Modelling Uranium Waste Residue Release and Transport Within a Near Surface Repository – 9137

S. Kwong, J.S. Small and O.R. Thompson
National Nuclear Laboratory
Hinton House, Risley,
Warrington, UK. WA3 6AS.

ABSTRACT

This paper presents results from coupled chemical and transport modelling of the near field of the Low Level Waste Repository (LLWR) in the UK. This modelling contributes to an understanding of the geochemical and hydrogeological processes controlling the release of uranium from the near field.

Legacy disposals of uranium at the LLWR are principally in the form of fluoride residues from uranium refining in the UK. Based on recent advances in the understanding of the kinetics of fluorite (CaF_2) dissolution, a conceptual model of uranium release from MgF_2 residues in these wastes has been formulated and implemented using the reactive chemical model PHREEQC. Using the PHAST reactive transport software, a coupled model of fluoride dissolution and contaminant transport has been developed. The model incorporates a realistic representation of groundwater flow at the LLWR site.

In the present demonstration model, release of uranium from five arbitrary locations within the trench area was modelled in order to illustrate the complex behaviour of the potential contaminant plume. Initial results from the reactive-transport model for a typical uranium fluoride waste residue are encouraging, with modelled concentrations of uranium and fluoride generally consistent with measured values. This builds confidence in the conceptual model for uranium leaching. The model predicts that uranium concentrations in groundwater will be limited to moderate levels. The significance of this, in terms of the effect on radiological risks arising from uranium, will be assessed as part of the 2011 Environmental Safety Case for the LLWR.

INTRODUCTION

The UK Low Level Waste Repository (LLWR) located in Cumbria has served as a national repository for LLW since 1959. Until 1988, LLW was backfilled into trenches excavated into glacial clays and covered with an interim cap. A post-closure radiological assessment was undertaken in 2002 [1], which highlighted potential doses that may arise from uranium disposals to the trenches. The near-field conceptual model that formed the basis of these calculations [1, 2] considered that the release of uranium would be limited by the low solubility of UO_2, which is stable under the prevailing reducing chemical conditions. A biogeochemical reactive transport model of the site [2] indicated that after periods of around 3,000 to 4,000 years, the trenches may re-oxidize to the conditions in the surrounding geosphere and uranium may potentially become more mobile. The radiological assessment of the groundwater pathway considering this scenario [1] determined that after 10,000 years Ra-226 and Pb-210 daughters of U-234 would arrive in the biosphere, leading to doses that may exceed the 1e-6 yr^{-1} risk target. It was recognised [1] that the primary chemical and physical form of uranium in the wastes may also affect the release, but this was not considered in this previous assessment [1].

The LLWR has since supported work to further advance the understanding of the performance of the facility, which will lead to the production of an Environmental Safety Case in 2011. Part of this work is aimed at improving understanding of the behaviour of key radionuclides in the near field. The work involves the interpretation of site data and the development of an updated conceptual and computational model that will form the basis of future assessment calculations. The calculations and improved conceptual understanding will input to optioneering studies to help ensure that radiological impacts from the trench disposals are managed to be As Low As Reasonably Achievable (ALARA).

Legacy uranium disposals at the LLWR comprise a significant proportion of fluoride residues. It is therefore important to gain an understanding of uranium release and transport at the LLRW repository taking into account the geochemical effects that slow the uranium release. A new concept has been developed [3] in which uranium release is controlled by the rate-limited dissolution of the fluoride wasteform. Initial results from this model have been presented earlier [3]. In the current study, a model is developed using the PHAST [4] code to examine in more detail the release and transport of contaminants in groundwater under the current hydrogeological conditions at the LLWR.

Certain site-specific information, such as the location of specific uranium disposals, cannot be made public on security grounds. Therefore, the modelling has been based on some representative uranium fluoride wastes assumed to be emplaced at arbitrary locations within the LLWR.

OVERVEW OF THE PHAST CODE

PHAST (**PH**REEQC **A**nd H**ST**3D) is a modelling tool for simulating groundwater flow, solute transport, and multi-component geochemical reactions in three-dimensional saturated conditions [4]. It is a versatile groundwater flow and solute-transport simulator, with capabilities to model a wide range of equilibrium and kinetic geochemical reactions. The flow and transport calculations are based on a modified version of HST3D that is restricted to consider constant fluid density and constant temperature. Geochemical reactions are simulated with the geochemical model PHREEQC [5], which is embedded in the PHAST code.

A three-dimensional Cartesian coordinate system and finite-difference techniques are used for the spatial and temporal discretisation of the flow and transport equations. A variety of boundary conditions are available in PHAST to simulate flow and transport, including specified-head, flux, and leaky conditions, as well as the special cases of rivers and wells.

MODELLING APPROACH

An overview of modelling strategy employed in the current chemical and transport modelling for the near field of the LLWR can be summarised as:

- A reactive model was developed to compute the dissolution rates of fluorite and the associated release of uranium from representative uranium fluoride residues at LLWR.
- A 3D flow and transport model of the shallow flow system[1] developed.
- Model calibration performed to obtain acceptable conformance between measured and modelled hydraulic heads.
- Transient transport simulations made using kinetic release of uranium (from fluoride residues) derived from the reactive model.
- Results of transport model compared to historic monitoring results.

The model domain covers a region of 1300 m x 1200 m x 15 m (in X-, Y- and Z-directions) and is discretised using 95, 75 and 10 cells respectively (Figure 1). Engineered features represented in the solute transport model include:

- Cut-off walls for restricting groundwater movement in some regions (assumed depth of 5 m);
- Trench clay base layer (assumed thickness of 0.5 m);
- Firebreaks (low permeability partition walls (not shown) between trench waste with assumed depth 4 m);
- Trench cap region for specification of lower infiltration (i.e. 0.054 m y^{-1} over the trench area with interim cap, and 0.263 m y^{-1} over the rest of the site area.

[1] The current model only considers the inventory located within the saturated zone which is subjected to groundwater transport.

