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Interpretation and Modelling: Hydrochemistry, to Support the Development of an Integrated Site Descriptive Model

Final Report

7 March 2012

AMEC Environment and Infrastructure UK Limited

7 March 2012
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Executive Summary

The objective of this report is to provide the Radioactive Waste Management Directorate (RWMD) of the Nuclear Decommissioning Authority (NDA) with an account of:

- The processes and tools that have been used on international radioactive waste management programmes for the processing, interpretation and modelling of hydrochemical data acquired through site characterisation;

- Any additional processes and tools that are used in other sectors for processing, interpreting and modelling hydrochemical data that may be applicable to a UK-based waste management site characterisation programme;

- The availability of resources (tools and specialist practitioners) for undertaking a future programme of processing, modelling and interpretation in the UK; and
  - The extent to which the required resources may vary in response to variations in the geological environment at the site(s) in the UK that are being considered; and
  - The identification of any gaps in available resources to support any UK-based site characterisation programme.

International Radioactive Waste Management Programmes

The approach to hydrochemistry at a number of international radioactive waste management programmes has been described and reviewed. These sites have been divided into the generic host rock types set out by RWMD, which are:

- Higher strength rocks. Work by SKB at Forsmark, Sweden and UK Nirex at Sellafield has been considered;

- Lower strength sedimentary rocks. Work by ANDRA at Bure, France; NAGRA at Benken, Switzerland; NUMO at Horonobe, Japan and LLWR at Drigg have been considered; and

- Evaporites. Work by US DOE at WIPP in New Mexico and BRG at Gorleben in Germany.

The approach to hydrochemistry work has been described in some detail for each of these case studies in terms of:

- End user requirements, where these could be identified;

- The data available for interpretation;

- The approach to data processing;
• The hydrochemical interpretation methodology, including which tools were used to aid interpretation;
• The hydrochemical modelling methodology, including the modelling software used;
• Remaining hydrochemical uncertainties following characterisation.

The principal lessons from the case studies can be summarised as follows:

• Understanding of objectives. Hydrochemical characterisation must be based on a clear understanding
  of the information requirements of end users (i.e. the needs-driven approach);
• Data quality and data management. The hydrochemical interpretation must be based on sufficient data
  of a suitable and known quality;
• Data requirements. The data requirements need to be managed to ensure that excessive and / or
  irrelevant data is not collected;
• Integration with other disciplines. Hydrochemical interpretation and modelling must be strongly
  integrated with the geological and hydrogeological disciplines;
• Lines of evidence. The final hydrochemical interpretation should make use of multiple lines-of-
  evidence to arrive at conclusions that are critical to the Environmental Safety Case (ESC);
• Analogue sites and underground rock laboratories (for site characterisation). The use of analogue sites
  and URLs has been found to be beneficial, particularly for lower-strength rocks;
• Programme. Most of the case studies have taken place over extended periods, which permitted time
  for interpretation between investigation campaigns. Shorter, more intense programmes impose
  constraints, notably the limited opportunity for later phases of site investigation to be informed by the
  understanding developed in preceding phases;
• Reporting. The production of comprehensive reports at each stage of investigation generally may
  provide benefits but is a potentially laborious process that may slow down the investigation and
  interpretation;
• Collaboration. Collaboration between organisations working in similar host media is essential.

The principal variations in the approach to hydrochemical investigations between the different host rock types were
identified as follows:

• Higher strength rocks. The hydrochemical interpretation was based on samples of flowing
  groundwater obtained from boreholes;
• Lower strength sedimentary rocks. In lower strength sedimentary rocks, the interpretation of the host
  rock hydrochemistry has largely been based on evaluation of porewater and in particular the
  development of porewater profiles to interpret the age and transport properties of the host rock. This
  is because it is not possible to obtain samples of groundwater. The hydrochemical characterisation of
lower strength sedimentary rocks has been dependent on investigations undertaken at underground rock laboratories;

- Evaporites. The hydrochemical interpretation of evaporites is generally limited to flowing horizons above and below the evaporite.

**Strategic Approach**

A strategic approach to hydrochemical interpretation and modelling has been set out based on NDA’s Proposed Strategy for the Geoscientific Aspects of Site Characterisation (NDA, 2011b) and the framework for site characterisation set out in NDA (2011a); by earlier work on a geochemistry strategy (Intellisci, 2008); and by information gathered in undertaking the current project.

The final approach to site characterisation will depend upon the host rock selected; the environmental setting; the proposed depth and design of the geological disposal facility; the proposed storage concept; and the extent to which the proposed site has undergone previous investigation and characterisation. Further development of the strategic approach is likely to be required following site selection.

The strategic approach considers the main tasks in the interpretation and modelling of hydrochemistry. For flowing groundwater as found in higher strength host rocks and aquifers above and below the host rock and for lower strength sedimentary rocks and evaporites the main elements of the strategic approach are:

- Identify the main parameters that vary over the investigation area and use these to identify and characterise water types (hydrochemical facies). Water types should also be assigned domains within the rock volume under investigation;
- Identify potential end-member water types (e.g. recharge) for use in groundwater mixing models;
- Use anthropogenic parameters, such as tritium, chlorofluorocarbons (CFCs) and nitrate to identify modern recharge and to determine the depth to which it has penetrated and domains where it has penetrated;
- Use graphical and statistical analyses of data for non-reactive solutes, or tracers, (e.g. chloride) and stable isotopes (e.g. $^{18}$O/$^{16}$O) to resolve solute sources and groundwater mixing ratios;
- Interpret groundwater isotope data (e.g. $^{18}$O/$^{16}$O, $^{14}$C, $^3$H, $^{36}$Cl, $^4$He), together with anthropogenic parameters, to derive the water-age at different locations. The interpretation of isotopes will require supporting geochemical and isotopic data for water samples and rocks, i.e. $^{13}$C/$^{12}$C, U and Th contents, estimates of natural neutron fluxes and the in situ rate of production of isotopes;
- Use the water-age distribution to establish solute travel times in the different parts of the groundwater flow system;
- Interpret and model (where necessary) groundwater mixing and geochemical reactions between water and rock that controlled the evolution of the present-day groundwater compositions and distribution
thereby identifying controls on the long-term future stability of compositions of groundwater entering the GDF and along solute transport paths leaving the GDF;

- Use non-reactive solutes and isotopes (chloride, \( ^{18}\)O/\( ^{16}\)O, \(^{4}\)He) to support and test hydrogeological interpretation of groundwater flow paths, to constrain groundwater sources and mixing, and to calibrate a palaeohydrogeological model.

Variations in the strategic approach for lower strength sedimentary rocks and evaporites were identified. The main differences are that:

- Lower Strength Sedimentary Rocks. The focus of the investigation of lower strength sedimentary rocks is likely to be recovery of samples for porewater analysis of the host rock. The principal interpretation will therefore be the construction of porewater profiles in the host rock supplemented by interpretation of hydrochemical data of flowing horizons above and below the host rock;

- Evaporites. There is unlikely to be any significant groundwater within the evaporite host rock and so the focus of the investigation and interpretation will be on more permeable strata above, and possibly below, the host rock. The presence of substantial quantities of soluble minerals means that groundwater chemistry may be substantially different (e.g. higher salinity) than for other host rocks.

**Other Sectors**

A review of approaches to hydrochemistry in other sectors was undertaken. The following fields of investigation were identified as being potentially particularly of relevance:

- Geothermal energy;
- Oil and gas, including oil shales;
- Carbon capture and storage (CCS);
- Marine studies;
- Water resources.

The review found only limited differences with the approaches used in radioactive waste management.

**Resources and Tools**

The availability of resources (tools and specialist practitioners) for undertaking a programme of hydrochemical data processing, modelling and interpretation has been considered. The review of tools considered the range and types of tools available; the operations that they perform; and the inputs required and the outputs generated. Tools were considered within 6 generic groups (Spreadsheets; Spatial data processing and visualisation; Statistics software; Hydrochemical database and visualisation; Bespoke tools; Aqueous hydrochemical speciation and reaction modelling programmes). The review considered the availability of tools. Most of the tools identified were readily
available, either freely or commercially. However, a programme of hydrochemical interpretation and modelling may also have requirements for bespoke tools, which would require specialist development skills.

The human resources required for hydrochemistry interpretation and modelling were identified in terms of the specialist skills required, the size of the team required and the experienced needed. Potential variations in resources for the different host rocks were also identified.

The review identified that hydrochemistry interpretation and modelling can be undertaken by a small team of specialist practitioners. Previous experience of site characterisation within the team would be highly beneficial, particularly so that the team are familiar with the information requirements of end users. It was considered that higher strength host rock is likely to require the greatest resources and evaporites the least.

The lack of availability of hydrochemists to undertake the work is not identified as a high risk, although the experienced senior advisors in this discipline are, and will continue to be, in short supply. However, the availability of resources will depend on the extent and timing of any programme.
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1. Introduction

1.1 Background

This report provides a review of hydrochemical interpretation and modelling for use in site characterisation for a geological disposal facility (GDF) for higher activity radioactive wastes.

The Radioactive Waste Management Directorate (RWMD) of the Nuclear Decommissioning Authority (NDA) is responsible for implementing geological disposal of higher activity radioactive waste in the UK. The implementation process envisaged is that, once a candidate site or sites for a GDF have been identified by Government, RWMD will undertake a programme of surface-based investigations at the site or sites to characterise the geosphere and biosphere.

The investigation would comprise detailed surface and subsurface investigations and would be required to acquire and interpret information on the geological, hydrochemical, hydrogeological and environmental conditions at one or more sites throughout all stages of the development and implementation of a GDF for the long-term management of higher activity radioactive wastes. The information acquired would be used: as an input to the development of the safety case; for engineering design of the disposal facility; for environmental assessment and to demonstrate confidence to stakeholders that the potential GDF site is adequately understood.

RWMD’s Site Characterisation Project (NDA, 2010) has objectives to:

- Develop approaches to the design and implementation of needs-driven information-led investigations (surface-based and underground investigations, etc) to meet the needs of information users within RWMD, Regulators and other key stakeholders;
- Undertake sufficient preparatory work such that, when required, the surface-based site investigations could be implemented in a timely and efficient manner; and
- Ensure that the necessary arrangements are in place so that resources will be available to support the subsequent implementation of site characterisation.

RWMD proposes to develop and present the information derived from site characterisation activities for a GDF in the form of a single integrated Site Descriptive Model (SDM). In this context RWMD in their “Site characterisation for a geological disposal facility, Status report March 2010” Report No NDA/RWMD/057 describes an SDM as follows:

“Taking into account the experiences of sister organisations and best practice in other sectors such as oil and gas it is anticipated that the characterisation of the site will best be undertaken by the development and progressive updating of a single integrated Site Descriptive Model, i.e. a model describing the geometry, properties of the bedrock and water, and the associated interacting processes and mechanisms, which will be used to address the information requirements of all the end users. Such an approach will ensure that:
The understanding of the different aspects of the geosphere such as the geology, hydrogeology and hydrochemistry is developed in a consistent manner; and

The different end users base their design and assessments on the same understanding and evidence base.

There are several elements to the preparation of a Site Descriptive Model, including:

- Definition of the volume of ground that needs to be included in the model;
- Subdivision of the model into geometric units so as to permit the description of spatial variability in a meaningful manner; and
- Assignment of parameters (values and/or statistical distributions) to the defined geometric units.

It is anticipated that, in a similar way to the approach adopted by SKB and Posiva, the integrated Site Descriptive Model will be divided into parts comprising clearly defined disciplines which may form either chapters or discipline-based models. The discipline-based models that are likely to be developed for UK sites comprise the following:

- Geology;
- Hydrogeology;
- Hydrochemistry;
- Geotechnical;
- Transport properties;
- Thermal properties; and
- Biosphere.

The Site Descriptive Model will provide the understanding of the characteristics of the site, sufficient to allow further qualitative and quantitative modelling to be undertaken as part of the development of the Environmental Safety Case.”

It should be noted that the SDM will describe the current situation at the site and where relevant the historical development of conditions at the site to support the conceptual understanding. It will not include prediction of the future evolution of the conditions at the site which will be included within the safety assessment work.

Past advice from RWMD’s High-Level Advisory Panel (previously GeoCAP) identified that further work was required to gain an increased understanding of the approach to undertaking interpretation and modelling activities of site characterisation data in order to support the development of descriptive site models.
RWMD has therefore commissioned work to provide a description of the state-of-the-art processes and techniques available for the modelling and interpretation of site characterisation data in each of the discipline areas identified above to support the development of facilities for the long term disposal of higher activity radioactive waste.

1.2 **Objectives of this Report**

The objectives of this report are to provide RWMD with an account of:

- The processes and tools that have been used on international radioactive waste management programmes for processing, interpreting and modelling hydrochemistry data acquired through site characterisation;
- Any additional processes and tools that are used in other sectors for processing, interpreting and modelling data acquired through site characterisation that may be applicable to a UK-based waste management site characterisation programme;
- The availability of resources (tools and specialist practitioners) for undertaking such a programme of processing, modelling and interpretation in the UK;
- The extent to which the required resources may vary in response to variations in the geological environment at the site(s) in the UK that are being characterised; and
- The identification of any gaps in available resources to support a UK-based site characterisation programme.

This report deals with the discipline of hydrochemistry and separate reports have been prepared for the other six disciplines identified above.

1.3 **Approach**

1.3.1 **Case Studies of International Radioactive Waste Management Programmes**

To meet the objectives a detailed description of the various techniques which have been adopted by radioactive waste organisations to translate acquired data into understanding to support site descriptions as part of their site characterisation programmes has been provided.

RWMD has identified three host rock categories that are considered potentially suitable to host a disposal facility for higher activity wastes, based on studies carried out in the UK and internationally, and which occur in the UK can be described as follows:

- Higher strength rocks, which would typically comprise crystalline igneous and metamorphic rocks or geologically older sedimentary rocks where any fluid movement is predominantly through discontinuities (e.g. fractures);
• Lower strength sedimentary rocks, which would typically comprise geologically younger sedimentary rocks where any fluid movement is predominantly through the rock matrix; and

• Evaporites, which would typically comprise anhydrite (anhydrous calcium sulphate), halite (rock salt) or other evaporites that result from the evaporation of water from water bodies containing dissolved salts.

It should be noted that the term lower strength sedimentary rock is an engineering description, rather than a hydrogeological or hydrochemical description. Fluid movement in a lower strength sedimentary rock may not be confined to the rock matrix.

A review of case studies by other radioactive waste organisations that cover the range of RWMD’s likely host rocks is provided in Sections 3 to 5. The case study sites reviewed are set out in Table 1.1. The review has focussed on hydrochemical surface-based investigations. However, it is apparent that some hydrochemical information can only be obtained from Underground Rock Laboratories (URLs) and, therefore, the results of these investigations have been considered where relevant.

This review of hydrochemical site characterisation for the development of a SDM to support the characterisation of a GDF was based on:

• Project team knowledge and discussions with those involved in the programmes, where possible;

• Publicly available reports; and

• Peer-reviewed literature.

The quantity and nature of readily-available information for the sites vary considerably and this influenced the level of review that could be undertaken.

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<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>
### Table 1.1 (continued)  Case Study Sites

<table>
<thead>
<tr>
<th>Host Rock Type</th>
<th>Country</th>
<th>Lead Organisation</th>
<th>Site/Area</th>
<th>Host Strata</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evaporites</td>
<td>USA</td>
<td>DOE Department of Energy</td>
<td>WIPP</td>
<td>Halite</td>
</tr>
<tr>
<td></td>
<td>Germany</td>
<td>BfS Das Bundesamt für Strahlenschutz (The Federal Office for Radiation Protection)</td>
<td>Gorleben</td>
<td>Halite</td>
</tr>
</tbody>
</table>

#### 1.3.2 Other Sectors

The following fields of investigation were identified as being potentially particularly of relevance:

- Geothermal energy;
- Oil and gas, including oil shales;
- Carbon capture and storage (CCS);
- Marine studies; and
- Water resources.

Hydrochemistry approaches in these sectors were identified through contacting researchers in appropriate fields and from a survey of the literature.

#### 1.3.3 Resources and Tools

Human resource requirements and tools used were identified in the review of case studies. Gaps in the available resources were then identified based on the understanding of the likely resource requirements.

#### 1.4 Links to Other Disciplines

This review concentrates on hydrochemistry. However, it is important that the understanding of the site results from an integration of activities across a range of disciplines. The principal links for hydrochemistry are to:

- Geomorphology:
  - The geomorphology of the site and its environs as an aid to interpreting the Quaternary history of the development of the site and the surficial distribution of the geological materials present at the site;
  - Description of the geological and geomorphological development of the site during the Quaternary;
• Geology and soils:
  - The nature, distribution and properties of the soils (drift deposits);
  - The nature, distribution and properties of sedimentary cover rocks at and around the site;
  - The nature, distribution and properties of deeper rocks;
  - The nature and characteristics of the structural geological features present at the site including folds, faults, bedding planes, joints, etc, together with an assessment of the manner in which the various features would be described (stochastically or deterministically);

• Hydrogeology:
  - The extent of the flow system and nature of its boundaries;
  - The nature of flow and solute transport within the different hydrogeological units (e.g. diffusion, advection, interaction between matrix porewater and mobile groundwater, the role of sedimentary structure, role of discontinuities [faults, fractures and joints], etc);
  - The hydraulic properties (e.g. transmissivity, hydraulic conductivity, porosity, storativity) to describe flow within the hydrogeological units;
  - Recharge and discharge areas, catchments and topography (to aid establishment of a water balance);
  - The influence of groundwater density on flow;
  - The flow history (paleohydrogeology);
  - Recharge rates;

• Hydrology and meteorology:
  - Surface water composition;
  - Precipitation and temperature;
  - Surface water flows;
  - Historical development, detailed description of current regime.

• Biosphere:
  - Hydrochemistry of shallow groundwater, soil waters and surface waters;
  - Baseline geochemical conditions of the surface environment.

• Climate: Historical and current climate;
• Marine (for coastal sites): Estuarine and marine systems need to be described in terms of geometry, water and sediment transport and the distribution and abundance of biota.

Hydrochemistry will also inform engineered barrier system (EBS) design.

1.5 This Report

1.5.1 Contributions

This report has been prepared by AMEC with contributions from:

• Dr Adrian Bath (Intellisci);
• Dr Russell Alexander (Bedrock Geosciences);
• Dr Nick Rukin (RUKHydro);
• Professor John Tellam (University of Birmingham).

1.5.2 Structure

The report first sets out (Section 2) the general objectives for hydrochemistry interpretation and modelling as an introduction to the case studies of international radioactive waste management programmes. Sections 3 to 5 then present details of the case studies for higher strength rock (Section 3), lower strength sedimentary rocks (Section 4) and evaporites (Section 5).

Section 6 summarises the principal lessons for RWMD from the case studies and also identifies potential site-specific factors of relevance to the hydrochemistry discipline.

Section 7 presents a review of approaches to hydrochemistry interpretation and modelling in other sectors to consider whether there are different approaches to those used in site characterisation for radioactive waste management that are potentially of interest to RWMD.

Section 8 presents a strategic approach to hydrochemistry interpretation and modelling for site characterisation based on the approaches taken at the case studies sites, on NDA’s overall strategic approach and on earlier work on a geochemistry strategy.

Section 9 considers the human and modelling resources required to deliver the strategy and identifies potential gaps in these resources.
2. Objectives for Hydrochemistry Interpretation and Modelling

2.1 Introduction

A hydrochemistry programme will generally consist of sampling, data acquisition and processing, interpretation and modelling that provides information that contributes to the overall SDM and general understanding of the GDF.

The focus for a site characterisation programme will be to develop an understanding of the deep geosphere at the depth of a GDF but it will also need to consider the hydrochemistry of as a contribution to the understanding of the biosphere and the geosphere-biosphere interface zone (GBIZ).

The general objectives of hydrochemical interpretation and modelling are outlined below.

2.2 End User Requirements

Hydrochemical interpretation and modelling will be based on data obtained primarily from laboratory analyses of groundwater samples from boreholes, porewater extracted from core samples and surface water samples, supported by field measurements of sensitive parameters. Additional information will also be taken from:

- Geology: Stratigraphy, lithology and petrology of rock samples, which will aid the understanding of rock-water interactions;
- Hydrogeology: Location of aquifers, aquitards, porosity, direction and rate of groundwater flow, nature of groundwater flow (fractures vs. intergranular);
- Interpretation of geophysical borehole logs and surface-based geophysical surveys, particularly in relation to determination of salinity with depth.

Hydrochemical interpretation and modelling will be undertaken to provide information to other disciplines or End Users. The key users of hydrochemical information and their hydrochemical information requirements are set out in Table 2.1.
Table 2.1  Key Users of Hydrochemical Information (NDA, 2011b)

<table>
<thead>
<tr>
<th>Information User</th>
<th>Information Requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Engineered Barrier System (EBS) design</td>
<td>Groundwater composition at GDF depth</td>
</tr>
<tr>
<td>Groundwater flow model:</td>
<td>Definition of groundwater bodies</td>
</tr>
<tr>
<td>Development of a conceptual understanding of groundwater flow, contaminant transport and boundary conditions</td>
<td></td>
</tr>
<tr>
<td>Geosphere pathways model:</td>
<td>Groundwater compositions at GDF depth</td>
</tr>
<tr>
<td>Hydrochemistry of transmissive faults and other flow paths down-gradient of GDF location</td>
<td></td>
</tr>
<tr>
<td>Geochemical description of radionuclide transport pathways including fracture minerals and adjacent rock matrix (near and far-field).</td>
<td></td>
</tr>
<tr>
<td>Long term performance</td>
<td></td>
</tr>
<tr>
<td>Biosphere and geosphere-biosphere interface zone (GBI/Z) models:</td>
<td>Hydrochemistry of shallow groundwater, soil waters and surface waters</td>
</tr>
<tr>
<td>Geochemical compositions of soils</td>
<td></td>
</tr>
<tr>
<td>Baseline geochemical conditions of the surface environment</td>
<td></td>
</tr>
</tbody>
</table>

2.3  General Approach to Interpretation and Modelling

The main tasks in any programme for the interpretation and modelling of hydrochemistry (for flowing groundwater) are:

- Construct an initial, desk-based conceptual model, which sets out the understanding of the site in advance of site characterisation. The model helps the interpretation and later modelling by providing the basis against which to test hypotheses;
- Identify the main parameters that vary over the investigation area and use these to identify and characterise water types (hydrochemical facies). Water types should also be assigned domains within the rock volume under investigation;
- Identify potential end-member water types (e.g. recharge) for use in mixing models;
- Use anthropogenic parameters, such as tritium, chlorofluorocarbons (CFCs) and nitrate to identify modern recharge and to determine the depth to which it has penetrated and domains where it has penetrated;
- Use graphical and statistical analyses of data for non-reactive solutes, or tracers, (e.g. chloride) and stable isotopes (e.g. $^{18}\text{O}/^{16}\text{O}$) to resolve solute sources and groundwater mixing ratios;
- Interpret groundwater isotope data (e.g. $^{18}\text{O}/^{16}\text{O}$, $^{14}\text{C}$, $^3\text{H}$, $^{36}\text{Cl}$, $^4\text{He}$), together with anthropogenic parameters, to derive the water-age at different locations;
- Use the water-age distribution to establish solute travel times in the different parts of the groundwater flow system. The interpretation of isotopes will require supporting geochemical and isotopic data for
water samples and rocks, i.e. $^{13}$C/$^{12}$C, U and Th contents, estimates of natural neutron fluxes and the in situ rate of production of isotopes;

- Interpret and model (where necessary) groundwater mixing and geochemical reactions between water and rock that controlled the evolution of the present-day groundwater compositions and distribution and therefore control the long-term future stability of compositions of groundwater entering the GDF and along solute transport paths leaving the GDF;

- Use non-reactive solutes and isotopes (chloride, $^{18}$O/$^{16}$O, $^{4}$He) to support and test hydrogeological interpretation of groundwater flow paths, to constrain groundwater sources and mixing, and to calibrate a palaeohydrogeological model.

The data obtained from the hydrochemical sampling and testing programmes will generally be interpreted to develop an understanding of some or all the following (developed from NDA, 2011b):

- The presence and nature of anthropogenic influences on groundwater composition;

- The identity and characteristics of different groundwater bodies and their distribution;

- The extent to which mixing of water from different bodies is occurring or has occurred;

- The compositions of the groundwater end-members from which the identified groundwater bodies have been derived by mixing and/or reaction;

- The nature of rock-water interactions that influence groundwater compositions under present-day conditions; conditions in the past; and into the future (in association with geochemical and petrological studies carried out as part of the preparation of the Geology SDM);

- The hydrochemical compositions of surface waters and groundwater that contribute to hydrogeological understanding of present day groundwater movements including recharge and discharge;

- The composition of groundwater in the regional volume of rock around a GDF (above, below and laterally) that might influence how chemical conditions evolve in the future;

- The ages and residence times of water and solutes in the groundwater system (based on isotopic and other data) to infer rates of groundwater movement and hence travel times for water and solutes;

- Which hydrochemical data can be used to calibrate and test models of groundwater movement and solute transport, including how they have evolved over a long period of time in the past (i.e. ‘palaeohydrogeological modelling’), including consideration of palaeo-climatic conditions;

- The presence of structural and stratigraphic controls on groundwater composition and movement;

- The chemical and microbiological conditions with the potential to affect long-term performance of Engineered Barrier System (EBS);

- The chemical conditions that may affect the engineering of an excavation, the possibility of any chemical or natural radiological hazards, and their influence on the short-term durability of introduced materials;
The composition of the groundwater at GDF depth that will re-saturate the backfill and buffer and eventually influence the dissolution, speciation and mobility of radionuclides when the primary containment (i.e. waste containers) is breached;

Factors relevant to radionuclide transport, e.g. presence and nature of colloids, bacteria, organics etc;

The distribution of trace elements, natural radionuclides and related stable nuclides that are analogues for the geochemical behaviour of waste-derived radionuclides.

Information on the hydrochemistry of the site will also typically be interpreted to:

- Characterise the undisturbed hydrochemical conditions at the site and describe the origin and flux of groundwater;
- Obtain specific data on parameters that are of importance for safety assessment and EBS design, such as pH, Eh, sulphates and chlorides;
- Identify water-age distribution within the rocks, including the possible presence of indicators of younger groundwater at GDF depth, e.g. the presence of dissolved oxygen (DO); and
- Develop an understanding of the palaeohydrogeology, in terms of locations of groundwater volumes with distinct compositions and hydrochemical properties at site model boundaries.

The priorities for data acquisition and the degrees of importance and relevance of individual parameters will be host rock and site-specific and will depend upon the rock type, hydrogeology, geochemical environment and many other factors.

It will also be necessary to characterise near surface hydrochemical conditions to meet some of the information requirements. The scope of shallow investigations will vary depending upon a range of factors, such as the extent and depth of glacial deposits. The hydrochemical information requirements of the SDM for the shallow system include:

- The presence and identity of different groundwater bodies, their distribution and extent to which mixing is occurring or has occurred; and
- The presence of anthropogenic influences on groundwater composition (e.g. presence of nutrients, persistent organic compounds, tritium).

The hydrochemistry SDM will need to make clear any uncertainties and to identify any key sensitivities within the interpretation and the models used.

### 2.4 Principal Outcomes and Priorities

The principal outcome of hydrochemistry interpretation and modelling will be a hydrochemistry SDM. The SDM will be designed to meet end user requirements. However, it will also be important to make it accessible, as far as it is possible to do so, to other stakeholders. To this end, the presentation of the SDM requires careful
consideration and it should include illustrations, schematic diagrams and even animation to illustrate patterns, areal and vertical distributions, changes over time etc.

The focus of the hydrochemical SDM should be to present the understanding of present-day undisturbed hydrochemical conditions at, above and below GDF depth and to provide an understanding of how these conditions have arrived. The SDM should also provide sufficient information to permit prediction of future changes.
3. Higher Strength Rocks: Case Studies

3.1 Introduction

Two case studies of international radioactive waste management programmes for higher strength rocks are presented here for work undertaken by SKB in Sweden and the investigations undertaken by UK Nirex Limited (Nirex) at Sellafield in Cumbria, UK.

3.2 SKB Forsmark

3.2.1 Background

Hydrogeochemical SDMs were developed by SKB, the Swedish Nuclear Fuel and Waste Management Company following investigations at candidate sites for deep GDFs at Forsmark and Laxemar-Simpevarp. Site investigation at these sites started in 2002, however, the design and implementation of investigative works was informed by many years of investigations and feasibility studies, most notably the work at Stripa between 1976 and 1992 and Äspö from 1995 to the present (SKB, 2009). Construction of the GDF is planned to begin in 2015 (SKB, 2010a).

This section concentrates on the hydrochemical interpretation inputs into the SDM for Forsmark. The geological history and setting of Forsmark is sufficiently similar to Laxemar-Simpevarp for the hydrochemical interpretation and modelling to not require separate review. The same approach is currently being applied to the shallow SFR site at Forsmark (e.g. SKB 2010a). There are also strong similarities with the setting and the investigations undertaken in Finland at Posiva Olkiluoto, with a high level of collaboration between the Swedish and Finnish programmes. SKB have kept a watching brief on the Olkiluoto work and were involved in the Palmottu project in Finland, both to provide wider input from similar crystalline host rocks with a similar palaeohistory.

The hydrochemical site investigation at Forsmark was completed in June 2007. Data obtained to this point (the ‘extended 2.3 data freeze’) form the basis of the hydrochemical conceptual model (SKB, 2008a). Sampling and hydrochemical analysis of groundwater, surface water and rainwater continued past the data freeze (Nilsson et al, 2010; SKB, 2007a). In addition, work towards addressing a number of specific knowledge gaps identified in a review of the SDM (SKB, 2010b) is ongoing. Recommendations for further works included: more specific studies of the sulphate-sulphide system; further investigation into the occurrence of U in Forsmark groundwater; studies of ion exchange; studies of redox kinetics, in particular the effects of micro-organisms; and a detailed future glacial scenario analogue study in Greenland.

3.2.2 Sources of Information

SKB’s work has been extensively reported in a series of detailed technical reports. Site Characterisation work at Forsmark was undertaken in two stages: initial (or preliminary) and complete. The characterisation from each stage is described in SKB (2005) and SKB (2008a) respectively. The site characterisation from the initial stage
(SKB, 2005) directly informed the production of the GDF safety case initial evaluation report (SKB, 2006a). At least two data collection ‘campaigns’ were undertaken for each stage and the results and interpretation following each of these campaigns were reported in detail.

For consistency across the site characterisation disciplines, the concept of ‘data freezes’ was introduced whereby each iteration of the site characterisation interpretation was based only upon site data collected up to a certain time, although data collection continued beyond the cut-off. The reports produced following ‘data freezes’ were reviewed by the Swedish Nuclear Power Inspectorate’s (SKI) review group (Insite) and SKB’s independent internal reviewers. The reviews generated lists of issues and questions that were subsequently investigated as part of the next data collection campaign or research and development (R&D) phase.

Following submission of the application for permission to construct the GDF at Forsmark, a period of long-term monitoring has begun. Hydrochemical data are being collected and quality checked as part of this programme (e.g. Nilsson et al, 2010) but it is not clear how these data will be used (SKB, 2007a).

### 3.2.3 End User Requirements

The aims, objectives and scope of the hydrochemical SDM at Forsmark (and Laxemar) are summarised in Table 3.1.

#### Table 3.1 Aims, Objectives and Scope of Hydrochemical Descriptive Modelling during Site Investigations at SKB Candidate Sites (after Smellie et al, 2002)

<table>
<thead>
<tr>
<th>Area</th>
<th>Activities</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aims</td>
<td>Develop a quantitative hydrogeochemical model based on site measurements&lt;br&gt;Use the quantitative model to construct a qualitative conceptual model that describes the important hydrogeochemical processes</td>
</tr>
<tr>
<td>Objectives</td>
<td>Describe the chemistry and distribution of groundwater in the bedrock and overburden, using direct chemical measurements and relevant information from geological and hydrogeological site investigations, and the hydrogeochemical processes responsible for its origin and evolution</td>
</tr>
<tr>
<td>Scope</td>
<td>To understand the origin and evolution of the groundwater chemistry&lt;br&gt;To understand the influence of the surrounding lithological types on the groundwater chemistry&lt;br&gt;To understand the influence of the fracture mineralogy (through water/rock reactions) on the groundwater chemistry&lt;br&gt;To understand the influence of hydraulic mixing processes on the present groundwater chemistry&lt;br&gt;To understand the influence of hydraulic mixing processes on the past composition of the groundwater (i.e. palaeohydrogeochemistry)&lt;br&gt;To allow assessment of future hydrogeochemical changes (i.e. forward predictions) at GDF depths</td>
</tr>
</tbody>
</table>

In addition to the requirements for hydrochemical characterisation, a number of GDF performance assessment “function indicators” were considered within the hydrochemical investigation, particularly following completion of
the draft GDF safety case in 2006 (SKB, 2006a). These were specified to ensure the long-term integrity of the GDF (SKB, 2006a), particularly to assess:

- Corrosion of the copper canisters used to store the waste;
- Degradation of the low hydraulic conductivity buffer and back-fill material; and
- The rate of transport of material in groundwater from the GDF.

Function indicators specified by SKB and their quantitative criteria are summarised in Table 3.2. The hydrochemical function indicators refer solely to the GDF host rock volume and should be fulfilled over the 1 Ma period used for the forward-looking safety assessment (SKB, 2006a).

Developing an understanding of processes that may lead to changes in the hydrochemistry at GDF depth was vital to meeting these requirements and required a detailed conceptual model of the hydrochemistry of the site and surrounding area.

The safety case and performance assessment considered a specific GDF design concept referred to as KBS-3, which comprises a single GDF based around a branching network of horizontal tunnels. The function indicators associated with this design concept may differ from those required by a different design, such as disposal in deep boreholes or vertical shafts.

### Table 3.2  SKB Hydrogeochemical Function Indicators for the GDF Host Rock Volume (after Anderson et al, 2000; SKB, 2006a and 2006b)

<table>
<thead>
<tr>
<th>Function Indicator</th>
<th>Function Indicator Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reducing conditions.</td>
<td>Eh must be &lt;0 mV and supported by the presence of reduced chemical species (Fe²⁺ or HS⁻) ± reducing bacteria¹</td>
</tr>
<tr>
<td>Ionic strength.</td>
<td>Concentration of divalent cations must exceed 40 mg/l as Ca²⁺ to avoid chemical erosion of buffer and backfill. Salinity as NaCl must not exceed 100 000 mg/l (1.7 M) to prevent swelling and reduction in hydraulic conductivity of buffer and backfill material².</td>
</tr>
<tr>
<td>Low DOC concentration.</td>
<td>DOC must be &lt; 20 mg/l.</td>
</tr>
<tr>
<td>Low colloid concentrations.</td>
<td>Colloid concentration must be &lt;0.5 mg/l</td>
</tr>
<tr>
<td>Low concentrations of corrosive species.</td>
<td>Important species are HS⁻ for the copper canisters and K and Fe for the buffer/backfill (concentrations not specified)</td>
</tr>
<tr>
<td>pH</td>
<td>pH must be ≤ 11, preferred range 6 - 10</td>
</tr>
<tr>
<td>Avoidance of chloride corrosion.</td>
<td>pH must be &gt; 4 and Cl must be &lt; 100 000 mg/l (3 M)</td>
</tr>
</tbody>
</table>

Notes:

¹ Eh measurements were not considered sufficiently reliable in isolation;
² Criteria are highly dependent on choice of material, buffer material may potentially have lower tolerance to salinity, 70 000 mg/l (1.2 M) threshold.
3.2.4 Setting

A brief summary of the current understanding of the Forsmark site is presented here based on the interpretation in SKB (2008a).

The Forsmark site is located in eastern Sweden on the coast of the Gulf of Bothnia 120 km north of Stockholm. The site investigation area covers approximately 12 km² and includes the Forsmark nuclear power plant and a disposal facility for low and intermediate level radioactive waste.

The investigation area is a low-lying coastal plain where ground surface elevations are less than 25 m above sea level (m asl). It is an area of hummocky topography interspersed with shallow lakes up to 2 m deep, some of which are connected to the Baltic Sea at high tide. There are no significant surface watercourses in the area.

The area was covered by up to 3 km thickness of ice during the last glacial maximum, approximately 18 ka ago. Since the glaciers melted the shoreline gradually regressed to the east due to isostatic rebound. Approximately 5-6 ka ago, the present-day Baltic basin was inundated by a more saline epi-continental sea known as the Littorina Sea. As the major drainage basins of continental Europe developed throughout the Holocene, the Littorina was replaced by the less saline Baltic. Approximately 2 ka ago, the Baltic shoreline regressed far enough for the Forsmark site to be exposed to meteoric processes and the present-day groundwater system began to develop. Ongoing isostatic rebound means that the site elevation relative to mean sea level is rising at approximately 6 mm/a.

3.2.5 Geology

Crystalline basement rocks of the pre-Cambrian Fennoscandian shield form the bedrock at the Forsmark site and are predominantly lithologically homogeneous, medium-grained meta-granites. The granites were intruded by more mafic rocks around the time of formation, leading to localised high temperature mineral alteration and lower temperature metasomatism by Fe-rich waters.

The bedrock is extensively fractured as a result of various phases of brittle deformation and the glacial history of the area. Fractures with open or partly open apertures are present down to approximately 400 m. Below 400 m, fractures are typically closed and very poorly connected. Fractures are variably mineralised, with the better connected and more transmissive features tending to be less mineralised.

Approximately 90% of the investigation area is covered by superficial deposits of late Pleistocene or Holocene age. These are predominantly tills with post-glacial clays and silts. There is also some peat and mudflats (gyttja) in the onshore area, particularly around the margins of the lakes.

3.2.6 Hydrogeology

The groundwater system at Forsmark has three components:
Surficial flow system in the till. Groundwater in the till is present at shallow depth. Shallow groundwater recharge and discharge is controlled by the small-scale variations in topography. Groundwater levels are controlled by the balance of precipitation and evapotranspiration. During dry weather when groundwater levels are low, lakes may contribute recharge to the till. There is clear disconnection between the till and shallow bedrock groundwater systems;

Shallow groundwater in the uppermost (weathered) bedrock. The shallow weathered bedrock system is confined by the till. It is a transmissive aquifer characterised by low hydraulic gradients. In simple terms, the weathered bedrock acts as a thin aquifer overlying an aquitard (deeper bedrock). The transmissivity is consistent with the occurrence of horizontal fracture zones and ‘sheet joints’ in the upper, weathered bedrock. In contrast, horizontal hydraulic gradients in the till are much higher. The shallow bedrock aquifer discharges to the sea; and

Deeper bedrock groundwater.

Groundwater heads in the till were generally higher than in shallow bedrock. Heads in the shallow bedrock are also lower than in the deeper bedrock. These observations suggest that the shallow bedrock system prevents significant interaction between the surficial and deep bedrock systems by intercepting infiltration from the till above and regional groundwater from below.

The water balance for the till and shallow bedrock aquifer suggests that the majority of recharge to these systems is discharged locally by surface seepage to lakes and water courses. Infiltration into the deeper bedrock aquifer was estimated to be approximately 0.1 mm/a.

Conceptually, the hydrogeological system was divided into three domains, as follows:

- Soil domain (i.e. the groundwater system in the superficial cover);
- Hydraulic conductor domain (i.e. fractures and deformation zones as well as the high transmissivity shallow bedrock aquifer); and
- Hydraulic bedrock domain (i.e. the rock matrix between fractures).

Within this conceptual model, groundwater is mobile within the soil and conductor domains and effectively immobile within the bedrock domain.

3.2.7 Hydrochemical Investigations

Site Characterisation Data

The candidate area for site investigation covered approximately 12 km². Investigation boreholes were drilled at 12 locations within and surrounding the candidate area to depths up to 1300 m below surface. In total, 25 cored boreholes and 38 percussion boreholes were drilled for the completed characterisation derived following the Stage 2.3 ‘data freeze’ (SKB, 2008a). Some 17 of the cored boreholes were sampled for bedrock hydrochemistry at various vertical intervals using packers, 10 boreholes were sampled for gases and microbes and 5 boreholes sampled for colloids. In addition, 76 shallow soil piezometers were installed to depths of approximately 10 m.
throughout the area and samples were taken from these for hydrochemical analysis. Samples of precipitation, surface water (including springs), and seawater were also analysed. The number of samples used for the complete site characterisation (SKB, 2008b) is summarised in Table 3.3.

