



University of HUDDERSFIELD

University of Huddersfield Repository

Small, J., Humphreys, Paul, Johnstone, T. J., Plant, R., Randall, M. G. and Trivedi, D. P.

Results of an aqueous source term model for a radiological risk assessment of the Drigg LLW site

Original Citation

Small, J., Humphreys, Paul, Johnstone, T. J., Plant, R., Randall, M. G. and Trivedi, D. P. (2000) Results of an aqueous source term model for a radiological risk assessment of the Drigg LLW site. Materials Research Society Proceedings (608). ISSN 0272-9172

This version is available at <http://eprints.hud.ac.uk/4269/>

The University Repository is a digital collection of the research output of the University, available on Open Access. Copyright and Moral Rights for the items on this site are retained by the individual author and/or other copyright owners. Users may access full items free of charge; copies of full text items generally can be reproduced, displayed or performed and given to third parties in any format or medium for personal research or study, educational or not-for-profit purposes without prior permission or charge, provided:

- The authors, title and full bibliographic details is credited in any copy;
- A hyperlink and/or URL is included for the original metadata page; and
- The content is not changed in any way.

For more information, including our policy and submission procedure, please contact the Repository Team at: E.mailbox@hud.ac.uk.

<http://eprints.hud.ac.uk/>

RESULTS OF AN AQUEOUS SOURCE TERM MODEL FOR A RADIOLOGICAL RISK ASSESSMENT OF THE DRIGG LLW SITE, UK

J.S. SMALL, P.N. HUMPHREYS, T.L. JOHNSTONE, R. PLANT, M.G. RANDALL, AND D.P. TRIVEDI

BNFL Research & Technology, Risley, Warrington, WA3 6AS, UK.

ABSTRACT

A radionuclide source term model has been developed which simulates the biogeochemical evolution of the Drigg low level waste (LLW) disposal site. The DRINK (DRIGg Near field Kinetic) model provides data regarding radionuclide concentrations in groundwater over a period of 100,000 years, which are used as inputs to safety assessment calculations. The DRINK model considers the coupled interaction of the effects of fluid flow, microbiology, corrosion, chemical reaction, sorption and radioactive decay. The model simulates the development of a period of reducing conditions resulting from degradation of cellulose and steel wastes. Under these conditions U and Th remain as solubility controlling solids for periods over 30,000 years and provide an important source of daughter nuclides such as Ra. The fraction of ^{14}C is followed through all reactions involving carbon. Less than 5% of ^{14}C is present as mobile aqueous species.

INTRODUCTION

Disposals to the UK LLW site at Drigg, owned and operated by British Nuclear Fuels (BNFL), are authorised by the Environment Agency under the terms of the Radioactive Substances Act 1993. A post closure radiological safety assessment (PCRSA) is being prepared to support the safety case for the Drigg site. An integral part of the PCRSA is the DRINK source term model which simulates the biogeochemical evolution of the Drigg near surface site. DRINK provides radionuclide concentrations within the near field which are input as radionuclide fluxes to a groundwater assessment model. Simulated activities of radionuclides remaining in the near field are used for the calculation of impacts associated with potential human intrusion. In addition to quantitative model inputs, DRINK helps provide a phenomenological understanding of the behaviour of the site over extended periods of time, which is a requirement of the regulatory guidance.

The Drigg site includes two disposal systems: 1) An original system operated from 1959 to 1988 comprising a series of parallel trenches excavated into glacial clays, back filled with LLW and covered with an interim water resistant cap. 2) Current disposal of compacted waste placed in steel ISO-freight containers, with void space filled with a highly fluid cement based grout. These containers are then disposed of in a series of open concrete vaults. Figure 1 illustrates the disposition of the two disposal systems. Drigg LLW contains a large proportion of cellulosic waste together with disposed steel and contaminated soil. Radionuclides with highest activities in the inventory include ^3H , ^{241}Pu , ^{137}Cs , ^{234}U and ^{90}Sr . The long-lived radionuclides ^{238}U and ^{232}Th have the highest molal concentration.

This paper outlines the functionality of the DRINK source term model and gives examples of its output. The results provide a simulation of the nature and timing of the chemical changes which occur during the degradation of wastes in the Drigg near field. The varying aqueous concentration of radionuclides is calculated considering their varying solubility under the simulated conditions.