Geology representation

The model represents an idealised geological structure of the site with four strata, namely top soil, clayey sand (Upper Clay), gravel and sandstone bedrock, over the whole model domain (Table I). Field data for part of the site region indicates that there are areas where the Upper Clay is absent. These areas are represented in the model, approximated as a number of rectangles (referred to as 'Hole') as shown in Figure 1. It is not clear if the absence of clay is more widespread than indicated. This information would be useful for the refinement of future detailed flow and transport models.

Hydraulic properties of the geological and other materials used in the model are presented in Table I. It is assumed that the waste is slightly more permeable than the top soil, while the firebreaks consist of compacted soil and are likely to be less permeable than the top soil. At the north of the site, there is a cut-off wall (for reducing groundwater flow into the trench waste region) constructed with low-permeability cement. This is assigned a very low hydraulic conductivity in the model of 3 to 4 orders of magnitude less than that of the top soil. There is a layer of low permeability clay at the base of the trenches. The clay base is assumed to have a hydraulic conductivity similar to that of cement. There remain significant uncertainties associated with the characteristics of the clay layer (e.g. homogeneity and continuity (below each trench), and variations in thickness). It is possible that the hydraulic conductivity of the clay base may be different from the value used here. More detailed information on the properties and characteristics of the clay base would enable an improved model representation.

The properties of the various materials represented in the near-field models are summarised in Table I.

Table I Values for the materials properties represented in the near-field model.

Geological materials						
Material	**Elevation (m)**	**Porosity (-)**	**Kx and Ky[a] ($m\ s^{-1}$)**	**Kz[b] ($m\ s^{-1}$)**	**D_{Long}[c] (m)**	**D_{Hor} and D_{Vert}[d] (m)**
Top Soil	11 to 15	0.2	7.50E-05	7.50E-06	5	0.5
Clayey Sand	9 to 11	0.2	1.00E-07	1.00E-07	5	0.5
Gravel	3 to 9	0.3	7.50E-05	7.50E-05	10	1
Sandstone	0 to 3	0.2	1.30E-05	1.30E-05	5	0.5
Other materials						
Waste	11 to 15	0.2	1.50E-04	1.50E-04	5	0.5
Clay base	10.5 to 11	0.1	5.00E-09	5.00E-09	1	0.1
Firebreak	11 to15	0.15	3.75E-05	3.75E-05	1	0.1
Cut-off wall	10 to 15	0.1	5.00E-09	5.00E-09	1	0.1

[a] K_x, K_y Horizontal hydraulic conductivity

[b] K_z Vertical hydraulic conductivity

[c] D_{Long} Longitudinal dispersivity

[d] D_{Hor}, D_{Vert} Horizontal and vertical dispersivity

Groundwater flow representation

The hydrogeological conceptual model for the LLWR site includes Upper and Lower groundwater systems. Within the trenches, the hydraulic head is variable and 'water mounds' are observed, where there are localised elevations in hydraulic head. The cause of these mounds is not clear and has not been investigated further in this study. A steady-state groundwater flow model was constructed to represent these key features of the hydrogeological conceptual model (see Figure 1).