Table 3.3 Sample Numbers used within the Final Site Characterisation at Forsmark ('Data Freeze' 2.3, including Samples from the Extended Data Freeze, Laaksoharju et al, 2008a)

<table>
<thead>
<tr>
<th>Type of Sample</th>
<th>Number of Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percussion boreholes</td>
<td>167</td>
</tr>
<tr>
<td>Cored boreholes (packer samples)</td>
<td>205</td>
</tr>
<tr>
<td>Process control *</td>
<td>13</td>
</tr>
<tr>
<td>Drilling sample</td>
<td>7</td>
</tr>
<tr>
<td>Tube sampling (multilevel collection from cored boreholes)</td>
<td>65</td>
</tr>
<tr>
<td>Shallow groundwater (piezometers and springs)</td>
<td>317</td>
</tr>
<tr>
<td>Seawater</td>
<td>277</td>
</tr>
<tr>
<td>Lake water</td>
<td>404</td>
</tr>
<tr>
<td>Stream water</td>
<td>398</td>
</tr>
<tr>
<td>Precipitation</td>
<td>31</td>
</tr>
<tr>
<td>Colloids</td>
<td>37</td>
</tr>
<tr>
<td>Microbes</td>
<td>50</td>
</tr>
<tr>
<td>Gases</td>
<td>42</td>
</tr>
<tr>
<td>Rock matrix porewater</td>
<td>91</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>2104</strong></td>
</tr>
</tbody>
</table>

* Duplicate samples were taken periodically so that parameters could be analysed simultaneously at different laboratories to determine analytical errors.

The most complete analyses of water samples measured the following parameters (Laaksoharju et al, 2008a; Nilsson et al, 2010):

- Eh, pH, Electrical Conductivity (EC) and temperature (continuously measured at the well head with pH and EC also measured in the laboratory);
- Uranine (fluorescein) concentration continuously measured at the well head. Uranine was added to the drilling fluid/flushing water to enable this water to be traced within the bedrock;
- Major ions (Ca, Mg, Na, K, HCO₃, SO₄, S total, Cl);
- Nutrients (NO₃, NO₂, NH₄, PO₄, total N, total P, organic carbon total and dissolved, SiO₂, Si total, chlorophyll, fulvic and humic acids);
- Minor ions and trace metals (Al, As, B, Ba, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, V, Zn, U, Th, Fe²⁺, Fe total, Mn, Li, Sr, Sc, Rb, Y, Zr, In, Sb, Cs, I, Br, F, HS⁻);
- Rare Earth Elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu);
- Dissolved gases (O₂, N₂, Ar, He, CO₂, CO, H₂, CH₄ and other short-chain aliphatic hydrocarbons);
- Isotope abundance and ratios (²H, ³H, ¹⁸O, ¹³C, ¹⁴C, ¹⁰B, ³⁴S, ³⁶Cl, ³⁷Cl, ⁸⁶Sr/⁸⁷Sr, ²²⁲Rn, ²²⁶Ra, ²³⁴U, ²³⁵U, ²³⁸U, ²³²Th, ²³⁶Th);
- Microbe abundance (adenosine triphosphate (ATP) concentrations, total numbers of cells for nitrate reducing, iron reducing, manganese reducing, sulphate reducing, acetogenic and methanogenic bacteria);
- Colloid concentrations.

**Hydrochemical Data Processing**

Prior to undertaking interpretation a quality-controlled dataset was assembled. The data processing methods used to evaluate sample quality and/or determine representative parameter values included:

- Analysis of time-series data collected during drilling and sampling (mainly for pH, Eh, uranine concentration);
- Statistical evaluation of groups of analyses and duplicate analyses, sometimes from two separate laboratories, to determine measurement precision;
- Calculation of charge balance error for major ions;
- Comparison of observed values between samples taken at different times or at other sample points;
- Comparison and correlation with other observed parameter values (e.g. microbiological parameters and inorganic chemistry);
- Comparison of observed values with data from other sites (Laxemar-Simpevarp, Posiva Olkiluoto);
- Sense checking of measured concentrations against known standards (e.g. gas concentrations compared with solubility).

The quality of the analyses or samples was categorised based on criteria such as the number of parameters measured and completeness of the isotopic analyses, the degree of drilling fluid contamination, charge balance error and the method of sampling. Five levels of quality were defined between 1 (best) and 5 (worst). Of the samples used in the bedrock interpretation, only 1% of the samples from cored and percussion boreholes were of category 1 and 19% were category 3 or better (i.e. the majority of samples were not of high quality) (Smellie et al, 2008a). Only the samples with category 3 or better were used for detailed modelling of Performance Assessment (PA) critical variables (e.g. redox conditions) whereas even the lowest category results were used in qualitative interpretation when supported by higher-category results.

Attempts to correct hydrochemical observations from cored boreholes for the presence of drilling fluids were made using a tracer (Gascoyne and Gurban in Kalinowski, 2008). A fluorescent dye uranine (fluorescein) was added to drilling fluid so that its presence in samples could be detected. Drilling fluid was typically shallow groundwater
pumped from a nearby well or borehole. It should, therefore, have been possible to post-process the results to correct for the presence of drilling fluid assuming a binary mixing model between formation water and drilling fluid, with or without reactions. This was unsuccessful for a number of reasons, including the following:

- Technical difficulties related to introducing and measuring the tracer due to variations in flushing rate (presumably in response to variations in drilling progress), variations in the rate at which the tracer was added to the flushing water and fluorometer drift;
- Background fluorescence;
- Sorption of the tracer to bedrock;
- Contamination of boreholes due to earlier hydraulic tracer testing (the Borehole Probe Dilution Tests).

Overall, the technique was assessed as useful for assisting with sampling (i.e. determining how much pumping may be required to remove the flushing water from a borehole prior to sampling) but it was not a practical means of correcting observations for drilling contamination. As a result, the bedrock hydrochemical SDM is based on uncorrected data. However, correction for the presence of drilling water was found to be of assistance in the qualitative interpretation of the surface hydrochemistry (Tröjbom et al, 2007).

The final data processing stage was to calculate mineral saturation indices and associated parameters (e.g. pCO$_2$ - partial pressure of CO$_2$) to account for degassing during sampling.

Raw data were stored on a central database (SICADA). A subset of these data was extracted to a second database (SIMON) following data processing and quality categorisation. The data from the SIMON database were used to compile the interpretation. It should be noted that the SICADA does not currently contain uncertainty values.

Collation of Related Information from Other Site Investigation Work Packages

Information was obtained from other work packages and work groups for input into the hydrochemistry SDM. This included the following:

- Geology: understanding of the palaeographic evolution of the site; bedrock domain, deformation zone and fracture domain concepts and 3-D mapping/realisations; bedrock mineralogy and geochemistry; fracture mineralogy and geochemistry; depth to saline water estimated from surface Transient Electromagnetic soundings;
- Hydrogeology: conceptual model of site hydrogeology; translation of geological domains into hydrogeological domains (e.g. identifying active flow zones); hydraulic properties including fracture zone transmissivity and matrix diffusion properties; water balance/flux data;
- Surface system: conceptual model of shallow groundwater chemistry (modern freshwater end-member); identification of interest areas for bedrock geochemistry (areas of potential deep groundwater discharge).

Collaboration between groups working on different components of the site investigation was vital, not least to avoid duplication of effort and to ensure consistency in the terminology used in the final SDM.
3.2.8 Hydrochemical Interpretation and Modelling

Methodology

The interpretation of hydrogeochemical data for site characterisation at Forsmark was iterated at each stage of investigation. The following steps were taken at each iteration:

- Assembly of a quality-controlled hydrochemical dataset (the SIMON database);
- Collation of related information from other site investigation work packages;
- Explorative analysis and visualisation of groundwater properties;
- Mathematical modelling;
- Site description;
- Uncertainty analysis;
- Further investigation and iteration of the site description.

For the purposes of interpretation, the surface system (depths down to 10 m) was treated separately from the bedrock system (depths below 10 m). The depth interval between 10 and 150 m below surface was an area of overlap between interpretations. The main reports for the systems are Tröjbom et al. (2007) for the surface system and Laaksoharju et al. (2008a) for the bedrock system. The following description included details from both interpretations.

Explorative Analysis and Visualisation of Groundwater Properties

The data obtained were evaluated semi-quantitatively in order to develop understanding of:

- Parameter ranges;
- The vertical and lateral distribution of properties;
- Patterns and trends within the data; and
- Similarities and differences between data from Forsmark and other sites or international standards (e.g. for isotopes).

The result of this phase was an SDM of the site hydrochemistry supported by a large number of figures and statistics. The initial SDM was used as the basis for numerical modelling and to guide further data collection during the later iterations of the SDM. Visualisation techniques and statistics were an important component of this phase and are discussed in more detail in the Tools Section (3.2.8).
In summary, the following steps were taken to develop the SDM:

- Classification of samples into water types based on major ion concentrations (Fresh – Mixed – Brackish Marine – Mixed – Brackish to Saline non-marine);
- Calculation/ visualisation of ‘traditional’ water types for dilute groundwater using hydrochemical diagrams (e.g. Piper diagrams, Langweiler-Ludwig plots);
- Principal Component Analysis (PCA) assisted in the grouping and initial classification of groundwater in the interpretation of surface and shallow groundwater hydrochemistry. PCA was used to separate out the sources of variation within the more saline groundwater that effectively had the same (Na-Cl) type when classified using ‘traditional’ types;
- Spatial visualisation and presentation of parameters. Scatter plots of parameter value vs. sample depth proved to be very useful at Forsmark and were used to present much of the data in the initial characterisation. These plots showed that the salinity increased with depth but also that the chemistry of the saline waters changed throughout the bedrock, particularly with respect to Mg concentrations;
- 3-D visualisation of element concentrations, as points or coloured as ‘zones’ corresponding to particular water types, helped to identify areas where more saline water was present near to the surface;
- Scatter plots were used to look for correlations between major ions, ion ratios, isotopes ($\delta^{18}O$) and other conservative elements (e.g. Br). Compositions of known end-members (for example Baltic Sea, local rain water, global meteoric water line) were included for comparison. These relationships indicated that mixing is an important process at Forsmark. The PCA from the shallow system supported these conclusions;
- Presentation of trace and rare earth element (REE) concentrations and their relationship with depth and other major ions. Difficulties were encountered interpreting REEs, which were attributed to: complex mixing relationships; relatively poor understanding of their mineral sources; and contamination during drilling. U concentrations were higher than expected in some samples, leading to further sampling, mineralogical investigation and modelling. Fingerprint diagrams – line diagrams listing REE elements on the category axis and element concentration on the value axis – were used to evaluate REE concentrations against established reference concentrations but were of limited interpretive value without additional information on the sources and sinks of these elements;
- Review of the abundance of micro-organisms, colloids and gases and qualitative interpretation with respect to sample depth, hydrochemistry and water types. Gases were evaluated with respect to saturation and found to be undersaturated. Methane was detected below 440 m depth in one borehole and methanogenic bacteria discovered throughout the deep groundwater system, albeit in low abundance. A relationship between Eh and the abundance of bacterial reducers was noted. Colloids were mainly Fe-Al species and although these colloids may transport U, they were not the source of the high U concentrations;
- More detailed evaluation of relationships between the water types and PA-critical parameters such as U, Ra and Rn, S-species and nutrients (N and P-species) (following the general requirements in Table 3.2). Important conclusions from these evaluations included: confirmation of both mineralogical and redox control over U mobility in the groundwater; recognition that most of the S in the system was derived from the brackish marine water type (Littorina Seawater) with ongoing $SO_4$
reduction (shown by $\delta^{34}$S); and confirmation that Ra, Rn and nutrient concentrations were low, as expected from other sites (Smellie et al, 2008a);

- Qualitative analysis of water-rock interaction, focussing on the carbonate phases in fractures. Groundwater tracers such as $^{86}$Sr/$^{87}$Sr, $\delta^{13}$C$_{\text{TIC}}$ and $\delta^{18}$O$_{\text{TIC}}$ (TIC is total inorganic carbon) were used in combinations with understanding of fracture mineral hydrochemistry (Sandström et al, 2008) to identify the dissolving phases that buffer pH within the bedrock and to determine whether there had been significant movement of the redox front over geological time. The evidence suggested that there had been no significant penetration of oxidising water into the bedrock during the Quaternary;

- Descriptive analysis of porewater chemistry and comparison to fracture water chemistry. Differences between ionic strength and isotope ratios were identified;

- Qualitative evaluation of groundwater residence times using indicators that accumulate in groundwater over time because their concentrations are not limited by equilibrium reactions (e.g. Sr, Rb, Cs, Li, $\delta^{18}$O, $\delta^{37}$Cl, $^{86}$Sr/$^{87}$Sr). These techniques generally supported the conclusions from the hydrogeological conceptualisation (i.e. young water at the surface, mid-Holocene age seawater below this and older water at greater depth);

- Calculation of groundwater residence time using quantitative indicators such as tritium, $^4$He, $^{14}$C, $^{36}$Cl. Tritium analysis confirmed that modern water was restricted to depths less than 200 m at the site. Tritium contamination in some of the deeper, more saline samples was attributed to contamination from de-ionised water during drilling or mixing with highly tritium-enriched water from the nuclear power plant near to the site. $^{36}$Cl and $^4$He suggest that the age of the oldest groundwater on site was in excess of 1.5 Ma ago. $^{14}$C suggested an age of 5-6 ka for the brackish marine water (Littorina seawater) but the carbonate chemistry of the site is too complex (controlled by too many mineral phases of different ages) to calculate reliable $^{14}$C ages for all of the groundwater.

The result was a hydrogeochemical SDM accompanied by visualisation of the present-day water type distribution. The model describes a system where present day water compositions are the product of mixing between different water bodies in the recent geological past, modified to a small degree by water-rock interaction. The extent of mixing between water bodies is controlled by the permeability of the fracture system, whereby younger water has penetrated to greater depths in the more permeable parts of the system. Schematic cross-sections in different orientations were used to present the data. The locations of these cross-sections were chosen to be consistent with interpretive elements from other work packages.

**Hydrochemical Modelling**

Hydrochemical modelling was used to increase confidence in the hydrochemical SDM and to extend its applicability beyond the range of observed data. Modelling was used for three main purposes, as follows:

i) Determination of end-member water compositions and calculation of mixing ratios using the mixing code M3;

ii) Conservative flow and transport modelling using CONNECTFLOW; and

iii) Water-rock and equilibrium reaction modelling using PHREEQC.
The proprietary model code ‘M3’ (Multivariate Mixing and Mass-balance, Laaksoharju et al., 1999; Gómez et al., 2006) was used extensively by SKB in the analysis of the surface and bedrock hydrochemistry at Forsmark. The model determines the composition of each sample in a dataset as a function of mixing between end-member water types. Variations between the predicted and the observed composition were attributed to water-rock interaction. The model was developed for the purpose of hydrochemical site investigation for radioactive waste disposal in systems where the groundwater composition is primarily a function of mixing between hydrochemically distinct water bodies. It is therefore applicable to the conceptual model of the groundwater system at Forsmark.

Exploratory analysis suggested that the groundwater composition at Forsmark was primarily the result of mixing of a small number of end-members. The compositions of these end-members were estimated from the exploratory analysis; from data obtained from other Scandinavian localities; and a detailed review of the literature (Gimeno et al., 2008). The end-members were then used in the M3 model to calculate mixing ratios of groundwater samples.

The sample and end-member water types used within M3 were iterated throughout the site investigation process (Gurban in Kalinowski, 2008). The final mixing model of the groundwater environment considered only groundwater samples (i.e. samples from surface water and shallow piezometers were excluded) and incorporated four end-members. The sensitivity of the M3 model to uncertainties in the end-member compositions was explored using Monte-Carlo analysis (Gimeno et al., 2008). The analysis confirmed that the conclusions from the M3 modelling were reasonably stable and also improved understanding of the end-member compositions.

The mixing proportions derived from the M3 modelling were used:

- To support the presentation of the conceptual model;
- To assist with calibration of the hydrogeological flow and transport model; and
- As a starting point for water-rock reaction modelling.

The variable-density, flow, heat and solute transport modelling package CONNECTFLOW (Serco) was used as the basis for the hydrogeological modelling undertaken at Forsmark (see Follin, 2008 for details), but was part of the hydrogeological SDM hence it is discussed only briefly here. The observed fracture and porewater hydrochemistry has been used to validate the discretisation of the CONNECTFLOW model area into zones of kinematic porosity (mobile water, i.e. fractures) and diffusion-accessible porosity (immobile water i.e. matrix) and to calibrate the solute transport elements of this model that will ultimately be used for GDF PA. Conservative parameters such as Cl and Br concentration, Cl/Br ratio and δ\(^{18}\)O were used in this calibration. HCO\(_3\) concentrations and end-member mixing ratios calculated by M3, which rely on concentrations of non-conservative elements, were also used to validate hydraulic modelling. The end-member mixing ratios calculated by the CONNECTFLOW model were in good agreement with the ratios calculated using M3 and provide informative visual outputs that were used to describe the overall hydrogeological and hydrochemical conceptual models.

Modelling of water-rock reaction and speciation-solubility processes in Forsmark groundwater was undertaken using PHREEQC (Parkhurst and Appelo, 1999, see Section 9.5.4). In addition to simple solubility and speciation calculations, more advanced applications of the PHREEQC model at Forsmark included:
• Modelling of redox potentials using an un-coupled version of the WATEQ4F thermodynamic database with the aim of determining which redox pairs, specifically which reduced mineral phases, were controlling the Eh of the groundwater (Gimeno et al, 2008). This modelling was validated for a small number of samples where Eh was measured accurately using the Chemmac probe (see Auqué et al, 2008). The resulting models of redox equilibrium species were used in coupled modelling of chemical conditions throughout the host rock (see below);

• Incorporating water-rock reaction and ion exchange into end-member mixing calculations in order to improve understanding of end-member compositions (Gimeno et al, 2008). This was particularly important for the pre-Littorina end-members where the chemical and isotopic compositions are not well constrained. The M3 model was adjusted to agree with the PHREEQC calculations and the pre-Littorina boundary conditions in the hydrogeological model could be improved as a result;

• Modelling the disturbance caused by the introduction of drilling water (modern meteoric signature) into old groundwater at GDF depth in order to evaluate the level of uncertainty with respect to the function indicator criteria (Molinero et al, in Kalinowski, 2008). It was shown to be highly unlikely that mixing, reactions and ion exchange would have contaminated the host rock to such a degree that a false positive would occur (i.e. the sample would meet the function indicator but the formation water would not). Reactive transport modelling was used to show that introduced oxygen would not penetrate further than 0.01 m into the host rock and would be consumed by reduced species (pyrite) within 2 years.

There has been no attempt at large-scale reactive transport modelling for the Forsmark site. However, coupled modelling, which simulates both transport and reactions (Auqué et al, 2006) was developed to link hydrochemistry and hydrogeology. With the coupled modelling approach, calculated end-member mixing proportions from each node within the CONNECTFLOW model were used to generate initial solutions in a PHREEQC model. PHREEQC was then used to mix these waters and equilibrate them with the host rock, accounting for processes such as ion-exchange and redox reactions. The models were run separately so there is no feedback from the PHREEQC model to the CONNECTFLOW model. The results were validated against observations. This approach has been used to visualise the distribution of function indicators at GDF depth (Gimeno et al, 2008) and forecast how the composition of groundwater may change in the future assuming a return to glacial conditions with and without anthropogenically-induced climate change (Sidborn et al, 2010 and Guimera et al, 1999).

Site Description, Further Investigation and Iteration of the Site Description

The site description was compiled based on the results of explorative analysis and modelling. Overall, the interpretation was successful and able to meet many of the end user requirements: characterising the chemistry of groundwater at GDF depth with precision and describing the evolution of that groundwater body over the past 10 ka. The interpretive methodology adopted was successful because it was tailored to the groundwater environment at Forsmark. Here, mixing between different groundwater bodies controls the groundwater chemistry and the method adopted was able to quantitatively analyse these mixing relationships. However, the thorough interpretation and modelling programme has identified a number of specific uncertainties related to limitations in the observed data set (see following section).

The site description has undergone iteration when additional details have become available from other site investigation programmes or when further data are collected that reduced uncertainties. At Forsmark, the site
description has undergone at least four iterations during the site investigation programme. The changes at each iteration were related to results from targeted investigations to address uncertainties through, for example drilling additional boreholes, analysing porewater chemistry and using isotopic tracers and gaseous tracers in new ways. As an example, further investigation of the sulphide system in the deep groundwater was requested following review by the internal reviewers and regulator (Tullborg et al, 2010). Despite this, the outline conceptual model of the evolution of the system and the main hydrochemical processes has remained consistent throughout the site investigation programme (Laaksoharju et al, 2008b). Alternative hypotheses have been developed during iteration of the SDM and have been tested against the observed data in order to increase confidence in the final model. This process was illustrated very effectively by Gimeno et al. (2008) who used simple scatter plots of Cl concentration and δ18O to test two hypotheses of the origin of the glacial end-member water.

3.2.9 Uncertainties

Uncertainties were considered throughout all stages of the site investigation processes and steps were taken to reduce or constrain them, including:

- Data categorisation to identify data quality and the uses to which it could be put (Section 3.2.5);
- Quality control procedures were put in place at the start of site investigation;
- There was a procedure for recording uncertainties, comments generated by internal and external review and areas where additional work is required;
- Analytical errors were evaluated and reported, with recommendations to present error bars on figures where possible and to include standard errors in the databases, which is currently not possible (Nilsson in Kalinowski, 2008). However, this information was not recorded in the SICADA database and so were not available for the modelling and interpretation;
- Techniques were developed to trace analytical errors throughout the interpretations and modelling and hence evaluate the sensitivity of the interpretation to these errors. This is particularly significant for the interpretation of porewater chemistry and the numerical modelling;
- Sensitivity analyses were undertaken within numerical models, including Monte Carlo analysis within the M3 model;
- Modelling has been used to assess the levels of uncertainty that are acceptable with reference to the function indicator criteria; and
- Coupled modelling has been used to help reduce uncertainties in both the hydrochemistry and hydrogeological interpretation and modelling.

In terms of the outcome of the site investigation for the bedrock environment (Laaksoharju et al, 2008a), confidence was high in the understanding of end-member water compositions and the processes affecting groundwater composition (mixing, redox reactions, ion exchange and carbonate buffering). This gave confidence to aspects of PA that were dependent on the SDM. However, confidence was low in some areas where uncertainties remained including the following:
• Understanding how the depth of the redox front may change over time (mainly due to lack of detail regarding fracture mineral phases at depths above 150 m);

• Sulphide concentrations, hence the processes responsible for generating sulphide in the deep groundwater (caused by the high level of disturbance in sulphide concentrations caused by drilling and sampling);

• Sources and sinks of methane and the mechanisms of gas bubble generation and transport in the bedrock environment; and

• Knowledge of the deep saline groundwater end-member outside the investigated rock volume.

The majority of these areas of low confidence were related to data availability and the limitations of data gathering techniques rather than to the interpretation.

Confidence in the surface hydrochemical assessment appears to have been lower but with less specific uncertainties and general areas of low confidence (SKB, 2008a). Understanding of the catchment-scale processes appears to be good, whereas information was lacking at the detailed scale, for example related to the chemical and biological processes that act as sources and sinks for specific elements.

3.2.10 Tools

Software tools used in the interpretation and modelling of hydrochemical data at SKB-Forsmark have included the following:

• Data management: bespoke databases SICADA, SIMON;

• Data processing, exploration and visualisation: Aquachem (hydrochemical data management and presentation), PHREEQC (data processing), OpenDX (3-D visualisation);

• Geochemical modelling: PHREEQC (solubility and speciation calculations, reactive transport, calculation of mixing with reactions);

• Hydrogeological and solute transport modelling: CONNECTFLOW (3-D variable density flow and solute transport); Core2D (2-D groundwater flow and reactive transport); DarcyTools (variable density flow and solute transport);

• Bespoke tools: Matlab (numerical data processing, operating environment for M3); M3 (PCA, end-member decomposition and mixing analysis); VBX-VI (surface catchment water quality mass balance model).

Further details on software tools are given in Section 9.1. It is noted that with the exception of PHREEQC, which is freely available and open source, the interpretive software tools used by SKB are all proprietary, commercial tools and that the solute transport modelling codes used are not widely applied outside the nuclear industry.
3.3  Nirex, UK

3.3.1  Background

Site investigations were undertaken by Nirex at Sellafield in West Cumbria, Northern England between 1989 and 1997 to assess the suitability of the area for development of a GDF. Preliminary investigations by Nirex also considered Dounreay (Caithness, northern Scotland) as a potential GDF location. However, for the latter part of these investigations the Sellafield area was favoured for investigation over alternative sites.

The investigation programme included the drilling and testing of 19 boreholes to depths of up to 1950 m below surface. There was a large amount of pre-existing geological, hydrometric and hydrochemical data when the site investigation programme began due to the presence of a regionally-important aquifer and mineral exploration in the area. The interpretation of the shallow hydrogeology of the site made extensive use of pre-existing data.

Hydrochemical investigations were conducted at two scales, as follows:

- Shallow groundwater investigations took place over a large area of ~200 km² covering the surface catchments of the rivers Ehen, Calder and Irt;
- Deep groundwater investigations focussed on a much smaller area between the coast and Lake District foothills immediately to the south of the Sellafield works. The area of interest for development of the GDF (the Potential Repository Zone, PRZ) was located within the deep investigation area.

The scope of the Nirex investigations as a whole considered a very much wider area, extending offshore for more than 50 km (Chaplow, 1996).

3.3.2  Sources of Information

The investigation programme at Sellafield ceased in 1997 when planning permission for a rock characterisation facility (RCF) at Longlands Farm was refused. Following dismissal of the planning appeal, Nirex completed reporting of the site investigation work and prepared a demonstration Performance Assessment for a GDF at Sellafield (Baker et al, 1997). The reports that resulted are the principal source of information for this review.

3.3.3  End User Requirements

The main objectives of the hydrochemical elements of the site investigation were (Bath et al, 1996):

- To assist in developing a conceptual model of groundwater flow through the PRZ and surrounding area;
- To investigate the evolution of the groundwater system over time and how it might have responded to external changes such as climate; and
- To measure the baseline hydrochemistry of groundwater within the PRZ.
Information requirements were not specified for the investigations and, to some extent, the programme of work was developed to address uncertainties as they were identified. Therefore, although the objectives set out above were achieved, the level of confidence is low in some aspects of the interpretation that were important for the Performance Assessment (Nirex, 1997b).

3.3.4 Setting

The Sellafield site is located on the coast of West Cumbria in Northern England. The investigation area included the western margin of the Lake District Fells, where ground elevations exceed 100 m AOD, and the coastal plain where elevations are typically between 30 and 60 m AOD. The area includes the catchments of three rivers: the Ehen, Calder and Irt. The rivers rise from mountain streams and lakes in the Fells and flow to the sea over the coastal plain.

Geology

The geology of the investigation area is transitional between the Lake District Massif basement rocks to the east and sedimentary rocks of the Irish Sea Basin to the west. These geological domains are separated by the Lake District Boundary Fault (Nirex, 1998c). Basement rocks are volcanic welded ignimbrites of the Ordovician Borrowdale Volcanic Group (BVG), which are thought to be in excess of 1 km thick throughout the investigation area. BVG rocks are found at outcrop in the east but covered by up to 1750 m of predominantly Mesozoic and Quaternary sediments at the coast. The sequence overlying the BVG is most complete at the coast and comprises Carboniferous Limestone, Permian Brockram breccias, Sherwood Sandstone and Quaternary terrestrial glacial sediments (tills, sand and gravel). The Sherwood Sandstone is by far the thickest group within the sequence, exceeding 1000 m thickness at the coast (Nirex, 1998c). The Mercia Mudstone overlies the Sherwood Sandstone offshore.

The BVG was the intended host rock for the RCF. The proposed location of the RCF was under the coastal plain approximately 3 km from the coast where the BVG lies at approximately 600 m depth.

Structurally, the area is dominated by the east-north-east trending lineaments that characterise the Lake District Massif (Michie, 1996). These lineaments have been reactivated over geological time in response to igneous intrusions and sedimentary processes in the Irish Sea Basin. Faulting and fracturing in the BVG is ubiquitous. Displacement and deformation within fault zones can be very extensive and several major deformation zones have been defined. North-west trending normal faults linked by shorter north-east trending faults are characteristic of the Mesozoic sequence onshore and into the Irish Sea Basin.

Hydrogeology

The hydrogeology of the Sellafield area is controlled by the topography, geology and the coastal setting of the site. The topography and coastal setting provide a contrast between inland topographically-driven flow systems and the coastal and offshore density driven flow systems. Differences in the permeability of the onshore rocks are also important, with the Sherwood Sandstone being an important aquifer formation in contrast to the relatively
impermeable BVG. At its simplest level, the hydrogeological conceptual model considered three main hydrogeological regimes within the area (Black and Brightman, 1996) as follows:

- The Coastal Plain regime (topographically driven flow within the Sherwood Sandstone aquifer and overlying Quaternary);
- The Irish Sea Basin regime (density driven flow throughout the geological sequence at the coast and into the Irish Sea Basin); and
- The Hills and Basement regime (predominantly topographically driven flow within the BVG beneath the Coastal Plain regime).

The interfaces between these regimes can be sharp and well defined or broader spatial transitions and there are internal controls on groundwater flow within each regime related to fluid density, geological anisotropy and recharge rates (Black and Brightman, 1996). Understanding the properties of the regime interfaces and the controls on their movement was considered vital for making informed, quantitative predictions about how the hydrogeological system will change in the future. The interpretation of groundwater hydrochemistry was important in defining the extents of the three regimes and characterising the nature of the interfaces between them.

3.3.5 Hydrochemical Investigations

Phases of Investigation

The Nirex investigations for site characterisation at Sellafield were undertaken in phases between 1989 and 1997. The elements of these phases relating to the hydrochemical characterisation and modelling were as follows:

- Exploratory investigations related to drilling and testing of deep borehole 1/1a (Nirex, 1989; Cave et al, 1990) and the production of a baseline information report (Nirex, 1990);
- Existing hydrochemical data for rivers, springs, boreholes and mine workings from the National Rivers Authority (precursor to the Environment Agency), Institute of Freshwater Ecology and other published sources were collated and quality checked during 1991 (Nirex, 1991). Recommendations were made for Phase 2 data collection;
- Water samples were collected and analysed during 1992-3 to augment the existing shallow hydrochemical data for rainwater, river baseflow, springs (including beach-front springs), shallow boreholes, located and re-opened 400-600 m deep iron ore exploration boreholes, and mine workings (Nirex, 1994);
- Samples of groundwater were collected during the drilling and testing of deep boreholes between 1992 and early 1997, although the majority of the work was completed before the end of 1994. Significant effort was put into data quality assurance and preparing an approved dataset to be used in the interpretive work. Results and preliminary interpretations were reported throughout the drilling and testing programme (Nirex, 1993; Nirex 1995; Bath et al, 1996);
• Geophysical logging of the deep boreholes, petrographic analysis of core samples and extraction of core porewater were undertaken following drilling and provided data that supported the hydrochemical interpretation (see Nirex, 1998a; Nirex 1998b; and Nirex, 1995 respectively);

• Addition of data to the shallow dataset in 1994-5 following further sampling of river baseflow, springs and rainwater (Nirex, 1996a). Hydrochemical data were also collected from shallow Quaternary Characterisation Boreholes that were drilled and tested in 1995 (Nirex, 1997a);

• Final interpretive reporting (Nirex, 1998a and c) and contribution to a demonstration Performance Assessment (Nirex, 1997b) during 1997-8 following refusal of planning permission for the rock characterisation facility.

Site Characterisation Data

Results from approximately 400 water samples were considered in the interpretation of surface water and shallow groundwater above the Saline Transition Zone (STZ, see below) (Nirex, 1998a). The dataset comprised chemical analyses of rainwater, surface water, springs, shallow groundwater, mine waters and depth samples from existing mineral (iron ore) exploration boreholes, in addition to interpreted data from samples of deeper groundwater from the Nirex investigation. The dataset included data that predated the Nirex investigation. Availability of analytical data for different types of sample is summarised in Table 3.4.

The characterisation of deep groundwater was based on data from 163 tests in 19 deep boreholes drilled as part of the site investigation programme (Nirex, 1998c). The deep groundwater chemistry dataset was supported by mineralogical data and porewater chemistry obtained from core samples.

Of these, 79 samples were determined to have <10% contamination by drilling fluid and were used in interpretation (see below). Analytical data types available for the deep drilling samples are summarised in Table 3.4 and a complete list of the data available for the deep boreholes can be found in Nirex (1998c) and references therein.

A large number of analyses were undertaken on water samples recovered from deep boreholes. However, much of these data were not used in the interpretation. The data that were not used included measurements of redox sensitive species and nutrients (Eh, pH, Fe – including Fe2+ – Mn, HS-, NH4+, NO3-, NO2-, HPO4-) and carbon isotopes, which were not considered reliable due to drilling fluid contamination.

Reactive gas analyses and Rare Earth Element (REE) analyses were also not utilised in the final interpretation, although there was some initial interpretation of dissolved He, Rn, CH4 and higher hydrocarbons, CO2 and the N2/Ar ratio (Richards et al, 1995) and the reactive gas dataset was utilised in the description of the hydrochemical baseline (Nirex, 1996b). Porewater chemistry data were also not used in the final interpretation due to concerns over their reliability.

Limited porewater data were obtained from extraction tests on drillcores from the sandstone at depths of ca. 450-1100 m. Porewater concentrations of chloride and sulphate were calculated using helium porosity data for the same core samples. Sulphate values gave the same pattern as chloride, so it was inferred that sulphide oxidation was not a dominant artefact. Insufficient work was done to derive reliable estimates of propagated uncertainties, so the interpretation of a comparison between these data and groundwater sample data was limited in its extent. The raw
data suggest that the porewater concentrations were similar to concentrations in the few available groundwater samples (Bath et al, 1996).

Porewater extraction by centrifuging (sandstone core samples only) as well as aqueous leaching extractions was carried out on drillcore samples from Borehole 3. Comparison of the centrifuged and leached chloride porewater concentrations gave limited calibration for the sandstone, but this was not possible for the BVG samples, for which porosity data were required to recalculate in situ concentrations. Again, large uncertainties mean that the resulting data patterns could not be interpreted with any rigour (Cave et al, 1994).

Golder Associates (2010) reviewed the Nirex investigation as part of NDA guidance on sampling for colloids and microbes. In the review, it was noted that water samples from deep boreholes for analyses of colloids and organics were severely compromised by the use of organic additives in the drilling fluid and that there was limited reporting of sample results. They also note that samples for microbial characterisation were not obtained from deep boreholes and that no samples for colloids and microbial analyses were taken from the shallow groundwater sources.

### Table 3.4 Summary of Analytical Data available for the Sellafield Hydrochemical Interpretation

<table>
<thead>
<tr>
<th>Sample Type/Data Source</th>
<th>pH, EC</th>
<th>Major Ions (including NO3)</th>
<th>Metals and Minor Ions</th>
<th>Stable Isotopes of Water and Tritium</th>
<th>Trace Elements, Gases and Other Stable Isotopes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Historic rainfall data</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Historic National Rivers Authority - NRA (now Environment Agency) surface water data</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Historic NRA groundwater data</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nirex rainfall monitoring</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Nirex Baseflow and spring surveys</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Nirex surveys of existing boreholes</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Nirex deep borehole samples</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
</tbody>
</table>

✓ = data type available for all sample; ✈ = some parameters from that data type are available for some samples.

**Sample Quality Assurance and Data Processing**

The final combined interpretation of shallow and deep groundwater chemistry for Sellafield was based on a dataset of 114 samples (79 from new deep boreholes, 22 from springs and 13 from shallow, existing boreholes) (Nirex, 1998c). These samples were considered to have good analytical reliability and included analyses for a wide range of parameters. Reported parameter values for the key dataset were estimates because they were derived from
measured compositions following correction for drilling fluid contamination and/or selected as representative for a site (e.g. depth interval in a borehole) from a suite of replicate samples.

Samples were selected for the key dataset following quality assurance. For existing datasets, a quality assurance process of primary and secondary data verification was adopted (Nirex, 1991). Primary verification used professional judgement and internal cross-checking of samples or determinands for consistency, plausibility, reported levels of uncertainty, how robust the sampling procedure was, and how complete the data were. This included the calculation of ion balance error and spatial comparisons between Ca and HCO₃ concentrations and groundwater levels. Secondary verification considered consistency between different samples and data types. It included use of scatter plots and Piper diagrams. Similar checks were carried out on data collected following sampling of surface water or shallow groundwater at existing monitoring points.

Chemical tracers were added to drilling fluid (fresh mains water with organic polymer thickener) to estimate the amount of drilling fluid (of known composition) in a groundwater sample. The tracers used were LiCl (1000 mg/l Li, ~6g/l TDS), KI (100 mg/l I) and NaNO₃ (250-500 mg/l NO₃) although the latter was found to be a poor tracer because NO₃ was not conservative in reducing groundwater found at depth (Nirex, 1998c).

Natural groundwater compositions for most inorganic ions and dissolved gases were then estimated from samples using Tracer Regression Analysis Programme (TRAP) to correct for tracer contamination (Nirex, 1998d). TRAP determined the amount of tracer in a sample using linear regression (or linear extrapolation) assuming that the natural groundwater has a negligible concentration of the tracer. Natural I and Li concentrations in groundwater were low, so this assumption was thought to lead to errors of ±2% on estimated natural groundwater compositions (Nirex, 1998c). However, the use of the LiCl tracer at concentrations around 1 g/l meant that Cl concentrations in the drilling fluid were very much higher than those in fresh groundwater. This meant that the compositions of fresh (non saline) groundwater from new boreholes were often not consistent with those from existing, shallow boreholes (Nirex, 1998a). Concentrations of redox-sensitive species, trace elements (e.g. U and Th), carbon isotope ratios and other isotope ratios (²⁶Cl/Cl, ⁸⁶Sr/⁸⁷Sr and δ³⁴S) were estimated from samples shown to be relatively uncontaminated by drilling fluid (Nirex, 1998c). However, tritium and carbon isotope abundances were so badly affected by drilling fluid contamination that they had limited interpretive value (Nirex, 1998c, d). Nonetheless, measured tritium concentrations were used to check calculated tracer mixing ratios in the deep groundwater samples because these were anticipated to contain no detectable tritium, in contrast to the water used for drilling (Nirex, 1996).

Attempts were made to validate the estimated compositions of deep groundwater by comparison with deep groundwater from other investigations in the UK as well as in Scandinavia and Canada. This had limited success due to the distinct character of the samples (Nirex, 1998c).

3.3.6 Hydrochemical Interpretation and Modelling

Methodology

The hydrochemical interpretation for site characterisation considered shallow and deep groundwater systems separately because the data availability and interpretation requirements were different. The division between the
two systems is referred to as the Saline Transition Zone (STZ), which corresponds to the part of the groundwater system where EC changes from being <10 mS/cm (~3 g/l TDS) to >17 mS/cm (~10 g/l TDS). The depth to the mid-point of the STZ varies between 200 m and 680 m below surface within the area of interest (Nirex, 1998a). The interpretation was undertaken by separate teams. Interim interpretations from the two work packages were integrated with other work programmes (e.g. geology, hydrogeology and groundwater flow modelling) at a high level by the technical experts supervising the work.

The approach to interpretation adopted for the two work programmes was similar. Initial data processing and quality assurance was followed by a review of the general spatial properties of the dataset, which allowed distinct water bodies to be defined. The hydrochemistry of each water body was then interpreted in terms of the sources of dissolved solutes, the implied residence time of the groundwater and the stability of the groundwater composition. The deep hydrochemistry work package had the greater relevance in terms of Performance Assessment given the proposed depth of the GDF and an apparent lack of interaction between shallow and deep systems over recent geological time. This is reflected in the final report on the hydrochemistry of Sellafield (Nirex, 1997c), which describes the interpretation of the deep hydrochemistry in greater detail than the shallow.

Definition of Water Types and the Spatial Distribution of Groundwater Bodies

The spatial distribution of groundwater bodies within the investigation area was determined using a small selection of parameters: salinity and EC; ion ratios between conservative species (e.g. Br/Cl ratios) and major ions; and stable isotopes of water. The parameters were used to identify characteristic attributes of different groundwater bodies and determine the distribution of these water bodies in space.

Three water types were identified from the selected properties and ratios (Table 3.5). These types were identified using scatter plots between the variables of interest (typically including Cl) and spatial plots presenting parameters of interest against depth in a single borehole or boreholes within a particular area of interest (e.g. the PRZ). Intermediate water types that evolved from mixing between the main types were also identified, relying on the conservative properties of Cl, Br and δ18O in the subsurface (Nirex, 1995).

Table 3.5 Water Types identified during Sellafield Site Investigations (Nirex, 1995, Nirex, 1998c)

<table>
<thead>
<tr>
<th>Water Type</th>
<th>Cl (g/l)</th>
<th>Br/Cl Mass Ratio</th>
<th>δ18O (% VSMOW)</th>
<th>Other Attributes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh to brackish waters</td>
<td>&lt;0.6</td>
<td>-</td>
<td>-6 to -7 (isotopically heavy sub-type)</td>
<td>Ca-HCO3 to Na-Cl type</td>
</tr>
<tr>
<td>Basement saline water</td>
<td>Typically 10 - 17</td>
<td>≥0.0018</td>
<td>-7 to -8 (isotopically light sub-type)</td>
<td>Na-Cl type, high Ca/Na, SO4/Cl ratios</td>
</tr>
<tr>
<td>Basinal brine</td>
<td>Up to 100</td>
<td>About 0.0009</td>
<td>About -5</td>
<td>Na-Cl type, low Ca/Na, SO4/Cl ratios</td>
</tr>
</tbody>
</table>

Note: VSMOW = Vienna Standard Mean Ocean Water
The spatial distribution of water types in the investigation area was determined using data from the deep drilling programme. Measured Cl concentrations, EC values, Br/Cl ratios and $\delta^{18}O$ ratios were plotted on geological cross-sections and contours of equal parameter value constructed. This interpretation showed a good, although not exact, correlation between the hydrochemical stratigraphy and the hydrogeological regime (Nirex, 1998c).