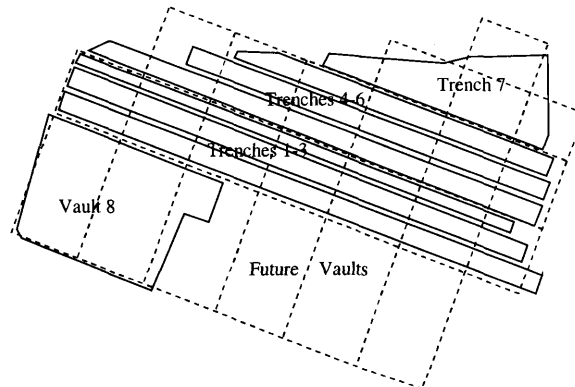


Figure 1. Plan view of the disposition of the Drigg Trench and Vault disposal systems (solid lines), and coincidence with the DRINK finite difference grid (dashed lines).

THE DRINK SOURCE TERM MODEL

The DRINK model utilises the BNFL biogeochemical reaction Generalised Repository Model (GRM) [1,2] to simulate the evolving geochemistry of the Drigg trenches and vaults. GRM considers kinetically controlled steel corrosion and microbial induced cellulose degradation reactions. The products of these processes are used to determine an evolving redox condition, taking account of kinetically controlled microbially mediated redox reactions between redox product species and species in groundwater (e.g. SO_4), and minerals in soils (e.g. $\text{Fe}(\text{OH})_3$). Redox potential (pe) is calculated by using standard mass action equations [3] considering the most oxidising couple. The resulting pe is used as a constraint for equilibrium speciation and mineral equilibrium calculations by a routine based on PHREEQE [4], which determines the pH and master species concentrations, including those radionuclides which are solubility controlled. GRM describes the 2-dimensional lateral groundwater flow in the saturated zone by means of a finite difference solver. The discretisation of the finite difference grid used in the DRINK model is shown in Figure 1. Vertical flow is considered on a cell by cell basis and is used to simulate the release of radionuclides from the unsaturated zone to the saturated zone. In DRINK, sorption is modelled using a distribution coefficient (K_d) which is selected taking into consideration the simulated geochemical model, and the types of sorbant surfaces present in the Drigg trenches and vaults. Radioactive decay is considered on a cell basis for dissolved, sorbed and precipitated phases, and for the unsaturated zone.

BIOGEOCHEMICAL EVOLUTION OF THE DRIGG SITE

Chemical conditions in the Drigg trenches is simulated to vary over a period of around 1000 years. During this time degradation of cellulose and steel corrosion result in the establishment of conditions more reducing and acidic than the local groundwater. Figure 2 shows examples of the time evolution of concentrations of solid and dissolved species. In the DRINK model the first stage of cellulose degradation is the hydrolysis of cellulose modelled by a first order kinetic reaction with a pH dependent hydrolysis constant [2]. The computation of the cellulose concentration in Figure 2a includes the presence of hydrolysis in the saturated zone, and the transfer of cellulose and other materials from the unsaturated zone resulting from settlement. In

effect cellulose in the saturated zone is replaced by that in the unsaturated zone until around 100 years when the unsaturated zone is depleted of cellulose. After this time an exponential decrease in cellulose concentration is simulated. Iron corrosion is modelled by a zero order kinetic reaction. In the saturated zone iron increases (Figure 2b) in concentration because of transfer from the unsaturated zone as a result of settlement.

Products of cellulose hydrolysis and corrosion are subject to microbial mediated redox reactions [1,2]. Glucose is metabolised by aerobic and anaerobic processes to yield CO_2 , while acetate and other volatile fatty acids (VFAs) are produced by fermentation. The processes of cellulose degradation, microbial mediated redox reactions, gaseous exchange and mineral equilibration have been considered by DRINK for the computation of the rate of CO_2 production displayed in Figure 2c. The acetate concentration versus time show in Figure 2d was calculated from the model including acetate production by fermentation, and consumption by redox reactions. Acetate, and H_2 produced during corrosion are the main electron donors in the model which are responsible for the reduction of species such as SO_4 in groundwater, and Fe(III) oxyhydroxide in disposed soils.

The pH determined by the PHREEQE speciation calculation (Figure 2e) shows the generation of acidic conditions associated with the formation of CO_2 and acetate. After around 800 years, the pH returns to that of the local groundwater, which is in equilibrium with calcite at $\log p\text{CO}_2 = -2$. p_e is determined by the $[\text{SO}_4^{2-}]/[\text{HS}^-]$ couple for the first 2,000 years of the DRINK simulation. The concentrations of sulphate and sulphide species indicate a period of more reducing conditions during the first 1,000 years during which time S(II) is the dominate oxidation state (Figure 2f). The environment is significantly more reducing than the local groundwater, whose redox condition is consistent with equilibrium with siderite and Fe(III) oxyhydroxide. After periods of 1,000 to 2,000 years the trenches reoxidise as a result of the presence of NO_3^- in groundwater.