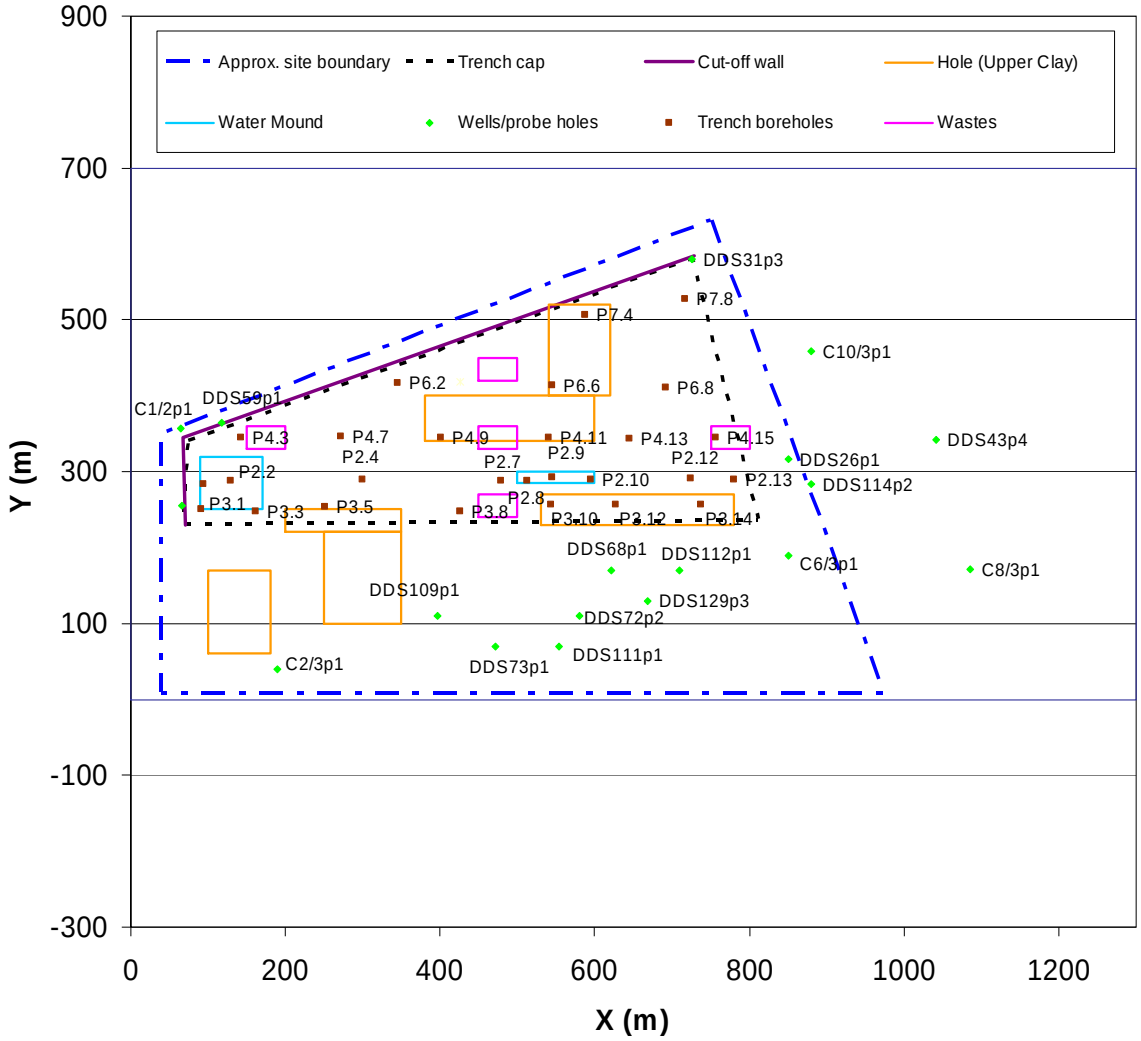

Figure 1 Near-field model domain showing probe holes, wells, and features represented in the models such as cut-off wall, wastes, water mounds and areas where clay was absent in the Upper clay (referred as 'hole').

The Upper groundwater system (Figure 2) is specified in the model over a near surface region (over depths 9 to 15 m Above Ordnance Datum (AOD) using a high hydraulic head of 16 m at the inflow boundary (X=0 m) which is then gradually decreased to 9m at the downstream boundary (X=1300 m). In a similar fashion the Lower/Regional groundwater system is specified with a high hydraulic head of 9 m at the boundary Y=900 m, and is gradually decreased to 4m at the downstream boundary (Y=-300 m), over the depth of 0 to 5 m AOD. As an approximation (when detailed information on flow directions is not available), the current model assumes that the ambient flows

within the Upper and Lower groundwater systems lie along the positive X- and negative Y-directions respectively. This work also demonstrate the ability to represent both the Upper and Lower groundwater systems in the model.

The PHAST model uses a grid system in Cartesian coordinates, such that the model domain and all features are represented by a rectangular cell or group of cells. PHAST allows the specification of head or flux boundary conditions at the model top surface to represent regions of elevated hydraulic head. In the current model, localised increases in hydraulic head related to two 'water mounds' within the trench area (Figure 2) are represented as two areas of elevated hydraulic head ('Water Mound' in Figure 1). The model uses a specified head boundary condition to represent the elevated hydraulic heads of 17.5 m and 18.5 m at the water mounds located at X ~ 100m and 600m respectively.

The near-field model also represents reduced infiltration over the trench area below the trench cap compared with the rest of the site area. The model uses infiltration values of 0.054 m y^{-1} and 0.263 m y^{-1} over the trench area (with interim cap) and the rest of the site area, respectively.

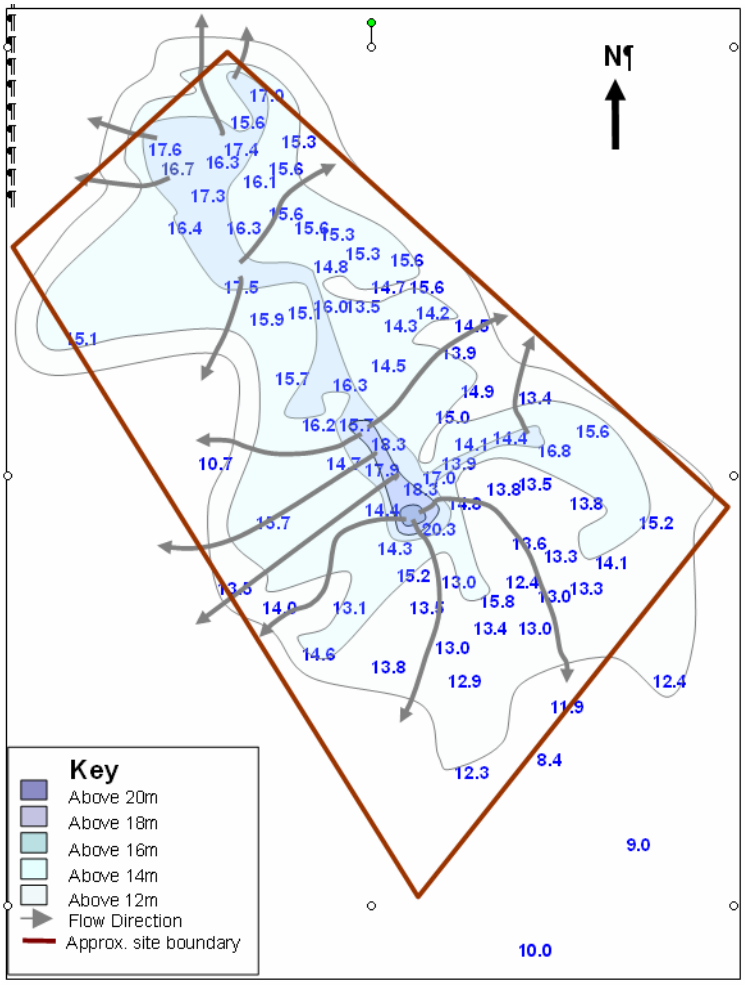

Figure 2 Levels of leachate and Upper groundwater and indicative flow directions (average of data from 1990-2005).

Uranium inventory and leaching model representation

Reference [3] describes a hydrogeochemical model developed with PHREEQC/PHAST that illustrated the effects of rate limited release of uranium (controlled by the dissolution of fluoride residues) to groundwater. This model considered a generic trench 20m wide and 100m in length, in which regions with disposed fluoride residues were located between two firebreaks. The model [3] used a simple representation of the flow field at the LLWR and was used to investigate the release behaviour from a number of representative uranium fluoride waste residues and the resulting uranium concentrations in leachate close to source. In the present demonstration model, five arbitrary regions of uranium waste (Figure 1) over the trench region were used to examine the complex behaviour of the potential contaminant plume that may develop. It was assumed that each waste region was associated with the same volume of fluoride waste. The model parameters for the wastes are summarised in Table II.