Borehole information on EC and Cl data were used to contour the estimated depth to the STZ. The resolution of the EC and Cl interpolation was improved using down-hole geophysics data. Logs of fluid conductivity and formation resistivity were used to support the interpretation of the elevation of the STZ. The interpretation of shallow formation resistivity was sometimes limited where saline drilling fluid had penetrated into the rock surrounding the borehole (Nirex, 1995). The STZ was shown to be deepest and thickest in the transitional area where the basement and basinal water meet but relatively shallow and apparently tightly constrained by the geological stratigraphy in the vicinity of the PRZ (Nirex, 1998a).

Separate interpretations of the origin and age of the shallow and deep groundwater were undertaken. These used different techniques due to the differences in available information and information requirements. However, a common thread between both interpretations was the interest in identifying areas where fresh and saline waters were mixing and the stability of the STZ over time.

**Shallow Groundwater**

The interpretation of shallow hydrochemistry was based on a large number of samples but a relatively small number of parameters. Existing data were vital in the interpretation of the shallow hydrochemical conditions, especially at depths less than 150 m below surface, but the dataset was restricted to simple chemical measurements (EC, pH, major ions and nitrate concentrations) (Nirex, 1998a). The dataset was augmented by samples taken during the Nirex investigations and analysed for $\delta^{2}H$ and $\delta^{18}O$. For the existing dataset, representative parameter values were estimated for each point from historic time-series (Nirex, 1994).

Interpretation of shallow groundwater chemistry concentrated on the following:

- Spatial interpretation of EC (or TDS) in terms of the constituent ions;
- Quantification of anthropogenic inputs and analysis of depth of penetration;
- Interpretation of water-rock interactions; and
- Evidence for mixing between shallow and deep groundwater.

The stages of the interpretation were synthesised into an interpretation of hydrochemistry that described the patterns of groundwater flow above the STZ and the age and origin of the groundwater.

The spatial interpretation of EC was undertaken using contour and scatter plots to show that EC decreased with distance from the coast. Scatter plots were also used to evaluate which ion species contributed to changes in EC. Plots of EC and NO$_3$ were used to evaluate the depth of penetration of modern recharge, these showed a sharp fall in NO$_3$ concentrations at 150 m, which was interpreted as the base of the present day active groundwater flow system. Stable isotope data of water were interpreted as showing that groundwater above the STZ had a meteoric
origin but that deeper water was recharged under different climatic conditions. Noble gas recharge temperatures calculated from measured concentrations of Ne, Ar, Kr and Xe in groundwater were used as proxies for ground temperatures at the time of recharge to suggest that deeper waters were recharged under cooler climatic conditions, probably in the late Pleistocene. A description of the theory and methodology of noble gas recharge temperature calculation is given by Stute and Schlosser (2000).

An understanding of the anthropogenic inputs into the groundwater system was used to differentiate between sources of Cl in the shallow groundwater (e.g. seaspray, fertilizer and manure) and chloride from deep, saline hydrogeological environment. Plots of NO₃ and Cl with depth showed an association at depths above 80 m. Below 80 m depth, Cl concentrations were lower and close to the levels expected in infiltrating rainfall (Nirex, 1998a). Stoichiometric calculations were undertaken to remove the fertiliser signature from estimated groundwater compositions, assuming no loss of NO₃, and the resulting ‘corrected’ freshwater compositions showed a linear increase in TDS with depth. This was taken to confirm water-rock interaction and mixing with deep saline water as being the main processes controlling groundwater chemistry (Nirex, 1998c).

Water-rock interaction was identified as an important control on the geochemistry of the shallow groundwater. The relationship between EC, Ca and HCO₃ concentrations showed that mineral dissolution, and possibly ion exchange, affects TDS. Hydrochemical speciation calculations were carried out using the MIX2 code (Plummer et al., 1975) (MIX2 is a geochemical reaction code that has been rendered obsolete by the development of PHREEQC).

Redox potentials in shallow groundwater were only measured in a small number of samples from close to the STZ. The transition from oxidising to reducing conditions appeared to be coincident with the top of the STZ (Nirex, 1998a). However, direct measurements of Eh were unreliable and strongly affected by drilling fluid contamination (Nirex, 1998c). Therefore, concentrations of U were used as a more reliable, albeit qualitative, proxy for estimating redox conditions. Concentrations of U were higher in the fresh groundwater than the brackish groundwater near to and within the STZ (Nirex, 1998c).

Overall, the interpretation of the shallow hydrochemical environment at Sellafield showed that there is an active groundwater system in the Sherwood Sandstone extending to depths of up to 150 m below the surface. Below this, older fresh-to-brackish waters occur which are thought to have been recharged before the last glacial maximum some 18 ka ago. The hydrochemical stratigraphy therefore suggests that the deep, saline waters are older still, implying very long-term stability in the hydrogeochemical environment at proposed GDF depth.

Deep Groundwater

The deep groundwater investigations below the STZ were concerned with the area of interest around the PRZ, a much smaller area than that for the shallow groundwater investigations. Groundwater compositions estimated following data processing were used in the interpretation, which considered the available range of inorganic and isotopic chemical parameters.

Interpretation of the deep groundwater hydrochemistry focussed on:

- The controls on chemistry, particularly pH and Eh in the PRZ;
- Understanding the origin of solutes and the implications for flow patterns;
- Constructing a descriptive model for palaeohydrogeology;
- Calculating groundwater residence times; and
- Evidence concerning hydrogeological and hydrochemical stability.

Two bodies of saline/brine groundwater were identified in the investigation area (Table 3.5) and the chemistry of both was interpreted using the same techniques. Initial spatial data exploration revealed the general relationships between these water bodies and general chemical characteristics. In contrast to the interpretation of the shallow groundwater, the interpretation of the deep groundwater chemistry placed greater reliance on measurements of environmental tracers (e.g. noble gases, $\delta^2$H, $\delta^{18}$O, $^{36}$Cl/Cl and $\delta^{34}$S).

Groundwater residence times were determined using a range of inorganic parameters and environmental tracers. Ratios of stable isotopes ($\delta^2$H and $\delta^{18}$O) showed that all deep waters, even the basal brines, had a meteoric origin because the ratios were too light (-8 to -5 %o vSMOW) to have originated from a seawater source (Nirex, 1998c). Therefore, Cl concentrations are a useful proxy for residence time as Cl will accumulate in the groundwater over time through water-rock interaction (evaporite dissolution). Differences in $\delta^{18}$O to Cl ratios were interpreted as indicative of groundwater recharged under different climatic conditions. Light $\delta^{18}$O ratios in brackish and saline groundwater contrast with heavy ratios in the brines with Cl concentrations in excess of 60 g/l. Relatively lighter isotope ratios than modern freshwater were taken to indicate recharge under cooler climates than present day whereas the relatively heavier ratios in groundwater indicated recharge in a warmer climate. Noble gas recharge temperatures support this interpretation (Nirex, 1998c). Based on comparison with other parts of the UK, light isotope ratios and noble gas recharge temperatures around 6°C were interpreted as being of late Pleistocene age, probably 18-30 ka ago (Edmunds et al, 2001). Quantitative evidence of groundwater residence time came from interpretation of $^4$He concentrations and $^{36}$Cl/Cl ratios. $^4$He accumulates in groundwater over time due to radioactive decay of U and Th in the host rock. $^4$He concentrations in groundwater were consistent with residence times in the order of several million years but there was uncertainty over absolute ages due to assumptions required in the calculation of ages from $^4$He concentrations (Nirex, 1998c). $^{36}$Cl/Cl ratios were used to estimate ages and showed that these waters were in excess of 1.5 Ma ago (Nirex, 1998c). This was consistent with the water body stratigraphy and the assumed ages of the isotopically light fresh and brackish waters.

The sources of the solutes in saline groundwater were interpreted using a range of isotopic tracers and ion ratios. Geochemical ‘finger-printing’ using Br/Cl ratios and $\delta^{34}$S$_{SO_4}$ suggests that salinity in the basinal groundwater results from dissolution of Triassic evaporites (Nirex, 1998c). Br/Cl and $\delta^{34}$S$_{SO_4}$ in Triassic halite and anhydrite respectively from the Cheshire basin closely match the ratios observed in the basinal groundwater at Sellafield. These ratios are distinct from the Br/Cl and $\delta^{34}$S$_{SO_4}$ values found in older (Permian and Carboniferous) evaporite minerals sampled from the deep Sellafield boreholes (Nirex, 1998c).

Br/Cl, I/Cl, B/Cl and $\delta^{34}$S$_{SO_4}$ in the basement waters were found to be different from those in the basinal waters. However, the source of salinity in the basement saline waters was thought to be the same as in the basal brines with the difference in ratios attributed to water-rock interaction in the volcanic basement (Nirex, 1998c). PCA was applied to the dataset and revealed similarities between the statistical behaviour of SO$_4$, Na, Mg, Br and Cl.
concentrations in the sample population, which suggests a common origin for the salinity in all of the samples. This is consistent with the interpretation of Br/Cl ratios and $\delta^{34}$S$_{SO_4}$. Br/Cl ratios showed closer association with Sr concentrations than Br concentrations in the PCA (Nirex, 1995). Sr is typically enriched in groundwater through incongruent dissolution of carbonates and silicates i.e. by water-rock interaction. This suggested that differences in Br/Cl ratio between water types could be attributed to differences in host rock geochemistry and water-rock interaction (Nirex, 1995). Alternatively, the basement waters may be derived from mixing between basinal waters and comparably ancient Lake District basement waters. PCA targeted at only the saline waters and brines tentatively indicated the existence of such a low Cl basement water end-member although this was not substantiated by the data collected (Nirex, 1998c).

Ratios of cation concentrations (e.g. Ca/Sr, Ba/Na and Sr/Na) were used along with $^{87}$Sr/$^{86}$Sr ratios to evaluate dissolved cation sources. Strontium isotopes are useful tracers of Ca sources because Sr substitutes for Ca in many minerals and Sr isotopes do not fractionate during dissolution. The Sr isotope ratio of seawater changes over time so carbonate and evaporite rocks of different ages can be distinguished based upon their isotope ratios. There was uncertainty in the interpretation but the Sr isotope ratios suggest that dissolution of Triassic calcite and anhydrite present in veins in the sandstone contributes most of the dissolved Ca and that older sources of Ca (e.g. Carboniferous Limestone) are relatively unimportant.

Mixing of saline basement and basinal water bodies was evident from the hydrochemical data. Br/Cl and $^{36}$Cl/Cl ratios showed very clear mixing relationships when plotted against Cl concentration. The existence of mixing was interpreted as showing that a mixing front had developed more recently than 1.5 Ma ago, because the mixing relationship shows that Cl had not reached secular equilibrium with the new host rock (Nirex, 1998c). This was consistent with the implied Pleistocene age of the basement water. The mixing relationship shows that the denser basinal waters are being displaced to the west by the topographically driven Hills and Basement flow system. Analyses of vein minerals suggest that there is ongoing dissolution of dolomite in the transitional area between the basement and basinal waters, showing that water with lower Mg/Ca ratios (basement water) is displacing water with higher Mg/Ca ratios (basinal water) in this zone (Nirex, 1998b). In contrast, the position of the STZ is shown to be relatively stable, having moved vertically by only tens of metres during the Quaternary, by the direct association between calcite crystal morphology and water salinity (Nirex, 1998b).

Redox potential and pH were difficult to measure reliably in water samples but are critical to performance assessment, so proxy techniques and geochemical speciation modelling were used to estimate the Eh and pH in the basement waters at GDF depth. For example, field measurements of Eh in the deep groundwater were between -100 and +150 mV down to depths of 1600 m below surface. In contrast, Eh determined from mineral stability diagrams and modelling was determined to be $-200 \pm 50$ mV based upon the detection of pyrite in some recent mineral precipitates, low concentrations of U in the groundwater and absence of methane (Nirex, 1995; Nirex, 1998c). pH was calculated to be $7.25 \pm 0.5$ using EQ3/6 (Wolery, 1992) (a geochemical speciation modelling code) assuming calcite, pyrite and haematite equilibrium.

The interpretation of the deep groundwater system is consistent with the conclusions from the interpretation of the shallow system, highlighting the relative stability of the hydrochemical system below the level of the active Sherwood Sandstone aquifer. However, dynamic behaviour was indicated at the interfaces between fresh and
saline water and between basement and basinal saline waters, which might have implications for the long-term stability of groundwater composition in the PRZ.

Links to Other Work Programmes

The interpretation of the hydrochemical environment was used to support other work programmes, most noticeably the hydrogeological modelling (e.g. Heathcote et al, 1996). 2-D and 3-D groundwater models were developed in various modelling codes to simulate the flow of groundwater and the salinity (TDS) distribution in the formations. A 2-D finite element hydrogeological model calibrated against temperature and hydrochemical data (chloride distribution) as well as hydrometric data were used as part of the demonstration performance assessment (Nirex, 1997b).

Site Description

The interpretation presents a coherent chronology of the evolution of groundwater chemistry at the site and identifies that stratigraphy is a significant control over the distribution of groundwater types. Limitations and uncertainties are related mainly to data acquisition but a number of these uncertainties could have been addressed though improved investigation design or having greater feedback between the interpretation and data acquisition process. The interpretation and modelling programme allowed a hydrochemical SDM to be developed for the groundwater bodies present within and surrounding the PRZ.

3.3.7 Uncertainties

A number of uncertainties are apparent in the interpretation of the hydrochemical environment at Sellafield:

- Uncertainties on calculated water compositions were large, particularly on the compositions of relatively shallow groundwater from the deep boreholes following correction for drilling fluid contamination. As a result, there was limited information on the composition of fresh groundwater between 150 and 300 m below surface. As a result, the depth (and spatial variability of this depth) of the active groundwater flow system may not be well understood;

- Ages of groundwater were not well constrained due to mixing and interpretative uncertainties. Although this was offset by interpreting water ages stratigraphically, the ages of the saline waters were imprecisely constrained. This has particular importance for the basement waters in the PRZ, which were estimated to be between 18 ka and 1.5 Ma ago based on geochemical ages and analogy with other localities in the U.K. Uncertainties of this magnitude were similar to the expected functional lifetime of the GDF of 1 Ma ago;

- Redox conditions: the distribution of redox sensitive species and pH in deep groundwater were imprecisely constrained and were acknowledged throughout the programme as areas of uncertainty;

- The hydrochemical stratigraphy at the coast was not well understood because of uncertainty over the location of the boundary between basement and basinal regimes. Basement waters may be rising towards the surface near to the coast as they are less dense than the basinal waters trapped at depth so a pathway between the PRZ and the coast may be present or developing. In addition, the extent of modern seawater in the aquifer was unknown;
• Interpretation focussed on flowing groundwater in deep boreholes. Analyses of sandstone porewater were not used in the final interpretation other than to provide supporting information on the depth of the STZ (Nirex, 1995). There was no sampling of porewater from crystalline basement rocks;

• Mineralogical and hydrochemical evidence suggested that the STZ has moved by tens of metres during the Quaternary. The hydraulic conditions and timescales under which the front moves were unclear from the hydrochemical data, but were informed somewhat by the hydrogeological modelling;

• Results of analysis of shallow groundwater from boreholes drilled to investigate the Quaternary sequence were not used in the hydrochemical interpretation. Their compositions appear to have been difficult to explain in the context of the hydrochemical conceptual model;

• The hydrochemical data existing prior to the Nirex investigations had been collected using sampling techniques and analysis outside the Nirex QA system. Consistency between samples from the same location over time improved confidence in which data were representative, but some uncertainties remained.

3.3.8 Tools

Tools utilised in the interpretation of hydrochemical data included the following:

• Data management: a bespoke database was developed to store the hydrochemical data and maintain a record of the quality assurance procedure;

• Data processing: the bespoke programme TRAP was used to correct for contamination of the water samples by drilling fluid; geochemical speciation and stochiometric modelling codes available at the time (e.g. MIX2, EQ3/6) were used to calculate mineral saturation indices and estimate pH and Eh from other hydrochemical data;

• Data presentation: geochemical diagrams (Piper and Schoeller plots) were produced using dedicated software; a statistical software package was used for PCA and to plot cluster (tree) diagrams; manually constructed cross-sections were used to present various aspects of the hydrochemistry;

More details on the specific interpretive value of these techniques are provided in Section 9.1.4.
4. Lower Strength Sedimentary Rocks: Case Studies

4.1 Introduction

Two detailed case studies are presented here for work undertaken by ANDRA in the Meuse Haute-Marne area of Northern France and work undertaken by NAGRA at Benken in Northeast Switzerland and at the Mont Terri Underground Rock Laboratory (URL). In addition, brief consideration has been given to work in Japan at Horonobe and to the Low Level Waste Repository at the village of Drigg, UK.

It is noted that there has been close co-operation between ANDRA and NAGRA and therefore there are strong similarities in the approach taken. For this reason, some of the detail presented in the first case study (ANDRA) is not repeated in the second case study (NAGRA). The Japanese work is of interest because the Japanese programme has, perhaps, been less reliant on following common approaches used elsewhere.

4.2 Specific Factors for Lower Strength Sedimentary Rocks

For lower strength sedimentary rocks, which in the case studies have generally low permeability, there is difficulty in obtaining groundwater samples by conventional pumping arrangements from boreholes within the host rock. These difficulties have been addressed by the measurement of porewater concentrations. However, groundwater samples have been obtained from flowing groundwater above and below the host rock.

As noted previously, the term lower strength sedimentary rock is an engineering description and is not synonymous with lower permeability rock.

The objectives of hydrogeochemical site characterisation that relate specifically to the expected properties and safety performance of lower strength sedimentary rocks that are in addition to the general hydrochemical properties such as groundwater compositions, are:

- To test whether fractures and more permeable layers in the host rock have any role in groundwater transmissivity at various scales from GDF-scale up to regional-scale;
- To demonstrate that small-scale and large-scale solute transport is controlled by diffusion (assuming fluid movement is confined to the matrix);
- To confirm the high effective solute retention capacity of the host formation;
- To establish and validate a model based on the rock fabric for in situ solute transport and retention at a range of scales;
- To study and quantify the potential for coupled chemical-hydro-mechanical processes that might affect water and solute movements (and hydraulic-mechanical properties), such as osmotic pressure gradients;
• To describe and parameterise for modelling the lateral flow of groundwater in aquifer layers either within, above or below the lower strength sedimentary rock sequence, so that they can be modelled as potential radionuclide release pathways and so that their palaeohydrogeology can be described as an analogue for future long-term evolution of the host rock; and

• To acquire mineralogical, petrographic and geochemical evidence for the evolution of the host rock fabric and of the palaeohydrogeological evolution of the porewater in the context of regional structural development in long (post-depositional) and shorter (glacial) timescales, for example in relation to erosion and river down-cutting respectively, or uplift due to tectonics/post glacial tectonics.

Many hydrogeochemical measurements and properties in lower strength sedimentary rocks have, perhaps, greater implications for hydrogeology and geotechnics. The performance of lower strength sedimentary rocks as a GDF host may be characterised by greater interdependence and coupling of the physico-chemical, hydraulic and mechanical properties than for higher-strength rocks.

4.3 ANDRA, Meuse/ Haute-Marne Area, France

4.3.1 Background

ANDRA has investigated a site in the Meuse and Haute-Marne area, the location of the Bure URL, since 1994. In the course of this investigation ANDRA have drilled 27 deep boreholes by 2006, many of which were partially cored, and collected thousands of water and drillcore samples. Excavations of two shafts for a URL at 445 m below surface started in 2001 and the URL became operational in 2004.

4.3.2 Sources of Information

A high-level synthesis of geological, hydrogeological and geochemical and hydrochemical findings of investigations is provided in the Dossier 2005 Argile (ANDRA, 2005a-e). This draws together information from design studies, scientific knowledge and safety analysis that demonstrate the feasibility of constructing a GDF and of demonstrating operational and long-term post-closure safety. The Dossier 2005 Argile focussed on the Callovo-Oxfordian (abbreviated to COx) shale as the potential host formation for a GDF for spent nuclear fuel and high-level waste in France. Dossier 2005 Argile comprises five ‘knowledge reference documents’ (ANDRA 2005a,b,c,d,e) among which, the most relevant for this review are those on ‘phenomenological evolution’ (ANDRA 2005b) and safety evaluation (ANDRA 2005c), both of which contain aspects of a SDM and thus rely on hydrochemical interpretation.

In addition to Dossier 2005 Argile, a compilation of seven overview papers describing the disciplinary conceptual models and supporting exploration data for the Meuse/ Haute-Marne area is contained in ‘A multi-disciplinary approach to the eastern Jurassic border of the Paris Basin, Meuse/Haute-Marne, Mémoire Société Géologique de France, no. 178, 2007’.

The Dossier 2005 Argile is supported by unpublished state-of-knowledge (‘Référentiels de connaissances’) and technical documents (‘Documents techniques’). These supporting documents are understood to provide
interpretation and modelling of site characterisation data in terms of geological environment, natural evolution of the site, near-field and far-field processes, and conceptual models for geology, hydrogeology and geochemistry but have not been seen in undertaking this review.

Additional information on data, data processing, interpretation and modelling for the Meuse/Haute-Marne area is provided in abstracts and proceedings from a series of conferences on ‘Clays in Natural and Engineered Barriers for Radioactive Waste Confinement’ organised by ANDRA.

AMEC understands that an update of the ‘Dossier 2005 Argile’ SDM and safety evaluation for the COx is planned for 2012.

4.3.3 **End User Requirements**

End user requirements are not explicitly stated in the documents reviewed.

4.3.4 **Geology**

The COx shale is a predominantly clayey formation that was deposited in a marine setting during the Dogger and Malm periods of the Jurassic between 180-135 Ma. It contains an average of 40-45% clay minerals, of which interstratified illite-smectite is the most abundant, with lesser amounts of illite, chlorite (<5%) and kaolinite (Elion, 2005). Carbonates comprise 22-37% of the argillite and are predominantly in the form of calcite with low amounts of dolomite and ankerite. Both detrital and secondary quartz are present. Pyrite is present and comprises 1-2% of the clay. The COx at Bure extends over the depth interval ca 410-555m and is an average of approximately 130 m thick.

The COx is overlain by the Tithonian and Oxfordian Limestone sequence and underlain by the Dogger Limestone sequence.

4.3.5 **Hydrogeology**

The COx is an aquiclude in which there is limited groundwater movement. Flowing groundwater occurs in the Tithonian and Oxfordian Limestone above and in the Dogger Limestone below the COx respectively.

4.3.6 **Information Requirements**

The principal long-term safety functions of the COx host rock (ANDRA, 2005a-e) are:

- Limiting the release of radionuclides from the engineered barriers and immobilising them in the GDF;
- Delaying and attenuating the migration of radionuclides that are released from the EBS into the geosphere; and
- Long-term stability.
The issues involving hydrochemistry data, interpretation, modelling and coupling with EBS processes (e.g. corrosion, cement degradation, bentonite performance) and other geosphere processes (e.g. hydrogeological, geomechanical) were:

- Chemical stability of host formation over time;
- Stable chemical environment provided by host formation;
- Capacity of host formation to retain wide range of chemical elements, particularly radionuclides;
- Capacity of the host formation to filter colloids;
- Good capacity to absorb chemical perturbations;
- Very small impact of engineering materials (cement, metals, etc), limited to immediate surroundings of engineered structures;
- Very slow groundwater flow in surrounding formations;
- Characterisation of whether the URL rock volume can be transposed to (i.e. is representative of) the surrounding area ~200 km²;
- Hydrochemistry of porewater promotes precipitation of some radionuclides;
- Very slow degradation/corrosion of cementitious and metallic materials;
- Geochemical impact of metals corrosion on host rock is very limited;
- Future hydraulic and hydrochemical evolution of host rock system is slow and limited;
- Slow transport of radionuclides through host rock;
- Straightforward and understandable evolution of host rock since deposition;
- Osmotic diffusion due to salinity gradient is balanced by Darcian water flow along hydraulic gradient; and
- Transport of solutes in system is interpretable in terms of diffusion and advection.

4.3.7 Hydrochemical Investigations

Investigations at the Bure site and surrounding area to date have comprised surface-based investigations and construction and operation of the URL. Thirteen boreholes have been drilled over the footprint of the URL. Most of these were vertical, but 3 boreholes were deviated. A further fourteen boreholes were drilled within a 15 to 20 km radius of the URL site within the ‘Transposition Zone’. This is an area of ~200 km² over which it is believed that the geological structure, mechanical properties, hydrogeology and hydrochemistry of the COx and adjacent formations that have been studied in detail at the Bure URL can be extrapolated with confidence.
The Bure URL plays an ongoing role in the geoscientific characterisation of the Meuse/ Haute-Marne site and specifically of the host formation. Data from experiments conducted in the galleries of the URL, for example using short boreholes drilled from the galleries to sample porewater in the host rock (the ‘PAC’ experiments), include measurement of parameters such as *in situ* pH and redox that are important inputs to hydrochemical interpretation.

**Groundwater in the COx Clay**

Porewater analysis provided the key dataset used in the interpretation of clay hydrochemistry. However, direct measurement of porewater hydrochemistry in intact rock is not possible. There was, therefore, an element of interpretation between analytical results and estimates of porewater concentrations.

The main method of obtaining hydrochemical information about porewater from drillcore samples from the COx formation was aqueous extraction, although squeezing was also used. In this process, crushed rock is mixed with a leaching solution to leach out porewater and rapidly soluble minerals (Mazurek et al, 2009, 2011). Core sample preservation and controlled leaching were undertaken to ensure that the composition of the leachate was closely related to *in situ* porewater composition.

The principal limitation of aqueous extraction of porewater is the potential for an unquantifiable degree of reaction between the leaching water and rock minerals. Consequently, aqueous extraction gives quantitative data only for conservative solutes, which are generally chloride and bromide and may include sulphate, where it has not been affected by sulphate mineral dissolution and/or sulphide mineral oxidation. Differences in the results of aqueous extraction and squeezing were used to determine the volume of anion-accessible porewater (not all porewater is accessible by anions such as Cl due to the charges on clay minerals).

Data for stable isotopes in water ($^{18}$O/$^{16}$O and $^{2}$H/$^{1}$H) and dissolved helium ($^{4}$He) in porewater in the COx formation were obtained by diffusive exchange and from outgassing respectively. In both cases, the raw analytical data from these tests require further processing and interpretation to adequately constrain *in situ* values and the associated uncertainties.

The potential effects of prolonged storage of preserved drillcores on the validity of results from aqueous extraction tests was investigated by mineralogical and geochemical studies of drillcores that had been stored for various periods prior to aqueous extraction (Techer et al, 2010) and this demonstrated that there were significant changes in core mineralogy and porewater composition due to oxidation and dehydration processes of both the mineral and organic components.

**Flowing Groundwater in Aquifers**

Flowing groundwater from higher permeability aquifers above and below the COx formation was sampled and analysed. Flowing intervals occur in the Tithonian and Oxfordian Limestone above and in the Dogger Limestone below the COx. In many cases, waters were sampled in boreholes for which the primary target was hydraulic testing and sampling of these aquifers, i.e. they were prioritised for this purpose over sampling the COx. The rationale for this is, in large part, the different drilling conditions that are appropriate for the different types of rock.
Flowing water samples in boreholes were obtained either by: (i) pumping and depth sampling in open borehole conditions; or by (ii) extraction and sampling of water using a downhole tool with a double packer arrangement to isolate a specific depth interval.

Groundwater samples were also taken, where possible, using pre-existing boreholes drilled for other purposes (e.g. hydrocarbon exploration, groundwater resource, geothermal), from the key aquifer formations at the regional scale, across an area far beyond the scale of the transposition zone. These were used to interpret the spatial variations of hydrochemistry and groundwater ages. The interpreted information was used to test the regional flow-transport groundwater model for consistency with the hydrochemical interpretation (Cornaton et al, 2010).

Mineralogy and Geochemistry of COx

General quantitative mineralogical analysis of the COx host rock was carried out for contents of major minerals (quartz, calcite, feldspar, plagioclase), important accessory minerals (primarily pyrite) and clay minerals (Yven et al, 2007). These data were required to interpret the degree of mineral heterogeneity in the host rock and the significance of that in the surface complexation/ ion exchange model of sorption properties (Grambow et al, 2010).

The natural organic material (NOM) content of the host rock was also determined. Data for in situ NOM, as well as for corresponding dissolved organic carbon (DOC) concentrations, were needed for modelling the potential effects on complexation of radionuclides in porewater solution and the sorption of radionuclides on to solid organic phases in the rock. The same data were also indicative of potential concentrations of natural colloids. In the case of the COx, NOM is up to 1% by weight of the total rock (Huclier-Markai et al, 2010). Specific information about complexing capacity of DOC was obtained by extracting NOM under reducing conditions and analysing functional groups (Grasset et al, 2010).

U and Th measurements were required to determine the rate of $^4$He generation.

Sampling and Analysis from the URL

Water samples collected in in situ experiments in the Bure URL form a major part of the hydrochemical data that will be used for interpretation and modelling (Delay et al, 2007). URL experiments involving in situ monitoring of pH and Eh, and sampling for analyses of easily-perturbed (or unstable) hydrochemical parameters i.e. HCO$_3^-$ and pCO$_2$, HS$^-$ and Fe$^{2+}$ (e.g. Tournassat et al, 2010), provide data for these parameters that are the main inputs to geochemical modelling of the full in situ hydrochemical conditions in the COx host rock (Table 3.3.1 in Dossier Argile - ANDRA,2005b, Tôme: Phenomenological Evolution of a Geological GDF; Altmann and Jacquot, 2005; Gaucher et al, 2010; Buschaert et al, 2007; Vinsot et al, 2008).

4.3.8 Hydrochemical Data Processing

Porewater

Boreholes targeted for recovery of drillcore from the COx were drilled with oil-based mud (OBM). Possible contamination of porewater was monitored by detection of the organic signature of the OBM.
Porewater concentrations were obtained from aqueous extraction test results. The leaching process also means that porewater is diluted and analytical results require processing to give porewater concentrations by using porosity measurements.

For conservative ions the porewater concentration can be derived from the leachate concentration where the ion-accessible (‘geochemical’) porosity of the rock is known. As a first approximation it was assumed that geochemical porosity was equal to the water-loss porosity or physical porosity. However, in clay-rich rocks the effective porosity for anions is likely to be reduced because anions are excluded from the portion of pore space affected by diffuse double-layers associated with permanent negative layer charge. Neglecting anion exclusion will lead to an underestimate of the true porewater concentration of anions, which could be by 50% or more. The measurement of physical properties and an understanding of their role and reliability in processing of data for porewater compositions are outside the scope of this review but should be noted as a key aspect of any study of sites with similar geology.

Arriving at a more accurate estimate of anion porewater concentration requires additional information on the geochemical porosity. Site-specific information requires additional testing of drillcore samples (Altmann and Coelho, 2005), but as an approximation a reduction factor for physical porosity to geochemical porosity can be adopted from similar material. Thus for example, an estimated reduction factor of 50% for the COx might be derived by analogy with the Opalinus Clay at the Mont Terri URL in Switzerland as the COx and Opalinus Clay have similar clay mineral contents.

**Flowing Groundwater**

Surface-based boreholes dedicated to sampling groundwater in aquifers were generally drilled by a reverse air-flush percussion method (replacing air by nitrogen in one case, J. Delay, ANDRA, personal communication). In some of the early boreholes, water-based drilling fluid was used with tracers to permit raw analytical data for water samples to be ‘corrected’ for mixing with drilling water (Kloppmann et al, 2001). However, for water samples collected from boreholes drilled with air flush, drilling water mixing was not an issue though the possibility of air intrusion into the formation causing bias in subsequent redox and DO monitoring data has been considered in processing of data for interpretation.

Comparison of tritium (³H) data with carbon-14 (¹⁴C) and chlorine-36 (³⁶Cl) data in water samples from the more permeable horizons indicated that there was widespread contamination that affected the validity of those isotope measurements (Jean-Baptiste et al, 2010). This underlines the difficulty in obtaining representative water samples for measurements of natural tracers at low levels and the need for caution when interpreting isotopic data in terms of groundwater residence times.

**Mineralogy and Geochemistry Data**

Conventional X-ray diffraction (XRD) methods were used to determine whole rock and clay fraction mineralogy of samples of the COx (Yven et al, 2007). These semi-quantitative estimates of mineral compositions were combined with analyses of whole rock geochemistry and measurements of cation exchange capacity (CEC) to improve
confidence in mineral compositions by calculating mineralogical ‘norms’ for each sample with typical estimated precision of about ±5%.

Although, discussion of the measurement of physical properties and the interpretation of those measurements is generally outside the scope of this report, the acquisition and processing of porosity data are important in the processing and interpretation of porewater hydrochemistry and of solute transport and retardation properties. Porosity data were acquired by direct and indirect methods including geophysical logging (nuclear magnetic resonance tool), imaging and autoradiography after 14C-PMMA impregnation, 2-D mapping with scanning electron microscopy (SEM), densitometry (dry density and grain density measurements), mercury injection porosimetry and gas adsorption tests (which also give specific surface area data). The resulting data and proxy data for porosity were found to differ in absolute values although the patterns in depth profiles were similar. A substantial amount of research-based interpretation has been involved in deducing porosity values that are relevant to different modelling purposes (Yven et al., 2007). A similar data processing and interpretative process was necessary to derive surface area data for various modelling purposes, e.g. proportions of porewater that is bound to mineral surfaces and in interstitial sites, porosities and sorption capacity (Yven et al., 2007).

4.3.9 Hydrogeochemical Interpretation and Modelling

Hydrogeochemical Interpretation and Modelling

The primary hydrochemical parameters of interest for EBS design are: (i) with respect to container corrosion: pH, Eh and other redox indicators including reduced sulphur species, total salinity; (ii) with respect to clay/bentonite barrier evolution: Na⁺, Ca²⁺, Mg²⁺, K⁺ and other potentially significant cations such as Fe²⁺, NH₄⁺.

Unstable parameters, including pH and Eh and redox-active solutes, cannot presently be reliably measured directly in porewater extracted from drillcore. These parameters and other hydrochemical parameters were determined by means of geochemical modelling using the PHREEQC code (Altmann and Jacquot, 2005). The resulting data were then tested for sensitivity to geochemical constraints such as pCO₂ and the composition of the equilibrium-controlling mineral assemblage. Thermodynamic modelling was used to evaluate redox conditions in host rock porewater for comparison with experimentally-measured Fe²⁺/Fe³⁺ ratios (Tournassat et al., 2010).

A more comprehensive geochemical model of porewater composition was developed in the ANDRA-BRGM (Bureau de Recherches Géologiques et Minières) ‘THERMOAR’ project, originally using data from the Opalinus Clay at the Mont Terri URL (Gaucher et al., 2006, 2010). An earlier model developed by Motellier et al. (2003) calculated ion exchange for three types of exchange sites, but did not take into account the SO₄²⁻ content in the mass balance and speciation. The improved model used analytical data for Cl⁻ and SO₄²⁻ obtained from aqueous extraction tests, for stable isotopic ratios ¹³C/¹²C and ³⁴S/³²S, and for exchangeable cations. The modelled composition used data from aqueous extraction for CEC analysis, ion exchange selectivity constants (Gaucher et al., 2004) and exchangeable cation population, and for total reducing capacity of rock (TRC). Model calculations were constrained by the partial pressure of CO₂ (pCO₂) (Gaucher et al., 2006), ion exchange equilibrium and geochemical equilibrium with observed mineral phases (Buschaert et al., 2007).
The hydrochemical modelling method for interpreting the *in situ* composition of porewater in the COx formation appears to be established as the primary interpretation tool used by ANDRA for hydrochemistry of host rock porewater. It provides an internally consistent and comprehensive hydrochemical dataset for near field modelling in the Environmental Safety Case. The dataset includes pH, Eh, alkalinity, ionic strength, major cations and anions, Fe, Si and Al (Buschaert et al, 2007).

**Hydrochemistry of Near- and Far-Field Groundwater with Respect to Radionuclide Speciation and Transport**

The hydrochemical dataset for porewater in the near-field COx formation appears to be adequate for modelling of radionuclide speciation although there is some uncertainty related to data on dissolved organic carbon (DOC), which in such rocks may have a significant effect on speciation. Approximate levels of DOC can be related to the organic carbon content of the rock which, in turn, is likely to be a major component of the total reducing capacity (TRC). *In situ* DOC concentrations have also been used as an indication of the potential abundance and character of colloids originating from the host rock (Huclier-Markai et al, 2010).

Water samples collected from more permeable horizons in the far-field rock formations (Tithonian aquifer and Oxfordian and Dogger limestones) included field analysis of easily-perturbed parameters including pH, Eh and DO. After data processing to identify perturbations and other sampling artefacts, the data from monitoring and analyses of water samples were used for modelling of radionuclide speciation.

A number of flowing, more porous, zones were identified but these horizons are discontinuous and could not be correlated at the kilometre scale (Mazurek et al. 2009). Groundwater in the Oxfordian limestone sequence is a Ca-Mg-HCO₃ type at shallower levels and of a general Ca-Mg-SO₄-HCO₃ type at deeper levels (ANDRA 2005b). Its mineralisation is low to moderate, and it is in chemical equilibrium with the dominant carbonate minerals. Based on the radiogenic data (absence of $^3$H, $^{14}$C generally below 3 pmC (percent modern carbon) Michelot and Massault 2004) and stable isotope compositions, groundwater in the Oxfordian limestone sequence was interpreted to have infiltrated during present-day (i.e. since the last glaciation) conditions and, at deeper levels, recharge appears to be from during colder climatic conditions with an average residence time in the order of 10 000 – 100 000 a (Mazurek et al, 2009 and references therein).

Meteoric groundwater movement through these limestones has probably been active since the system emerged from marine cover at ca. 65 Ma.

It is noted that the strata outside the COx were identified as not performing a safety function and were therefore modelled in a simplified way in the safety evaluation (ANDRA, 2005c).

Groundwater in the Dogger limestone sequence is of a general Na-Cl chemical type and is more mineralised than that in the Oxfordian limestones. It shows a large variation in solute concentrations over the investigation area and is generally interpreted as a mixture of Holocene meteoric and old (Eocene) formation water with an average residence time in the order of 0.1 to 1 Ma, based on the absence of measurable $^3$H and $^{14}$C, the stable-isotope composition of water, and high contents of He and $^{35}$Cl (Mazurek, 2009 and references therein).
Natural Tracers Evidence of Solute Transport

Hydrochemical and isotopic data for conservative natural tracers in the COx host rock and overlying rock provided evidence for the mechanisms of solute transport and for the hydrodynamic stability of solute transport through the host rock over a long timescale. The natural tracers of primary interest were those for Cl, 18O/16O, 2H/1H and 4He. Data for the distributions of these tracers in depth profiles of porewater through the host rock and overlying limestone were interpreted in two stages, as follows: (i) qualitative examination of the variations of tracer concentrations in relation to concentrations at the upper and lower hydrogeological boundaries of the host rock porewater system and in relation to structural discontinuities such as faults, and (ii) numerical simulation of the tracer profile using a diffusion-advection model.

Numerical simulations of porewater profiles were used to investigate the sensitivity of the profile to a number of parameters including diffusion coefficients, advection velocity, porosity, and geochemical porosity reduction factor. In addition, a range of initial conditions were considered. The main initial condition that was varied was time at which groundwater in the bounding higher permeability horizon(s) became active in terms of groundwater flow. Flow in these aquifers introduced younger, fresher water that created a concentration contrast with the underlying (or overlying) low permeability host rock. As a result of this concentration gradient, diffusion of solutes would have occurred out of the host rock and into the aquifer.

The interpretation and modelling approach was first developed at Mont Terri URL (Pearson et al, 2003) and was further developed and then applied at Meuse/ Haute-Marne (Mazurek et al, 2009). The hydrogeological boundaries at the top and base of the COx/ low permeability system were inferred to be flowing horizons in the Oxfordian and Dogger Limestones.