The evolving biogeochemical conditions associated with cellulose degradation and steel corrosion involve reactions between minerals considered by the PHREEQE module. A simplified mineral assemblage is considered comprising calcite and Fe(III) oxyhydroxide representing the reactive component of disposed soil. Under the acidic and reducing conditions simulated for the Drigg trenches calcite and Fe(III) oxyhydroxide dissolve during the early stages of the model. Siderite precipitates during the first 1,000 years of the model and is the main corrosion product under the simulated conditions, calcite and Fe(III) oxyhydroxide reprecipitates after 800 years as the chemical composition of leachate waters return to that of the local groundwater (Figure 2g).

pH buffering of the Drigg vaults

The chemical buffering effect of the Portland Cement based grout used as a backfill material in the Drigg vaults is simulated by the inclusion of two end-member phases to represent the calcium silicate solid-solution (CSH) [5]. Figure 2h shows the variation in concentrations of the calcium rich end member (CEMCSH), the silica end member (CEMSIO) and calcite. The variation in these concentrations is consistent with a carbonation reaction where CO_2 reacts with CSH to produce calcite and where the CSH becomes more silica-rich. Two phases of carbonation are simulated, a rapid period during the first 100 years where CO_2 generated from cellulose degradation contributes to the reaction, and a slow carbonation phase due to the presence of CO_2 in inflowing groundwater. The DRINK model simulates that it takes around 10,000 years for the calcium end member to be dissolved. During this time the pH is around 11 (at 10 °C). Despite the establishment of alkaline conditions the vaults are computed to undergo a similar pattern of biogeochemical evolution as the Drigg trenches described above. Reducing conditions are established as a result of cellulose degradation and steel corrosion reactions, reoxidation occurs over a period of 2,000 to 10,000 years. Under alkaline conditions different secondary mineral phases are produced with Fe(II) hydroxide and FeS formed as corrosion products.