The present near-field reactive transport model follows the conceptual model of uranium release developed previously [3], which makes use of a fluorite dissolution mechanism [6] controlled by H^+ and Ca^{2+} ion activities[2] (a) such that the dissolution rate (r) is expressed as:

$$-r = k\left(\left(a_H^+\right)^2 \Big/ \left(a_{Ca}^{2+}\right)\right)^{\alpha} \qquad \text{(Eq. 1)}$$

where k is the rate constant and α is the order with respect to the H^+ activity versus the Ca^{2+} activity.

Reference [6] provides values for the rate constant (k) and α for the dissolution of fluorite powders in specific size fractions and pH values between pH 2.57 and pH 5.08 at 25°C and 100°C. The current implementation within the near-field model releases approximately 0.00026 moles of U to the groundwater for every mole of MgF_2 dissolved. Effectively this release model provides a constant source term, since a constant uranium content for the fluoride residue is considered. The rate of release will also vary with the composition (e.g. Mg, Ca, F, pH) of the groundwater, but in this model these parameters are assumed to be constant. In more detailed models, with varying groundwater composition, the source term may not be constant. Similarly, where the uranium content of the residue varies, or different fluoride solubility limits occur in different regions of the trenches, the source term would vary spatially. Further details of the release mechanism and model implementation are given in [3].

Table II Location and volume of fluoride waste used in the model

Waste[e]	**Approximate waste location**	
	X (m)	**Y (m)**
WF1	150	330
WF2	450	420
WF3	750	330
WF4	450	240
WF5	450	330

[e] Assuming each waste volume of about 6,000 m^3.

[2] Activity here is the thermodynamic quantity approximately equivalent to molal concentration.

MODEL RESULTS

Calibrated near-field groundwater flow model

The near-field groundwater flow model was calibrated against the time averaged hydraulic heads at a number of wells and probe holes (see Figure 1). Values for the material properties represented in the near-field model are shown in Table I. The groundwater flow model was calibrated by varying the representation of the water mounds (e.g. intensity, size, location) in the model. Hydraulic head data from a total of 47 monitoring wells and probe holes were used to calibrate the numerical model. It should be noted that the target heads are for the Upper groundwater system only. This makes sense since, in the model, fixed heads were specified at all perimeters and at the water mounds.

In order to replicate the observed heads (Figure 2), the two water mounds were represented in the model as two rectangular areas of elevated hydraulic head with parameters as given in Table III.

Table III Parameters for the water mounds represented in the calibrated near-field groundwater flow model.

Model feature	X1, X2 (m)	Y1,Y2 (m)	Head (m)
Water Mound 1	90, 170	250, 320	17.5
Water Mound 2	500, 600	285, 300	18.5

Figure 3 shows a comparison of the modelled heads for the calibrated model and observed heads. It can be seen that the model heads compare favourably with the observed heads, with two prominent water mounds (Figure 2). The presence of the water mounds is significant in influencing the groundwater flows, such that the decreasing hydraulic head away from the water mound causes radial outward flow locally. The overall flow pattern is rather complex with local flow direction dependent on relative location to the water mounds.

The head comparison in the trench area is presented in Table IV and shown graphically in Figure 3. Within the trench area, heads are predicted to within 1 m of the observed values at 18 out of the 29 locations, with the others (with the exception of six) to within 2 m of the measured values. The head comparison is good overall, with the trend well predicted. The comparison also shows that good agreement is obtained at locations that are fairly well spread out within the trench area. This indicates that the overall flows are likely to be well represented[3], while heads at a small number of locations are less well predicted. This is due to the influence of localised effects not accounted for in the model. For example, at P2.2 the model undepredicts the groundwater head by 2.2m, with heads in the surrounding area (e.g. P2.1, P2.4, P3.1, P3.3, P4.3) all predicted to well within 1m. This is also the case for probe hole P2.10 where the observed head is over 21m, with the model head under-predicted by over 4m.

[3] In a separate model run (not shown), the evolution of the tritium plume was modelled using the calibrated groundwater flow model over a 10 year period. The modelled tritium result is consistent with observations at the site. This builds confidence in the ability of the PHAST model to represent the near-field hydrogeology of the LLWR site.