The general pattern of the Cl profile is of increasing concentrations with depth to the centre of the COx, suggesting that out-diffusion was mainly to the upper aquifer and not to lower aquifers. However, the data showed some scatter and were not consistent between adjacent boreholes. Stable isotope ratios showed similar patterns whilst 4He concentrations increased continually with depth. The shape of the Cl profiles was consistent with diffusion as the only transport process. The only constraint on the initial Cl concentration was that seawater (~19000 mg/l) was probably a maximum limit. Diffusion modelling assumed a range of initial conditions between seawater and the maximum currently observed in each borehole profile (about 2150 mg/l). For each initial condition Cl concentration the model was used to evaluate the diffusion time for the modelled profile to match the data. The model was fairly insensitive to the range of uncertainty in initial Cl. The time required to achieve good fits between the modelled and observed profiles ranges from 11 to 1.2 Ma ago.

Similar modelling of data for the Cl and stable isotope ratio depth profiles in the 2000 m deep borehole EST433 at the Meuse/ Haute-Marne site by ISRN (Bensenouci et al, 2010) concluded that the system had evolved by upwards diffusion from a deep Triassic aquifer and also by lateral advective transport in the Dogger Limestone.

An analytical solution using diffusion of Cl out of the COx and hydrodynamic dispersion in the advective system was used to simulate the distribution of Cl and stable Cl isotopes, 37Cl/35Cl, in the Oxfordian/ Tithonian aquifers that overlie the COx formation (Lavastre et al, 2005; Buschaert et al, 2007). From the best fit to observed Cl and δ37Cl data, a residence time for groundwater in the Oxfordian limestone of about 100,000 years was estimated. It
was also concluded that the vertical heterogeneity of Cl in the aquifer is better accounted for by hydrodynamic dispersion rather than simple diffusion.

**Coupling between Hydrochemistry and Hydraulics: Osmotic Effects**

Coupled thermo-hydraulic-mechanical-chemical (THMC) processes are potentially important in clay-rich, low permeability lower strength host rock formations. One of the issues for the interpretation of site characteristics at the Meuse/ Haute-Marne site is the significance of and processes associated with the apparently high hydraulic head in porewater in the COx relative to heads in the Dogger and Oxfordian groundwater (Chapter 3 in Dossier 2005 Argile). A model for osmotic interpretation of overpressure development within the pores of clay-rich rock was developed (Guetin et al 2007) based on a triple layer model for sorbed ions and water at the clay surface that calculates the activity of water taking into account the solute concentrations, the electrical charge due to clay mineral structure and the proportion of clay minerals in the rock. A separate model for electro-osmotic effects was also developed (Lemaire et al 2007).

**Groundwater Evolution, Ages and Palaeohydrogeology**

Samples from more permeable horizons in the far-field rock formations were subject to full hydrochemical analyses, analysis for environmental isotopes and for dissolved gases including noble gases. Interpretation of hydrochemical and isotopic data from these samples comprised (Buschaert et al, 2007):

- Graphical interpretation of solute concentrations and stable isotope ratios to identify correlations and to interpret water sources, evolution of water quality by water-rock reaction and mixing (Dewonck and Buschaert, 2006);

- Interpretation of groundwater ages from isotopic (\(^3\)H, \(^{14}\)C, \(^{36}\)Cl) and dissolved helium (\(^4\)He) data using various data processing and residence time calculation methods (Buschaert and Giffaut, 2005; Fourré et al, 2010);

- Interpretation of palaeo-temperatures of water recharge from noble gas concentrations using corrections for ‘excess air’ contents and calculations based on solubility-temperature relationships (Dossier 2005 Argile).

Groundwater compositions in the Oxfordian and Dogger limestones were interpreted by inverse modelling using the PHREEQC code, which showed that they were consistent with out-diffusion of porewater solutes from the COx formation plus ion exchange and mineral dissolution (Rebeix et al, 2010).

A hydrogeological conceptual model was constructed at the regional scale of the eastern Paris Basin (~200,000 km\(^2\)), by integrating structural, geological, hydrogeological and hydrogeochemical data (Cornaton et al, 2010). The model was calibrated against groundwater heads and used to derive model groundwater ages and ‘lifetime expectancy’ values (i.e. transit times of groundwater along flow paths to discharge). These were then compared with groundwater and porewater ages interpreted from hydrochemical and isotopic data. The regional groundwater model was used to provide constraints on the future transient boundary conditions for the groundwater model in the safety case.
Hydrogeochemical Stability

The hydrogeochemical stability of near-field and far-field groundwater compositions was interpreted by geochemical equilibrium modelling of water-rock reactions, solution-mineral equilibria and buffering processes. The objective was to show that the hydrochemistry of near-field groundwater will change only slightly and slowly, if at all, in response to future internal and external perturbations. Long-term stability of the key parameters pH, redox, salinity, and cation proportions, was of particular interest. Perturbations that were considered included: the thermal perturbation caused by heat-producing wastes in the early post-closure period; hyperalkaline impacts from cementitious materials; out-diffusion of waste and container components including corrosion by-products; long-term hydrogeological evolution of the far-field groundwater flows; and climate-driven changes such as permafrost (ANDRA, 2005a-e).

Organic Geochemistry and Biogeochemistry

A model for near-field biogeochemical conditions was reported by Albrecht and Libert (2010). It apparently comprised two approaches: one based on mass balance; and the other on thermodynamics and did not use kinetic parameters. Nothing more is currently known about this interpretation method.

Colloids and Microbes

There is limited mention of colloids and microbes in the work set out in the Dossier 2005 Argile. An identified requirement property of the EBS and geosphere COx is that it filters colloids. Migration of colloids has therefore been excluded from the safety case.

4.3.10 Uncertainties

ANDRA (2005b and 2005c) recognised that there were a number of remaining uncertainties, particularly related to:

- Spatial variation within the host rock;
- Inaccuracy in measurements;
- Scaling from laboratory and borehole observations to the much larger host rock volume; and
- Simplifications necessary to enable modelling.

For hydrochemistry the main uncertainties were:

- Porewater composition. The limitations of porewater sampling mean that the composition of porewater has to be calculated from an understanding of the measured parameters and mineralogy. Uncertainties in the measured concentrations (due to drilling fluid penetration), physical properties (effective porosity) and mineralogy mean that the calculated porewater composition is subject to uncertainty. However, agreement in results from different boreholes suggested good agreement;
Diffusion coefficients varied across a range of values. Some of the uncertainty was thought to be due to ionic strength (for anions) and sorption (for cations), both of which are uncertain. Sensitivity analysis was used to examine the effect of varying diffusion coefficients on transport phenomena.

Overall, hydrochemical uncertainties were regarded as being “under control” (ANDRA, 2005c).

4.3.11 Tools

Specific tools that have been developed for application to hydrochemistry in this type of host rock include:

- Spreadsheet calculation tools for storing raw experimental results and related parameters and for carrying out calculations that use those raw data to derive in situ porewater concentrations and isotopic ratios. Uncertainties in those derived results are also calculated from the individual errors in raw experimental data and other parameters by Gaussian error propagation;

- Models for the electrical interactions between ions and mineral surfaces that control the distributions of anions and cations in porewater and the relationship between physical and ion-accessible porosity. The objective of these tools is to estimate the ‘anion-accessible porosity factor’ that must be applied to the physical porosity to derive the in situ porewater concentrations from the results of porewater extraction tests. Such models are bespoke and are areas of ongoing research within the Andra and Nagra programmes;

- A geochemical equilibrium and reactive transport code that models the future evolution of the near-field and far-field systems due to both natural processes and interactions between groundwater and components of the engineered barrier system. The aim is to develop a modelling tool that has a geochemical reaction model coupled with a 2-D/3-D hydraulic model for groundwater movement and solute transport. The geochemical codes PHREEQC or CHESS were coupled with flow-transport module MT3D or CAST3M. These are mainly off-the-shelf codes. CHESS is a similar code to PHREEQC developed by Ecole des Mines in Paris that has been particularly customised for solution-surface interaction modelling;

- Software platform (‘Alliances’) for THMC processes were developed jointly by ANDRA/CEA/EDF (Montarnal et al, 2007) as bespoke software to facilitate flexibility, integration and coupling;

- Analytical or numerical diffusion-advection-dispersion solute transport model for simulating natural tracer profiles with time-dependent boundary conditions – analytical model as reported by Lavastre et al (2005), Buschaert et al (2007); numerical model developed from the FLOTRAN code as reported by Mazurek et al (2009). The main features of this type of model are the ability to model of time-dependent boundary conditions and transport as diffusion (in 3D) and advection (in 1D across a mudrock sequence and in 2D in the adjacent bounding aquifers). The FLOTRAN code was developed for Nagra; and

- A physico-chemical conceptual model and calculation method for simulating osmotic influences on hydraulic pressures (Guetin et al, 2006; Lemaire et al, 2007). Such models are based in bespoke calculations, potentially as spreadsheet tools, analytical solutions or numerical models.
4.4 Swiss Project Opalinus Clay (Entsorgungsnachweis), Benken

4.4.1 Background

In 1980 NAGRA began a regional geological investigation programme in Northern Switzerland, which consisted of regional seismic campaigns, hydrogeological investigations, tectonic analyses and deep boreholes. This work was undertaken in the search for a site for a high-level waste (HLW) GDF.

In 1985, the Swiss authorities called for sedimentary rocks to be investigated as potential hosts for geological disposal of HLW. Initially effort was concentrated on two formations: the Opalinus Clay and the Lower Freshwater Molasse. As part of a regulatory review in 1994, HSK (now ENSI, the Swiss Federal Nuclear Safety Inspectorate) along with two independent governmental review bodies (KNE and KSA) decided to concentrate on the Opalinus Clay for HLW and the Brauner Dogger for ILW. This became the Entsorgungsnachweis Project Opalinus Clay, which was carried out by NAGRA.

In 1996 NAGRA constructed a URL in the Opalinus Clay at Mont Terri in NW Switzerland. The Mont Terri URL has been used as an international research site to conduct numerous experiments on clays and to characterize the Opalinus Clay. Work at Mont Terri was carried by NAGRA and a wide group of radioactive waste implementers, regulators, universities and research institutes (see, for example, Bossart and Thury, 2007 for discussion). NAGRA term the Mont Terri research site the ‘Regional Analogue’ (sometimes also known as a ‘self analogue’) for the Opalinus Clay.

The Swiss Federal Office of Energy’s Sectoral Plan (SFOE, 2008) sets out a three-stage siting process for deep geological disposal.

- Stage 1: Selection of geological siting areas for L/ILW and HLW. The main focus of stage one is on identifying suitable siting areas based on safety and geological criteria. Three geological siting regions have been proposed for a repository for HLW. The three siting regions with the Opalinus Clay host rock have been confirmed within the Sectoral plan. These are: Zürich Nordost (Zürcher Weinland), North of Lägern and Jura Ost and are characterised by a simple and stable underground geological situation. In addition, six geological siting regions have identified for LLW and ILW and been included in the Sectoral Plan. These are: Südranden, Zürich Nordost, North of Lägern, Jura Ost, Jura-Südfuss and Wellenberg. All of these site are characterised by lower strength sedimentary potential host rocks, which include the Opalinus Clay, the Brauner Dogger, the Effingen Beds and the marl formations of the Helveticum;

- Stage 2: Selection of at least two sites each for L/ILW and HLW. In stage 2 the focus is on participation: the proposed siting regions have an opportunity to participate in the specification of the repository projects and in studies on the socio-economic effects and spatial planning impacts;

- Stage 3: Site selection and general licence procedure for L/ILW and HLW. The remaining sites will be studied in greater detail in stage 3 and the site-specific geological information will be supplemented if necessary by carrying out further geological studies.

The area of Benken in the Zürich Nordost (Zürcher Weinland) siting region of Northeast Switzerland was identified as a potential site of a GDF. Intrusive investigations at Benken were limited to a single deep borehole, which was
drilled in 1998-1999. This single borehole was used as a proving hole for a detailed 3-D seismic survey of the Opalinus Clay formation in Northeast Switzerland. The work at Benken was integrated with ongoing research at the Mont Terri URL, Benken is situated some 150 km west of Mont Terri.

All of this work fed into the site performance assessment which included a demonstration that (NAGRA, 2002a):

- A suitable geological environment for the GDF existed (siting feasibility);
- Construction and operation of a GDF was practicable in such an environment (engineering feasibility);
- Long-term safety from the hazards presented by the wastes was assured for such a GDF (safety feasibility).

4.4.2 Sources of Information

The focus of this review has been publicly available summary reports written in English. References written in other languages (principally German) are identified in the reference list. Publications include research reports by NAGRA and collaborating organizations, scientific papers and conference proceedings.

A significant body of the work undertaken by NAGRA is contained in unpublished research reports. In addition, as a result of NAGRA’s collaboration with industrial partners, some of the data and interpretation has been assigned commercial-in-confidence status and is therefore not readily available.

The overall objective of the investigations at Mont Terri and Benken was to investigate the suitability of the Opalinus Clay as a GDF host rock. At Benken, NAGRA investigation comprised a single deep borehole to obtain baseline data for the Opalinus Clay and neighbouring rock formations and to calibrate new and existing seismic data with these results. Existing borehole data came from the earlier North Swiss Crystalline campaign of the 1980s and 90s (NAGRA, 1985). Additional shallow boreholes were also drilled at Benken.

4.4.3 End User Requirements

End user requirements have not been explicitly stated in the documents reviewed. The relevant properties of the host rock for long-term safety were summarised as follows (NAGRA, 2002b):

- Diffusion is the dominant transport mechanism, with advection playing either only a secondary role or none at all;
- Fault zones in the Opalinus Clay do not represent preferential flow-paths, which can be explained by an efficient self-sealing mechanism; and
- Stable, reducing geochemical conditions are present.
Specific aims of the Benken borehole included (NAGRA, 2001):

- Determining the thickness, bedding and lithological and mineralogical/ petrographical composition of the full sedimentary sequence;
- Characterising the fracture and fault systems and determining their spatial orientation;
- Investigating the rock mechanical properties of the Opalinus Clay and determining the stress field and temperature conditions in the formation;
- Investigating transmissivities and hydraulic potentials in aquifers and aquitards;
- Investigating the hydrochemistry and isotope hydrogeology of deep groundwater in aquifers and of porewater in aquitards; and
- Acquiring geophysical reference data for calibration of seismic images.

The Benken borehole also had two main hydrochemical objectives (NAGRA, 2001):

- To study the physico-chemical and isotopic composition of the deep groundwater in regional aquifers and in the water-bearing strata above and below the Opalinus Clay; and
- To characterise the porewater in the Opalinus Clay and surrounding (above and below) low permeability formations.

4.4.4 Geology

The sedimentary rocks in the Benken area are nearly horizontally bedded (Gimmi and Waber, 2004). The sedimentary sequence comprises Triassic and Tertiary sediments beneath Quaternary deposits. There are no large faults present in the area. The stratigraphy in the Benken borehole has been assumed to be representative of the entire siting area.

Tertiary deposits comprise a 124 m thick Lower Freshwater Molasse (marls and sandstones). The underlying Jurassic deposits (the Cretaceous is absent) comprise the Upper Malm, a thick (252 m) sequence of limestone with thin marl intercalations. The Malm shows karstification. Beneath the Malm, Dogger sediments were found, consisting of about 200 m of marine claystone and marls with thin layers of limestones, sandstones and iron ooliths. These sediments also contain the Opalinus Clay Formation (113.2 m). Below this, the Lias comprises about 40 m of marine marls, silt- and claystones, and thin limestone beds.

The underlying Triassic sediments consist of alluvial (sand and dolomite breccias) and evaporite sequences (anhydrite and, gypsum) and dolomite, below which are dolomites and limestones, laminated dolomites, marls, claystones, and thick anhydrite bands and halite (64 m), and then a 34 m thick sequence of dark grey to black claystones with thin sandstone and dolomite layers.

A similar sequence is found at Mont Terri. Structurally, Benken is simpler as bedding is near horizontal, whereas at Mont Terri the sedimentary sequence has been subject to folding and forms an overthrust anticline.
At Benken, the Opalinus Clay occurs at a depth of 540-622 m, in a low permeability sedimentary sequence that extends from 400 to 710 m below the surface. The Opalinus Clay is between 110 and 120 m thick. The potential host formation also includes the overlying Brauner Dogger clay, which is 70 to 100 m thick. For comparison, the Opalinus Clay is ~160 m thick at Mont Terri.

4.4.5 **Hydrogeology**

The hydrogeological environment at Benken consists of limestone aquifers and clay aquicludes. The limestones have some karstic development, particularly in overlying limestones. Groundwater flow in the Opalinus Clay, other clays and evaporites is considered to be practically absent.

4.4.6 **Hydrochemical Investigations**

A wide range of information was available for the Opalinus Clay from work at Mont Terri and from earlier programmes. The understanding of the Opalinus Clay developed at Mont Terri, and other sites, was augmented by work at Benken, which in summary included:

- 2-D seismic surveys conducted for Projekt Gewähr (NAGRA, 1985);
- Earlier deep boreholes drilled for Projekt Gewähr (e.g. Blaesi, 1987) as well as information from a range of other deep boreholes drilled in the region for gas and oil exploration;
- A focused 3-D seismic campaign in the Zürcher Weinland (Birkhauser et al, 2001);
- One deep borehole at Benken;
- Examination of material from a range of road and rail tunnels which cut through the Opalinus Clay in Switzerland (e.g. Schaeren and Norbert, 1989);
- Informal discussions with oil and gas exploration companies; and
- Hydrochemical sample handling.

Standard hydrochemical sampling techniques were employed, including (NAGRA, 1996):

- Use of tracers in drilling fluids to assess sample contamination;
- Measurement of EC, temperature, pH and Eh on-site during drilling;
- Measurement of sensitive parameters (EC, temperature, pH, alkalinity and Eh) during groundwater sample collection. Alkalinity was titrated immediately on-site and samples for redox analysis were ‘fixed’ on-site; and
- Collection of samples for gas, stable isotopes and noble gas analysis (on-site) with corrections for gas lost during sampling.
Conventional groundwater sampling was not possible in the Opalinus Clay or in the over and underlying clay-rich formations due to their low permeability. Porewater analysis therefore formed the principal basis for hydrochemical interpretation of the Opalinus Clay, supported by mineralogical analysis of the clay. Porewater extraction and analysis shared many of the methods previously described for ANDRA although many of the methods were developed at Mont Terri (e.g. Bath et al, 2001; Degueldre et al, 2003; Wersin et al, 2004). These methods included:

- Extraction of samples for $^{18}$O and $^2$H analysis for interpretation of isotope ratios ($\delta^{18}$O and $\delta^2$H) using vacuum extraction (early samples) or diffusive-exchange (later samples);
- Squeezing samples to provide water for analysis for major and minor element chemistry and stable isotope content; and
- Samples were also collected to determine porewater noble gas concentrations.

Comments on the limitations of porewater sampling and analysis are provided in Section 4.2 on the ANDRA work.

In addition, analysis of rock samples was undertaken to determine cation-exchange capacity and concentrations of soluble salts.

Supporting data for modelling of diffusion profiles was obtained from laboratory measurements of diffusion coefficients, porosity and sorption coefficients.

Measurement and theoretical evaluation work were undertaken to understand the mobility of colloids (Voegelin and Kreuschmar, 2002).

### 4.4.7 Hydrochemical Data Processing

Since 2005, NAGRA has operated a peer review system using both internal and external reviewers as part of their project management system under ISO 9001:2000, which post dates Project Opalinus Clay. Details of NAGRA’s assessment of the data quality or the Opalinus Clay project is only included in unpublished internal reports and have not been seen.

The hydrochemical dataset was periodically frozen to permit data handling and interpretation. The dataset includes details of data uncertainties.

The development of geochemical and thermodynamic databases (GDB and TDB) used during Project Opalinus Clay was controlled by a series of checks on the validity of the assumptions and procedures and the quality of the data generated by modelling (Wersin and Schwyn, 2004). Quality assurance measures included: regular discussions and audits within the project team; external peer reviews of Technical Reports; and a workshop with international experts where the geochemical databases and underlying approaches were presented (NAGRA 2002c). In addition, for a number of cases, the consistency of the data was checked by additional geochemical calculations carried out by the project team.
Tracers were used during drilling to permit correction for penetration of drilling fluid in pumped water samples. Continuous measurements of tracers showed that tracer concentrations fell to low levels after a short period of time in the more permeable formations. The exception was the Malm Limestone, which yielded little water and tracer contents remained high even after several days of pumping. Corrections were applied to samples with elevated tracer concentrations.

It was recognised that there were a number of sources of contamination and uncertainty as a result of the method of porewater analysis, including (Pearson et al., 2003):

- Contamination from the drilling fluid;
- Modification of porewater chemistry during storage (oxidation and evaporation); and
- Contamination and modification of porewater during the extraction process (degassing, fractionation and pressure effects on solubility).

Measures were developed to minimise the effect of these on the analysis.

### 4.4.8 Hydrochemical Interpretation and Modelling

The focus of interpretation for Benken was porewater chemistry in the Opalinus Clay and the immediately overlying Dogger. Comparatively little effort was expended on the overlying and underlying permeable strata.

The principal method of interpretation of the Opalinus Clay was the production of porewater profiles for stable isotopes ($\delta^{18}$O, $\delta^2$H, $\delta^{37}$Cl), chloride, noble gases (He, Ar) and ratios of noble gas isotopes ($^{4}$He/$^{3}$He, $^{40}$Ar/$^{36}$Ar). Porewater profiles for the Opalinus Clay were developed for both Mont Terri (Mazurek et al., 2011, Pearson et al., 2003) and Benken (Gimmi and Waber, 2004). At Benken, the interpretation found some differences in the profiles, with clearly defined profiles being produced for $\delta^{18}$O, $\delta^2$H, a more variable profile for chloride and flat profiles for excess helium (based on limited data).

Stable isotope data were also examined using plots of $\delta^{18}$O‰ VSMOW vs. $\delta^2$H‰ VSMOW.

Work on colloids (Voegelin and Kretzschmar, 2002) concluded that colloid-facilitated transport of radionuclides in Opalinus Clay was unlikely due to the absence of fracture flow.

### Palaeohydrogeological Interpretation

A palaeohydrogeological interpretation of the potential GDF site was built up from a range of data sources, including: commercial boreholes, tunnels through the Opalinus Clay as well as data from the Benken borehole and the Mont Terri URL. The basic model assumes that, after deposition in a shallow marine environment at ca. 180 Ma, connate porewater was modified by expulsion during compaction and diagenesis. A highly saline event, probably related to the underlying late Triassic evaporites, was preserved in fluid inclusions in diagenetic carbonate cements. Current salinity is about 30% of seawater, but the stable isotope signature cannot be explained by simple mixing of marine and meteoric waters (Pearson et al, 2003).
Loss of salinity from the Opalinus Clay may have occurred during the early Tertiary when a karstic groundwater system was active in the overlying Malm limestone for at least 20 Ma and by diffusive exchange with groundwater in the aquifers above and below the Opalinus Clay in the Quaternary. In the Opalinus Clay, the mineralogy has changed little since diagenesis and is expected to remain largely unchanged in the future (NAGRA, 2002b) and can therefore be considered stable.

For NaCl, the main changes over the next 1 Ma will be out-diffusion, but amounting to only 20% of the total NaCl present (Gimmi and Waber, 2004). Hydrogeological measurements in numerous boreholes and tunnels across Switzerland indicate that a significant increase in the hydraulic conductivity of isolated fault zones in the Opalinus Clay will only occur if the overburden is less than 200 m. At Benken, the clay currently lies at 650 m and is expected to be 450 m after 1 Ma (NAGRA, 2002b).

Modelling

A reference porewater was defined for the Opalinus Clay (Pearson et al, 2003) based on chemical and mineralogical analyses of cores from the Benken borehole, various studies performed at the Mont Terri URL and geochemical modelling.

The modelling was based on chemical thermodynamics and included equilibria with carbonates and cation exchange with the clay fraction. Modelling used the PHREEQC and EQ3 codes. An important aspect in the modelling was the estimation of chloride concentrations and pCO₂ as these were the only two independent variables in the model. Chloride concentrations in porewater were estimated from leaching of Benken cores and experimental data obtained from Mont Terri. Sulphate concentrations were estimated by assuming a current marine SO₄/Cl ratio and back-calculating to the measured chloride content. For pCO₂, Pearson (2002) proposed a nominal value of 10⁻².² bar, corresponding to the most likely value based on extensive modelling results along with two bounding values of 10⁻¹.⁵ and 10⁻⁻³.₅ bar, which were calculated assuming the combination of SO₄ and Cl concentrations that lead to the highest and lowest possible pH values.

The redox potentials were derived assuming equilibrium between sulphate, pyrite and siderite, which resulted in Eh values of about -140 to -250 mV. The assumption of sulphate/ pyrite equilibrium was considered reasonable given the very long residence time of porewater, even though the catalytic role of sulphate-reducing bacteria in Opalinus Clay remains uncertain (NAGRA 2002b).

A reference mineralogy was also established for the Opalinus Clay and included CEC and other properties (NAGRA 2002b). The cation exchange properties were observed to be similar to those of MX 80 bentonite (Wyoming Bentonite containing approximately 85% Na/Ca-montmorillonite and 15% accessory minerals). MX 80 bentonite has been proposed for use as backfill and has been the subject of detailed analysis. These similarities include:

- Sodium (Na⁺) is the main exchangeable cation; and
- The total amount of exchangeable cations per unit volume of porewater is similar in both clays (3.9 eq/l in bentonite vs. 2.1 eq/l in Opalinus Clay). The CEC is larger in the bentonite due to the
higher smectite content but the overall exchangeable cations per unit volume are similar due to the higher solid/liquid ratio in Opalinus Clay.

Although the use of a reference water and the use of a reference host rock mineralogy are simplifications, they are probably justified when the general homogeneity of the Opalinus Clay Formation is assessed (e.g. Allia, 1996; Boisson, 2001) and are unlikely to significantly bias site characterization. It is, however, of note that many important parameters were not measured directly and were derived from interpretation and modelling.

Porewater profiles were modelled assuming diffusion was the only transport process (Gimmi and Waber, 2004) using analytical solutions. Models were produced based on assumptions regarding the starting boundary conditions (i.e. concentrations in the overlying aquifer and the activation time) and measurements of diffusion coefficients and anion-accessible porosity (for chloride). The models also included consideration of isotopic fractionation (for stable isotopes). Modelling was undertaken for both Benken and Mont Terri.

Initial conditions were based on maximum measured concentrations (excluding outliers) in porewater (Gimmi and Waber, 2004). Boundary conditions were based on measured concentrations in the underlying aquifer and a range of values for the overlying Malm aquifer.

The models were used to develop porewater profiles for comparison with measured porewater profiles. The comparison was used to inform the understanding of contaminant transport processes. Some of the profiles could not be explained by diffusion alone, and a requirement for a scaling factor for anion exclusion was identified. The modelling provided information on the evolution of porewater within the Opalinus Clay and hence the age of porewater and its palaeohistory.

**Interpretation for End User Requirements**

Geochemical retention is an important safety feature in the Swiss GDF concepts for SF/HLW/ MOX and L/ILW (Wersin and Schwyn, 2004) and was taken into account by applying solubility limits and \( K_d \) values for the safety-relevant radionuclides. The NAGRA methodology defined quality-assured TDB and associated models, similar to the HARPHREEQE geochemical model and the HATCHES databases (SERCO, 2007) used in the UK. Within the Swiss programme, there was less concern about geochemical models, and more focus on the TDB and its relationships to site hydrochemistry. Thus NAGRA’s first TDB (I Core data; Pearson and Berner, 1991) focused on the ‘normal’ parameters of interest to hydrochemistry as this was intended to act as a framework on which all the other work could be based.

The second TDB (I Supplemental data 05/92; Pearson et al, 1992) then addressed specific radionuclides and so was of more direct relevance to the SA. By the time the Opalinus Clay became the prime focus of the Swiss programme, the methodology had developed further into an integrated approach which embraced not only hydrochemistry and TDBs, but also laboratory sorption and diffusion data for both the Opalinus Clay and the backfill. As Wersin and Schwyn (2004) note, the applied methodology can be separated into three parts, as follows:
Part one consisted of establishing the geochemical foundations, which included:

- An extensive update of the NAGRA/PSI thermodynamic database (Hummel and Berner 2002; Hummel et al. 2002);

- Derivation of the geochemical boundary conditions (e.g. porewater pH and Eh) in the different compartments of the disposal system (Curti and Wersin 2002; Schwyn et al. 2003; Pearson 2002) and

- Generation of experimental sorption data in clay (e.g. Baeyens and Bradbury 1995a,b; Lauber et al. 2000; Glaus et al. 2001) and cement (e.g. Bradbury and Sarott 1995; Wieland and Van Loon 2002) systems.

Part two involved the derivation of scientifically-sound retention data, i.e. the solubility limits (Berner 2002; 2003) and sorption values (Bradbury and Baeyens, 2003a,b,c; Wieland and Van Loon, 2002) for safety-relevant radionuclides, under GDF conditions;

Part 3 of the overall procedure involved the critical evaluation and, if necessary, adaptation of the values for use in safety assessment calculations.

As such, the development of the understanding of the Opalinus Clay hydrochemistry moved forward as an integrated part of a much larger, safety assessment-focussed effort which relied on the ongoing research at Mont Terri. Indeed, much of the Opalinus Clay hydrochemical understanding has come about more indirectly than would be the case in a more traditional programme and this must be taken into account when transferring the Swiss approach to understanding low permeability, argillaceous host rocks elsewhere.

Porewater profiles and their interpretation by diffusion-only models appear to have provided the principal basis for estimating the age of groundwater within the host rock.

4.4.9 Uncertainties

Although uncertainties remain in the hydrochemical understanding, NAGRA believe that they have demonstrated that the selected site is sufficiently safe and that “remaining uncertainties do not put safety in question” and that “the information basis for the wastes and the engineered barrier system is adequate and draws on more than 20 years of work in Switzerland and wide experience abroad” (NAGRA, 2002a).

4.4.10 Tools

All modelling tools utilised to date are standard, well-tested off-the-shelf software packages such as EQ3 and PHREEQC. The TDBs utilised in the modelling were NAGRA’s own well publicised and tested systems which are an integral part of NAGRA’s extensive research programme in this area (cf. Wersin and Schwyn, 2004).

Diffusion modelling was based on analytical solutions (Gimmi and Waber, 2004) to the particular model domain.
4.5 Horonobe, Japan

4.5.1 Background

Work in Japan is of potential interest because the Japanese have undertaken investigations using a different approach to elsewhere. European programmes have largely cooperated and collaborated with each other to the extent that there are strong similarities between approaches.

The most advanced and relevant work in terms of hydrochemical interpretation and modelling has been the work with JAEA at Horonobe in northwest Hokkaido (see Ota et al, 2007 for programme details). A number of other URLs exist or have existed in Japan but the Horonobe URL programme is of most interest as it has effectively been planned in the same manner as a GDF site characterisation, including the development of a SDM. Horonobe has been the subject of a research programme to study sedimentary formations in Northern Japan as potential host rocks for a GDF. Phase 1 of the research was surface-based investigations. Phase II investigations took place during tunnel excavation and Phase III consists of research within a URL. The Horonobe site is not planned for use as a GDF and is therefore similar to the regional analogue concept of NAGRA.

The Horonobe area of Hokkaido was chosen as a research area on the basis of:

- Geology: The presence of argillaceous sediments which are representative of the Neogene sedimentary formations that are widespread across Japan and had previously been identified as a potential GDF host rock (JNC, 2000);
- Location: The site’s proximity to the coast allowed examination of coastal processes of relevance to potential coastal repositories (e.g. presence of saline groundwater, the impact of repeated regressions/transgressions on the site hydrochemistry).

The Japanese work was not specifically identified by NDA RWMD as of interest and is therefore only covered briefly to highlight areas of potential interest to NDA.

4.5.2 Sources of Information

The primary source of information is a series of JAEA reports on the work at Horonobe. A summary is provided in Ota et al. (2010), which explains the background to the research and details work carried out to 2005.

4.5.3 End User Requirements

The following end user requirements can be identified for the siting of the investigation area and development of the URL research facility:

- The presence of argillaceous sedimentary formations and associated groundwater at GDF depth (minimum between 300-500 m);
• Existence of sediments mechanically strong enough for tunnel and cavern construction at GDF depth (Kubota et al, 2003);

• Low enough groundwater gas content to ensure safe construction and operation (natural gas and oilfields are present in the very near vicinity and have been subject to exploration and exploitation);

• Coastal/near coastal site to permit research on coastal influences; and

• Available data from existing boreholes (e.g. HMPC, 1990; JNOC, 1995) to provide a baseline regional and site-scale description of the hydrochemistry of the deep groundwater.

The work was designed to provide the following information:

• Initial state (baseline) hydrochemistry at disposal depth and suitability for engineering design;

• Description and understanding of boundary conditions (e.g. infiltration zones) in the shallow geosphere and at the surface;

• Development of a hydrogeological conceptual model for integration with the site hydrochemistry; and

• Provision of sufficient data to enable development of a conceptual model of the 4-D evolution of the palaeohydrogeology of the URL site and the Sea of Japan coastal environment (Niizato et al, 2010).

4.5.4 Setting

Horonobe is situated in Northeast Japan. Parts of the investigation area have an oceanic climate and other parts an inland climate. The geology of the Horonobe area consists of Cretaceous basement rock overlain by a sedimentary sequence of shale, diatomaceous mudstone, fine-grained sandstone, conglomerate, sandstone and siltstone. The geological structure in the Horonobe area is divided by faults. The site lies in an area of generally low permeability formations.

4.5.5 Hydrochemical Investigations

Hydrochemical investigations in Phase I used information from deep boreholes.

4.5.6 Site Characterisation Data

The following site characterisation data were used to inform the hydrochemical interpretation:

• 2-D, 3-D and 4-D geophysical data for the URL site and the coastal zone were examined to check existing geological information;

• Geomorphological and archaeological information to allow reconstruction of the temporal changes to the coastline over the last 2 Ma (Niizato et al, 2007);
• Samples of core from boreholes were used to understand lithology, mineralogy, geochemistry, palaeontology, stratigraphy, porosity, permeability and structure. Surface based site characterisation was based on analysis of results from 11 deep boreholes to depths of between 470 and 1020 m, and a number of shallow boreholes;

• Groundwater samples including returned drilling fluids, samples taken during drilling tracer clean-up and long-term observation. Most samples were analysed for a wide range of parameters. Currently, gas and microbial analyses are ongoing, but there is no colloid sampling;

• Matrix porewater samples obtained by squeezing. Samples were analysed for a restricted range of parameters (some major ions and stable isotopes of H and O) due to limited sample volume obtained (Charlton et al, 2005; Oyama and Suzuki, 2006);

• Fracture minerals and related data (including a few fluid inclusion samples; e.g. Barnes and Milodowski, 2004); and

• Full structural analysis of several fractures and significant shear zones/ active faults (THERP, 2007).

Groundwater samples for hydrochemical analysis were handled as follows:

• Basic on-site sample check (e.g. sample turbidity, smell) and simple quality control against a basic checklist for groundwater samples (see Kunimaru et al, 2011, Amano et al, 2011);

• Surface monitoring data for pH, Eh (Pt and Au electrodes), Oxidation-reduction potential - ORP (Pt and Au electrodes), EC, DO, temperature and drilling fluid tracer content. No discrete downhole interval sampling was carried out;

• Basic on-site handling and transport procedure for cores destined for porewater analysis (Kunimaru et al, 2011b, Amano et al, 2011).

The hydrochemical dataset was periodically frozen, but there is currently no formal quality management system in place for data release and no data manager has been designated. The dataset does not include details of data uncertainties. A simplistic evaluation of analytical error ranges and reproducibility has been undertaken based on JISO – Japan Industrial Standards Organisation procedures (Kunimaru et al, 2010).

The hydrochemical data were categorised using an adapted and updated version of SKB’s Expert System (Smellie et al, 2008, Kunimaru et al, 2010, 2011, Amano et al, 2011). Samples were assigned to 5 quality categories with Categories 1 to 3 being of use for modelling and palaeohydrogeological studies and Categories 4 and 5 only of use for conceptual model development.

4.5.7 Hydrochemical Interpretation and Modelling

The following activities were undertaken as part of hydrochemical interpretation and modelling:

• Preliminary comparison of mineralogy, groundwater and porewater (Kemp et al, 2002);

• Preliminary gas data interpretation (Metcalfe cited in Kunimaru et al, 2010);
• Geochemist’s Workbench (GW) analysis (Metcalfe cited in Kunimaru et al, 2010; Arthur and Zhou cited in Kunimaru et al, 2010);

• Open system isotopic fractionation modelling (Kai, cited in Kunimaru et al, 2010);

• PCA to evaluate mixing using the M3 code was attempted on two separate occasions. The first (Laaksoharju, cited in Kunimaru et al, 2010) identified three end-members for groundwater, and the second (Yamamoto et al, 2006), only two;

• Inverse geochemical modelling was used to explain hydrogeochemical evolution of present-day groundwater by water-rock reactions (Hama et al, 2007). The analysis identified two groundwater end-members and the presence of very old groundwater (>1.5 Ma ago) at GDF depth;

• Basic PHREEQC analyses (e.g. Sasamoto et al, 2007a);

• Multivariate geostatistical analysis (using Piper plots etc; Sasamoto et al, 2007a, Sasamoto et al, 2007b);

• Last Glacial Maximum stable isotope signature derivation and hydrochemical mixing and reaction model (Teramoto et al, 2008);

• 2-D, 3-D and 4-D visualisations of baseline variations, interpolation between data points, kriging etc (e.g. Niizato et al, 2010, Amano et al, 2011);

• Groundwater dating using natural decay series and \(^{4}\text{He}/^{3}\text{He} \) ratio (CRIEPI, 2011) indicates groundwater ages of greater than 1 Ma.

**Interpretation for End User Requirements**

The following interpretation has been undertaken to meet end user requirements:

• Inverse geochemical modelling to explain hydrogeochemical evolution of present groundwater by water-rock reactions and groundwater mixing;

• Identification of ‘reference water’ compositions, however, this topic is still the subject of discussion;

• Geochemical modelling of redox couples to understand redox at disposal depth and buffering processes;

• Geochemical modelling of pH and carbonate system and of buffering processes at disposal depth;

• Geochemical modelling of silica diagenesis impacts on the site hydrogeology;

• Using natural tracers (chloride and stable isotopes) with reliable uncertainties to calibrate the palaeohydrogeological model;

• Distribution of groundwater ages from isotopic data and in situ production estimates and using these to test the hydrodynamic groundwater travel times;

• Interpretation of evidence from natural system for matrix diffusion;
Construction of semi-quantitative model of palaeohydrogeology for past climate episodes at local (URL), district (Horonobe area) and regional (eastern seaboard of the Sea of Japan) scales.

The hydrochemical interpretation of the Horonobe site has not evolved in a linear fashion, as shown, for example, by the application of M3 modelling on two occasions. In addition, there was extensive unpublished work over a number of years that was only synthesized in Kunimaru et al. (2010). There is also an absence of an overarching palaeohydrogeological conceptual model for the site (which is currently still being developed: cf. Niizato et al, 2010). There are several reasons for these anomalies and they include:

- Lack of a rigorous QMS during sampling means that many artefacts were introduced into the groundwater and porewater datasets and incorporated into models. Despite the use of atmosphere-controlled glove boxes during core sampling, all porewater collected to date have indications of oxidation, probably introduced during on-site sample handling and transport;
- Modellers were remote from the URL programme and so lacked awareness of data limitations;
- Data was released in an ad hoc manner, rather than through a controlled release process. As a result, work has been undertaken and published on different versions of the dataset;
- QMS is now being addressed in a programme of work (e.g. Kunimaru et al, 2010, Amano et al, 2011 etc) which is also addressing ‘retro-QA’ i.e. retrospective QA of older data.

4.5.8 Tools

All modelling tools utilised to date are standard, well-tested, off-the-shelf software packages such as Geochemist’s Workbench (GWB), PHREEQC, M3 etc. In addition, the TDBs utilised in the modelling have been JAEA’s own well-publicised and tested systems which are an integral part of JAEA’s extensive ongoing research programme in this area (Kitamura et al, 2010). The electronic versions of the JNC-TDB are publicly available as input files to the geochemical calculation programs PHREEQE, PHREEQC, EQ3/6 and Geochemist’s Workbench (GWB).

4.6 Low Level Waste GDF, West Cumbria

4.6.1 Background

A brief review of work at the Low Level Waste Repository (LLWR) is included here. The LLWR site in Cumbria has been used for disposal since 1957. Waste disposal at the site was historically in shallow trenches but disposals since 1995 have been to concrete lined vaults.

4.6.2 Sources of Information

The recently-submitted 2011 Environmental Safety Case (ESC) (LLWR, 2011) provides details on the site’s geological and hydrogeological setting. The interpretation of the site hydrochemistry was limited to a review of non-radioactive hydrochemistry data collected as part of the site’s environmental monitoring programme is also included within the ESC (Entec, 2010). The ESC describes the site hydrogeology in some detail.
Hydrochemistry was considered in more detail in an earlier Post-Closure Safety Case (PCSC) (BNFL, 2002), which included a Far-Field Geochemical Interpretation, which was based on characterisation work undertaken prior to the earlier ESC. It appears that no further hydrochemical characterisation has taken place since 2002.