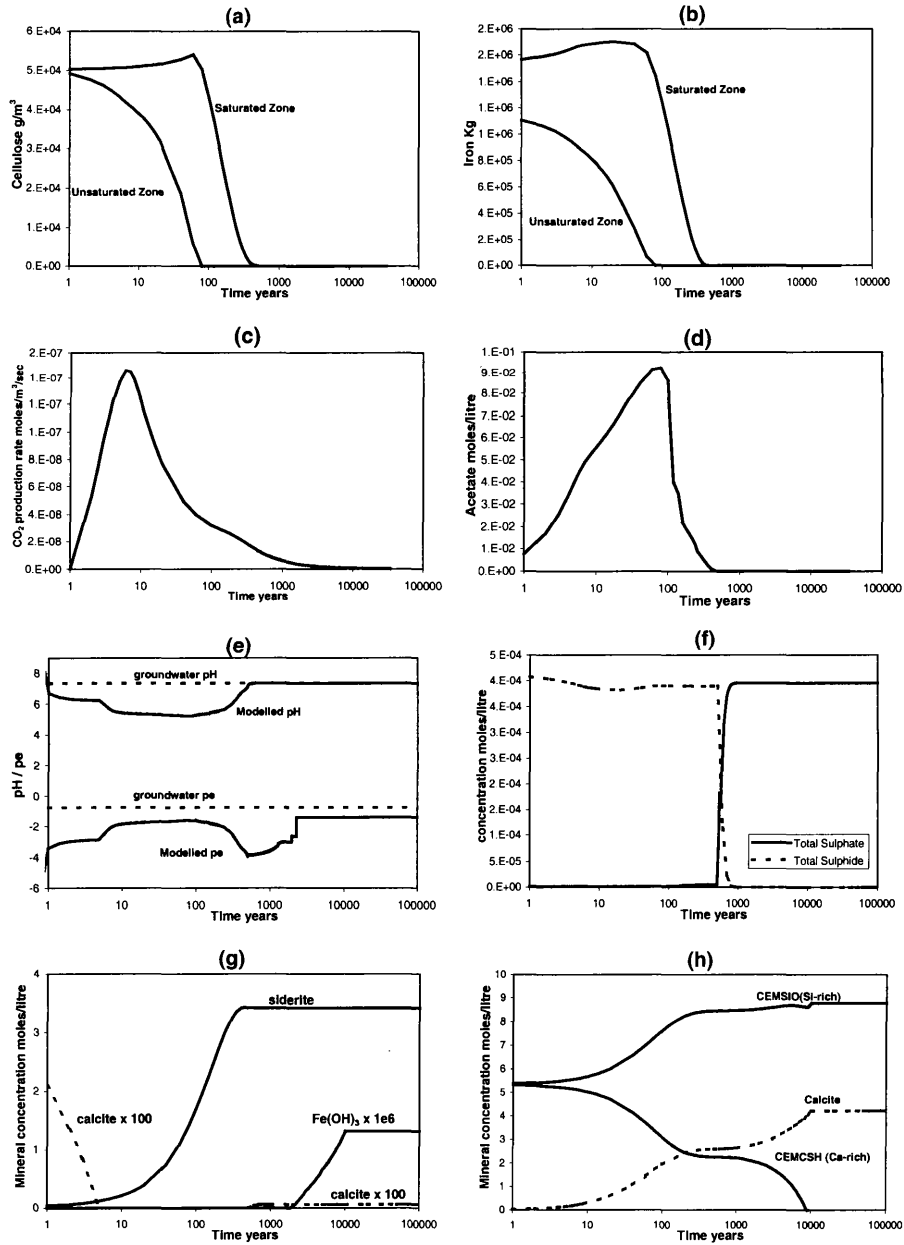


Figure 2. a-g Concentration profiles of waste materials, and degradation products simulated by the DRINK model for a representative model cell from the Drigg trenches, (h) simulated evolution of cement minerals in the Drigg vault saturated zone.

RADIONUCLIDE RELEASE MECHANISMS AND NEAR-FIELD CONCENTRATIONS

The DRINK model considers the time variation in pH, pe and aqueous speciation to determine changing solubility controls over radionuclide elements. In the DRINK model all isotopes of a particular element are combined for the purpose of determining solubility. The principal solubility controlled radionuclides are Th and U and their aqueous concentrations under representative trench conditions are illustrated in Figure 3a. Uranium solubilities are simulated to be at minimum values during the first 1,000 years as a consequence of the reducing conditions, which stabilise the U(IV) solid phase UO_2 . After reoxidation of the trenches UO_2 solubility increases as consequence of U(VI) aqueous speciation. At approximately 30,000 years UO_2 completely dissolves and U concentration decreases sharply. Under the alkaline vault conditions U concentration is solubility controlled by U(IV) species within a concentration range of $1e-9$ to $1e-10$ moles/litre. Thorium solubility is very strongly influenced by the generation of high concentrations of acetate during the first 200 years (Figure 2d), with Th-acetate being the dominant aqueous species under the acidic conditions of the trenches. When acetate concentration is low, Th concentration is at a low and constant level because of the dominance of the $Th(OH)_4$ species which is unaffected by pH variation. Under the alkaline vault conditions Th solubility is unaffected by Th-acetate complexing. As a consequence of these solubility controls U and Th are retained as solids within the Drigg site. This has important implications for maintaining the concentration of sorption controlled daughter nuclides such as ^{226}Ra , (Figure 3a) which increase in concentration over the 1,000 to 30,000 year period. The rate of generation of ^{226}Ra is lower after 10,000 years when solid U dissolves. The behaviour of other sorption controlled radionuclides is illustrated in Figure 3b. Sorption controlled release is characterised by a washout of the radionuclide, exemplified by Tc which is assigned a minimal K_d value. Other radionuclides such as ^{90}Sr are influenced by decay while Am concentration increases as a result of ingrowth of ^{241}Am from ^{241}Pu decay.

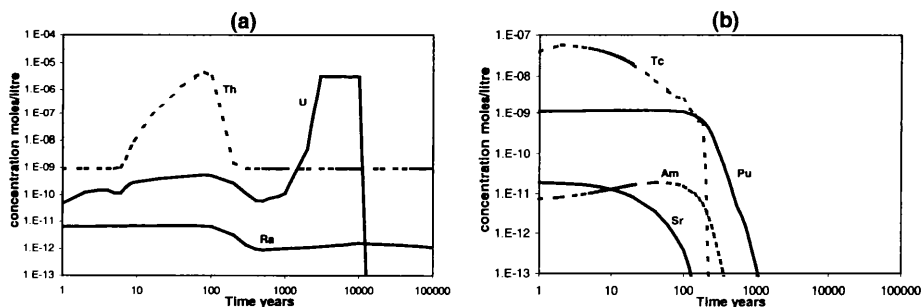


Figure 3. Variation in radionuclide elemental concentrations in the Drigg trenches influenced by (a) solubility controlled processes, and (b) sorption controlled processes.