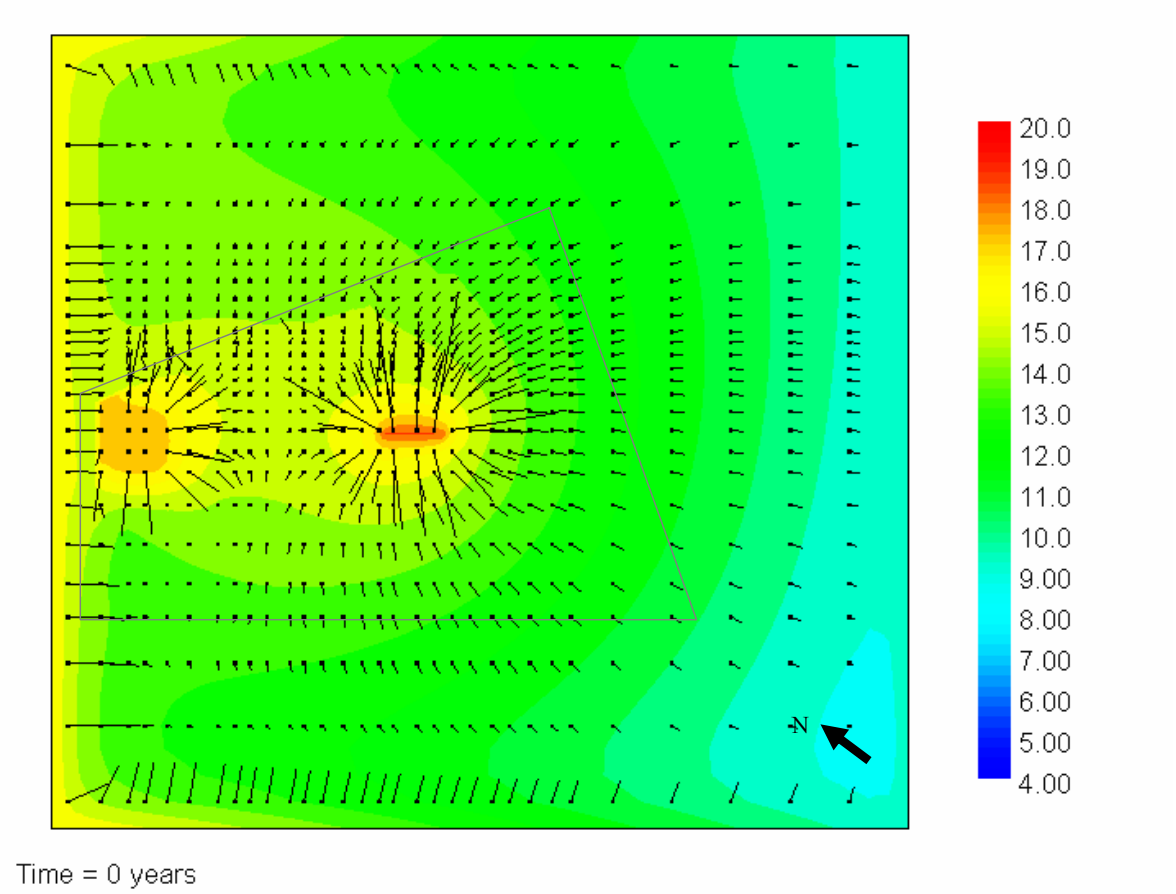

Figure 3 Computed hydraulic heads (m AOD) and velocity vectors from the calibrated groundwater flow model (top, the approximate site boundary shown in grey), and comparison of modelled and observed heads at trench bore holes (bottom).

Beyond the trench area, modelled heads are predicted to within 1 m of the observed values at 10 out of the 18 locations, with most of the others (except two) to within 3 m of the measured values (Table V). Although the overall head comparison is good and the trend well predicted, there are larger differences (>2 m) between the computed and observed heads at a number of 'isolated' locations. These localised discrepancies are related to the effects of heterogeneity not included in the model. For example, the model under-predicts the groundwater head by over 2 m at C1/2p1 and DDS126p1 (Figure 1), with heads at a number of nearby locations predicted to within 1 m of the observed values (e.g. 0.8m at DDS59p1; 0.9 m at P2,1; 0.2 m at P3.1). A similar situation also occurs at DDS114ps that was over-predicted by 3.6 m, while much better predictions are obtained at the nearby locations (e.g. within 0.4 m at DDS26p1 and 0.6m at P2.13). The average head differences between the modelled and observed heads are 1.06 m and 1.3 m for the trench areas (29 probe holes) and the surrounding region (18 wells) respectively. These average head differences would have been lower if the isolated large discrepancies were not included in the statistics.

Table IV Comparison of modelled and observed heads at the trench probe holes (see Figure 1).

Trench probeholes	X	Y	Observed head (m)	Model head (Basecase)	Difference $Head_{Model - observed}$
P2.1	93.7	283.4	16.36	17.30	0.9
P2.2	129.8	288.5	19.67	17.50	-2.2
P2.4	299.5	289.3	15.52	14.90	-0.6
P2.7	478.3	288.2	18.34	15.99	-2.3
P2.8	512.5	288.7	17.30	17.31	0.0
P2.9	544.3	292.4	17.77	18.38	0.6
P2.10	595.4	290.1	21.05	16.80	-4.3
P2.11	661.4	290.0	13.01	14.39	1.4
P2.12	723.5	291.0	13.38	13.51	0.1
P2.13	780.6	289.6	12.29	12.85	0.6
P3.1	90.6	250.0	16.74	16.98	0.2
P3.3	161.8	247.5	16.42	16.70	0.3
P3.5	251.2	253.9	17.29	15.04	-2.3
P3.8	425.3	248.2	16.38	15.14	-1.2
P3.10	543.6	256.3	14.41	15.81	1.4
P3.12	628.0	255.9	14.65	14.88	0.2
P3.14	737.9	256.9	13.00	13.35	0.3
P4.3	142.1	345.1	16.46	16.59	0.1
P4.7	271.0	346.0	15.38	15.06	-0.3
P4.9	400.4	344.6	14.85	14.96	0.1
P4.11	540.2	345.4	13.86	15.98	2.1
P4.13	645.3	344.0	13.35	14.61	1.3
P4.15	755.9	344.5	12.34	13.16	0.8
P6.2	345.4	416.5	15.60	14.75	-0.9
P6.4	426.2	417.7	14.28	14.75	0.5
P6.6	544.6	413.1	15.74	14.76	-1.0
P6.8	692.2	410.5	14.20	13.64	-0.6
P7.4	586.9	506.9	15.64	13.88	-1.8
P7.8	717.4	527.0	15.45	13.01	-2.4

Table V Comparison of modelled and observed heads at wells/probe holes (see Figure 1) in the LLWR site.