This review focuses on the work described in BNFL (2002), but takes into account the revised geological and hydrogeological interpretation set out in LLWR (2011).

4.6.3 **End User Requirements**

For the 2002 PCSC, a description of hydrochemistry was required:

- To provide a description of the hydrogeochemical system at the LLWR site that can be used by the Post-Closure Safety; and

- To fulfil the relevant requirements of the regulatory guidance (Environment Agency *et al.*, 1997), in particular the need for site related information.

4.6.4 **Setting**

The LLWR lies close to the Irish Sea coast in a low lying setting. Geologically and hydrogeologically, the regional setting for LLWR is the same as that described for Nirex (Section 3.2).

The LLWR is underlain by a thick and complicated sequence of Quaternary Deposits over the Ormskirk Sandstone. Hydrogeologically, the facility lies within the Coastal Plain regime (topographically driven flow within the Sherwood Sandstone aquifer and overlying Quaternary) defined by Nirex.

In the vicinity of the LLWR site, groundwater generally flows from the Lake District hills towards the coast.

The 2011 ESC divides groundwater into Upper and Regional regimes, the Upper regime lies entirely within Quaternary Deposits, whereas regional groundwater includes drift and sandstone.

The direction of flow in the Upper Groundwater is predominantly downwards with only limited lateral migration, whereas regional groundwater is dominantly laterally to the south-west (towards the coast). Groundwater from this zone discharges to the inter-tidal zone and off-shore.

The 2002 PCSC (BNFL, 2002) used an event-based lithostratigraphic approach to characterise the geology on the basis of depositional history. The 2011 ESC (LLWR, 2011) used a lithofacies approach to characterising the geology and hydrogeology, which allowed the grouping of geological units with similar hydraulic properties.
4.6.5 Hydrochemical Investigations

Site Characterisation Data

The 2002 hydrochemistry interpretation was based on information provided by earlier geological, hydrogeological and geochemical investigations.

The investigation included:

- The sampling and analysis of on-site boreholes for major element, trace element, colloidal, organic material and stable isotope groundwater chemistries;
- Detailed mineralogical studies.

In addition to site-specific information, data were also taken from off-site sources, notably the Nirex Quaternary borehole network (see Section 3.3) and off-site rainfall data.

Quality Control

A similar approach to data control for sampling and analysis as used by Nirex was adopted for the 2002 PCSC (see Section 3.3.5). This included a multi-step data screening procedure to eliminate samples identified as contaminated and screening for samples with charge-balance errors.

4.6.6 Hydrochemical Interpretation and Modelling

Interpretation

Groundwater was generally of a similar composition with few exceptions. Hydrochemical data were visualised using Piper and Stiff diagrams and frequency histograms. The depth distribution of a range of parameters was also considered. The LLWR groundwater was found to be predominantly fresh water, Ca-Na-HCO₃-Cl composition. The groundwater composition was generally similar throughout the site including samples taken from both the Upper and Regional groundwater systems. Some samples from the Upper groundwater display a greater NaCl signature, representing a larger contribution from seaspray.

Limited statistical analysis was also undertaken (co-variance analysis) to look for any correlation between major elements.

Cross-plots were used to consider end member composition of mixing using conservative natural tracers (principally Cl) and also stable isotopes. The primary contributor to groundwater chemistry was found to be meteoric water, with a concentration factor of approximately three required to account for the concentrations of Na and Cl in groundwater. Stable isotope data also indicated that meteoric recharge was the main process controlling δ²H and δ¹⁸O composition, with sediment-water interaction processes being minimal.

A reference groundwater for use in biogeochemical and experimental use was determined.
A significant feature at LLWR is the presence of a plume of tritium-contaminated groundwater that had as its source the trenches. Engineering of the trenches, including a cap and cut-off walls has limited the release of tritium in recent years. The presence of the plume provides a strong indication of the pathway that is likely to be taken by any other substances that escape from the trenches and has therefore been used to aid the understanding of the site hydrogeology.

**Modelling**

Water-rock interactions were considered through calculations of mineral saturations using PHREEQE and the use of activity ratio diagrams that relate equilibrium phase relationships between minerals to the composition of coexisting fluids. In addition, measured redox conditions were compared to modelled redox based on ion-pairs.

Water-rock interactions indicated that the major reactions affecting the overall evaporated rainwater composition were ion-exchange, sorption and carbonate equilibrium.

The long operational history of the site meant that pre-disposal characterisation was not undertaken prior to the earlier disposals. The site has been subject to geological characterisation; however, hydrochemical interpretation and modelling inputs to the ESC were limited. A review of non-radiological hydrogeochemistry in Leachate (Entec, 2010) presented an analysis of the data collected in various monitoring programmes at the site. The monitoring data that were collated and reviewed were not collected with the purpose of determining the site hydrochemistry. The review does not constitute a detailed characterisation of the site hydrochemistry. No modelling of hydrochemistry has been undertaken for the ESC (LLWR, 2011).

Due to the absence of detailed interpretation and modelling of hydrochemistry the LLWR is not discussed further.

**4.6.7 Uncertainties**

Uncertainties in the PCSC were discussed in BNFL (2002) in general terms regarding the representativeness of the data used but few specific examples are given. It appears that the principal uncertainty was the effect of the site on the geosphere.

**4.6.8 Tools**

The PHREEQE code was used to undertake modelling.

The bespoke bio-geochemical code (LLWR near field kinetic - DRINK model) was used in modelling the LLWR near-field (which is outside the scope of this report). However, it requires an input groundwater composition to define boundary geochemical conditions. There was therefore an end user requirement to define a standard or reference groundwater.
5. Evaporite Case Studies

Two case studies for evaporites have been reviewed for sites at WIPP (USA) and Gorleben (Germany). Both sites are located within predominantly halite deposits. The principal difference between the sites is that WIPP is located within a layered sedimentary sequence, whereas Gorleben is located within a salt dome.

5.1 Specific Factors for Evaporites

Within evaporites, the host rock does not contain groundwater in the conventional sense, although isolated pockets of brine are typically found. The absence of groundwater means that hydrochemical investigation requirements for the host rock are very limited and investigations concentrated on strata immediately above and below the host rock. In particular investigations have concentrated on flowing horizons.

The objectives of hydrogeochemical site characterisation that relate specifically to the expected properties and safety performance of evaporites that exist in addition to the general hydrochemical properties such as groundwater compositions, are:

- To assist in the demonstration of the absence of flowing groundwater within the host rock from GDF-scale up to regional-scale; and
- To describe and parameterise for modelling the lateral flow of groundwater in aquifer layers either within, above or below the evaporite sequence, so that they can be modelled as potential radionuclide release pathways and so that their palaeohydrogeology can be described as an analogue for future long-term evolution.

5.2 Waste Isolation Pilot Plant (WIPP), USA

5.2.1 Background

The Salado formation, an evaporite, is the host rock for the United States Department of Energy’s (US DOE) Waste Isolation Pilot Plant (WIPP). WIPP is located 42 km east of Carlsbad in New Mexico, United States. WIPP was first identified as a potential GDF site in 1974 and was developed as a R&D facility in 1978. The site was first investigated in 1975. Initial characterization was completed in 1978. Additional holes have been drilled since then to meet specific information requirements. A decision was made by US DOE to proceed with construction of WIPP in 1981, when the first exploratory shaft was excavated. Underground excavation began in 1982 and was initially completed in 1989. An application for a site licence was submitted in 1996 and the site was certified to accept waste in 1998. The site was granted an operating certificate in 1998. Long-term monitoring has continued since 1999. In addition, some further characterisation work, including drilling of additional boreholes has been undertaken since 1999.

The WIPP GDF is situated at 655 m below ground level.
5.2.2 Sources of Information

There is a large body of published information on WIPP, which reflects the fact that it has been licensed to accept wastes since 1998. Much of this information is contained within the Compliance Certificate Application (CCA). Site characterisation has been ongoing since the site was first investigated until the present day, including post-licensing. However, characterisation to support the original CCA was completed in 1996. Compliance recertification applications have been made in 2004 and 2009. These include some updates to the site conceptual model as a result of the collection of additional information and further interpretation. This review focuses on the site characterisation described in Siegel et al. (1991), which forms part of the 1996 CCA.

Further characterisation activity has been undertaken at the site to address uncertainties, notably long-term observations that contradicted the original conceptual model. The model suggested that there were no inputs of modern water to aquifer formations above WIPP, but observations showed increases in groundwater levels in the overlying Culebra Dolomite which indicated a degree of connection to modern recharge.

5.2.3 End User Requirements

Information from site characterisation has been used to develop and screen Features, Events and Processes (FEPs) to develop conceptual, mathematical, and computational models to evaluate the efficacy of natural and engineered barriers in meeting environmental performance standards.

The principal end user of hydrochemistry was groundwater flow modelling, which required information to support the hydrogeological conceptual model.

5.2.4 Site Setting

Geology

The WIPP host rock, the Salado Formation, is an evaporite which comprises predominantly halite (NaCl), with some accessory evaporite minerals such as anhydrite (CaSO₄), gypsum (CaSO₄·2H₂O), polyhalite (K₂MgCa₃(SO₄)₄·2H₂O), and magnesite (MgCO₃).

The Salado evaporite is underlain by the Castile Formation and overlain by the Rustler Formation. The Castile is composed of bedded anhydrite and limestones. The Rustler Formation contains five members: (1) Los Medaños: A lower member of siltstone/ mudstone and containing anhydrite and halite (2) the Culebra Dolomite; (3) the Tamarisk which is predominantly gypsum/ anhydrite; (4) the Magenta member a dolomite/ sulphate unit; and (5) the Forty-niner member (mudstone, halite and anhydrite).

The Culebra Dolomite is approximately 7 to 8 m thick. It exhibits significant spatial heterogeneity in: the types of porosity, the amount of fracturing, and the amount of porosity-filling cements, which are generally gypsum, with some halite.
The geology is laterally variable. Halite beds are commonly found in association with mudstones to the east of the WIPP site, and halite beds and/or cements are present in the mudstones and clastics of the lower Los Medaños over much of the WIPP site. To the west of the WIPP site, a large subsidence trough known as Nash Draw has formed due to dissolution of the upper Salado Formation, which has given rise to evaporite karst in the Rustler Formation.

To the east of the WIPP site, the Culebra is deeply buried and contains few fractures. The fractures and primary porosity that are present are filled with sulphatic and/or halite cements. In the area of the WIPP site, the presence and continuity of fracturing and sulphatic fracture fillings within the Culebra were difficult to predict (Siegel and Lambert, 1991).

**Hydrogeology**

The Salado halite is essentially dry, but there are isolated quantities of intergranular brine (USDOE, 2004). Consequently, the deposit does not have groundwater flow in the conventional sense.

The Culebra Dolomite is the first major water-bearing unit above the GDF and was the focus of hydrogeological and hydrochemical investigations. The Culebra Dolomite is also the most transmissive member of the Rustler, although its transmissivity varies over several orders of magnitude. Water movement in the Culebra Dolomite is predominantly within fractures in regions of extensive fracturing and little porosity-filling cements. The Magenta Dolomite also forms an aquifer.

The halite beds associated with mudstones and halite cemented clastic sediments of the lower Los Medaños form aquicludes.

### 5.2.5 Hydrochemical Investigations

**Phases of Investigation**

Investigations began at the site in 1976 and by 1978 some 47 boreholes had been drilled. Since 1978 additional boreholes were drilled to collect specific information. The hydrochemical site characterisation used in the CCA (Siegel et al, 1991) was based on information collected up to 1989.

Application for a Compliance Certificate was made in 1996 and certification was given in 1998. The site began operating in 1999. However, since the certificate was granted, further hydrochemical investigations have been undertaken to improve the conceptual model for the site.

In addition, the site is subject to routine monitoring of groundwater and the results have been used to update the understanding of the site.
Hydrochemical Data

Data in and around the area of the WIPP site have been collected over a span of 50 years (1960 to 2010), including data collected on behalf of the WIPP project and historic data from the region around WIPP (data collected prior to 1976). Groundwater samples have been collected specifically for WIPP since 1976, and include:

- Historic data collected by the United States Geological Survey (USGS) from the region around WIPP since 1960;
- 1976 to 1986: Data collected by the USGS and Sandia National Laboratories (SNL);
- 1985 to 1995: Data collected by Westinghouse Electric Corporation (WEC) from most of the available Culebra wells and a small number of Magenta, Dewey Lake, and Santa Rosa wells;
- 1995 to Present: WEC has collected two rounds of samples each year on seven newly installed wells, known as WQSP wells, (6 Culebra and 1 Dewey Lake). Twenty-nine rounds were completed by December 2009; and
- 2000 to Present: SNL collected water samples in non-WQSP wells. Opportunistic samples have also been collected during drilling of new wells.

The hydrochemical data included in the 1991 (Siegel et al, 1991) site characterisation consisted of a large number of water analyses. Samples were predominantly taken from the Culebra Dolomite. Mineralogical analysis was also undertaken on core samples.

In detail, the analysis available for the 1991 site characterisation consisted of:

- Groundwater samples from 70 sites (107 sampling horizons) analysed for major ions and minor solutes;
- Mineralogical analysis of cores from 12 cored boreholes aligned in 3 transects through the Culebra member. Over 100 samples were analysed by: optical microscopy, quantitative X-Ray Diffraction and X-ray fluorescence;
- Isotopic analysis for $\delta^2$H and $\delta^{18}$O undertaken on water samples from 70 locations comprising 6 from Magenta; 21 from Culebra; 17 from Rustler/ Salado contact zone 3 from Dewey Lake, 16 from the Capitan Limestone 1 from alluvium and 5 at the surface;
- Values of $\delta^2$H from water of crystallisation of gypsum in Dewey Lake and veins in the Rustler measured at 11 horizon sites (20 samples);
- $\delta^{13}$C and $^{14}$C measured in water from 16 horizon-sites at 12 wells (21 samples);
- Tritium measured in 7 wells;
- Total U and U isotopes taken from 5 Rustler/ Salado contact locations 9 Culebra locations 2 Magenta 1 potash mine, 1 rainfall and 1 spring;
- 87Sr/86Sr in gypsum and anhydrite in 29 carbonates from Dewey Lake veins, Rustler Veins and Salado and Castile;
- Concentrations of members of four oxidation-reduction (redox) couples and platinum electrode potential measurements obtained from 21 wells in the Culebra and used to calculate apparent Eh values;
- Groundwater samples from 21 Culebra wells analyzed for total organic carbon (TOC); and
- Stable isotopes analysed in carbonates from the Magenta and Culebra members (43 tests).

The data were subject to a critical evaluation procedure before use (Siegel et al. 1991), which placed greatest reliance on samples obtained following lengthy pumping that had reached stability in terms of easily measurable parameters. It was also assumed that results were reliable if they have been reproduced by repeat sampling. Details of this procedure have not been seen. Samples obtained as part of the WIPP investigation were preferred to other samples.

Additional data collected since 1989 includes:

- Groundwater samples from new and existing boreholes primarily in the Culebra Formation. Groundwater samples were analysed for a range of parameters, including isotopes;
- Mapping of catchment basins in Nash Draw;
- Correlation of geophysical logs from exploratory potash and oil and gas holes around the WIPP site;
- Detailed evaluation of post-depositional processes (e.g. dissolution);
- Collection of information on potash industry water usage and disposal;
- Evaluation of borehole plugging and abandonment records; and
- Modelling of various scenarios that could introduce water into the Culebra.

5.2.6 Hydrochemical Interpretation and Modelling

Hydrochemical interpretation focussed on the Rustler Formation and in particular the Culebra Dolomite, where the majority of samples were taken. The focus on the Culebra was due to it being the first flowing groundwater above the Salado.

The presence of evaporites within the Rustler Formation and underlying Salado Formation meant that the interpretation was based largely on understanding dissolution and equilibrium between dissolved and mineral phases. This approach requires knowledge of evaporite geochemistry and the behaviour of minerals in high concentration solutions.
Visualisation

Visualisation in Siegel and Lambert (1991) included:

- Contouring of major ions and other solutes;
- Contouring ratios of Br/Cl, Na/Cl, Na/K, Sr/Ca, and other minor/major solute ratios.
- Use of trilinear plots (Piper diagrams etc.) used to evaluate water types and assist in the water typing approach; and
- Results of isotope analysis were compared to SMOW and deviations from SMOW were attributed to a profound degree of water-rock interaction and to partial evaporation from the unsaturated zone / capillary fringe.

Water Typing

A water typing approach was taken to distinguish the waters encountered (Siegel et al, 1991). The data show that Culebra groundwater is predominantly Ca-Mg-SO₄ to Na-Cl type, with very little HCO₃, which was thought to be due to the depth and age of Culebra groundwater that has had sufficient time to react with SO₄ phases along the flowpath.

Trends and patterns in the major ion aqueous geochemistry and ionic strength of Culebra waters were identified by organizing the waters into groups based on hydrochemical facies proposed by Ramey (1985), which was expanded by Siegel et al. (1991) and is set out in Table 5.1. More recently, Domski and Beauheim (2008) added a fifth facies (facies E) and also identified transitional A/B and B/C facies.

Hydrochemical facies were used to map the occurrence of different groundwater within the area of interest both spatially and with depth. Facies were used to qualitatively assess the age and hydrochemical evolution of groundwater.

The 1991 conceptual model (Siegel et al. 1991) for the chemical evolution of waters in the Culebra tentatively identified the major sources and sinks for many of the solutes. It proposed that solutes are added to the Culebra by dissolution of evaporite minerals. The solubility of gypsum and calcite increased with salinity and therefore dissolve to maintain chemical equilibrium with groundwater. However, equilibrium is not maintained between groundwater and dolomite. In addition, clays within the fractures and rock matrix exert some control on the distribution of Li, B, Mg, and Si via sorption, ion exchange, and dissolution.
Table 5.1  Hydrochemical Facies at WIPP

<table>
<thead>
<tr>
<th>Hydro-chemical Facies</th>
<th>Characteristics</th>
<th>Origin</th>
<th>Location</th>
<th>Concentration (Molal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>NaCl brine with high TDS</td>
<td>Marine signatures of old waters (long flow paths) that have dissolved halite and/or mixed with connate brine.</td>
<td>Found in a general north-south cluster along the Rustler mudstone/halite margins</td>
<td>2-3</td>
</tr>
<tr>
<td>A/C</td>
<td>Facies A/C are less saline than facies A, and likely result from the mixing of relatively dilute facies C with facies A water.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>A dilute CaSO$_4$ water with low TDS</td>
<td>Relatively recent recharge through gypsum layers overlying the Culebra in the southern part of Nash Draw</td>
<td>South and southwest of WIPP</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>C</td>
<td>Variable composition and moderate TDS</td>
<td>Meteoric waters that have dissolved CaSO$_4$, overprinted with mixing and localised processes.</td>
<td></td>
<td>0.3-1.6</td>
</tr>
<tr>
<td>B/C</td>
<td>Facies B/C and C form a broad north-south band that parallels Nash Draw</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>Potash contaminated waters with a high K/Na weight ratio of 0.21 attributed to contamination from refining at potash mining facilities</td>
<td></td>
<td>3-7</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>Na-Mg Cl brines</td>
<td>NaCl brines with diagenetic signatures represent primitive brines present since deposition of the Culebra.</td>
<td>Eastern, halite side of the Rustler mudstone/halite margins.</td>
<td>6.4-8.3</td>
</tr>
</tbody>
</table>

Groundwater Ages

Siegel et al. (1991) used isotopic data to demonstrate that no significant recharge had occurred for ~12000 to 16000 years. The hydrogeological interpretation indicated that modern flow within the Culebra at and near the WIPP Site was generally from north-to-south with limited or negligible modern vertical flow into and out of the Culebra. Hydrochemical and isotopic data suggested that the identified flow direction was not uniformly applicable over the past 10,000 years. The present-day north to south regional groundwater flow was not consistent with the salinity distribution at the WIPP Site. This was because a hydrochemical facies having low salinity was found downgradient of more saline water to the north.

Mineralogical and isotopic studies of sulphates in the Rustler demonstrated an absence of vertical recharge to the Culebra. Specifically, much of the anhydrite in the Tamarisk member above the Culebra had not been hydrated to gypsum in the presence of fresh water and in addition $^{2}H/^{1}H$ ratios in gypsum throughout the Rustler were not consistent with significant water-rock interaction. The discrepancy between modern flow direction and solute distribution was explained by a change in flow direction in the last 30,000 to 12,000 years.
Such a model was consistent with generally eastward increase in $^{234}$U/$^{238}$U activity ratios that indicate recharge from a near-surface Pleistocene infiltration zone, flowing from the west-northwest. The model is also consistent with the radiocarbon-derived age of groundwater in the Culebra.

The absence of tritium in the Culebra also indicated that no modern recharge had occurred.

The concept of normative salt assemblages was used to identify mixing end members. Normative water results from the quantitative equilibrium assemblage of salts that would precipitate from a natural water if evaporated to dryness under ideal equilibrium conditions at 25° C and atmospheric pressure. The SNORM code (Bodine and Jones, 1986) was used on waters from the Rustler Formation to identify four end-members, as follows:

- **Type 1**: brines containing normative alkaline earth chloride salts and low Cl/Br ratios, which may result when connate waters are involved in dolomitization;
- **Type 2**: dilute solutions contain normative alkalki-bearing carbonates that suggest dissolution of detrital silicates through carbonic acid hydrolysis in a weathering/recharge zone;
- **Type 3**: dilute sulphate rich solutions produced when surface-derived fresh waters dissolve anhydrite/gypsum (and little else);
- **Type 4**: saline halite-rich brines produced when fresh water dissolves anhydrite/gypsum and halite.

The compositions of most waters in the Rustler Formation could be produced by mixing of the above four end-member brines (Bodine et al., 1991).

**Modelling**

PCA was used (Siegel and Lambert, 1991) to define relationships between waters. The analysis was used to refine the hydrochemical facies and to suggest the nature of chemical reactions and mixing that control groundwater composition.

Mineral saturation indices were used to provide insight into chemical processes that control solute concentrations in groundwater. Saturation indices were calculated for minerals commonly observed in rocks overlying the Salado using the code PHRQPITZ (Plummer et al, 1988). This uses the Pitzer model for ion-interactions. The analysis found that:

- All waters were saturated with respect to gypsum;
- All waters were undersaturated with respect to halite;
- All waters were undersaturated with respect to anhydrite, with the exception of a single location.

The results were also used to identify differences between samples collected and model analysis. Potential errors identified as being due to sampling: loss of CO$_2$ during sample collection leading to supersaturation of carbonates; uncertainty in pH; laboratory error; and model input choice: e.g. use of inappropriate activity scales for NaCl brines.
PHRQPITZ was also used for exploratory analysis to evaluate the composition of waters along hypothetical flow paths. Reaction path models could account for most of the observed variation in Na, Cl, SO₄, Mg and K. An attempt was also made to evaluate the role of clay minerals through ion exchange, sorption and silica diagenesis but this was hampered by the limitations of the available data.

5.2.7 Uncertainties

Uncertainties have been addressed throughout the site characterisation programme and are the subject of ongoing investigations. Characterisation has continued to the present day to improve the understanding of the Culebra groundwater flow regime. This in part reflects the significant variation in the hydraulic properties of this aquifer (hydraulic conductivity varies by 6 orders of magnitude). Hydrochemistry has been used to support the understanding of the aquifer.

The uncertainty in the Culebra hydrochemistry has limited impact as it has not been directly used in PA.

In the 2004 CCA US DOE (USDOE, 2004) state that their regulator (the US EPA) ‘has concluded that the groundwater hydrology information for the various geologic and hydrostratigraphic units at the WIPP site identified the important characteristics of the PA and was therefore technically sufficient.’

5.2.8 Tools

The following tools were used in the characterisation:

- PCA was used to evaluate mixing relationships between water types;
- The SNORM code was used to undertake normative analysis;
- PHRQPITZ is a United States Geological Survey (USGS) model code capable of making geochemical calculations in brines and other electrolyte solutions at high concentrations using the Pitzer approach for activity-coefficient corrections. It is now obsolete as current versions of PHREEQC include complete implementation of the Pitzer specific ion interaction approach.
5.3 Gorleben, Germany

5.3.1 Introduction

The Gorleben site lies in the state of Lower Saxony at the eastern boundary of the former West Germany. The area of investigation extended over approximately 390 km² and across the Elbe into the former East Germany.

Site characterisation works commenced in 1979 and were terminated in 2000 when a moratorium was imposed on investigation works for a maximum of 10 years. All documented work reviewed for this report relates to the investigations carried out prior to the moratorium. AMEC understand, however, that further works are planned (and may have commenced) at Gorleben.

The site geology and hydrogeology of the Gorleben site and surrounding area are complex. As a result of this complexity, it is not possible to arrive at a simple explanation of the geology and hydrogeology of the site. The complexity also has implications for the study of the site hydrochemistry.

In broad terms, the geology consists of Tertiary and Quaternary sedimentary strata overlying a salt dome. The salt within the dome is the proposed GDF site. The overburden is of highly variable thickness but is up to 430 m thick.

The overburden contains a number of aquifers separated by aquitards, which are generally arranged in layers. The generally layered structure has been deformed by the salt dome and, in addition, is interrupted by an erosional trough and a deeply incised, infilled glacial channel, which contains a mixture of highly permeable material and clays.

The surface based hydrochemistry investigations that terminated in 2000, concentrated on the overburden, and on tracing the pathway taken by solutes in groundwater in overlying strata. The evaporite deposits were investigated by cored boreholes and also within a URL. The general absence of water within the evaporite means that the investigations at the URL were of little interest to the hydrochemical interpretation.

The overall objective of the investigation described by Kinge et al. (2007) was to provide an interpretation of potential migration paths for contaminants from the surface of the salt dome and into the biosphere via groundwater.

5.3.2 Sources of Information

The understanding of the work has largely been taken from three summary Bundesanstalt fur Geowissenschaften und Rohstoffe (BGR) reports published in 2007 (Kinge et al, 2007, Kothe et al, 2007 and Borneman et al. 2007), which describe the hydrogeological investigation, the geological investigation and the investigation of the salt deposit respectively. Kinge et al. (2007) note that the investigation data and detail is located within internal BGR reports that are not generally accessible.
5.3.3 Information Requirements

The hydrochemical information requirements for the investigation are not explicitly stated in the documents reviewed.

5.3.4 Site Setting

The site characterisation area lies within the Elbe valley at low elevation (13 to 17 m above sea level). The climate is of a continental type. Recharge is variable across the area. The water table is close to surface in the lower lying areas, resulting in evaporation exceeding mean rainfall. Recharge is concentrated in the more elevated areas away from rivers but is limited to less than 80 mm/yr over much of the area and only exceeds this value in areas of arable farming where the water table lies at depths in excess of 1.5 m.

Geology

The geology of the site and surrounding area is described in detail in Kothe et al. (2007) and is summarised in this section. The geology is complex and therefore some simplification is necessary to arrive at a succinct description.

The geological structure of the area investigated has the following main features:

- The Gorleben salt dome (diapir), which fully penetrates Triassic and Cretaceous deposits and partially penetrates Tertiary deposits. The dome is approximately 14 km long and up to 4 km wide. It continues to the northeast as the Rambow salt dome at reduced width. Salt is found at its shallowest within 250 m of the surface and extends to 3400 m below ground level. The salt dome is believed to have developed from the Cretaceous onwards;

- Rim synclines: The upwelling of the salt dome has resulted in the development of synclinal structures (rim synclines) to either side within the overlying sediments;

- An erosional trough over the western part of the Gorleben Dome associated with glaciation;

- A glacial channel (the Gorleben Channel), which cuts through the overlying sediments down to the evaporite. The channel is up to 200 m deep, 7 km long and is 1 to 1.5 km wide.

The Tertiary deposits are fully developed within the rim synclines, but are much thinner over the salt dome. They consist of layered silts, clays and sands. A notable clay layer (Rupelian Clay) forms a regionally important aquitard that separates shallow groundwater from deeper, more saline groundwater and therefore forms the base of the upper groundwater flow system. Above this lies the Eochatthian sequence of silts, which are fully developed in the rim synclines but thinner over the dome. A 25 m thick sand and silt layer (Neochattian) overlies the Eochattian. Above this are the Lower Brown-Coal Sands. These contain localised lignite seams. Above the Lower Brown Coal Sands lies the Hamburg Clay, which is a sequence of clays, fine sands and silts between 60 and 100 m thick. The Hamburg Clay is, however, thin or absent to the south. The Upper Brown Coal Sands overlie the Hamburg Clay but are only present as relics in the study area. They contain a high fraction of fine grained sediments.
Older Quaternary deposits are restricted to those within an erosional trough and in Glacial Channels. In the Gorleben Channel these consist of sands with a thickness of 10 to 50 m overlain by silts and clays (Lauenburg Clay Complex) and then by silts and clays laid down in the Holstein interglacial. In the erosional trough, a sand deposit is found over an area of 3 km² overlain by finer grained deposits. Due to their location within these features, older deposits are not areally extensive. Younger deposits from the Saalian Glaciation are more widespread and are highly variable, consisting of sands, glacial tills and silts and clays generally formed within lakes.

The upper Pleistocene deposits consist of highly permeable sands and gravels (Weichsalian Lower Terrace).

Recent flood plain deposits are also found in the lower lying areas of the study area associated with the flood plain of the Elbe and its tributaries.

**Geochemistry**

The primary focus of geochemical investigation was the salt (evaporite) deposit. The evaporite deposits are primarily sodium-chloride but also include anhydrite, mudstone and carnallite (a potassium-magnesium chloride mineral). The mineralogy of the evaporite was established from the results of geochemical analysis by modelling using the code ZECHMIN-7. As this is not an explicit hydrochemical model it is not discussed further.

Overall water content of the brine was found to be very low (0.1 to 2%). Free water, where encountered, was limited to pockets of brine that ceased to flow after a short term. This was taken to suggest that discontinuities within the salt are limited in extent and not connected over any appreciable distance.

Overburden rock geochemistry was established based on the following analyses:

- Carbonate content 103 samples;
- Organic carbon content 99 samples;
- Heavy minerals 157 samples;
- Clay mineral analysis 180 samples.

The analysis was primarily used to confirm geological mapping and does not appear to have been used in the hydrochemical analysis.

**Hydrogeology**

A simple division of the more permeable deposits has been established to describe the hydrogeology. These units have been divided into an upper and lower aquifer (Kinge et al. 2007), which are as follows:

- The Lower aquifer: The lower aquifer consists of the Lower Brown Coal Sand and Neochattian with the Rupelian Clay as it base and the Hamburg Clay as it upper boundary. It also includes the channel sands within the Gorleben Channel, where the Lauenburg Clay Complex forms the top. It also includes the sand deposits in the erosional trough;
The Upper aquifer consists of permeable near surface deposits (Weichsalian and Saalian sands) but also includes glacial tills and silts.

The Rupelian Clay, Hamburg Clay and Lauenburg Clay Complex form aquitards, as does the evaporite.

A further subdivision has been made into four hydrogeological domains as follows:

- The Rim synclines to the northwest and southeast of the salt dome, which developed as a result of the uplift of the salt dome;

- The Gorleben Channel (and other erosional channels) that cut north-northeast to south southwest across the area. The channel cuts into the salt over an area 5 km long by 1 to 1.5 km wide. The lower part of the channel is filled with permeable deposits in direct contact with evaporite and is overlain by low permeability deposits;

- The erosional trough of the western part of the salt dome, which is bounded on all sides by low permeability deposits except where cut by the Gorleben Channel in the east. The erosional trough is only weakly separated from the Upper Aquifer;

- The transition zone between the Gorleben and Rambow salt domes, which is heavily faulted as a result of salt uplift. Faults were identified as potential pathways for groundwater movement. In this area the Upper and Lower aquifers are locally in contact due to erosion of the intervening areas during glaciation.

### 5.3.5 Hydrochemical Investigations

Hydrogeological and hydrochemical investigations concentrated on the Tertiary and Quaternary deposits and their interface with the evaporite. Older deposits of Triassic and Cretaceous age have not been characterised in detail as they lie at depth to either side of the salt dome.

The investigation at Gorleben was divided into a southern and northern area, which related to the parts of the investigation area within the former West and East Germany respectively, although investigations continued past re-unification of Germany. The scope of investigation within these areas comprised (Kinge et al. 2007):

#### Southern Area

- 158 exploration boreholes;
- 322 water level observation and sampling boreholes;
- 4 pumping wells for long-term pumping tests;
- 22 exploration boreholes.

#### Northern (Domitz-Lenzen) Area

- 76 Groundwater observation wells;
• 12 observation boreholes for pumping tests.

Across both areas, geophysical investigations were undertaken comprising: 549 borehole profiles; 16 seismic reflection profiles; and 82 downhole seismic profiles.

The Geological investigations included:

• 44 boreholes to investigate the salt surface;
• 4 deep boreholes into the salt;
• 4 deep borehole at the flanks of the salt dome to 2000 m;
• 2 pilot shafts to 1000 m.

Salt exploration boreholes were cored through the salt but openholed above the salt.

The hydrogeological investigation included:

• 4 long-term pumping tests;
• Short term pumping tests in observation wells;
• Soil (pedological) mapping to determine recharge characteristics;
• Permeability testing of drill cores;
• Sorption tests on sediments.

The data used in the hydrochemistry interpretation were based on:

• Analysis of groundwater samples from 404 observation wells, including pre-existing wells. In total some 1400 samples were subject to chemical analysis and a subset was also analysed for isotopes;
• Porewater samples from clay layers;
• Results of geophysical logging of 106 investigation boreholes using formation density, specific electrical resistance and natural gamma. Geophysics was supplemented with sampling data to distinguish salinity classes. The primary dataset used in the hydrochemical interpretation was EC and density. These were calculated from the full dataset.

In freshwater, an empirical correlation between formation resistivity and groundwater analyses was established for the more permeable strata.

5.3.6 Hydrochemical Interpretation and Modelling

Water was not generally present in the host rock formation and therefore the interpretation and modelling of hydrochemistry focussed on groundwater in the overlying sedimentary sequence.
Salinity

Because groundwater is in direct contact with soluble evaporite minerals in the Gorleben Channel, the hydrochemical interpretation focussed on chloride (and/or total dissolved solids - TDS) as a tracer for groundwater movement. Salinity or TDS was used as a key factor (but not the only factor) in identifying water types and establishing groundwater movement at Gorleben. An advantage of using salinity/TDS when compared to other tracers is that it allowed the use of both groundwater analysis and geophysical measurements. Groundwater salinity was divided into 6 classes, as follows:

<table>
<thead>
<tr>
<th>Class</th>
<th>Concentration (g/l TDS)</th>
<th>Water Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>&lt;1</td>
<td>Fresh water</td>
</tr>
<tr>
<td>2</td>
<td>1-10</td>
<td>↓</td>
</tr>
<tr>
<td>3</td>
<td>10-50</td>
<td>↓</td>
</tr>
<tr>
<td>4</td>
<td>50-100</td>
<td>↓</td>
</tr>
<tr>
<td>5</td>
<td>100-200</td>
<td>↓</td>
</tr>
<tr>
<td>6</td>
<td>&gt;200</td>
<td>Brine</td>
</tr>
</tbody>
</table>

Following classification of geophysical logs and water samples into salinity classes, cross-sections and maps were used to establish the spatial and vertical distribution of TDS. In detail, the distribution of TDS both laterally and vertically was quite complex reflecting the distribution of aquifers and aquitards.

Unsurprisingly, TDS were highest where groundwater was in direct contact with evaporites and generally decreased towards the surface. However, some saltwater highs (where high salinity water was found close to surface) were identified in the Elbe River Valley, above the southwestern end of the Gorleben salt dome and at the western end of the Gorleben Channel.

Water Types

A water typing approach (i.e. hydrochemical facies) was used to classify waters in the overburden into the following types:

- **Calcium-sulphate.** These waters were interpreted to result from recharge through shallow low carbonate near-surface sediments. The main influence on water quality was identified as weathering of feldspars. These waters have a low TDS/salinity (<150 mg/l);

- **Calcium-bicarbonate waters** were found at greater depth where carbonate was more abundant in sediments (TDS 250 mg/l);

- **Sodium-bicarbonate waters** were formed as a result of cation exchange in freshwaters flushing through previously saline aquifers;

- **Sodium-chloride waters** result from dissolution of evaporite.
Pie charts were used to characterise these water types.

The occurrence of these different water types was used to determine the likely reactions taking place between groundwater and sediments, which were considered to be silicate weathering, carbonate dissolution, sulphate reduction, cation exchange and halite dissolution.

Plots of water composition were used to examine the evolution of water, including the following:

- Sodium: chloride ratio vs. TDS;
- Sulphate vs. TDS;
- Bicarbonate vs. TDS.

**Water-rock Interaction**

Based on the results of groundwater sampling, three main processes of water rock interaction were interpreted to be occurring in the overburden:

- Alkalisation ion exchange between groundwater and sodium clay minerals resulting in increased sodium in groundwater at the expense of calcium and magnesium. This process only affects low mineralised waters;
- Alkali-earth alkalisation: In salt bearing sediments, minerals were enriched and waters depleted in sodium. There was also some degradation of feldspars and clay minerals leading to the release of calcium, magnesium and strontium;
- Sulphate reduction. Sulphate reducing conditions were interpreted to be generated by the oxidation of abundant organic material and by presence of salinity.

**Groundwater Ages**

Isotopes were used to investigate the age of groundwater. Isotope analysis was undertaken for isotopes of carbon ($^{14}$C), hydrogen (including deuterium ($^2$H) and tritium ($^3$H)) and oxygen ($^{16}$O and $^{18}$O).

Isotopic water compositions were reported as deviation from standard mean ocean water (SMOW). The data were plotted on a $\delta^2$H vs. $\delta^{18}$O plot against the Global Meteoric Water Line (GMWL) and the deviation from this were used to evaluate the likely ambient temperature of water at the time of recharge, which was supported by interpretation of noble gas content. However, an alternative local meteoric line was found to provide a better fit than the GMWL (Suckow, 1993).

Samples that deviated from local meteoric line were separated into groups and explanations sought for their isotopic composition. A group of samples showed enrichment in $^{18}$O and were freshwater samples from shallow groundwater. These are samples from an area where evaporation exceeds recharge.
A relationship between TDS and δ\textsuperscript{18}O isotope values was established diagrammatically (TDS vs. δ\textsuperscript{18}O) and also mapped across the study area. The interpretation of these plots led to the following divisions:

- Class 1 salinity groundwater had δ\textsuperscript{18}O values from -8.1 to -9.1 ‰. These waters also included those that contained tritium and some with little tritium which probably relate to recharge in interglacial periods. Glacial waters δ\textsuperscript{18}O values were believed to be around 2‰ lower than interglacial waters;

- Class 2 to 4 salinity waters showed increasingly negative δ\textsuperscript{18}O values with increasing salinity;

- Class 5 and 6 salinity waters had variable δ\textsuperscript{18}O signatures. Most of these samples were from the deep aquifer within the Gorleben Channel (in direct contact with the evaporite), the Lower Brown Coal Sand and from the lower aquifer in the rim synclines;

- The upper and lower limits of the δ\textsuperscript{18}O were taken as end members and other waters believed to be the result of mixing between end members. Four groups of exceptions to this general mixing trend were identified as follows:
  - shallow fresh waters enriched in δ\textsuperscript{18}O by evaporation;
  - fresh water samples from the Hamburg Clay which are strongly depleted in δ\textsuperscript{18}O values;
  - saline water from the Lauenburger Clay Complex;
  - saline water from the Lower Brown Coal Sands and the deep channel sands.

The distribution of the various isotopic compositions were mapped spatially. Samples were taken from 82 wells in the southern area and all wells in the northern area for all isotopes and from all wells for \textsuperscript{18}O.

The tritium detection limit improved during the programme (it was rather high before 1985) and older data were rejected in the analysis. Tritium provided information on the occurrence of recent recharge. In general, tritium was only found in shallow groundwater (tritium was plotted against depth) with the exception of 5 deeper wells where leaking casing was identified as the likely cause. As a result of the identification of elevated tritium the results from these boreholes were discounted for further use in the interpretation.

Dating using \textsuperscript{14}C was constrained by the presence of organic matter (e.g. lignite) within the sediments. This organic matter has no \textsuperscript{14}C due to its age and therefore when released dilutes \textsuperscript{14}C in groundwater or decreases the C-\textsuperscript{14}/C-\textsuperscript{12} ratio. As a result, \textsuperscript{14}C measurements gave unrealistically high ages (Buckau et al, 2000). The \textsuperscript{14}C readings were used with reservation and in combination with other isotope data to give order-of-magnitude ranges of groundwater age rather than to date groundwater. \textsuperscript{14}C was plotted against TDS to identify and group water samples and identify older water.

A general relationship was found between TDS and \textsuperscript{14}C with a decline in \textsuperscript{14}C with increasing TDS. Samples from within the clays had higher \textsuperscript{14}C compared to the general relationship and also had low δ\textsuperscript{18}O suggesting that they were derived from a glacial period.
Noble Gas Analysis

Analysis was undertaken for the noble gases He, Ne, Ar, Kr and Xe at 14 observations wells and on core samples and was used to support the interpretation of groundwater age.