^{14}C modelling

Carbon 14 is treated separately from other radionuclides because of the complication of considering the stable isotopes (^{12}C and ^{13}C) which behave in a virtually identical chemical manner. The approach adopted in DRINK is to assign ^{14}C to the reactive cellulose phase, and to recalculate the fraction of ^{14}C in all carbon species, minerals, gases and microbial substrates at each reaction and transport step, but neglecting isotope fractionation effects. The detailed biogeochemical modelling of cellulose degradation and mineral precipitation is therefore central to modelling ^{14}C release. Figure 4 shows the redistribution of the whole ^{14}C inventory during the

DRINK simulation. The majority of the ^{14}C is redistributed to siderite and calcite which form as secondary precipitates, approximately 10% of the inventory remains as inert organic material (humins). Less than 5% of the ^{14}C inventory is present as acetate or carbonate species, which is thus available for release from the near-field; an even smaller amount is present as gaseous CO_2 .

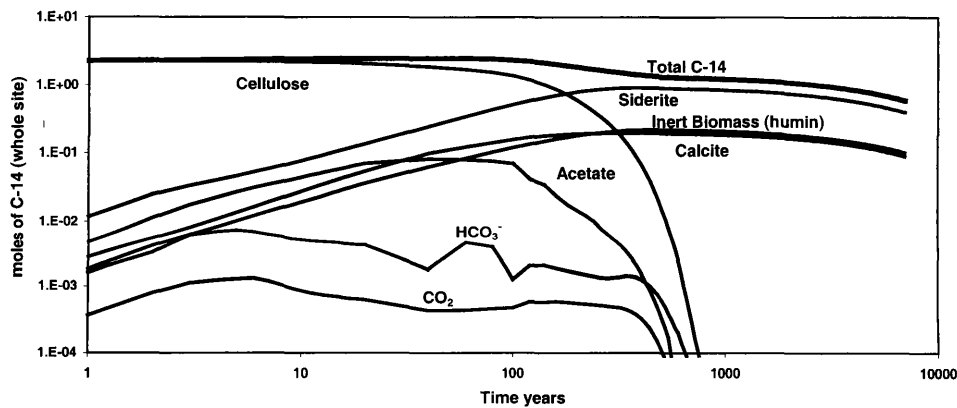


Figure 4. Variation in the distribution of C-14 between solid, aqueous and gaseous species for the whole of the Drigg site.

CONCLUSION

The DRINK model simulates that waste degradation results in the development of reducing and acidic conditions in the Drigg trenches during the first 2,000 years after site closure. Following this, the trenches reoxidise and chemical conditions return to that of the local groundwater. In the Drigg vaults a cementitious backfill maintains an alkaline environment for over 10,000 years. Using this model the varying solubility of U and Th in the trenches and vaults has been calculated over a period of 100,000 years. U and Th are retained within the site as solids and provide a source for daughter radionuclides such as Ra. The distribution of ^{14}C between aqueous species and solids minerals and microbial substrates has been calculated on the basis of the model of cellulose degradation and reactive chemical transport. Less than 5% of the ^{14}C inventory is present as mobile species. The continuously varying aqueous concentrations of radionuclides calculated by DRINK are directly input to a geosphere and biosphere groundwater risk assessment model used for the Drigg PCRSA. In addition the DRINK model supports the Drigg post closure safety case by contributing to the phenomenological understanding of the behaviour of the site.

REFERENCES

1. Manton, S., Johnstone, T., Trivedi, D. P., Hoffmann, A. and Humphreys, P. N., *Radiochimica Acta*, **68**, 75-79 (1995).
2. Humphreys, P. N., Johnstone, T., Trivedi, D. and Hoffmann, A., in *Scientific Basis for Nuclear Waste Management XVIII*, edited by T. Murakami and R.C Ewing. Mat. Res. Soc. Proc., **353**, 211-218 (1995).
3. Stumm, W. and Morgan, J.J. *Aquatic Chemistry*. 2nd Ed.. Wiley, New York (1981), p449.
4. Parkhurst, D.L., Thorsteson, D.C. and Plummer, L.N. PHREEQE – A computer program for geochemical calculations, USGS Water Resour. Invest., 80-96 (1980).
5. Berner, U.R. *Waste Management* **12**, p201,219 (1992).