Well	X	Y	Observed head (m)	Model head (m)	Difference $Head_{Model - observed}$
C1/2p1	60.0	358.6	17.00	14.86	-2.1
DDS126p1	65.5	255.4	17.60	15.04	-2.6
DDS59p1	120.4	367.0	15.30	16.15	0.8
C2/3p1	195.8	43.1	15.10	13.24	-1.9
DDS109p1	403.5	113.5	10.70	13.93	3.2
DDS73p1	486.1	78.4	15.70	13.56	-2.1
DDS111p1	553.1	74.9	13.50	13.37	-0.1
DDS72p2	586.8	108.3	14.00	13.64	-0.4
DDS68p1	624.3	171.4	13.10	13.98	0.9
DDS129p3	666.5	125.1	14.60	13.26	-1.3
DDS112p1	707.0	164.4	13.80	13.21	-0.6
DDS31p3	723.1	587.2	13.40	12.73	-0.7
DDS26p1	847.2	321.2	11.90	12.32	0.4
C6/3p1	861.2	199.5	12.30	12.07	-0.2
C10/3p1	887.8	456.5	12.40	12.05	-0.4
DDS114p2	891.9	280.9	8.40	12.04	3.6
DDS43p4	1041.7	341.6	9.00	10.84	1.8
C8/3p1	1085.3	171.9	10.00	10.06	0.1

Uranium residual reactive transport model

As noted earlier, similar volumes of uranium fluoride residue waste were assumed for each of the five arbitrary locations across the site (see Figure 1 and Table II). The near-field reactive transport model examined the combined effects of groundwater transport and kinetically controlled reactions of contaminant release from the uranium containing fluoride residues. Effects represented in the model include dilution/dispersion, pH buffering and equilibrium mineral dissolution/precipitation.

Figure 4 shows the computed uranium concentrations over a period of 10 years. A number of plumes are seen to develop downstream of the residue accumulations. The influence of the water mounds on the flow field is apparent, causing the plume to migrate in different directions according to the local flow directions (Figure 3), dependent on the relative position to the water mounds. The plumes developed from wastes at the north (e.g. WF1, WF2 and WF5) are seen to migrate towards the east, while the uranium plumes originated from wastes WF3 and WF4 migrate towards the south-east and south-west respectively.

The transport of an unretarded tracer (which is instantaneously released from the wastes) has also been modelled. Figure 5 shows the tracer plumes to develop in a similar fashion (to the uranium plumes) but to evolve more quickly (i.e. Tracer plumes after 2 years are comparable to uranium plumes after 4 years). The tracer plume (unlike the uranium plume) reduces in concentration by 2 orders of magnitude after 10 years, as all of the tracer is released at the start of the simulation.

The uranium plume that develops downstream of the locations of the fluoride residue wastes, ranges in concentration from a maximum of 1.83E-8 mol kg^{-1} of water in the vicinity of the waste locations to around 1E-9 mol kg^{-1} of water over distances of the order of hundreds of metres from the waste locations (Table II). The modelled concentrations of uranium are generally consistent with the measured concentrations in leachate [3], although some significantly higher concentrations are measured than in the current model run. Reference [3] remarks that the higher concentrations that occur in a number of sampling points are likely to be associated with anomalously high fluoride concentrations. These could result from effects of a more soluble form of fluoride residue disposed in the vicinity of the area, or residues that contain a higher uranium content. It should be noted that sorption of uranium is not represented in the current model and this will over estimate the rate of uranium migration away from the fluoride waste locations, but would not explain the highest measured uranium concentrations occurring in specific regions.

The results for fluoride show a similar pattern of distribution to that of uranium, but over a higher concentration range (Figure 5). This reflects the kinetically limited release of both of these species from the waste residues. The concentrations of fluoride result from the dissolution of the fluoride residue. The concentrations of fluoride modelled are comparable to the concentrations of fluoride measured in vent probes, which range from 4E-4 to 4E-6 mol kg^{-1} of water in most of the samples in a recent study [3]. This good agreement between the model and site measurements, particularly for fluoride, provides further confidence in the model's ability to represent the combined effects of chemical leaching and groundwater transport.

Figure 4 also shows isometric views of iso-surfaces of uranium concentrations over 10 years. The plumes from the different wastes show differences in migration characteristics. Besides the differences in migration directions, the plumes also show differences in the depth to which they penetrate. The plumes from WF2 and WF5 are seen to penetrate to deeper depths. Closer examination reveals two different mechanisms at work. The plume from WF2 initially migrates eastwards and eventually migrates outside of the trench cap area, where there is higher infiltration (0.263 m y^{-1} compared with 0.054 m y^{-1} over the trench area with interim cap). This higher rate of infiltration leads to greater vertical movement of the plume. For the plume from WF5, it can be seen that only the north-east part of the plume penetrates to deeper depths. This is caused by an area of missing clay beneath the waste ('hole' in Figure 1).