Porewater Profiles

Core samples were taken through the Hamburg and Lauenburg Complex clays in 4 boreholes and were subject to porewater analysis. Porewater samples were analysed for major ions, stable isotopes and helium. Helium (\(^{4}\)He) was used as a tracer as it was anticipated to be generated by radioactive decay of uranium and thorium decay-series elements within the clay minerals. Through estimation of the rate of helium production the age of the porewater could therefore be estimated.

The data were used to establish vertical porewater profiles of the helium excess (when compared to the solution equilibrium with the atmosphere (\(^{4}\)He)), TDS, \(\delta^{18}\)O and \(\delta^{2}H\) through the Lauenburg Clay.

A simple model was used to establish that the porewater profile of \(^{4}\)He\(_{exc}\) could be explained by the difference between the rate of helium production and the rate of transport by molecular diffusion. The model estimated that around 80,000 years would be required to establish the diffusion profile. This was interpreted as good evidence for a lack of advective flow in the clay. The lack of advection was also supported by profiles of stable isotopes of oxygen and hydrogen that were taken to demonstrate that glacial signature water in the clays had only been displaced by younger waters at the margins.

The profile of \(^{4}\)He against depth through the Hamburg Clay showed a more complex picture due to the layered geology of this unit. Layering affects the rate of helium production, which is higher in clay layers and lower in sands and silts. \(^{4}\)He showed a logarithmic increase with depth. Upward diffusion was suggested as explaining the distribution.

Overall, it appears that porewater profiles of \(^{4}\)He were useful in demonstrating the evolution of clay porewater and demonstrating that the clays were effective aquitards.

Wider Interpretation

Hydrochemistry was a key input to understanding the likely evolution of groundwater flow. The conceptual history was based on understanding the evolution of TDS. The highest TDS were in the channel in contact with evaporite in the lower aquifer. This aquifer shows density layering. High TDS water in the channel was identified as the most likely source of high TDS water in deeper groundwater to the north in the lower aquifer within the rim syncline, which forms a closed basin.

Isotopic data provided information on formation ages.
Modelling

There is no readily-available information to suggest that hydrochemical modelling was undertaken for the Gorleben project. Numerical modelling of groundwater flow and density variant modelling was used to support the development of the hydrogeological conceptual model.

Summary

The complex geology and hydrogeology of the Gorleben area required (or appears to have required) extensive investigation through a large number of boreholes and samples.

The principal method of hydrochemical characterisation of Gorleben was to trace the evolution of groundwater that had been in contact with evaporites. This groundwater started off with elevated salinity and could therefore be traced on the basis of TDS. Comparison of other parameters, such as sodium with TDS provided information on rock water interaction.

As saline water is denser than fresh water this has an effect on the distribution of TDS that needs to be accounted for in the interpretation.

Stable isotopes were of use in determining relative ages of groundwater and in evaluating the role of aquitards.

The interpretation of hydrochemistry at Gorleben was largely based on the use of maps, vertical sections and cross sections to arrive at a 3-D overview.

Underground Rock Laboratory (URL)

Two shafts and associated drifts have been used to explore the salt formation. The focus of this investigation was on the geology and structure of the salt. The general absence of water within the evaporite meant that no hydrochemistry characterisation was undertaken as part of this investigation.

Uncertainties

The hydrochemical interpretation appears to be robust with few explicit uncertainties. However, the complexity of the shallow flow system is likely to mean that there is considerable uncertainty regarding the lateral and vertical distribution of hydrochemical and other parameters.

Tools

Only simple tools appear to have been used in the interpretation, such as spreadsheet models and simple hydrochemistry diagrams. Modelling to simulate porewater profiles in clay horizons was used, but the models used are not stated.
6. Lessons from the Case Studies and Site Specific Factors

6.1 Lessons

A key element of RWMD’s approach is to incorporate the lessons learned in previous work. This section summarises lessons from the case study programmes. The intention is to provide RWMD with the benefit of previous experience. It is not intended as a critique of the case studies.

6.1.1 Understanding of Objectives

Hydrochemical characterisation, including data acquisition, interpretation and modelling must be based on a clear understanding of the information requirements of end users (the needs-driven approach). The type, quantity, quality of data required for the interpretation need to be set out in advance. The objectives of the investigation must be communicated to, and understood by, all involved in the project, including those taking samples, laboratories and other disciplines.

Clear objectives should avoid the collection of unnecessary data and the missing of important data requirements and, therefore, reduce the requirements for follow-on investigations and will aid decision making during site characterisation.

6.1.2 Data Quality and Data Management

The hydrochemical interpretation must be based on sufficient data of a suitable and known quality. Data must also be traceable from its origin to the point of use. Data management is therefore critical to the successful outcome. Hydrochemical interpretation and modelling will rely on data collected from a range of sources. This may include existing data from third party organisations, data obtained using different techniques (e.g. porewater from rock cores and pumped groundwater samples), and modelled values. It is therefore important that data management measures are put in place at the outset of site characterisation and that they are maintained for the duration of the project. Data consistency is also vital. Data may be derived from several sources and must be able to be compared e.g. through the use of standard notation and units.

It should be noted that RWMD has developed a Data Management System (DMS) that includes rigorous QA/QC procedures, including:

- Assignment of quality flags;
- Data managed as records (as data changes following processing, previous data are stored);
- A controlled vocabulary to minimise semantic misunderstandings;
• Sample tracking (chain of custody).

The DMS will be the only source of data available to those involved in RWMDs site characterisation programme.

The quality systems used by Nirex at Sellafield and by SKB represent well documented and robust systems for assuring groundwater sample data from various sources that were obtained by different methods and determining the use to which the data could be put. A combined interpretation of data form different origins was possible because the data were quality assured according to defined schemes and were accompanied by estimates of measurement or model error/uncertainty.

Standards for analysis of hydrochemical parameters are detailed in Quintessa (2008).

6.1.3 Data Requirements

It is apparent that the programmes reviewed in Sections 2 to 5 have collected large quantities of data and also that much of these data were not used in the final interpretation. For example at ANDRA, Cl and Sr isotopic data have not been used in the interpretation. S and C stable isotope data also have not led to safety-relevant interpretations, though in certain cases these data might be significant for understanding diagenetic history of the argillite and/or in detecting sampling artefacts such as pyrite oxidation.

However, without prior knowledge it is probably not possible to be certain which data are essential to the interpretation and which are not essential. Early data should therefore be interrogated to identify useful datasets and eradicate superfluous data. The additional effort and costs of collecting potentially superfluous data, for example by undertaking analysis for substances that may not be used in the SDM, need to be considered against:

• The cost of obtaining samples in the first place;
• The difficulty of obtaining additional samples; and
• The potential future costs should the analysis be required at a later date, which might involve return visits to obtain additional samples, or in the extreme case, require an additional borehole compared to the cost of analysis that might not be used.

For the simpler measurements, the analytical costs are likely to be small in the context of the overall investigation and therefore it is sensible to consider a broad range of analysis where sample size permits.

6.1.4 Approach to Interpretation

Although the overall approach to hydrochemical interpretation and modelling in the different host rocks can be described in similar terms, in detail the different host rocks require substantially different approaches, as set out below.
Higher Strength Rocks

Interpretation of the hydrochemistry of higher strength rocks has mainly been based on samples of flowing water taken from boreholes, supported by porewater samples. The results of analysis have been used to:

- Identify the main parameters that vary over the investigation area and use these to identify and characterise water types (hydrochemical facies) within the host rock volume;
- Identify potential end-member water types (e.g. recharge) for use in mixing models;
- Use anthropogenic parameters, such as tritium, chlorofluorocarbons (CFCs) and nitrate to identify modern recharge and to determine the depth and locations to which it has penetrated;
- Use graphical and statistical analyses of data for non-reactive solutes, or tracers, and stable isotopes to identify solute sources and groundwater mixing ratios;
- Interpret groundwater isotope data, together with anthropogenic parameters, to derive the water-age at different locations, notably at GDF depth;
- Evaluate the water-age distribution to establish solute travel times in the different parts of the groundwater flow system;
- Interpret and model groundwater mixing and geochemical reactions between water and rock that controlled the evolution of the present-day groundwater compositions and distribution and therefore control the long-term future stability of compositions of groundwater entering the GDF and along solute transport paths leaving the GDF;
- Use non-reactive solutes and stable isotopes to support and test hydrogeological interpretation of groundwater flow paths, to constrain groundwater sources and mixing, and to calibrate a palaeohydrogeological model.

Lower Strength Sedimentary Rocks

In lower strength sedimentary rocks, the interpretation of any flowing groundwater above and below the host rocks was similar to the interpretation of higher strength rocks (water typing etc). However, the interpretation of the host rock has been based on evaluation of porewater. This places some limitations on the interpretation because reliable measurements can only be obtained for a limited number of parameters. Greater reliance has therefore been placed on the use of models to derive calculated parameters and to interpret water age-distribution within the host rock.

For porewater, two principal interpretations are required, as follows:

- Description of in situ hydrogeochemical conditions that will be experienced by the EBS. Data acquisition and interpretative modelling for in situ hydrogeochemical conditions (pH, redox, water-rock buffering, cation distributions in porewater and exchange sites) are dependent on porewater analysis supported by URL experiments. ANDRA and NAGRA have used a hydrochemical modelling methodology that derives an internally-consistent set of parameters for in situ hydrogeochemical conditions. This addresses the technical difficulties of measuring easily-perturbed parameters and delivering a robust dataset;
Use of natural tracer evidence for solute transport mechanism and parameters. A large dataset is needed to characterise the distribution of tracers and to provide adequate input for interpretative modelling that will evaluate it in terms of solute transport mechanism and long-term palaeohydrogeological evolution.

These interpretation modes are independent of each other and each requires a data acquisition and research strategy that is customised for this type of host rock and for the specific site conditions. Specifically, many of the sampling and data acquisition methods and interpretation approaches and tools, which are based on porewater sampling, are distinct from those that would be employed for a higher strength, fractured hard rock environment, based on sampling of flowing water.

The interpretation of porewater profiles using diffusion models was based on analytical solutions for different initial conditions and boundary conditions. However, interpretation can give non-unique matches. In addition, errors in hydrochemical and physical properties data are propagated in the interpretation to give relatively large overall uncertainties. Therefore, sensitivity analysis for model parameters and boundary conditions is essential to assessing uncertainties and producing credible conclusions. It is noted, however, that good fits between measured and modelled porewater profiles for boundary conditions that fit within the plausible range of understanding of the paleohydrogeology at both Bure (ANDRA) and Benken (NAGRA) provide confidence in the approach.

Evaporites

The hydrochemistry of evaporites is limited to flowing horizons above and below the evaporite. The primary function of hydrochemical interpretation for this host rock is to provide supporting lines-of-evidence to the hydrogeological model. It is of note that very little use was made of the hydrochemical interpretation in PA modelling of WIPP.

There are a number of features of interpretation that are unique to evaporites, including:

- The pathway for evaporite movement can be traced using simple indicators, such as total dissolved solids or EC provided that there are no other evaporites in the rock sequence (e.g. Gorleben) but not where overlying strata contain soluble minerals (WIPP);
- Evaporite dissolution is an irreversible process;
- Water that is present within evaporites has generally been found to be immobile and isolated and is therefore of limited interest;
- The general absence of mobile or recoverable water in the host rock means that there will be few, if any samples and therefore no/ limited hydrochemistry to interpret;
- The chemistry of highly mineralised waters requires different geochemical models incorporating Pitzer calculations of activity. However, combining low salinity and high salinity waters in the same model does not currently appear to be possible;
- Density is important in understanding the movement of groundwater in association with evaporates;
- The normative approach to water typing was useful at WIPP.
6.1.5 Lines of Evidence

The hydrochemical interpretation should make use of multiple lines-of-evidence to arrive at conclusions regarding the SDM. For example, the understanding of the water-age distribution should be based on information from radio isotopes, supported by stable isotopes, major ions and by hydrogeological models of groundwater flow. The use of multiple lines-of-evidence is important in providing confidence in the robustness of the interpretation.

When using the lines-of-evidence approach, where contradictory sets of data are identified, the cause of the difference needs to be explored and resolved.

WIPP provides two examples of how contradictory data led to an improved understanding of the descriptive model, as follow:

- Relatively low salinity water was found down hydraulic gradient of more saline water, when the direction of flow indicated that high salinity water should have been present. The discrepancy was attributed to a change in groundwater flow direction in the past; and

- A water level response to recharge was found in waters identified as being relatively old. Early versions of the conceptual model had assumed that, therefore, there was no modern recharge. Following further investigation the water level response was concluded to be due to recharge to overlying aquifers creating a pressure response.

6.1.6 Integration with Other Disciplines

Hydrochemical interpretation and modelling must be integrated with the geological, hydrogeological and biosphere understanding to develop an internally consistent site descriptive model. The integration needs to be maintained throughout site characterisation as the descriptive models are iterated.

6.1.7 Analogue Sites

Analogue sites have been used by ANDRA, NAGRA and NUMO to improve the understanding of the host rock in lower strength sedimentary rocks at locations away from the proposed GDF. Similarly, SKB’s work at Forsmark was built on earlier work at Stripa and Äspö. The benefits of using analogue sites include:

- Minimising disturbance of the host rock around the GDF during characterisation. The use of the Mont Terri analogue site meant that NAGRA’s investigation at Benken could be restricted to 3-D seismic surveys, shallow boreholes and a single deep borehole;

- Ability to develop and test sampling techniques and approaches prior to use at the GDF site;

- Freedom to undertake a range of R&D, including the use of destructive techniques, without the concern of creating potential pathways;

- They are useful in building teams and capabilities and in undertaking collaboration with other programmes.
Whilst analogue sites provide a range of benefits, their use has not been described in the strategic approach provided here.

The implementation and interpretation of both NAGRA and ANDRA, has been dependent on research and methods development carried out at the Mont Terri URL in Switzerland. Much of that experience has now been developed to the point where the methods and models can be regarded as generically applicable to lower strength clay-rich host rock with similar properties to the Opalinus Clay and COx Formation. It is also of note that the similarities between Opalinus Clay and bentonite mean that the model may be extended to a wide range of potential host rocks (possibly most/many lower strength sedimentary rocks). However, different types of lower strength host rock, for example one in which homogeneity, thickness and lateral continuity are not such reliable and dominant features and in which solute transport mechanisms and hydrochemistry are more complex, may require additional research.

6.1.8 Colloids and Microbes

Sampling and analysis for colloids and microbes presents numerous challenges (Golder Associates, 2010) that need to be overcome. Information on the occurrence and nature of colloids and microbes is required for PA and may, therefore, be important. However, the use of these analyses to support hydrochemical interpretation appears to be limited to indicating whether some important, microbially mediated reactions are occurring.

In addition, the work of Golder Associates (2010) concluded, from a review of existing safety assessments, that there were few direct colloids and microbes data inputs to safety analysis. However, they identified several aspects of the understanding of present-day conditions and of the future evolution of a site that could impact the performance of the EBS and the geosphere barrier, including: microbially-mediated corrosion and colloid-facilitated radionuclide transport. These aspects require adequate information and data to support semi-quantitative calculations, scoping models and qualitative lines of argument in an ESC. Golder Associates (2010) also noted that the information requirements and data for colloids and microbes in an undisturbed host rock environment have to be considered in the context that potentially be more significant sources of colloids, microbes and organics may be introduced by construction and operation of a disposal facility, which in turn may influence the impact and significance of data uncertainties in the ESC.

Work on colloids and microbes in evaporite host rocks was not reported in the references considered for this review, suggesting that they are unimportant. The presence and role of colloids and microbes in lower strength sedimentary rocks also appears to be the subject of debate.

6.1.9 Collaboration

Collaboration between organisations working in similar host media is common, particularly when undertaking R&D, for example, the Mont-Terri URL is being used by several research groups to research techniques for interpreting hydrochemical data from lower strength sedimentary rocks and NAGRA, Posiva and SKB have worked collaboratively to develop methodologies for crystalline rocks.

In crystalline rocks, examples of interpretive approaches that have resulted from research collaboration between programmes include SKBs M3 multivariate statistical model, Posiva’s Chemmac method of measuring in-situ Eh
and a modelling approach to determine redox speciation where direct sampling is difficult. In lower-strength rocks, ANDRA and NAGRA have developed a geochemical modelling methodology for estimating *in situ* hydrogeochemical conditions that addresses the technical difficulties of measuring easily-perturbed parameters and delivers a consistent set of porewater estimates. Hydrochemical interpretation of porewater in the Opalinus Clay (NAGRA) was assisted with the discovery that the Opalinus Clay has very similar properties to bentonite, the properties of which are described extensively in academic and commercial literature.

However, it is also important to recognise that approaches developed for one site may not be applicable to another site, even if the host rock is similar. Whilst the ANDRA/NAGRA approach developed at the Mont Terri URL might be appropriate for the Opalinus Clay and lower strength sedimentary rocks within similar geological settings with comparable mineralogical characteristics, the approach should not be considered generic for lower-strength rocks without further demonstration.

Data from other investigations also provide important information on achievable measurement and modelling precision, which may assist in the setting of initial information requirements before site investigation.

### 6.1.10 Programme

Most of the case studies have taken place over extended periods, particularly if work at analogue sites and development work at other sites are included. The extended programme has permitted time for interpretation between investigation campaigns. In contrast, the Nirex site investigation and PA were completed in a short period (under 10 years). In terms of the hydrochemistry, the work appears to have been successful because the conceptual model developed at the outset of the programme was comprehensive (see Chaplow, 1996 and other papers within the same journal volume). The initial stages of site investigation were therefore carefully planned and had clear objectives. However, the short programme imposed constraints, notably the limited opportunity for later phases of site investigation to be informed by the understanding developed in preceding phases.

### 6.1.11 Reporting

The production of comprehensive reports at each stage of investigation (as done by SKB) provides substantial benefits as it allows for peer review, which is essential to ensuring the confidence of stakeholders. Stakeholder confidence is particularly important in the UK because of the volunteer approach to siting of a GDF. It also permits integration with other disciplines. However, it can also be laborious, resource intensive and may slow down the investigation and interpretation.

A balance, therefore, needs to be sought to ensure sufficient reporting to enable peer-review and integration without it becoming excessively onerous.
6.2 Site Specific Factors

This section addresses factors of hydrochemistry that can show significant variation between sites. It must be recognised, however, that many aspects of hydrochemistry (and other disciplines) are inherently variable over space. As a result, site characterisation will always be required to define a site’s hydrochemistry.

Site-specific factors identified here are those that might not always be anticipated at the design stage of a site characterisation programme. This section is therefore presented as a check list of such factors that may need consideration within the interpretation and modelling of hydrochemistry. The purpose of the checklist is to ensure that site-specific factors are considered in the design of site characterisation investigations and in subsequent interpretation.

Further work may be required to investigate the approach to dealing with site-specific factors in site characterisation and in interpretation and modelling.

Many of the site-specific factors identified have overlap with other disciplines, notably geology and hydrogeology. It is therefore likely that they will also be identified within those disciplines.

Table 6.1 Site Specific Factors

<table>
<thead>
<tr>
<th>Site-Specific Factor Potentially affecting Hydrochemistry</th>
<th>Detail</th>
<th>Area Affected</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geology and mineralogy</td>
<td>Minerals present</td>
<td>Water rock interaction</td>
</tr>
<tr>
<td></td>
<td>Accessibility of minerals</td>
<td>Water rock interaction</td>
</tr>
<tr>
<td></td>
<td>Soluble substances</td>
<td>Water rock interaction</td>
</tr>
<tr>
<td></td>
<td>Recent precipitates</td>
<td>Water rock interaction</td>
</tr>
<tr>
<td></td>
<td>Analogues for radionuclides</td>
<td>Water rock interaction</td>
</tr>
<tr>
<td></td>
<td>Sorption properties of minerals</td>
<td>Water rock interaction</td>
</tr>
<tr>
<td></td>
<td>Presence of soluble minerals</td>
<td>Groundwater density. Dissolution of evaporites will result in more dense (saline) groundwater</td>
</tr>
<tr>
<td></td>
<td>Groundwater salinity</td>
<td></td>
</tr>
<tr>
<td>Location</td>
<td>Proximity to coast</td>
<td>Composition of recharge. Coastal rainwater generally has a marine signature compared to rainfall further from the coast.</td>
</tr>
<tr>
<td></td>
<td>Depth to saline water under present day conditions.</td>
<td></td>
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<tr>
<td></td>
<td>Recent coastal regression (presence of marine water)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Latitude and altitude</td>
<td>Location relative to past glaciation</td>
</tr>
<tr>
<td>Site-Specific Factor Potentially affecting Hydrochemistry</td>
<td>Detail</td>
<td>Area Affected</td>
</tr>
<tr>
<td>----------------------------------------------------------</td>
<td>--------</td>
<td>--------------</td>
</tr>
<tr>
<td>Climate (present day and historic)</td>
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<td></td>
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<tr>
<td>Recharge rates/changes of sea level</td>
<td>High recharge potentially more diluting, changes of sea level may change the salt content in bedrock</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Topography</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Recharge and discharge locations</td>
<td>Steep slopes less likely to have recharge – so more variation in recharge</td>
<td></td>
</tr>
<tr>
<td>Elevation</td>
<td>More elevated ground can create driving heads for deeper groundwater flow.</td>
<td></td>
</tr>
<tr>
<td>Human activity</td>
<td></td>
<td></td>
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<tr>
<td>Presence of nutrients</td>
<td>Nitrate, organic substances</td>
<td></td>
</tr>
<tr>
<td>Persistent organic compounds</td>
<td>Evidence of modern recharge</td>
<td></td>
</tr>
<tr>
<td>Anthropogenic Influences</td>
<td></td>
<td></td>
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<tr>
<td>Mining</td>
<td>Oxidation of sulphide minerals</td>
<td></td>
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<tr>
<td></td>
<td>Increased dissolution due to weathering of exposed minerals</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Connections between aquifers resulting in mixing of water types</td>
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<tr>
<td>Groundwater pumping</td>
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<td></td>
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<tr>
<td></td>
<td>Pumping effects on groundwater flow direction and moved zone boundaries, creating new water composition when mixing groundwater</td>
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<tr>
<td>Thermal gradients</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Increased thermal gradients</td>
<td>Reaction rates</td>
<td></td>
</tr>
</tbody>
</table>
7. Hydrochemistry in Other Sectors

7.1 Sectors Reviewed

Approaches to hydrochemical interpretation and modelling in the following sectors were identified by RWMD as being potentially of relevance:

- Geothermal energy;
- Oil and gas, including oil shales;
- Carbon capture and storage (CCS), also known as CO₂ sequestration;
- Mineral exploration;
- Water resources.

The first four of these sectors make use of deep boreholes for exploration and production and therefore have some similar requirements to site characterisation for a GDF.

In addition, consideration has been given to studies in the following sectors, where use is made of hydrochemistry to aid interpretation:

- Marine studies;
- Surface water chemistry.

The general uses of hydrochemistry in these areas are compared to those used in site characterisation for GDFs in Table 7.1.

The uses of hydrochemistry in these disciplines are as follows:

- Oil and gas and oil shale exploration use hydrochemistry as an aid to prospecting. The primary goal of analysis is to identify the presence of hydrocarbons through, for example, analysis of gases;
- Geothermal energy extracts heat from depth for use in power generation through the injection (if required), heating and recovery of hot water. The primary focus of geothermal investigations is in determining whether there is a sufficient source of heat and sufficient transmissivity to extract that heat. The primary hydrochemical interests are in providing an understanding of the source of heat in terms of its temperature (and hence resource potential); the source of water; and the impact of any added water on the original flow porosity;
- CCS involves injection of large quantities of CO₂ into deep formations, including exhausted oil and gas fields and deep saline aquifers. The two main concerns from a hydrochemical perspective are: the effect of upward migration of CO₂ on shallow groundwater; and the displacement of large quantities of formation water by the injected CO₂ (Lemieux, 2011). The presence of CO₂ in shallow groundwater
can lower the pH of groundwater leading to mobilisation of metals (e.g. As and Pb). Mobilisation of brines can also adversely affect shallower groundwater quality;

- Mineral exploration uses hydrochemistry as an aid to prospecting;
- Water resources uses hydrochemistry primarily to evaluate the age of groundwater to determine whether abstracted groundwater is modern recharge or older (fossil) water and hence to determine whether water use is sustainable. Hydrochemistry is also used to evaluate sources and fluxes of diffusion pollution from agriculture (e.g. nitrate). Regional groundwater resource models make use of hydrochemistry at the conceptual model stage.

The focus of this review has been on looking for alternative approaches to those used in the radioactive waste disposal programmes or potentially interesting developments.

### 7.2 Interpretation

#### 7.2.1 General Water Chemistry

Interpretations of major determinands are typically very similar across all disciplines. Minor and trace determinands for which there are no relevant solubility controls have long been used to indicate relative age, their build-up in solution resulting from incongruent dissolution of the phases in which they occur as impurities (e.g. Edmunds and Smedley, 2000), and further quantification may prove useful. Minor and trace elements may also be used for end-member mixing analysis by assuming conservative behaviour (Barthold et al., 2011). In water management studies, this technique has been used to identify and quantify mixing between groundwater and surface water (e.g. Ladouche et al., 2001 used Si, Ba and U). Recent work to describe the baseline hydrochemistry of fresh groundwater bodies in the UK (Shand et al., 2007) provides a useful reference data set for minor and trace elements in British groundwater, which may be of value when applying minor and trace elements in site characterisation.

The rare earth elements (REEs) are of interest in radioactive waste disposal as analogues for transuranic elements (e.g. Menager et al., 1992). There has been a considerable amount of work undertaken in recent years on both field and laboratory investigations of the behaviour of the REEs, in the context of mining, geothermal, marine, surface water, and regional groundwater studies (e.g. Willis and Johannesson, 2011; Johannesson and Burdige, 2007; Xiong, 2011; Cetiner et al., 2005; Peiffer et al., 2011). As a result there is a greater understanding of the behaviour of REEs in aqueous environments that, in the long run, should improve the security of interpretations of sources, and therefore flow pathways. REE isotope ratios offer further opportunities to constrain process interpretations (see below).


7.2.2 Stable Isotopes

All disciplines commonly use a range of stable and unstable isotopes to determine source, estimate residence time, and deduce reaction pathways (Kazemi et al., 2006).

The isotopes $^2$H, $^{18}$O, and $^{13}$C are often used in many of the sectors (e.g. Taran et al., 2008 (geothermal); Tan et al., 2011 (oil field brines)) to assist in the understanding of groundwater age and origin. The use of Sr isotopes ($^{87}$Sr and $^{86}$Sr) is commonplace in studies of both fresh and saline groundwater (McNutt, 2000). The use of these isotopes can improve the resolution of $^{14}$C age dating by identifying carbonate sources in aquifers (Bishop and Lloyd, 1990). Stable Sr isotopes are also used for mineral exploration (e.g. Piqué et al., 2008) and geothermal investigations (Peiffer et al., 2011).

The isotopes $^{34}$S and $^{18}$O$_{SO_4}$, ($^{18}$O within sulphate) together with $^{15}$N$_{NO_3}$ and $^{18}$O$_{NO_3}$ have been widely used in shallow systems both in the UK (e.g. Fukada et al., 2004; Bottrell et al., 2008) and internationally (see Kendall and McDonnell, 1988). They are tracers of sulphur and nitrate sources, particularly anthropogenic sources of N, as well indicators of redox processes. They have also been used in deeper systems (e.g. the geothermal system of Dotsika et al., 2010) to identify sulphur sources and to track reaction pathways. Although sulphur isotopes have been used in site investigation for radioactive waste disposal, nitrogen isotopes have not been commonly applied in this context.

Boron isotopes ($^{11}$B/$^{10}$B) have been used to identify groundwater sources and distinguish between flow systems (e.g. Williams et al., 2001 (oilfield); Wu et al., 2011 (submarine hydrothermal)), and can also indicate reaction pathways (Alexander et al 2011). In water resources studies, $\delta^{11}$B has been applied as a tracer of anthropogenic contamination (e.g. Vengosh et al., 1994).

Transition metal stable isotope variations have been found to be large enough to be measured and may be of use in determining solute sources and geochemical processes. Species of interest include $^{56}$Fe, $^{65}$Cu and $^{66}$Zn. The geochemistry and applications of transition metal isotopes are areas of ongoing research (e.g. Welch et al. (2003); Kiczka et al. (2010); Zhu et al. (2000), Marechal and Albarede (2002); Mathur et al. (2005), and Maher et al. (2011)). Applications have been focussed on the marine environment, where the sensitivity of Fe, Zn and Cu isotopes to sorption, redox and biogeochemical processes is being investigated (e.g. Rouxel et al., 2008). There is also application of transition metal isotopes in mineral prospecting (e.g. Mathur et al., 2005 used $^{56}$Cu in an investigation of a porphyry copper deposit). Chen et al. (2008) and Borrok et al. (2009) describe applications of Fe and Zn isotopes sediment and solute sources in surface waters but transition metal isotopes are not widely applied in water resources.

A few studies have been undertaken on stable isotopes of Ca and Li. Variations in $^{44}$Ca generally appear to be small in minerals, including biotic precipitates, though slightly greater (up to 4 per mille) in soils and this seems to be connected with root processes (Holmden and Bélanger, 2010). Though ion exchange may cause some fractionation, Holmden and Bélanger (2009) suggest that concentrations will often be conservative below the soil zone. $^7$Li may prove useful for determining solute sources, especially as lithium is generally mobile, though it may be prone to preferential uptake of $^6$Li during clay authigenesis (Witherow et al., 2010). A little work has been
undertaken on $^{30}$Si in groundwater (presumably as a means of helping to correct for Si reactions in $^{32}$Si dating), including in studies of silicate reactions (Georg et al. 2009).

The determination of the isotopic composition of REEs (e.g. $^{143}$Nd/$^{144}$Nd) can increase their usefulness in identifying solute sources and therefore flow pathways. As with Sr isotopes, the interpretative value of solute isotope ratios is greatly increased by conjunctive measurement of the same isotope ratios in minerals. Most use appears to have been in fluvial and marine studies, particularly related to oceanic trace element loading/sources, mixing of water bodies, and the investigation of reaction pathways (Amakawa et al., 1996; Tricca et al., 1999; Johannesson and Burdige, 2007).

The stable isotopes of conservative elements such Br and Cl are often applied in both shallow and deep groundwater studies. $^{37}$Cl and $^{81}$Br provide a means of identifying solute sources, especially of brines (e.g. Davis et al., 2001; Eggenkamp and Coleman, 2000; 2009). Mazurek et al. (2011) discuss the use of $^{37}$Cl in comparison with $^2$H$_{2}O$ and $^{18}$O$_{2}O$ and other data in the context of interpreting diffusion-controlled solute distributions in mudrocks. $\delta^{37}$Cl has also been applied as a tracer of diffusion from mudrocks into aquifers with groundwater residence times of order 400 ka (Lehman et al., 2003a). Variations in $^{81}$Br and $^{37}$Cl in groundwater to depths of 4 km in shield areas that look potentially useful for determining sources and processes have been reported (Shouakar-Stash et al, 2007) and Stotler et al, 2010), but these studies were not able to resolve the causes for the variations observed.

Noble gas isotopes ($^{81}$Kr and $^{36}$Cl) have been used to estimate groundwater age for waters in excess of one million years old (Sturchio et al, 2004).

### 7.2.3 Stable Gaseous Tracers

The use of gaseous tracers in groundwater investigations is becoming more prevalent in both shallow and deep groundwater. He and the other stable noble gases are commonly used as indicators of groundwater residence time and recharge conditions respectively. Over the past 10 years, there has been significant development in the interpretation and modelling of noble gas concentrations in groundwater through the measurement of noble gas stable isotope ratio, which has improved the resolution of the interpretation (Aeschbach-Hertig et al., 1999; Peeters et al., 2003). The degree of supersaturation of dissolved noble gases (‘Excess Air’) has been shown to be useful in differentiating different water bodies (e.g. Ingram et al., 2007; Osenbrück et al., 2009). Anthropogenic gaseous tracers such as CFCs and SF$_6$ are becoming more commonly applied in water resources investigations as indicators of groundwater age and flow pattern (e.g. Gooddy et al, 2006; Busenberg and Plummer, 2008) although, like $^3$H, these tracers are applicable only in modern groundwater.

In deeper groundwater, the build up of $^4$He in porewater is relatively frequently used for estimating age in oilfields (e.g. Tan et al. 2011) and around underground gas storage caverns (e.g. Lee et al. 2011). $^3$He/$^4$He ratios are often used to distinguish between crustal and mantle sources of He in geothermal investigations (e.g. Fourré et al., 2011; Banerjee et al., 2011). Significant use has also been made of a range of noble gas isotope ratios in the investigations of deep mine waters in South Africa that have revealed deep abiotic hydrocarbon gases, ~3km deep microbial communities, and 2 billion year old fluid components (Lippmann et al., 2003; 2011).
7.2.4 Environmental Radioactive Isotopes

Groundwater age dating is an area of ongoing hydrochemical research. A range of commonly applied techniques are described by Loosli et al. (2001), many of which have been introduced in the case studies in Sections 3 to 5 (e.g. the use of $^3$H, $^4$He $^{14}$C and $^{36}$Cl). Radioisotopes and their decay products are commonly used tracers for groundwater age dating but other methods using hydraulic and geochemical modelling, climate analogues and trace element accumulation have also been used to date groundwater.

There are several methods for dating young groundwater that are commonly applied in water resources and contamination clean-up investigations. $^3$He/$^4$He dating is widely applied to dating groundwater up to 100 years old (Solomon and Cook, 2000, Murphy et al., 2011). Short-lived noble gas isotopes such as $^{19}$Ar and $^{85}$Kr have been used to date groundwater that had apparent ages of 100s and 10s of years respectively (e.g. Ekwurzel et al., 1994; Sidle, 2006). Some work has been undertaken using $^{32}$Si, an isotope that would allow dating to about 1000 years, but a major problem is accounting for exchange with solid phases (Fifield and Morgenstern, 2009) and the half life appears to be poorly known.

Very old groundwater requires different tracers. For example, $^{129}$I has been used for very old systems due to its very long half life of 15.7 Ma (Moran et al, 1995. It has also been in the Stripa and Milk River systems (Fabryka-Martin et al., 1989; 1991). $^{81}$Kr has been used (Collon et al, 2000) to date groundwater up to 40 000 years old and $^{85}$Kr analysis of shallow groundwater has been used to identify waters up to a few decades old (Sidle, 2006). The use of $^{36}$Cl in dating has been applied for some time in groundwater investigations (e.g. Davis et al., 1998; also see the case studies in Section 3). However, problems with estimating the initial concentrations and other issues have not been completely resolved, but some useful interpretation is possible as shown by for example Lehmann et al. (2003b), Genereux et al. (2009), and Kulongoski et al. (2008), the former using $^{81}$Kr and $^4$He as constraints to obtain age.

Ra and other U and Th series isotopes have been used in several submarine groundwater discharge studies to locate the groundwater fluxes rather than to determine age directly (e.g. Charette et al., 2003; Breier and Edmonds, 2007). Similarly, radon, particularly the $^{222}$Rn isotope (half life 3.8 days), is not used so much for water dating but rather as a tracer of groundwater-surface water interaction as groundwater typically has a much high $^{222}$Rn abundance than surface water (e.g. Cook et al., 2003).

All the methods listed in this section have advantages and disadvantages, but use of multiple isotope tracers (e.g. $^{81}$Kr, $^{36}$Cl, $^4$He along with $^{238}$U/$^{230}$Th/$^{226}$Ra) is most likely to provide unique ages of the system.

7.2.5 Geochemistry

Geochemical analysis of rock and mineral samples is vital to constrain interpretation of hydrochemistry. Apart from the usual geochemical analysis of aquifer material, sampling and interpretation of fluid deposits, e.g. vein materials, including fluid inclusions, have been an active area of research in several disciplines over the last decade or so (Blyth et al., 2009). For example, Richard et al. (2011) used fluid inclusion analysis of Cl, Br, and $^{37}$Cl to deduce the origins of ore-forming brines in U deposits in the Athabasca Basin of Canada. Other examples include Heijlen et al. (2008) (mineralizing fluids); Derome et al. (2005) (U deposits from brines); Kendrick et al. (2011)
(inert gas isotopic ratios to interpret metamorphic fluid compositions). However, many fluid inclusions may be of ages beyond that relevant to site characterisation.

### 7.2.6 Aqueous Models and (Reactive) Solute Transport Models

Models commonly applied in the field of site investigation for radioactive waste disposal are also applied in other sectors. PHREEQC and TOUGHREACT are widely cited in water resources and CCS investigations (e.g. Cantucci et al., 2009; Belkhiri et al., 2010; Lemieux, 2011) though a range of other solute transport other models have been used (see Johnson et al., 2004 and Zheng et al., 2008). As in the nuclear sector, challenges encountered during modelling mainly relate to the availability of reliable geochemical and thermodynamic databases and the approaches underlying them (Birkle et al., 2009; Lemieux, 2011). There is, therefore, value in developing unique databases, as done at Benken (Wersin and Schwyn, 2004).

The use of kinetic models is still comparatively rare, but they have been used for CCS (Cantucci et al., 2009).

Over the last few years an increasing number of studies have attempted to model the movements of groundwater solutes through aquifer systems, comparing the results against field sample analyses (e.g. Plummer et al., 2004; Bester et al., 2006; Trowsdale and Lerner, 2007; Howard and Maier, 2007; Michael and Voss, 2008; Furlong et al., 2011). In doing this, it has become apparent that local-scale movement and dispersion of solutes, including both in the aquifer and during sampling, have to be taken into account in some detail and with some care (e.g. Goode, 1996; Zhao et al., 1998; Varni and Carrera, 1998; Bethke and Johnson, 2002; Weissmann et al., 2002; Jones et al., 2006). Bethke and Johnson (2008) summarise some of the issues.

It is of note, however, that many of the case study sites show strong evidence for deep groundwater stability.

### 7.2.7 Geothermometry

Hydrochemical geothermometers use the composition and temperature of water to estimate reservoir temperatures at depth using temperature-dependent water-rock equilibria. Geothermometry has been developed for a number of mineral systems, including quartz, chalcedony, albite, microcline, calcite, muscovite and paragonite.

Geothermometry methods were first developed in the 1970s and continue to be investigated and refined (Verma and Santoyo, 1997; Can, 2002; Levet et al., 2006; Ferguson et al., 2009) to make use additional minerals and to use modelling to aid interpretation. Recent applications include for oil field brines (Birkle et al., 2009) and for geothermal energy (Han et al., 2010 and Dotsika et al, 2010).

### 7.2.8 Methods of Sample Classification and Statistical Analysis

Over the past 20 years, techniques for classifying groundwater samples based on suites of measured parameters have developed beyond standard empirical techniques such as Piper/ Durov plots and major ion water types. In water resources, the concept of hydrochemical facies is widely used (e.g. Krothe and Bergeron, 1981) and has been further developed into more quantitative classification systems that are widely applicable to shallow groundwater
environments (e.g. Stuyfzand, 1999). Increasingly, multivariate statistical techniques (such as cluster analysis, Q-mode factor analysis and PCA) are being applied to classify groundwater (e.g. Suk and Lee, 1999) and explore complex data sets, such as trace element abundances (Chen et al., 2007). Multivariate statistics have already been applied during site characterisation (see Sections 3-5) but the application and interpretation of the results is developing, mainly through water resources and water quality/pollution clean-up applications. More advanced data mining techniques, including statistical and artificial intelligence methods designed to identify patterns within (often) large data sets, have been applied to shallow groundwater quality investigations by a few researchers (e.g. Peeters et al. 2007 and Lischeid, 2009) and may have application to site characterisation.

7.3 Summary Findings

In the sectors identified in Section 7.1 groundwater chemistry is used for furthering understanding of the dominant groundwater processes: this often includes determining flow pathways, residence times, palaeoenvironmental conditions, and reaction pathways. In addition, some use is made of chemistry for looking at operational issues, especially interaction with engineering structures. It is also apparent that most hydrochemical investigations, irrespective of sector, have included analysis for a range of major ions and often a range of minor and trace determinands.

Some recent work on geothermal investigation has included less commonly analysed elements including Tl, Hf, Ta, Nb, Ga, In, and Ge (e.g. Peiffer et al., 2011), and, though these have yet to demonstrate major insights, this may change as analytical techniques and understanding of aqueous geochemistry are developed, and this is an active research area (e.g. Wood and Samson, 2006; Xiong, 2009).

Gas compositions are commonly analyzed for in CCS, geothermal, volcanic, and earthquake studies, especially in the context of release to ground surface (e.g. Beaubien et al., 2008; Gal et al., 2011). Gases typically include CO$_2$, Rn, and He.

As in radioactive waste management, isotopes (stable and non-stable) have also been used extensively in research as an aid to the dating of groundwater.

