1 Closure Strategies, Reprt number EP135637, Minerals Down Under, p545.
- Parkhurst, D.L. and Appelo, C.A.J. (1999). User's guide to PHREEQC (version 2) - A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. USGS Water Research Investigation Report 99-4259. Washington, D.C., United States Geological Survey. 312 pp.

- Prommer, H., Barry, D.A. and Zheng, C. (2003). MODFLOW/MT3DMS based reactive multicomponent transport model. *Ground Water* 42: 2247-257.
- Şengör, S.S., Mayer, K.U., Greskowiak, J., Wanner, C., Su, D., Prommer, H. (2015). A reactive transport benchmark on modeling biogenic uraninite re-oxidation by Fe(III)-(hydr)oxides. *Computational Geosciences*, 15 p. Article in Press.
- Tokunaga, T.K., Kim, Y., and Wan, J. (2009). Potential remediation approach for uranium-contaminated groundwaters through potassium uranyl vanadate precipitation. *Environmental Science & Technology* 43 (14), 5467-5471.

SWAC (2012).

- Wersin, P., M.F. Hochella, Jr., P. Persson, G. Redden, J.O. Leckie, and D.W. Harris (1994). Interaction between aqueous uranium (VI) and sulfide minerals: Spectroscopic evidence for sorption and reduction. *Geochimica et Cosmochimica Acta.*, 58, No. 13, pp. 2829-2843.

CONTACT US

t 1300 363 400
+61 3 9545 2176
e enquiries@csiro.au
w www.csiro.au

FOR FURTHER INFORMATION

Henning Prommer
t +61 8 9333 6272
e Henning.Prommer@csiro.au

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