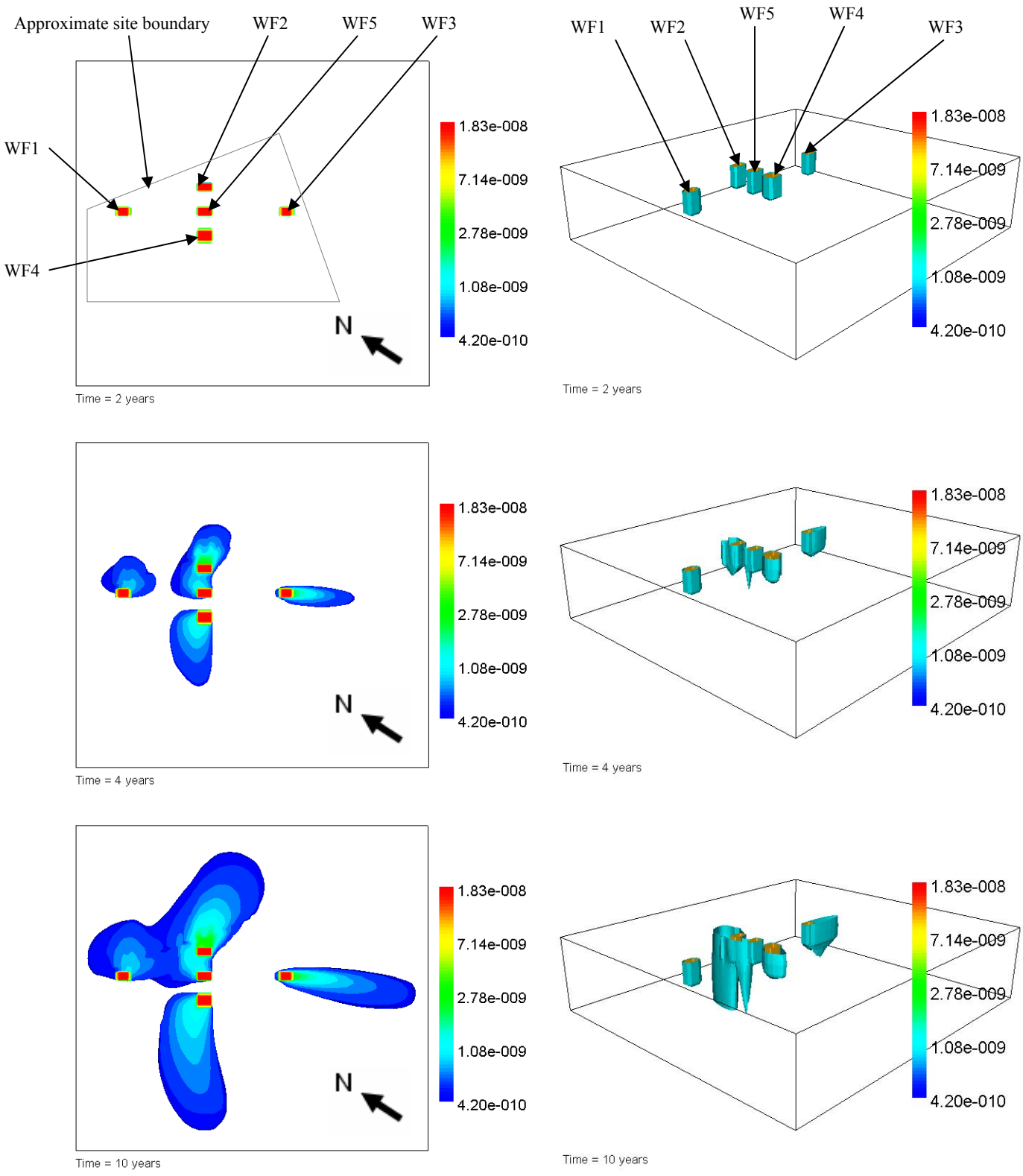

Figure 4 Modelled uranium concentrations (mol kg^{-1} of water) after 2, 4 and 10 years, showing plan view with threshold minimum at 5E-10 (left) and isometric view of iso-surfaces of 1E-8 and 1E-9 (right).

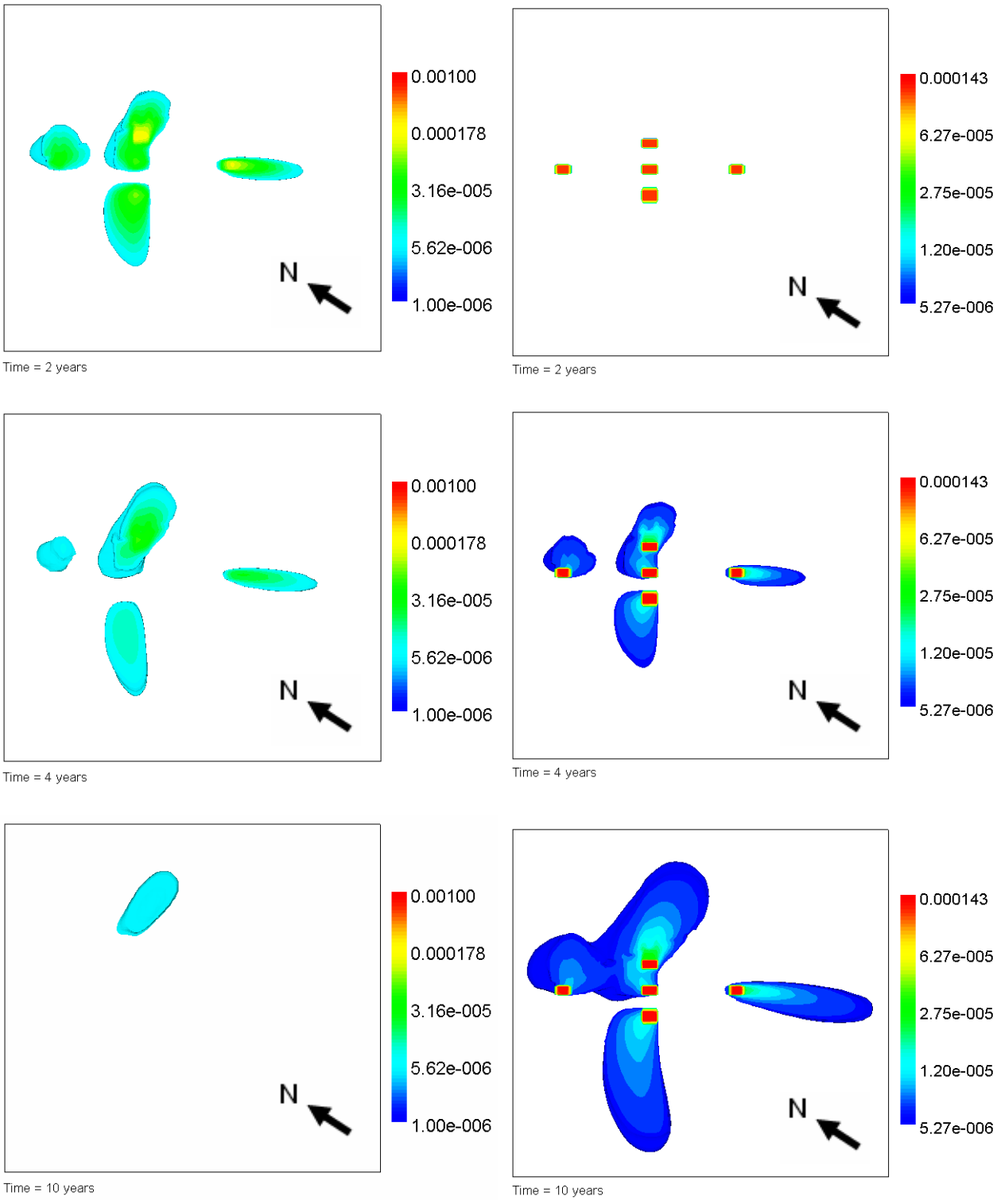

Figure 5 Modelled concentrations (mol kg^{-1} of water) after 2, 4 and 10 years for Tracer (left) and Fluoride (right), plot with threshold minimum at 5E-6 and 6E-6 respectively.