Overall, no major new approaches not already used in radioactive waste disposal were identified by the review; all of the disciplines are tackling the problems of investigating groundwater and solute processes. Information requirements for each discipline are similar as are interpretation and modelling approaches.

To date, little field scale work has been undertaken for CCS and work reported to date has been generally been confined to laboratory and modelling studies (Lemieux, 2011). According to Lemieux (2011) the fieldwork that has been undertaken has demonstrated that field-scale processes are significantly more complex than those observed in models and laboratory experiments.

It is also apparent that the requirements of CCS and site characterisation for a GDF are most similar, but GDF site characterisation is significantly more mature and it is therefore likely that information flows will be from radioactive waste research to CCS rather than the other way. However, the additional research required may identify new areas of interest.
Finally, data mining may have some uses in identifying trends and patterns in large datasets.
8. **Proposed Strategic Approach**

8.1 **Introduction**

A strategic approach to the interpretation and modelling of hydrochemistry for site characterisation is proposed in this Section. The strategic approach set out here has been informed by RWMD’s Proposed Strategy for the Geoscientific Aspects of Site Characterisation (NDA, 2011a); by the Geological Disposal: Site Characterisation for a Geological Disposal Facility (NDA 2011b), which sets out information requirements and the range of activities that could be necessary to adequately characterise a site for a GDF in the UK; by earlier work on a geochemistry strategy (Intellisci, 2008); and by information gathered in undertaking the current project. RWMD’s overarching strategy (NDA, 2011b) has been taken as illustrative for the purposes of informing the strategic approach here. The final approach to site characterisation will depend upon the host rock selected; the environmental setting; the proposed GDF depth and design; the proposed storage concept; and the extent to which the proposed site has undergone previous investigation and characterisation. Further development of the strategic approach is likely to be required following site selection.

The three geological host rock environments that represent the generic options for siting of a GDF (NDA 2011b), are as follows:

- **Higher strength rocks** - these would typically comprise crystalline igneous and metamorphic rocks or geologically older sedimentary rocks where any fluid movement is predominantly through discontinuities (e.g. fractures);

- **Lower strength sedimentary rocks** - these would typically comprise geologically younger sedimentary rocks where any fluid movement is predominantly through the rock matrix; and

- **Evaporites** - these would typically comprise anhydrite (anhydrous calcium sulphate), halite (rock salt) or other evaporites that result from the evaporation of water from water bodies containing dissolved salts.

The strategy set out here provides a general framework for hydrochemical interpretation and modelling for a base case of higher strength rocks, but also identifies specific requirements for the other generic potential host rocks (lower strength sedimentary rocks and evaporites).

Hydrochemical interpretation will commence at an early stage in site characterisation and will be iterated as more information becomes available. Early data collection is important and baseline data need to be collected before the geological and hydrochemical systems are perturbed by investigations. Iterations in the interpretation should be used to inform further data acquisition that will most effectively test the suitability of the model and improve understanding of geosphere features and processes.

The strategic approach to hydrochemistry interpretation and modelling will need to be integrated with other site characterisation activities, notably: geophysics, hydrogeology and solute transport properties and modelling, biosphere characterisation, and in the identification of research needs.
The principal outcome of hydrochemical interpretation and modelling for site characterisation will be a hydrochemistry SDM. The principal objective of the SDM will be to meet the information requirements of end users. However, it will also be important to make it accessible, as far as it is possible to do so, to stakeholders. To this end, the presentation of the SDM requires careful consideration and it should include illustrations, schematic diagrams and even animation to illustrate patterns, areal and vertical distributions and changes over time.

The focus of the hydrochemical SDM should be to:

- Present the understanding of present-day undisturbed hydrochemical conditions in the host rock at, above and below GDF depth. In detail this will include:
  - Baseline hydrochemistry, including the distribution and values of safety-relevant parameters and any hazardous or anomalous geochemical conditions;
  - The water-age distribution;
  - The concentrations and fluxes of natural analogue solutes and mobile species (colloids, microbes, gases) at all depths from the host rock to the biosphere;

- Provide an understanding of how these conditions have been arrived at using:
  - Interpretation and modelling of groundwater mixing;
  - Evaluation of water-rock interaction and geochemical/isotopic compositions of secondary minerals to inform the understanding of palaeohydrochemistry and palaeohydrogeology.

The SDM should also contribute to the hydrological model for shallow groundwater and interactions with surface waters, including characterisation of the geosphere-biosphere interface zone (GBIZ) and should provide sufficient information to permit prediction of future changes.

8.2 Overview

8.2.1 Hydrochemical Interpretation for Site Characterisation

The main tasks in the interpretation and modelling of hydrochemistry for flowing groundwater (higher strength host rocks and aquifers above and below the host rock for evaporites and lower strength sedimentary rocks) are:

- Identify the main parameters that vary over the investigation area and use these to identify and characterise water types (hydrochemical facies). Water types should also be assigned domains within the rock volume under investigation;
- Identify potential end-member water types (e.g. recharge) for use in mixing models;
- Use anthropogenic parameters, such as tritium, chlorofluorocarbons (CFCs) and nitrate to identify modern recharge and to determine the depth to which it has penetrated and domains where it has penetrated;
• Use graphical and statistical analyses of data for non-reactive solutes, or tracers, (e.g. chloride) and stable isotopes (e.g. $^{18}$O/$^{16}$O) to resolve solute sources and groundwater mixing ratios;

• Interpret groundwater isotope data (e.g. $^{18}$O/$^{16}$O, $^{14}$C, $^{3}$H, $^{36}$Cl, $^{4}$He), together with anthropogenic parameters, to derive the water-age at different locations;

• Use the water-age distribution to establish solute travel times in the different parts of the groundwater flow system. The interpretation of isotopes will require supporting geochemical and isotopic data for water samples and rocks, i.e. $^{13}$C/$^{12}$C, U and Th contents, estimates of natural neutron fluxes and the in situ rate of production of isotopes;

• Interpret and model (where necessary) groundwater mixing and geochemical reactions between water and rock that controlled the evolution of the present-day groundwater compositions and distribution and therefore control the long-term future stability of compositions of groundwater entering the GDF and along solute transport paths leaving the GDF. This is the field of palaeohydrogeology;

• Use non-reactive solutes and isotopes (chloride, $^{18}$O/$^{16}$O, $^{4}$He) to support and test hydrogeological interpretation of groundwater flow paths, to constrain groundwater sources and mixing, and to calibrate a palaeohydrogeological model.

Hydrochemical sampling techniques have previously been described in Quintessa (2008) and are not covered here. However, it is important that the limitations of sampling are understood when considering the interpretation of hydrochemical data.

The information requirements should be reassessed before the start of each stage of characterisation, based on review and interpretation of data collected to date and on the identification of remaining uncertainties. Preliminary interpretations should be supported by interim (scoping) calculations.

8.2.2 Information Requirements from Hydrochemistry

Investigations for a GDF will be based on the need-driven information requirements an initial consideration of which is presented by RWMD in its Status Report (NDA, 2011b). In relation to interpretation and modelling of hydrochemistry, the status report sets out the information requirements for the descriptive hydrochemistry model as follows:

"The purpose of the model is to describe the chemistry of the groundwater system, and specifically the chemical environment in which the disposal facility would be located. The descriptive hydrochemistry model is a necessary input to the Environmental Safety Case (ESC) and to the design of the facility to be developed. Of particular importance is the demonstration that groundwater flow in the host formation is relatively stagnant and that groundwater at the GDF is not well-connected with the more active near-surface groundwater flow regime.

The acquisition and interpretation of hydrochemical data will contribute towards the development of a number of the other descriptive, discipline-based models and to the general understanding of the GDF. These models will integrate hydrochemical information with other site characterisation datasets and generic process models for the Engineered Barrier System (EBS), geosphere and biosphere. These key users of hydrochemical information and their information requirements are set out in Table 2.1."
Additionally hydrochemical interpretation and modelling may be required within the SDM to meet the following end user requirements:

- Identification of reference water composition(s);
- Interpretation of the redox conditions and biogeochemical processes at GDF depth to obtain a model of redox that will be applicable to performance of the EBS and to speciation of redox-sensitive radionuclides;
- Geochemical modelling to interpret the state of redox equilibrium between Eh measurements and redox-sensitive solutes (Fe, S) and to understand the reduction-oxidation processes (sulphate reduction, methane-CO₂ equilibria, Fe(II)-Fe(III) equilibria) in groundwater at GDF depth. It should be noted that the sampling process is likely to disturb the system and this must be taken into account in the modelling (this also applies to the next point);
- Geochemical modelling of pH and carbonate system and of buffering processes at GDF depth;
- Using the water-age distribution to test the hydrodynamic groundwater travel times;
- An assessment of sorption and reversibility of solutes on to natural colloids;
- Interpretation of evidence from natural systems for solute retention processes i.e. sorption, matrix diffusion because these processes are the primary mechanisms for retarding transport of radionuclides; and
- Interpretation of microbial population data and development of an understanding of microbologically-mediated chemical conditions especially with respect to redox.

8.3 The Characterisation Strategy

8.3.1 Overview

A characterisation strategy is set out in (NDA 2011a), which consist of the following stages:

- Stage 0 Investigations: Desk Based Studies for Site Selection;
- Stage 1.1 Investigations. Regional geophysics, geological mapping and other non-invasive surveys;
- Stage 1.2 Investigations. First campaign of deep drilling plus further regional surveys;
- Stage 2.1 Investigations. Further deep drilling, further regional surveys, 3-D seismic survey, Quaternary studies, Seismic monitoring network, preliminary geotechnical investigation;
- Stage 2.2 Investigations. Further deep drilling, geotechnical design;
- Stage 2.3 Investigations. Post completion testing in boreholes;
- Stage 2.4 Baseline monitoring.
A number of data freezes are planned at the end of Stages 1.1, 1.2, 2.1, 2.2 and 2.3. Following each data freeze, hydrochemical interpretation would begin.

8.3.2 Planning for Site Characterisation

Data Processing

A data management system will be required at the outset of the process (see Section 6.1.2), which should be designed to accommodate all potential datasets. Data used in interpretation and modelling require processing to provide a quality assured dataset with clear traceability to the data sources and in which the level of uncertainty is quantified.

Data acquired from site characterisation will require processing, which will include:

- Basic checking, QC, etc;
- Downhole monitoring data for pH, Eh, DO and EC – processing and calibrations with dedicated software;
- Correction for drilling fluid contamination;
- Evaluation of error ranges and reproducibility;
- Recalculation of dissolved gas data to in situ;
- Detection of unreliable data;
- Classification of data quality;
- Conversion of porewater analysis results to porewater concentration.

Uncertainties in the data should be identified, characterised and flagged.

Data Requirements

The data required for various aspects of hydrochemical interpretation and modelling are set out in Table 8.1.
### Table 8.1 Hydrochemistry Data Requirements for Interpretation and Modelling

<table>
<thead>
<tr>
<th>Data</th>
<th>Geochemical Model of Redox and Water-rock Reaction</th>
<th>Groundwater Age</th>
<th>Hydrochemical Variability</th>
<th>Baseline Hydrochemistry</th>
<th>Analogue Geochemistry and Natural Fluxes</th>
<th>Past Hydrochemical Conditions and Palaeohydrogeology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundwater</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eh, pH,</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Major ions (Na, Ca, Mg, HCO₃, Cl, SO₄)</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Br</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Redox-active solutes (NH₄/NO₃, SO₄/HS, Fe₃+/Fe²⁺)</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dissolved organic carbon (DOC)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Electrochemical/ thermodynamic data for redox couples</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Radioisotopes §H, §C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>§Cl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Stable isotopes (§O/¹⁶O and §H/¹H)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>§¹⁴C values for extracted DOC if appropriate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>§¹²C/¹³C ratios</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Other trace elements contents (e.g. B) of rock for calculation of natural thermal neutron flux</td>
<td>X</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Microbiological data</td>
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<td>X</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Colloids data</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Dissolved organics</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Data</td>
<td>Geochemical Model of Redox and Water-rock Reaction</td>
<td>Groundwater Age</td>
<td>Hydrochemical Variability</td>
<td>Baseline Hydrochemistry</td>
<td>Analogue Geochemistry and Natural Fluxes</td>
<td>Past Hydrochemical Conditions and Palaeohydrogeology</td>
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<td>----------------</td>
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<td>------------------------</td>
<td>---------------------------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>Natural radionuclides</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Porewater profiles of natural tracers (Cl-, Br-, δ18O, 4He) in lower strength sedimentary rocks</td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Gases</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Redox-active dissolved gases (CH₄/CO₂)</td>
<td>X</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Noble Gases (He, Ne, Ar, Kr, Xe)</td>
<td></td>
<td>X</td>
<td></td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>General dissolved gases (e.g. N₂)</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td><strong>Rock Geochemistry</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U and Th content</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Thermodynamic data for mineral dissolution reactions</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Kinetic data for mineral dissolution reactions</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reactive mineral surface area</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Mineral abundances in host rock</td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Mineral composition</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 8.1 (continued)  Hydrochemistry Data Requirements for Interpretation and Modelling

<table>
<thead>
<tr>
<th>Data</th>
<th>Geochemical Model of Redox and Water-rock Reaction</th>
<th>Groundwater Age</th>
<th>Hydrochemical Variability</th>
<th>Baseline Hydrochemistry</th>
<th>Analogue Geochemistry and Natural Fluxes</th>
<th>Past Hydrochemical Conditions and Palaeohydrogeology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cation exchange capacity,</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exchangeable cations</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cation exchange equilibrium constants.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Petrographic and minerals composition data for secondary minerals</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(calcite, pyrite, iron oxides, clays) in fracture-filling assemblage</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>in higher strength rocks</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>
Interpretation and Modelling Requirements

A number of separate interpretations and or models will be developed and refined as additional data becomes available. The input data required for each of these are set out in Table 8.1 and the approach to interpretation in Table 8.2.

Table 8.2 Modelling Requirements

<table>
<thead>
<tr>
<th>Activity</th>
<th>Interpretation Method</th>
<th>Tools</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geochemical model of redox and water-rock reaction</td>
<td>Establish rigorous quality control criteria for input hydrochemical data, especially for Eh, pH, redox-active solutes and microbial data. Evaluate pH and possibility of perturbation by CO₂ outgassing: assume calcite equilibrium and Ca²⁺ concentration and recalculate pH to <em>in situ</em> conditions. Calculation of electrochemical potential (Eh) for redox couples, assuming both homogeneous and heterogeneous equilibria, at <em>in situ</em> conditions; compare with measured Eh. Comparison of microbial populations and other biogeochemical parameters. Forward and inverse modelling of groundwater compositions to deduce potential water-rock reactions and to interpret hydrogeochemical evolution, studying whether local equilibrium assumption is valid or kinetics of reactions have to be taken into account; investigating hydrochemistry of fracture minerals and matrix minerals; studying effects of rock alteration on hydrochemistry and vice versa.</td>
<td>Geochemical speciation reaction and equilibrium model (e.g. PHREEQC). Thermodynamic database Reaction kinetic parameters Crossplots (e.g. Eh vs pH, microbial populations versus Eh, etc)</td>
</tr>
<tr>
<td>Groundwater ages and solute travel times</td>
<td>Evaluate evidence for recent recharge using ³H (adjusted for radioactive decay and trend of atmospheric ³H over time), NO₃ and organic chemicals Evaluate evidence for deep groundwater age using U decay series and ⁸¹Kr Undertake geochemical modelling of evolution of dissolved inorganic C, using measured HCO₃⁻ and ¹²C/¹³C data and assumed values for initial inputs, also ¹²C/¹³C of calcite in reacting mineral assemblages; calculation of ¹⁴C ages by adjusting for dilution effects. Calculation of in situ production rate of ³⁶Cl by thermal neutron irradiation of ³⁵Cl taking account neutron flux in rock due to U and Th and neutron absorption Calculate ³⁶Cl/Cl ratio for local secular equilibrium and compare with measured ³⁶Cl/Cl Estimate atmospheric ³⁶Cl input and calculate decay age for measured ³⁶Cl. Calculation of <em>in situ</em> production rate for ⁴He due to radioactive decay of U and Th Experimental measurement of efficiency of ⁴He due to radioactive decay of U and Th; Experimental measurement of efficiency of ⁴He loss from rock matrix Modelling of groundwater residence times from <em>in situ</em> ⁴He accumulation, influx from external sources, rate of loss Establish palaeoclimatic dependence of ¹⁸O/¹⁶O and ²H/H; Estimate temperature and altitude coefficients Compare variations of ¹⁸O/¹⁶O and ²H/H with respect to modern precipitation Construct palaeohydrogeological conceptual model.</td>
<td>Geochemical reaction code for modelling, DIC, ¹³C/¹²C and ¹⁴C Spreadsheet calculations for ³⁶Cl and ⁴He including calculation of natural neutron flux and <em>in situ</em> production rate for ³⁶Cl.</td>
</tr>
</tbody>
</table>
Table 8.2 (continued) Modelling Requirements

<table>
<thead>
<tr>
<th>Activity</th>
<th>Interpretation Method</th>
<th>Tools</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrochemical variability, groundwater flow and mixing</td>
<td>Use graphical crossplots, to identify 2- and 3-component mixtures Br versus Cl to identify sources of salinity (Note Br can be reactive under some conditions); also δ¹⁸O versus Cl etc. Use trilinear (Piper) diagrams, Schoeller diagrams etc to identify water types and to illustrate end-member water compositions, mixed groundwater and groundwater evolution pathways Use statistical analysis of hydrochemical and isotopic data to analyse water mixing patterns and to quantify mixtures in terms of proportions of end members. Use coupling of hydrochemical indicators of water sources and mixing with palaeohydrogeological modelling using transient flow and solute transport model Use specific tracers (i.e. Cl-, Br, δ¹⁸O, δ²H) to identify end-member water sources, or use principal components analysis</td>
<td>Spreadsheet and graphical tools Multivariate analysis codes Flow and solute transport with transient boundary compositions (e.g. CONNECTFLOW code)</td>
</tr>
<tr>
<td>Baseline hydrochemistry</td>
<td>Use interpretative methods described above for pH, redox and Eh, groundwater ages, groundwater mixing and hydrochemical variability Use graphical representation of variations and correlations with natural and artefact disturbances of hydrogeological and geochemical conditions</td>
<td>As above</td>
</tr>
<tr>
<td>Analogue geochemistry and natural fluxes</td>
<td>Use expert geochemical interpretation of elemental sources and sinks and mass transfers Use expert interpretation of, for example, U and Sr isotope data as tracers of natural mass transfers</td>
<td>Geochemical speciation and equilibrium code (e.g. PHREEQC) with thermodynamic database for trace elements and source/sink mineral phases.</td>
</tr>
<tr>
<td>Past hydrochemical conditions and palaeohydrogeology</td>
<td>Expert mineralogical and geochemical interpretation of morphology, composition and associated mineralogy. Expert isotope geochemical interpretation of isotopic compositions of mineral growth zones and of correlations with geochemical and trace element variation. Geochemical equilibrium and water-rock reaction modelling of secondary mineral deposition and bedrock alteration Comparison with case studies in the literatures (e.g. EQUIP and PADAMOT research projects for EC/Nirex).</td>
<td></td>
</tr>
</tbody>
</table>

8.3.3 Desk-based Studies for Site Selection

Investigation

The overall objective of this stage is to test the suitability of the identified site as a potential location for a GDF. The range of geoscientific information that will be available at this stage will vary widely dependent upon the site and especially on the extent of existing geophysical survey data and/or existing borehole information.
**Hydrochemical Data and Supporting Information**

For hydrochemistry, sources of data and supporting information are likely to include:

- Hydrogeological and hydrochemistry data from Environment Agency and British Geological Survey (BGS), water company records, local authority private well records, commercial boreholes, topographic maps showing springs and seepages, scientific literature on groundwater and surface waters in the region (water levels, abstraction rates, water quality);

- Geochemical data from BGS;

- Lithological and mineralogical data on relevant rock formations in scientific literature;

- The location of groundwater observations points (wells, boreholes etc.);

- Mapped location of springs, wetlands, streams;

- Existing information on interaction between surface water and groundwater (baseflow);

- Existing data on surface water quality;

- Surface water flows;

- Information from analogue areas (e.g. outcrops of the host strata) and interpretation of analogue geological conditions (investigations in similar host rocks).

**Hydrochemical Interpretation**

Interpretation at this stage is likely to take the form of:

- Construct an initial, desk-based SDM for hydrochemistry, which sets out the understanding of the site in advance of site characterisation. This initial SDM should cover hydrochemistry across the region and with depth. It should also be integrated with an initial hydrogeological SDM. The initial hydrochemistry SDM should be based on previous experience/ expert judgement; topography, expected groundwater circulation patterns, proximity to the coast, conditions in analogue groundwater systems, water-rock reactions and lithological variations. The initial SDM will help plan characterisation and aid later interpretation modelling by providing the basis against which to test hypotheses;

- An initial estimate of the distribution of salinity with depth and laterally;

- An initial assessment of the likely geochemistry and reactivity of rocks and minerals (e.g. evaporites, carbonates, sulphides, organics including hydrocarbons, ore potential) that will affect the composition of groundwater.

**Planning for Later Phases**

The initial interpretation will be used to plan the next stage of development by:
• Providing an expected distribution of groundwater salinity and expected distribution of gamma intensity based on information of U, Th, K distribution in rock formations to inform geophysical surveying;

• Identifying existing groundwater supplies (wells, boreholes, springs) of potential use for access for geophysical logging and sampling;

• Identifying the need for soil sampling where additional detail beyond that in existing geochemical databases is required;

• Aiding the specification of analytical requirements for groundwater and soil samples;

• Identification of targets for sampling of groundwater in existing boreholes and springs;

• Providing initial estimates of redox and pH conditions in groundwater at GDF depth.

8.3.4 Non-invasive Surveys

Investigation

This stage comprises non-invasive work, including regional geophysical surveys and geological mapping. It may include an initial campaign of surface water sampling. The surveys require only a limited hydrochemistry input, linked to hydrogeological mapping of water features. This might include sampling of water flows from large springs, analyses of water samples for pH, major elements, $^{14}$C, $^3$H, stable isotope ratios and sampling of soils at large-scale spacing, analyses for U and other indicator trace elements.

Hydrochemical Data and Supporting Information

Data might include:

• Results of geophysical surveys;

• Geological mapping;

• Hydrogeological mapping;

• Results of surface water sampling analysis;

• Results of soil analysis.

Hydrochemistry Interpretation and Modelling

Limited hydrochemical interpretation will be undertaken at this stage, which could include:

• Interpretation of EM geophysics in terms of variations of salinity variations in groundwater;

• Interpretation of directions of groundwater flows and distribution of groundwater ages;
• Interpretation of airborne gamma radiometry in terms of distribution of natural U-Th in soils and shallow rocks;

• Preliminary model for water-rock reaction and of groundwater compositions in relation to rock lithologies;

• Preliminary model of the hydrochemistry of the biosphere;

• Identification of potential baseline geochemistry issues.

Hydrochemical Outputs

The following information should result from the interpretation:

• Revised assessment of groundwater salinity and age-distribution;

• Prediction of hydrochemistry in preliminary boreholes.

This information will contribute to decisions on locations of preliminary boreholes.

Planning for Later Phases

The principal activity at this early stage is planning for subsequent stages of characterisation.

The following activities linked to hydrochemistry are likely to be required and to require planning:

• Establish methods for groundwater and soil sampling. More detail is provided in Quintessa (2008) and Kunimaru et al (2011). The latter publication has been field-tested and adapted based on feedback from the field team;

• Provide hydrochemical predictions for salinity, redox, pH, and other key parameters at, above and below GDF depth, including estimation of uncertainty ranges) and information about rock geochemistry and mineralogy as inputs to assist in borehole location;

• Contribute to setting targets for surface geophysics (e.g. EM survey for salinity);

• Contribute to setting targets for borehole geophysics and for drillcore sampling for geophysics and geochemical calibration;

• Provide inputs to the specification of deep borehole investigations, including:
  - Tracer(s) to be used in drilling fluid and monitoring requirements for tracer inputs and outputs during drilling;
  - Water samples required during drilling including method and quality criteria;
  - Water samples required from post-drilling hydrogeological testing in boreholes including method and quality criteria;
- Hydrochemical targets for deep boreholes (particularly if any are prioritised for hydrochemistry) in site area;

- Sampling methods and frequency for cores and fracture minerals to be obtained for petrographical and geochemical analysis and for porewater extraction;

- Analytical requirements for monitoring of pH and Eh (field measurements) and major and trace element hydrochemistry, isotopic analyses, dissolved gas analyses (laboratory measurements);

- Contribution to borehole installation design and specification of sampling methods;

- Advice on downhole geophysical logging methods (e.g. resistivity for salinity, gamma for U and Th distribution);

- Porewater extraction methods and analytical requirements for matrix water analyses;

- There will also be a requirement to input into the design of other investigations that may take place, such as shallow boreholes and sampling of precipitation, streams, springs, etc and soil sampling for biosphere data.

8.3.5 Preliminary Deep Drilling Investigation

The first campaign of deep drilling is likely to consist of a number of deep boreholes. Boreholes would be used for a variety of purposes, including sampling and in-situ testing. The purpose of these early boreholes would be to establish the main features of the site that might impact its suitability to host a GDF. Groundwater monitoring instrumentation would be installed in each borehole on completion of drilling.

Hydrochemical Data and Supporting Information

The following data should be available for interpretation at the end this stage:

- Geological borehole logs to include lithology, secondary fracture-fill minerals;

- Geophysical borehole logs;

- Petrographic and geochemical analyses of whole rock, mineralogical, microchemical, stable isotopic and U-Th content of rock;

- Groundwater quality for samples taken during drilling of deep boreholes, analyses of pH, salinity, major elements, plus drilling fluid tracer;

- Representative samples of flowing groundwater from completed boreholes from GDF depth and in the surrounding host rock in higher strength rocks and in any underlying and overlying permeable strata (all host rocks);
Groundwater quality from samples taken from shallow boreholes (field measurements of pH and Eh, monitoring of drilling water tracer, major and trace elements, tritium, $^{14}$C, stable isotopes, $^{36}$Cl);

- Dissolved gas concentrations ($\text{CH}_4$, $\text{H}_2$, $\text{N}_2$, noble gases, $^4\text{He}$, radon in groundwater);
- Microbial populations (concentrations, size and compositions) especially redox-mediators;
- Concentration of dissolved organics and colloids;
- Stage secondary minerals especially calcite, Fe-oxides, pyrite and other redox-reactive minerals;
- Porewater concentrations from GDF depth and in the surrounding host rock of salinity, major ions, stable isotope ratios;
- Surface water quality of streams, soil waters, rainwater (analyses for pH, major ions, stable isotope ratios, $^{36}$Cl).

**Hydrochemical Interpretation and Modelling: Higher Strength Rocks**

Interpretation will depend upon the data collected but is likely to consist of the following:

- Visualisation and graphical interpretation of hydrochemical variability using cross-sections, cross-plots, hydrochemical plotting (mainly based on major ions);
- Identification of key natural tracers (e.g. Cl, stable isotopes) and evaluation of their usefulness;
- Water typing to determine the number and distribution of different water types in the area of interest;
- Identification and characterisation of possible end-members for mixing that results in the present-day water types and preliminary interpretation of origins of mixing end members;
- Initial estimation of mixing proportions of components;
- Interpretation of groundwater flow directions based on the hydrochemical interpretation;
- Assessment and geochemical modelling of water-rock reactions, pH-controlling and redox-controlling processes in groundwater, particularly at GDF depth;
- Interpretation of the distribution of anthropogenic tracers ($^1\text{H}, \text{NO}_3$) to determine the depths of penetration of recent recharge;
- Geochemical modelling of the carbon isotope system;
- Interpretation of groundwater age: Interpretation of naturally-occurring $^{14}$C data to determine groundwater ages, evaluate $^4\text{He}$ data to estimate groundwater residence times and mixing ratios using estimates of in situ $^4\text{He}$ production from the uranium and thorium content of rocks; Interpret $^{14}$C and $^{13}$C/$^{12}$C data using a geochemical model to obtain groundwater ages; Interpret naturally occurring $^{36}$Cl data in terms of chloride residence times and groundwater ages using estimates of atmospheric inputs of $^{36}$Cl (for dilute groundwater) or of in situ isotopic production (for saline groundwater);
• Description of the baseline hydrochemistry for site area;

• Interpretation of trace element geochemistry of groundwater and rocks/minerals in terms of estimated fluxes of natural analogue elements, e.g. U, REEs, Ra, Cs, Sr, Cl, I;

• Interpretation of hydrochemical and isotopic compositions for deep groundwater and of microchemical/isotopic zoning of secondary minerals in terms of past hydrochemical conditions, e.g. redox, salinity, and palaeohydrogeology;

• Integration with other disciplines. The hydrochemistry interpretation must be integrated with the other disciplines, notably geology and hydrogeology at all stages of the investigation.

Hydrochemical Interpretation and Modelling: Lower Strength Sedimentary Rocks

The interpretation of low strength rocks is likely to be based primarily on water quality obtained from analysis of porewater (assuming low permeability clay-rich rocks), augmented by water quality from flowing groundwater above and below the host rock. Analysis of porewater is likely to be restricted to a limited number of parameters (major ions and stable isotopes). The principal interpretative output at this stage will be porewater profiles for key tracers (e.g. chloride, stable isotopes) and for ratios of these. Water quality from above and below the host rock will be used to identify current boundary conditions.

Low permeability strata are likely to require the following additional tasks:

• Development of porewater profiles to show the distribution of tracers through the host rock and evaluate patterns;

• Interpretation of tracer (Cl and stable isotopes) porewater profiles in terms of matrix diffusion and palaeohydrochemical equilibrium between generally immobile matrix porewater and mobile groundwater. The interpretation may be used to calibrate these processes in the palaeohydrogeological model. The interpretation can also be used to establish system boundaries;

• Measure the capacity of rocks/minerals in the GDF location to control the relevant hydrochemical conditions, i.e. redox, pH, TIC, Fe(II)/Fe(III), SO4–/S2–;

• Modelling of porewater composition based on the measured porewater concentration and rock geochemistry to provide estimated porewater compositions at GDF depth and in the wider host rock (above and below the GDF and laterally).

Hydrochemical Interpretation and Modelling: Evaporites

For evaporites, the focus will be on groundwater outside of the evaporite (above the contact zone). The focus of the interpretation will be on using salinity to evaluate the pathway taken by groundwater that passes over the contact with the evaporite. The interpretation of high salinity waters will require consideration of density flows and the use of models incorporating Pitzer models of activity. However, water encountered within the evaporite will require evaluation to determine whether it is immobile and hence indicates stability of the host rock.
For layered evaporites the investigation will also need to consider the hydrochemistry of underlying strata. However, for salt domes (diapirs) this will not be the case.

**Hydrochemical Outputs**

The preliminary interpretation will result in an initial SDM including the following information:

- The groundwater composition above, at and below GDF depth in terms of groundwater type, salinity, redox, pH, carbonate content, organics (for radionuclide solubility and speciation and for EBS materials performance model);
- Visual and statistical analysis of the spatial variability of groundwater composition;
- Visualisation of the depth and spatial variation in the penetration of recent groundwater infiltration;
- Mixing and dilution pathways for groundwater;
- Water-age distribution.

**Planning for Later Phases**

The interpretation to date will identify information gaps and assess remaining uncertainties in the hydrochemical description of the site. An understanding of the likely variability both vertically and laterally will be used to assess where additional information is required. Information from the hydrogeological interpretation will be used to identify the groundwater hydrochemistry upgradient of GDF, beneath the GDF and downgradient along potential discharge paths.

At this stage, the output will:

- Assess uncertainties in key hydrochemical parameters versus the required level of confidence;
- Assess the degree of heterogeneity in the material properties of the fracture minerals and matrix mineralogy, consider need for additional samples for transport properties;
- Interpret the range of uncertainty in travel times and solute residence times and in the understanding of past hydrogeological and geochemical stability;

8.3.6 **Further Intrusive Investigations**

Further campaigns of intrusive investigation, primarily focussed on deep drilling but also including shallower boreholes and other monitoring will be undertaken to address remaining uncertainties. These subsequent stages will be informed by the results of earlier drilling and used to target uncertainties in the SDM.

Specific hydrochemical sampling and analysis requirements may be identified from earlier stages, requiring specific hydrochemical investigations (including 'hydrochemical boreholes').
Hydrochemical Data and Supporting Information

A similar range of data but with greater spatial and depth coverage is anticipated as for the initial intrusive investigation supported by longer-term monitoring from earlier boreholes. Data requirements will depend upon the findings of the earlier borehole. Additional analysis may be undertaken to address uncertainties in the descriptive model.

Interpretation and Modelling

The hydrochemical interpretation developed as a descriptive model in earlier stages will be refined and further developed with the additional information. Additional interpretation is likely to take the form of:

- Further graphical interpretation of hydrochemical variability, interpretation of origins of component groundwater and solutes, and estimation of mixing proportions of components; interpretation of groundwater flow directions;
- Interpretation and geochemical model of water-rock reactions, pH-controlling and redox-controlling processes in groundwater;
- Confirmation of baseline hydrochemistry for site area;
- Interpretation of trace element geochemistry of groundwater and rocks/ minerals in terms of estimated fluxes of natural analogue elements, e.g. U, REEs, Ra, Cs, Sr, Cl, I;
- Interpretation of hydrochemical and isotopic compositions of deep groundwater and of microchemical/isotopic zoning of secondary minerals in terms of past hydrochemical conditions, e.g. redox, salinity, and palaeohydrogeology.

Hydrochemical Outputs

The information provided by hydrochemical interpretation and modelling will comprise a revised hydrochemical descriptive model, including:

- The distribution, spatial variability and ranges of concentrations of
  - key parameters for GDF EBS performance: pH, redox, salinity, microbial populations, organics, sulphide/ sulphate, carbonate, etc;
  - groundwater compositions for radionuclide solubility and speciation at GDF depth range and in downgradient potential transport pathways: salinity, redox, pH, carbonate, organics.
  - hydrochemical conditions at 300-500 m below GDF depth and/ or upgradient of area.
- A model of the long-term stability of geochemical conditions for reference evolution and various scenarios, supported by palaeohydrochemical evidence; including model of microbial mediation and dependence on sulphide/ sulphate, methane and other redox-reactive species;
- Statistical analysis of spatial variability of groundwater compositions; penetration of recent groundwater infiltration to GDF depth range; mixing/dilution of deep groundwater at shallow depths (0-300m); confirmation of presence/absence of anisotropic ‘fast’ flow pathways;

- Hydrochemical comparison of mobile groundwater and immobile matrix water, interpretation in terms of matrix diffusive exchange, implications for palaeohydrogeology and radionuclide speciation;

- Abundances of indicator species for potential hazards and environmental/ore conditions (e.g. radon, ore pathfinders, arsenic, hydrocarbon, fluoride, etc);

- Hydrochemical input to detailed hydrological model of biosphere; pathways, transport and mixing through the geosphere-biosphere interface zone (GBIZ);

- Site Descriptive Models of hydrochemistry for use in Performance Assessment.

### 8.3.7 Long Term Monitoring

Results of longer-term groundwater monitoring (over timescales of years) will largely be groundwater analyses and in situ measurements that will provide information on temporal variability and will also allow measurements to be collected for systems that are slow to equilibrate following drilling. Longer term measurements will feed into the later revisions of the SDM.

### 8.3.8 Integration with Other Disciplines

The results of the hydrochemical interpretation will need to be integrated with other disciplines, which will require the following tasks:

- Use the hydrochemical interpretation to contribute to the hydrological model for shallow groundwater and interaction with surface waters, including characterisation of the GBIZ;

- Use chloride and other geochemical and isotopic data to identify areas of groundwater discharge;

- Interpret mineralogy and geochemical/isotopic compositions of secondary minerals in terms of palaeohydrochemistry and palaeohydrogeology;

- Make qualitative interpretations of calcite morphology to interpret the past variations of groundwater salinity and thus of palaeohydrogeological stability;

- Use Fe, Mn and rare earth elements (REEs) contents of secondary calcite and other minerals to interpret the past stability or variability of redox conditions;

- Use $^{18}\text{O}/^{16}\text{O}$, $^{13}\text{C}/^{12}\text{C}$ data to identify calcite sources and qualitative ages, also to interpret carbon biogeochemistry;

- Quantify the concentrations and estimate the fluxes of natural analogue solutes and mobile species ( colloids, microbes, gases) from GDF depth to the biosphere;
• Interpret dissolved concentrations of U, Th, Ra and other analogue solutes e.g. Cs, Ba, La and REEs to show that natural geochemistry is consistent with assumptions in the radionuclide transport model;

• Interpret variations of concentrations of colloids, microbes and gases in terms of understanding their sources, compositions, reactions and transport/retention mechanisms;

• Establish baseline hydrochemical conditions and identify any hazardous or anomalous geochemical conditions or scenarios:
  - Describe the chemical compositions of undisturbed groundwater and surface waters in the potential siting area;
  - Interpret dissolved gas compositions (CO₂, CH₄, Rn, H₂) in shallow groundwater and in soil gases;
  - Interpret the production, concentrations and outgassing of Rn, CH₄ and any other hazardous dissolved gases at GDF depth;
  - Identify any other geochemical conditions that pose potential environmental hazards (e.g. As, F), that could affect the performance of the EBS system in a GDF (e.g. sulphide mineral oxidation), or could influence radionuclide solubility, speciation and mobility (e.g. F, HCO₃, organics).

8.3.9 Considerations for Lower Strength Sedimentary Rocks and Evaporites

The base-case concept for the strategic approach set out in this section is a GDF at 300-1000 m depth in a higher strength host; overlain by a sequence of sedimentary rocks several hundred metres thick. This forms the basis of RWMD’s overall strategic approach (NDA, 2011a).

NDA (2011b) has identified two other potential generic host rocks: lower strength sedimentary rocks and evaporites.

There are significant differences to the strategic approach required for these other potential host rocks. In general, lower strength sedimentary rocks and evaporites are likely to be in areas that are fairly flat-lying and laterally persistent. This means that the areal geology is likely to be relatively laterally extensive, although salt domes, such as Gorleben, form an exception. It also means that vertical anisotropy will probably be an important feature of the hydrogeology. Both the predictability and the anisotropy have implications for the strategies for hydrogeological and hydrochemical characterisation.

In addition, lower strength sedimentary rocks and evaporites are contained within sedimentary sequences, which may contain higher permeability formations, i.e. aquifers, above and potential below the host rock, which may not be the case for the higher strength rock. However, structural anomalies (e.g. diapirs, large scale thrusts) mean that general assumptions need to be verified by site characterisation.

The key difference with evaporites is that the host rock may not contain water, which means that no hydrochemical interpretation can be provided.
A brief outline of some of the more significant likely differences between the strategy for the higher strength rocks and the lower strength and evaporite rock variants are given in Tables 8.3 and 8.4 respectively. It should be noted that these are generalisations to which there are, in most cases, well-known exceptions.