DISCUSSION

A 3D PHAST model has been developed to model the trench area of the LLWR near field. The model includes the representation of engineered features such as a cut-off wall, firebreaks and interim trench cap. The model also represents hydrogeological features such as the Lower and Regional groundwater systems, and regions of water mounding identified from observational data. The calibrated groundwater flow model was used to investigate the behaviour of contaminants released from a number of uranium fluoride residue wastes at arbitrary locations across the LLWR site.

Groundwater flow model

Hydrology

The calibrated near-field groundwater flow model, gives good water level comparisons with observations over most of the model domain. The modelled heads are predicted to within 1 m of the observed values at 28 out of the 47 locations. Good agreement is achieved over a fairly wide area of the trench area, but with small 'pockets' of high discrepancies at a small number of locations. This indicates that the overall flow field is likely to be well represented. The inclusion of the water mound representation in the model is essential in replicating the hydrological conditions observed at the LLWR site, where areas of elevated water levels are evident within the trench area. The water mounds cause localised outward radial flow in an otherwise essentially uni-directional flow field (predominantly towards the south-east).

The representation of the Regional/Lower groundwater system in the model is important as the hydraulic gradients (and hence direction of groundwater flow) are different from that of the Upper groundwater system. The hydraulic gradient for the Upper groundwater system decreases from the north-west to the south-east, whilst the hydraulic gradient for the Lower groundwater system decreases from the north-east to the south-west.

Geology

The current model uses the recent geological interpretation for the site. This provides a generalised illustration of geology, but does not provide a detailed analysis of potential small-scale variations. This may be a possible cause for the isolated large head differences (between model and observation) associated with the observed large local gradients that were not accounted for in the current model.

The model represents an Upper clay layer, which contains areas where the clay is absent, estimated from site data (not shown). It is not clear if areas where the clay is absent are more widespread (which is probable) than indicated by site data. More detailed information on the geological characteristics and distribution of the Upper clay layer would be useful in refining the groundwater flow model. This may help resolve the discrepancies between modelled and observed heads at isolated areas.

Uranium residual reactive transport model

The near-field reactive transport model developed here demonstrates the potential value of such modelling in improving the understanding of contaminant migration from the LLWR trenches, accounting for the hydrogeochemical conditions. Initial results from the reactive-transport model are encouraging, with modelled concentrations of uranium and fluoride consistent with measured concentrations.

Sorption of uranium is not represented in the model and, as such, the current model will over estimate the rate of uranium migration and the extent of the plume. Sorption for uranium could be readily represented within the PHREEQC/PHAST geochemical model, with data based on recent sorption studies for uranium.

CONCLUSION

A 3D reactive transport model has been constructed using the PHAST code. The dissolution of fluoride waste materials is represented as a control on the release of uranium from the wasteform. The model includes the representation of typical fluoride residues that exist in the LLWR inventory. The modelled concentration ranges of fluoride (4E-4 to 4E-6 mol kg^{-1} of water) and uranium (2E-8 to 1E-9 mol kg^{-1} of water) in the plume are generally consistent with measured levels, although some significantly higher uranium concentrations are measured in isolated locations, these may represent fluoride residues which have higher solubility, or perhaps may represent residues with a higher uranium content.

The model results show that the uranium plumes penetrate to different depths, which relate to variations in infiltration and local geological features (i.e. local absences of clay underlying the trenches). This near-field model demonstrates the value of modelling in contributing to an understanding of the complex migration behaviour of contaminants at the LLWR site, under the influence of hydrogeological and chemical conditions.

The modelling supports the concept that the slow dissolution of the fluoride residues may hinder the release of uranium to groundwater. The model results may be used as a basis to reassess the radiological impact of the LLWR uranium disposals.

ACKNOWLEDGEMENTS

This work was funded by the UK Low Level Waste Repository (LLWR).

REFERENCES

1. BNFL. Drigg Post-Closure Safety Case: Overview Report (2002).

2. Small. J.S., Abraitis, P.K., Beadle, I.R. Johnstone, Kelly, P. Pettit, C.L. and Stevens, G.A. A comparison of site characterisation data and modelling results from a radiological assessment of the Drigg low level radioactive waste disposal site. Materials Research Society Symposium, Scientific Basis for Nuclear Waste Management XXVII**,** p905-910 (2004).

3. Small, J.S., Lennon, C., Kwong, S. and Scott, R.J. Development and Validation of a Model of Uranium Release to Groundwater from Legacy Disposals at the UK Low Level Waste Repository, Scientific Basis for Nuclear Waste Management XXXI, Materials Research Society Symposium Proceedings, Sheffield (2007).

4. Parkhurst, D.L., Kipp, K.L., Engesgaard, P., and Charlton, S.R. PHAST-A Program for Simulating Ground-Water Flow, Solute Transport, and multicomponent Geochemical Reactions, U.S. Geological Survey, Techniques and Methods 6-A8, 154p (2004).

5. Parkhurst, D.L. and Appelo, C.A.J.. User's Guide to PHREEQC (Version 2) – A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport and Inverse Geochemical Calculations. U.S. Geological Survey, Water Resources Investigations Report 99-4259 (1999).

6. Zhang, R., Hu. A. and Zhang, X. Experimental study of dissolution rates of fluorite in HCl-H_2O solutions. Aquatic Geochemistry, **12**, p123-159 (2006).