### Table 8.3  Key Differences between Lower Strength Sedimentary Rocks and Higher Strength Rocks in Site Characterisation

<table>
<thead>
<tr>
<th>Stage</th>
<th>Key Differences of Lower Strength Sedimentary Rocks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desk Study</td>
<td>Topography is likely to be less pronounced</td>
</tr>
<tr>
<td></td>
<td>Surface outcrops of bedrock are likely to be sparse except where excavated by e.g. road/rail cuttings</td>
</tr>
<tr>
<td></td>
<td>More information on regional hydrogeology and hydrochemistry is likely to be available due to the presence of aquifers</td>
</tr>
<tr>
<td></td>
<td>There may be direct or indirect (i.e. from analogous regions) information on the occurrence of saline groundwater</td>
</tr>
<tr>
<td></td>
<td>3-D geological structure may be simpler and comprise horizontal (or near-horizontal) bedding</td>
</tr>
<tr>
<td></td>
<td>Predictions of hydrogeology will probably be concerned with the degree of anisotropy due to sedimentary bedding, i.e. lateral transmissivity &gt; vertical transmissivity</td>
</tr>
<tr>
<td></td>
<td>Aquifers may feature more obviously in the sequence, e.g. thin aquifers in a sequence of generally lower permeability sedimentary rocks. The occurrence of these and their lateral persistence will be an important feature</td>
</tr>
<tr>
<td>Non-invasive investigations</td>
<td>Seismic reflection surveying may be an important source of information about sedimentary structure</td>
</tr>
<tr>
<td></td>
<td>There may be more existing boreholes and wells providing opportunities for hydrochemical sampling</td>
</tr>
<tr>
<td>Initial Invasive investigation</td>
<td>The focus of the investigation of lower strength sedimentary rocks is likely to be recovery of samples for porewater analysis of the host rock</td>
</tr>
<tr>
<td></td>
<td>It may not be possible to obtain depth-samples of groundwater from the host formation</td>
</tr>
<tr>
<td></td>
<td>Obtaining samples from flowing layers above and below the host rock will be important</td>
</tr>
<tr>
<td></td>
<td>Geophysical logging should identify higher permeability layers especially those at the upper and lower boundaries of the low permeability formation</td>
</tr>
<tr>
<td></td>
<td>The principal interpretation will be the construction of porewater profiles in the host rock. supplemented by interpretation of hydrochemical data of the flowing horizons</td>
</tr>
<tr>
<td></td>
<td>Geochemical modelling will be required to estimate the range of redox and pH conditions in the host formation due to sample volume limitations</td>
</tr>
<tr>
<td></td>
<td>Sampling from shallow boreholes should focus on sampling of higher permeability layers.</td>
</tr>
<tr>
<td>Further invasive investigations</td>
<td>Fewer additional boreholes may be required that focus on the spatial variability of hydrogeological and hydrochemical properties of higher permeability layers through the site area</td>
</tr>
<tr>
<td>Underground rock laboratory for site characterisation</td>
<td>Tests and samples from boreholes drilled from a URL are likely to be important in confirming the hydrogeological properties and the in situ hydrochemical conditions (pH, Eh) in the host formation</td>
</tr>
</tbody>
</table>
Table 8.4  Key Differences between Evaporites and Higher Strength Rocks

<table>
<thead>
<tr>
<th>Stage</th>
<th>Key Differences of Evaporite Rocks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desk Study</td>
<td>Topography is likely to be less pronounced</td>
</tr>
<tr>
<td></td>
<td>There are unlikely to be surface outcrops of the host rock</td>
</tr>
<tr>
<td></td>
<td>More information on regional hydrogeology and hydrochemistry is likely to be available due to the presence of aquifers</td>
</tr>
<tr>
<td></td>
<td>There may be direct or indirect (i.e. from analogous regions) information on the occurrence of saline groundwater</td>
</tr>
<tr>
<td></td>
<td>3-D geological structure may be simpler and comprise horizontal (or near-horizontal) bedding, although evaporites can be present as diapirs / domes</td>
</tr>
<tr>
<td></td>
<td>Predictions of hydrogeology will probably be concerned with the degree of anisotropy due to sedimentary bedding, i.e. lateral transmissivity &gt; vertical transmissivity</td>
</tr>
<tr>
<td></td>
<td>Aquifers may be important features in the sequence, e.g. thin aquifers in a sequence of generally lower permeability sedimentary rocks. The occurrence of these and their lateral persistence will be an important feature</td>
</tr>
<tr>
<td>Non-invasive investigations</td>
<td>Land-based seismic reflection surveying may be an important source of information about sedimentary structure</td>
</tr>
<tr>
<td></td>
<td>There may be more existing boreholes and wells providing opportunities for hydrochemical sampling</td>
</tr>
<tr>
<td>Initial Invasive investigation</td>
<td>The absence of groundwater in evaporites means that the hydrochemistry of the host rock is not the focus of investigation</td>
</tr>
<tr>
<td></td>
<td>The presence of soluble minerals means that groundwater interacting with the host rock can be readily traced</td>
</tr>
<tr>
<td></td>
<td>Flow may take place under density gradients</td>
</tr>
<tr>
<td></td>
<td>Obtaining samples from flowing layers above and below the host rock will be important</td>
</tr>
<tr>
<td></td>
<td>Geophysical logging should identify higher permeability layers especially those at the upper and lower boundaries of the low permeability formation</td>
</tr>
<tr>
<td></td>
<td>Geophysical logging should be used to aid the delineation of salinity and correlated to groundwater salinity</td>
</tr>
<tr>
<td></td>
<td>The principal interpretation will be hydrochemistry of flowing groundwater in aquifers above and below the host rock</td>
</tr>
<tr>
<td></td>
<td>Sampling from shallow boreholes should focus on sampling of higher permeability layers.</td>
</tr>
<tr>
<td>Further invasive investigations</td>
<td>Additional boreholes will focus on the spatial variability of hydrogeological and hydrochemical properties of the higher permeability layers through the site area.</td>
</tr>
</tbody>
</table>
9. Hydrochemistry Resources

This Section considers the availability of resources (tools and specialist practitioners) for undertaking such a programme of hydrochemical data processing, modelling and interpretation. Consideration has been given to the extent to which the required resources may vary in response to variations in the geological environment at the site that are being characterised. Potential gaps in available resources to support a UK-based site characterisation programme are considered.

9.1 Hydrochemistry Tools

9.1.1 Introduction

This section describes the tools that can be used to aid the interpretation and modelling of hydrochemistry. The tools described are computer software packages that assist the tasks described in the Strategic Approach (Section 8). Tools that are solely used to present or visualise data are not described unless they have specific value for quality assurance or for deriving information.

Six categories of tools (computer software programmes) that are necessary for interpretation and modelling of hydrochemistry data have been identified. Software tools have been assigned to basic (e.g. spreadsheets), specialist and modelling groups. The applicability of these tool types will be dependent upon the type of site being investigated and the specific local hydrogeology and hydrochemistry. The relationship between these tasks and the types of tool is set out in Table 9.1.

Because the Strategic Approach to interpretation varies between different geological environments, the tools required will also vary.

For each group of tools the role of the tool in interpretation and modelling has been summarised and the inputs and outputs described together with the tools requirements and potential limitations. Where names of tools are used in this Section it is for the purposes of providing examples.

The expertise required to operate the types of tool in each group is listed. Specific computer hardware requirements are not identified. The ready availability and low cost of high-powered computers mean that the application of the tools identified is unlikely to be constrained by hardware.

There is currently a wide range of tools that are commercially or freely available in each of the categories identified. The capabilities of the available tools in each class may differ so minimum capabilities have been summarised where possible. For the more advanced tools, particularly modelling packages, the choice of package will be based on expert judgement of those working on the site characterisation. In some cases it may be necessary to develop bespoke tools that are tailored towards specific data types or information requirements.
The current availability and functionality of tools is such that a programme of hydrochemical interpretation is highly unlikely to be compromised by the lack of an appropriate tool. However, the project team must have the knowledge, experience and skill to select and operate appropriate software tools.

Table 9.1  Software Tools used in the Interpretation of Hydrochemical Data

<table>
<thead>
<tr>
<th>Interpretation Task</th>
<th>Basic Software</th>
<th>Specialist Software</th>
<th>Modelling Programmes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Spreadsheets</td>
<td>Spatio Data Processing and Visualisation</td>
<td>Hydrochemical Database Package</td>
</tr>
<tr>
<td>Data processing and validation</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Hydrochemical processing</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Data management</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Exploratory analysis</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Statistical modelling</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Hydrochemical modelling</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Coupled flow and transport modelling</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Example tools</td>
<td>MS Excel</td>
<td>ArcGIS/ArcInfo Quantum GIS Surfer</td>
<td>Aquachem, Geochemist's Workbench TOUGHREACT</td>
</tr>
</tbody>
</table>

9.1.2  Basic Software Tools

Spreadsheets

Spreadsheets are basic data processing and visualisation tools that will be used throughout interpretation and modelling. Flexibility, accessibility and familiarity are the main advantages of spreadsheets over the specialist tools. The main value of spreadsheets comes in the initial stages of interpretation where they can be applied to the following:

- Quality assurance of raw data using visual or arithmetic techniques;
- Data processing (conversion of raw data to useable information);
- Visualisation of quality assured data for exploration and classification;
- Basic statistical characterisation, including PCA;
- Presenting quality-assured data in graphs and tables;
- Reformatting data and data manipulation for use in more specialist tools or models;
- Presentation of output from specialist tools and models in graphs and tables;
- Sharing data between groups working on related components of site characterisation.

Spreadsheets do not have fixed input requirements. Most spreadsheets are able to generate data outputs in a wide range of digital file formats to facilitate data transfer to or from other software packages. Charts and tables for inclusion in reports can be generated using spreadsheets.

The spreadsheets used for interpretation and modelling must, at a minimum, have the capabilities to address the applications listed above. Spreadsheets are able to carry out advanced tasks in the hands of experienced users (see the following section on Bespoke Tools) but it is often more appropriate to use software specifically designed for these tasks than build a complex spreadsheet that is difficult to audit. Traceability and reliability tend to be compromised if spreadsheets are used for calculations that would more easily be implemented in a specialist software package, where developers of licensed specialist software provide verification of calculation methods.

Spatial Data Processing and Visualisation

Understanding spatial variability in data collected during site investigation is an important aspect of hydrochemical interpretation and modelling. Tools that allow presentation of spatial datasets and spatial analysis will be used during site characterisation for the following:

- Visual consistency checks between neighbouring observations;
- Quality assurance using spatial statistics;
- Data characterisation and grouping;
- Estimation of parameters by spatial interpolation from discrete observations (e.g. contours);
- Comparison between hydrochemical data and other spatial data sets (e.g. geological structures, hydrogeological observations and interpolations);
- Presenting and communicating data, interpretation and model results.

Tools of this type include Geographical Information Systems (GIS), contour-generating packages, Computer Aided Design software (CAD) and 3-D visualisation packages.

Input requirements for most tools of this type are very flexible but all datasets must have Cartesian grid references in order to be displayed in context. Outputs will typically be maps, cross-sections or 3-D plots that present processed data to aid interpretation and communicate conceptual models.
There are several types of tool that are used to process and visualise spatial data. Each tool type has different strengths and limitations, which are summarised in brief in Table 9.2.

For the purposes of interpretation, ease of use is thought to be the main consideration when selecting tools. The case studies have shown that presenting data spatially on maps and cross sections is useful for interpretation (e.g. Nirex 1998a; Laaksoharju et al., 2008b). Until recently, 3-D visualisation has been used only rarely and appears to be used to confirm interpretations derived from 2-D visualisation rather than to develop new ideas (e.g. Laaksoharju et al., 2008b). However, recent work at the SFR site (SKB, 2010a) makes heavy use of 3-D visualisation to deal with complexity. The increased use of 3-D visualisation partly reflects increased familiarity with 3-D software.

<table>
<thead>
<tr>
<th>Tool Type</th>
<th>Strengths</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>GIS</td>
<td>Ease of use</td>
<td>Bias towards surface-based data (vertically spaced data can be difficult to view)</td>
</tr>
<tr>
<td></td>
<td>Widely used/format compatibility</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Toolboxes can be added to increase functionality (contouring, 3-D visualisation)</td>
<td></td>
</tr>
<tr>
<td>Contour-generating packages</td>
<td>Accessible and flexible for mathematical analysis of spatial data</td>
<td>Interpolations limited to 2-D (surfaces or sections)</td>
</tr>
<tr>
<td></td>
<td>Built-in spatial statistical functions</td>
<td></td>
</tr>
<tr>
<td>CAD</td>
<td>Widely used/format compatibility</td>
<td>Requires experienced users</td>
</tr>
<tr>
<td></td>
<td>Mathematical capabilities</td>
<td>Focussed towards presentation and design rather than interpretation</td>
</tr>
<tr>
<td></td>
<td>3-D visualisation and interpolation allows improved understanding of complex data</td>
<td></td>
</tr>
<tr>
<td>3-D visualisation packages</td>
<td>3-D visualisation and interpolation allows improved understanding of complex data</td>
<td>Requires experienced users</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Limited familiarity</td>
</tr>
</tbody>
</table>

9.1.3 **Specialist Software Tools**

**Statistics Software**

Statistical analysis software has a range of applications in the interpretation of hydrochemical data. The main benefit of using specific statistical software is for multivariate analysis, such as Analysis of Variance, (ANOVA), cluster analysis and PCA. Multivariate statistical analysis can be used to:

- Identify relationships between hydrochemical parameters, providing improved understanding of the sources and sinks of specific solutes;
- Assist in the definition of groundwater types; and
- Estimate the number and composition of hydrochemical end-members.
Quality assured data are used as input to the statistical analysis. Most statistical packages interface easily with databases and/or spreadsheets. Some data processing may be required to select appropriate variables for inclusion in the analysis and to transform skewed data (see below). However, this can usually be done within the specialist software.

Multivariate statistical analysis is used to increase confidence in initial interpretations and provide insight into the relationships between hydrochemical parameters. The outputs from multivariate tests therefore tend to be used to inform data exploration and the development of a conceptual model. Groundwater types or end-members defined using PCA may be used as inputs in more advanced models (e.g. coupled modelling at SKB Laxemar, Laaksoharju et al. 2009).

Capability in multivariate analysis is a requirement for any statistical software being considered for hydrochemical applications. Other statistical capabilities of these packages are likely to be of more limited use in hydrochemical analysis or can be used more readily in spreadsheets.

The use of this software requires an understanding of, and experience in the use of, statistics to ensure that the techniques are applied appropriately. Data may require transformation before analysis to ensure that the assumptions of normality required by parametric tests are satisfied. Data scaling may be necessary to avoid parameters with very high values and/or large ranges disproportionately affecting the analysis. The patterns and correlations in the data must be well understood before attempting multivariate analysis because the choice of variables to use in the analysis is important: for example including correlated variables (e.g. Cl, EC and TDS) can bias results; whilst including derived data such as ion ratios, calculated pCO₂ and noble gas temperatures can be informative, the resulting outputs must be checked for hydrochemical credibility.

Confidence limits and/or levels of significance are routinely calculated by statistical packages when multivariate analysis is undertaken. These limits should be used as part of input sensitivity analysis on any modelling work dependent on the outputs from multivariate modelling.

**Hydrochemical Database and Visualisation**

Hydrochemical database packages, such as Aquachem (Schlumberger Water Services) and Geochemist’s Workbench (Rockware), are designed to store, manipulate, model and present hydrochemical data. For site characterisation, these tools have the following applications:

- Quality checking, e.g. automatic calculation of ion balance errors;
- Data processing e.g. conversion of concentration units and calculation molar/molal ratios from measurements of mass concentration;
- Data exploration and presentation e.g. generation of standard hydrochemical diagrams such as Piper and Durov plots that are difficult to generate from spreadsheets;
- Speciation calculation using built-in or linked speciation codes to model mineral saturation indices, redox speciation, dissolved gas partial pressures etc.
Quality assured data are readily imported into hydrochemical database tools, which are designed to interface easily with other databases and spreadsheets.

Data that has been processed or quality checked in the hydrochemical database is an output that must be exported back into the main site characterisation data management system for use in other tools. Other outputs will include figures and tables that can be used in interpretation and reporting.

Although hydrochemical databases are a useful means of storing data during interpretation, these tools are not a substitute for a site characterisation data management system. Hydrochemical database tools typically have rigid data structure requirements, which may not be consistent with site characterisation data management and quality procedures. The user must consider how data integrity is maintained where hydrochemical databases are used for quality checking and data processing.

RWMD plans to have a robust data management system (DMS) in place before any data or information has been acquired and these plans are well-advanced. The DMS for site characterisation will hold all data acquired during site characterisation, from its initial generation e.g. as laboratory analysis (raw), through subsequent stages of processing and interpretation. This will be managed by modelling the data as records (using a records management system) where data is extracted and contained within a relational database (e.g. oracle) to allow interrogation through a search engine. Raw data from laboratory will be subject to approval from the Principal Investigator (hydrochemistry) and assigned a quality rating, it will then be uploaded to the DMS to share with others. However, the tools to undertake any processing and interpretation will lie outside the DMS. Processed results will be imported into the DMS as new records.

Bespoke Tools

The case studies have identified that bespoke software packages have been used in hydrochemical interpretation and modelling. It is possible that specific data processing or interpretive tools may be needed as part of the site characterisation process. Examples include SKB’s M3 code (Laaksoharju et al., 2009) and Nirex’s TRAP (Nirex, 1998c).

In general, bespoke tools will be developed to make routine tasks quicker and / or to tailor generic software to the available dataset, information requirements and specific aspects of the hydrochemical environment at a site. Likely applications of bespoke tools in site characterisation therefore include but are not be restricted to:

- Automation of routine data processing associated with each phase of groundwater sampling (e.g. calculation of radiocarbon ages from observed data);
- Pre-processing of data for model input (e.g. formatting data from site characterisation databases for use in modelling);
- Undertaking calculations tailored to specific information requirements; and
- Post-processing of model output (e.g. automated plotting of modelled and observed data to aid calibration).
Bespoke tools can be programmed from scratch using native computing languages or developed by modification of existing software. The bespoke tools may range in complexity from an automated spreadsheet to standalone software.

Bespoke tools aim to improve the flow of raw data (input) to information (output) when compared to off-the-shelf software tools. However, before developing a new tool, the value of the benefits need to be considered against the time required to develop and validate the tool (and hence its cost). There are also risks associated with developing new tools, including:

- Failure to design the tool appropriately with respect to available input data, process uncertainties and output requirements;
- Failure to validate the tool;
- Failure to achieve confidence in the tool outputs amongst the wider project team and other stakeholders;
- Failure to produce adequate user documentation making the tool vulnerable to staff changes and open to abuse;
- Use of flawed conceptual models leading to a flawed understanding of the issues to be modelled.

The limitations of bespoke tools are principally related to managing the risks outlined above. Technical limitations should not be encountered because the tools should be designed to maximise the capability of the tool for the intended application.

### 9.1.4 Modelling Tools

**Aqueous Hydrochemical Speciation and Reaction Modelling Programmes**

Hydrochemical processes and water-rock reactions in the subsurface can be simulated using dedicated hydrochemical modelling programmes or codes. Examples include USGS PHREEQC (pH, Redox and Equilibrium model written in C, Parkhurst and Appelo, 1999) Rockware’s Geochemists Workbench and TOUGHREACT (Xu et al, 2011, Xu et al, 2004a,b).

In the context of site characterisation, aqueous hydrochemical speciation and reaction modelling programmes are used to:

- Evaluate possible impacts of sampling on groundwater compositions and therefore inform sampling methods and strategies;
- Derive calculated parameters such as pCO₂ partial pressures and mineral saturation indices from hydrochemical data;
- Assist in the interpretation of hydrochemical data from water samples with reference to the known hydrochemistry of the groundwater environment;
• Estimate key parameters that it may not be possible to measure *in situ* (e.g. Eh and pH of pore waters); and

• Develop models that describe how the hydrochemical environment has evolved during the recent geological past.

For all but the simplest applications of speciation models (e.g. calculation of saturation indices), the following data are required to support speciation and reaction modelling:

• Quality assured hydrochemical dataset from groundwater or porewater samples;

• Mineralogical data describing the mineral assemblage(s) present, the geochemical composition of the minerals and associated laboratory measurements (e.g. porosity, fraction of organic carbon, cation exchange capacity); and

• Databases of geochemical properties for the mineral and aqueous phases present.

The overall aim of speciation and reaction modelling is to develop a numerical model that is able to reproduce observed data and therefore test and inform the descriptive model of the hydrogeochemical environment. The quality checked dataset is used to calibrate this model.

Simulation of observed data may be improved by incorporating mineralogical data from the site into the model. In a simple model, this stage will verify the mineral phases participating in water-rock reactions. In more complex models, laboratory data on the chemical composition of the minerals and their geochemical properties can be used to build confidence in the stochiometric elements of the modelling.

All geochemical speciation and reaction models rely on databases of geochemical properties. These properties include, among others, equilibrium constants, reaction rate expressions and parameters required to calculate activity coefficients and their dependence on ionic strength and temperature. Standard databases for a wide range of aqueous and mineral species are provided with most modelling packages. However, there may be a need to extend the standard databases using (in increasing order of reliability) analogy with other minerals, values from the academic literature, laboratory data from similar site investigation programmes or data collected from the site investigation. Sensitivity analysis should be carried out to determine how uncertainty in geochemical parameters affects the conclusions and information derived from the modelling. Sensitivity analysis may identify research requirements.

Outputs from modelling include: simulated solution compositions; lists of the mineral phases that control hydrochemistry through rock-water interaction; and estimates of the rates at which chemical changes in hydrochemistry have occurred over time. These outputs can be validated against observed hydrochemical and geochemical data as well as existing interpretations. Calibration of the model, either manually or using inverse modelling, allows parameters of interest to Performance Assessment to be estimated. Such parameters may include: diffusion coefficients and kinetic expressions related to redox-sensitive species. Outputs should also include sensitivity analysis considering both uncertainties in the measured data and in the geochemical parameters controlling the calculations. The results of the sensitivity analysis will allow confidence limits to be applied to
derived parameters. Using an inverse modelling calibration method such as PEST (Doherty, 2004) can aid in sensitivity analysis.

The modelling tool should have the following capability:

- Carry out speciation and equilibrium calculations. This allows parameters such as pCO₂ to be estimated and field measurements of pH and Eh to be validated;
- The tool must be customisable to allow the user to add new phases to the model or vary existing equilibrium constants.

In addition, the ability to simulate reaction kinetics, transport and diffusion, isotope systematics and dissolved gases are advantageous but may not be essential at the interpretation and modelling stage as shown by the Nirex investigations at Sellafield (Nirex, 1998c). Whether reactive transport modelling is attempted as part of site investigation will depend on nature of the site and the information requirements.

Features that may be desirable for interpreting complex systems include customisability (the ability to edit the model code to simulate a particular aspect of the hydrochemistry) and modularity (the ability to link the hydrochemical model to other models). Built-in pre and post-processing capabilities may speed up the modelling process and allow output to be visualised and interpreted more quickly. Some hydrochemical database packages such as Geochemists Workbench and Aquachem offer pre and post-processing for hydrochemical models.

One of the limitations of many hydrochemical speciation and reaction modelling codes is the treatment of saline water and brines. It is common for model codes to use an extended Debye-Hückel equation to determine activity coefficients for dissolved species. Whilst this is appropriate for fresh and brackish groundwater, the relationship breaks down at higher ionic strengths (e.g. the TOUGHREACT model is considered reliable in NaCl dominated solutions with concentrations up to 6 M, Xu et al., 2004). This limitation can be addressed using Pitzer-type calculations that can be used to calculate activity coefficients in high ionic strength solutions (Pitzer, 1979). PHREEQC and Geochemists Workbench incorporate this type of functionality. It should be noted that the Pitzer approach is not appropriate for dilute solutions and it is therefore challenging to model the hydrochemistry of both dilute waters and brines. In the cases studied fresh and saline waters have been interpreted separately using different techniques.

The standalone transport modelling capabilities of hydrochemical modelling codes may be limited to simple 1D or 2-D cases with steady state flow fields. These capabilities are sufficient for quantitative interpretation of water-rock interaction and estimating the impacts of drilling and sample collection on water chemistry (e.g. Molinero et al., in Kalinowski, 2008). However, more advanced modelling codes should be used to interpret the spatial distribution of water chemistry throughout the site. Using dedicated flow and transport models has been shown to benefit both the hydrogeological and hydrochemical aspects of site investigation (Follin, 2008).

The SNORM code can be used for normative analysis of saline water. The code was developed by USGS (Bodine and Jones, 1986). It calculates the salt norm from the chemical composition of natural water (see Section 5.2). SNORM proportions solute concentrations to achieve charge balance. It quantitatively distributes the acceptable solutes into normative salts that are assigned to allow only stable associations based on the Gibbs Phase Rule,
available free energy values, and observed low-temperature mineral associations. Results from SNORM identify three main categories of water: meteoric, connate marine-like waters and diagenetic waters. The solute source or reaction process is generally indicated by the presence or absence of diagnostic normative salts and their relative abundance. As a result salt norms can be used to identify lithologic sources; to identify the relative roles of carbonic and sulphuric acid hydrolysis in the evolution of weathering waters; to identify the origin of connate water from normal marine, hypersaline, or evaporite salt resolution processes; and to distinguish between dolomitization and silicate hydrolysis or exchange for the origin of diagenetic waters.

9.2 People

9.2.1 Specialist Practitioners

The understanding of the resource requirements and skills used for hydrochemical interpretation and modelling has been based on:

- The understanding of resources used in the site characterisation programmes developed in Sections 2 to 5;
- The project team understanding of the skills required to undertake the work set out in the NDA’s Strategy (NDA, 2011b) and Site Characterisation (NDA, 2011a);
- The resources and skills required to deliver the strategic approach set out in Section 8.

Hydrochemical interpretation involves two different types of modelling:

- Coupling of solute transport and non-reactive hydrochemical evolution with groundwater flow, and
- Simulations of reactive mass transfers and long-term buffering of hydrochemical conditions by water-rock reactions.

Modelling of radionuclide transport and retention for a performance assessment is not part of hydrochemical interpretation for site characterisation. However, it will have much in common with solute transport modelling. Coupled modelling of non-reactive solute transport and groundwater flow is typically undertaken by groundwater modellers as part of the hydrogeology task, but requires strong integration of hydrochemical modelling with groundwater modelling and also with radionuclide transport modelling. Therefore, there should be common conceptualisation of processes, especially with regard to solute retention (e.g. by matrix diffusion) across models. Reactive mass transfer modelling of, for example, pH and redox buffering and cation hydrochemistry, which is relevant to EBS evolution in the safety case involves conventional water-rock reaction modelling, albeit with a long time frame and thus uncertainties about controls by reaction kinetics and local equilibria.

Overall, resourcing for hydrochemical modelling requires two distinct modelling approaches and therefore different types of expertise. This is possibly a difficult and critical area for resourcing because it is an area of continual model development and innovation, and also because it will require the interfaces with groundwater flow modelling and safety assessment modelling to be managed to achieve cost-effective, coherent and focused output.
Where hydrochemical modelling is required, principally the coupled modelling of non-reactive solute transport, the key resource will be hydrogeological modellers with the ability to work with and develop or adapt coupled modelling approaches especially with regard to transient hydrochemical and hydraulic boundary conditions. These hydrogeologists should have understanding of the acquisition of hydrochemical data and of the basics of water-rock reaction, but the quantitative modelling expertise of physical processes will be more central to the task than hydrochemical specialism. On the other hand, water-rock reaction modelling of long-term hydrochemical evolution requires hydrogeochemical theoretical knowledge combined with expertise in the use and customisation of one or more of the reactive mass transfer software packages identified in Section 9.1.

9.2.2 Scale of Resources

From our understanding of the case study programmes and the requirements of the strategic approach set out in Section 8 of this report, it appears that hydrochemical interpretation would be undertaken by a hydrochemistry-led team. The size of the team would vary in response to:

- The host rock, with higher strength rocks generally requiring the most resources and evaporites the least;
- Reporting requirements. Variations in the frequency of reporting; the number and types of reports; the level of detail and the level and extent of review can have a very large impact on the resources required. A significant reporting burden would require additional resources;
- The scope and specification of the work required. A tightly specified and focussed hydrochemistry interpretation and modelling project would obviously require fewer resources than a more broad-based one;
- The characterisation programme. A short intense programme may require a dedicated team, a longer more intermittent programme may only require inputs from time to time;
- The method of procurement of hydrochemical skills;
- The resources available.

It should be noted that there are strong links between data acquisition and interpretation and modelling. A prerequisite of interpretation is that resourcing requirements of preceding tasks have been met. Data acquisition is likely to require many of the skills and experience required for interpretation and therefore should be resourced from the same team.

Given the uncertainties set out above, it is not easy to determine the resource requirement. The scale of resources required for the case studies have been considered. However, they are not explicitly stated and would be difficult to determine, because:

- Interpretation and modelling can be difficult to separate from planning of investigations, sampling and data acquisition as it is likely that some or all of the same project team will be involved in all these aspects;
• Many of the programmes are long running and therefore back-calculating the time and resources involved in just interpretation and modelling is likely to be difficult;

• Work on individual programmes has been spread over a number of organisations and individuals;

• Many programmes included research that does not form part of the RWMD strategy. Separation of research activity from core programme activity is difficult, even for those involved in those programmes;

• Not all the work undertaken on some programmes was used or, in some cases, effort was duplicated.

9.2.3 Specialist Skills

Hydrochemical interpretation and modelling will require several hydrochemists. The skills required and the approach to the interpretation of hydrochemistry will depend upon the host rock (see Strategic Approach). Hydrochemical skills and related skills that are likely to be required for hydrochemical interpretation and modelling include:

• Graphical interpretation using visualisation techniques;

• Understanding of isotope chemistry;

• Development of bespoke mixing models (e.g. M3);

• Statistical analysis (Principal Component Analysis);

• Geochemistry and understanding of rock-water interaction;

• Hydrochemical modelling (e.g. PHREEQC);

• High salinity environment (evaporite host rock).

In addition to hydrochemistry, the interpretation team may require skills in the following areas:

• Geology (geological structures, mineralogy, geochemistry);

• Hydrogeology (groundwater flow, solute transport modelling, diffusion (lower strength sedimentary rocks));

• Modelling and model development;

• Statistical analysis;

• Database analysis/ data management;

• Microbiology;

• Biosphere (interaction between hydrochemistry and the biosphere).
9.2.4 Experience

In addition to general hydrochemical and hydrogeological experience, the interpretation team will require experience of the following:

- Interpretation of deep groundwater;
- Groundwater dating techniques for relevant host rock;
- Modelling of in situ natural neutrogenic isotope production;
- Trace element low temperature hydrochemistry;
- Petrographic analysis;
- Statistical analysis;
- Solute transport modelling of natural tracers.

In addition, the team needs to be led by someone that has both the relevant scientific knowledge and experience and also specific knowledge of the data and qualitative information flows from site characterisation and interpretation right through to the safety case.

9.2.5 Resources Variations

The resources required will vary, to some extent, with the host rock selected, as follows:

**Higher Strength Rocks**

The interpretation of hydrochemistry in higher strength rocks is likely to be based on data acquired at the surface from boreholes and will require greater resources to undertake sampling and data acquisition on site, when compared to other host rocks. In addition, because flowing groundwater is potentially present at GDF depth, there will need to be a strong integration of the hydrochemical and hydrogeological interpretation teams.

**Lower Strength Sedimentary Rocks**

The hydrochemical interpretation of lower strength sedimentary rocks is likely to be based on a greater element of laboratory-based data acquisition, notably porewater analyses and more limited site-based data acquisition. Site-based data acquisition is likely to be limited to testing and sampling and analysis of flowing groundwater in underlying and overlying strata. Hydrochemical interpretation and modelling will primarily relate to porewater compositions and modelling of solute transport/retention in a diffusion-dominated porous medium. Hydrochemical interpretation and modelling of permeable strata will be similar to conventional water resources interpretation.
Modelling of porewater will be required to (a) understand how porewater profiles have developed; and (b) to determine porewater composition at GDF depth. Due to the limitations of porewater analysis, measurement of critical parameters, such as pH and Eh cannot be done in situ and therefore will need to be modelled.

Resourcing hydrochemical interpretation and modelling for a lower strength host rock would probably best be done by integrating it with the laboratory-based data acquisition, as has been done by NAGRA and ANDRA.

**Evaporites**

The hydrochemical interpretation of evaporites will be limited as conventional groundwater is unlikely to occur within the host rock. Site-based data acquisition is likely to be limited to testing and sampling and analysis of flowing groundwater in underlying and overlying strata. However, where the evaporite lies within a low permeability sequence then porewater samples may also be required (as with lower strength sedimentary rocks).

Hydrochemical interpretation and modelling of permeable strata will be similar to that used for conventional water resources interpretation.

Experience of work with evaporites and high salinity waters will be required.

### 9.2.6 Resource Gaps

It is not apparent, from the understanding of the work required that there are substantial resource gaps that require RWMD-action at the present time. The key resource is the lead hydrochemist.

Possible difficulties in resourcing hydrochemical staff from within the UK are:

- Identifying a suitable technical lead with relevant experience of site characterisation;
- There is a limited pool of practising, commercially-available hydrochemists resident in the UK (assuming a commercial procurement route);
- The potential that no single organisation is capable of fielding a suitably strong team;
- Competition from other site characterisation programmes or from other areas requiring similar skills (e.g. geothermal energy, shale gas, CCS);
- Some areas of interpretation are likely to require inputs from research groups;
- Maintaining continuity of resources and commitment should the work be episodic.

Many of these difficulties can be overcome through the use of resources from outside the UK, where the resource pool is larger and where resources may become available as other programmes move to different stages.

Methods to mitigate any resourcing issues include:
• Establishment of lead-in tasks to permit early contractor involvement and to ensure that capabilities are retained or enhanced;

• Subdivision of work into discrete work packages;

• Construction of multi-organisation teams;

• Identification of research issues and sponsorship of relevant university-based research to promote development of additional hydrochemists with relevant research interests and to establish strong links with the research community.

Resourcing of this task will need to consider both long and short term requirements. It is likely that a site characterisation programme will run over a number of years with periodic bursts of activity and periods of limited activity. Resourcing will therefore require some form of planning to maintain continuity by, for example:

• Having a detailed plan that sets out the activities to be done;

• Periodic reporting of all activity to date so that earlier work does not need to be revisited;

• Spread of work across a team to reduce reliance on individuals;

• Ensuring continuity of staff and adequate succession planning.

Gaps Elsewhere

A review of groundwater sampling methods (Quintessa, 2008) identified possible gaps related to groundwater sampling in deep boreholes. The key gaps were related to a lack of UK-based laboratory facilities and people with the skills to undertake work, notably for investigations of lower-strength sedimentary rocks.
10. Summary and Conclusions

This report provides a review of hydrochemical interpretation and modelling for use in site characterisation for a GDF for higher activity radioactive wastes.

10.1 Case Studies

The approach to hydrochemistry at a number of sites has been reviewed. These sites have been divided into the generic host rock types set out by NDA RWMD, which are:

- Higher strength rocks. Work by SKB at Forsmark, Sweden and UK Nirex Ltd. at Sellafield has been considered;
- Lower strength sedimentary rocks. Work by ANDRA at Bure, France; NAGRA at Benken, Switzerland; NUMO at Horonobe, Japan and LLWR have been considered; and
- Evaporites. Work by US DOE at WIPP in New Mexico and BRG at Gorleben in Germany.

The approach to hydrochemistry has been described in some detail for each of these case studies. The principal lessons from the case studies can be summarised as follows:

- Understanding of objectives. Hydrochemical characterisation must be based on a clear understanding of the information requirements of end users (i.e. the needs-driven approach);
- Data quality and data management. The hydrochemical interpretation must be based on sufficient data of a suitable and known quality;
- Data requirements. The data requirements need to be managed to ensure that excessive and/or irrelevant data is not collected;
- Data management. A central DMS must provide the single source for all data and be readily accessible to all persons working on the site characterisation programme;
- Integration with other disciplines. Hydrochemical interpretation and modelling must be strongly integrated with the geological and hydrogeological disciplines;
- Lines of evidence. The final hydrochemical interpretation should make use of multiple lines-of-evidence to arrive at conclusions that are critical to the Environmental Safety Case (ESC);
- Analogue sites and underground rock laboratories (for site characterisation). The use of analogue sites and URLs has been found to be beneficial, particularly for lower-strength rocks;
- Programme. Most of the case studies have taken place over extended periods, which permitted time for interpretation between investigation campaigns. Shorter, more intense programmes impose constraints, notably the limited opportunity for later phases of site investigation to be informed by the understanding developed in preceding phases;
• Reporting. The production of comprehensive reports at each stage of investigation generally may provide benefits but is a potentially laborious process that may slow down the investigation and interpretation;

• Collaboration. Collaboration between organisations working in similar host media is essential.

The principal variations in the site investigation approach between the different host rock types were identified as follows:

• Higher strength rocks. Groundwater samples are obtained principally from boreholes and include direct sampling of flowing groundwater from GDF depth;

• Lower strength sedimentary rocks. Groundwater samples of flowing groundwater can only be obtained from any aquifers above and below the host rock. Information on the hydrochemistry of the host rock was obtained from porewater taken from rock cores, but this only included a limited suite of analysis due to the small volume of sample that could be obtained and the changes in samples as a result of the porewater extraction process;

• Evaporites. Groundwater is generally absent from evaporites and therefore site investigation for hydrochemistry was limited to flowing groundwater in any aquifers above and/or below the host rock.

As a result of the differences in the investigation approaches outlined above, the interpretation and modelling of the host rock hydrochemistry also varied. The principal differences in the approach to hydrochemical interpretation and modelling were as follows:

• Higher strength rocks. The interpretation concentrated on determining and characterising groundwater chemistry throughout the host rock volume, including upgradient, at the GDF and downgradient in terms of mixing of end-members. Direct sampling of groundwater also permitted estimates of groundwater age distribution using stable isotope ratios and radio-isotopes. Models were principally used to assist in the estimation of mixing ratios;

• Lower strength sedimentary rocks. In lower strength sedimentary rocks, the interpretation of the host rock hydrochemistry was largely based on evaluation of porewater and in particular the interpretation of porewater profiles. These were interpreted to estimate the time required to simulate the observed profiles. Interpretation of the hydrochemistry of flowing water in aquifers was used to characterise water in these horizons and to evaluate any interaction with the host rock. Modelling was used to: simulate porewater profiles and to determine the composition of porewater chemistry for parameters that could not be directly measured;

• Evaporites. The absence of groundwater meant that the hydrochemical interpretation of evaporites was limited to evaluating the fate of water that has been in contact with evaporites and to the characterisation of any flowing horizons above and below the evaporite in terms of their water type and age.

10.2 **Strategic Approach**

A strategic approach to hydrochemical interpretation and modelling has been set out based on RWMD’s Proposed Strategy for the Geoscientific Aspects of Site Characterisation (NDA, 2011b) and the framework for site
characterisation set out in (NDA 2011a); by earlier work on a geochemistry strategy (Intellisci, 2008); and by information gathered in undertaking the current project.

The final approach to site characterisation will depend upon the host rock selected; the environmental setting; the proposed depth and design of the geological disposal facility; the proposed storage concept; and the extent to which the proposed site has undergone previous investigation and characterisation. Further development of the strategic approach is likely to be required following site selection.

The strategic approach considers the main tasks in the interpretation and modelling of hydrochemistry. For flowing groundwater as found in higher strength host rocks and any aquifers above and below the host rock for lower strength sedimentary rocks and evaporites are:

- Identify the main parameters that vary over the investigation area and use these to identify and characterise water types (hydrochemical facies). Water types should also be assigned domains within the rock volume under investigation;
- Identify potential end-member water types (e.g. recharge) for use in groundwater mixing models;
- Use anthropogenic parameters, such as tritium, chlorofluorocarbons (CFCs) and nitrate to identify modern recharge and to determine the depth to which it has penetrated and domains where it has penetrated;
- Use graphical and statistical analyses of data for non-reactive solutes, or tracers, (e.g. chloride) and stable isotopes (e.g. \(^{18}\)O/\(^{16}\)O) to resolve solute sources and groundwater mixing ratios;
- Interpret groundwater isotope data (e.g. \(^{18}\)O/\(^{16}\)O, \(^{14}\)C, \(^{3}\)H, \(^{36}\)Cl, \(^{4}\)He), together with anthropogenic parameters, to derive the water-age at different locations. The interpretation of isotopes will require supporting geochemical and isotopic data for water samples and rocks, i.e. \(^{13}\)C/\(^{12}\)C, U and Th contents, estimates of natural neutron fluxes and the \textit{in situ} rate of production of isotopes;
- Use the water-age distribution to establish solute travel times in the different parts of the groundwater flow system;
- Interpret and model (where necessary) groundwater mixing and geochemical reactions between water and rock that controlled the evolution of the present-day groundwater compositions and distribution thereby identifying controls on the long-term future stability of compositions of groundwater entering the GDF and along solute transport paths leaving the GDF;
- Use non-reactive solutes and isotopes (chloride, \(^{18}\)O/\(^{16}\)O, \(^{4}\)He) to support and test hydrogeological interpretation of groundwater flow paths, to constrain groundwater sources and mixing, and to calibrate a palaeohydrogeological model.

Variations in the strategic approach for lower strength sedimentary rocks and evaporites were identified. The main differences are that:

- Lower strength sedimentary rocks. The focus of the investigation of lower strength sedimentary rocks is likely to be recovery of samples for porewater analysis of the host rock. The principal interpretation
will therefore be the construction of porewater profiles in the host rock supplemented by interpretation of hydrochemical data of flowing horizons above and below the host rock;

- Evaporites. There is unlikely to be any significant groundwater within the evaporite host rock and so the focus of the investigation and interpretation will be on more permeable strata above, and possibly below, the host rock. The presence of substantial quantities of soluble minerals means that groundwater chemistry may be substantially different (e.g. higher salinity) than for other host rocks.

10.3 Other Sectors

A review of approaches to hydrochemistry in other sectors was undertaken. The following fields of investigation were identified as being potentially of particular relevance:

- Geothermal energy;
- Oil and gas, including oil shales;
- Carbon capture and storage (CCS);
- Marine studies;
- Water resources.

The review found only limited differences with the approaches used in radioactive waste management.

10.4 Resources and Tools

The availability of resources (tools and specialist practitioners) for undertaking a programme of hydrochemical data processing, modelling and interpretation has been considered. The review of tools considered the range and types of tools available; the operations that they perform; and the inputs required and the outputs generated. Tools were considered within 6 generic groups (Spreadsheets; Spatial data processing and visualisation; Statistics software; Hydrochemical database and visualisation; Bespoke tools; Aqueous hydrochemical speciation and reaction modelling programmes). The review considered the availability of tools. Most of the tools identified were readily available, either freely or commercially. However, a programme of hydrochemical interpretation and modelling may also have requirements for bespoke tools, which would require specialist development skills.

The human resources required for hydrochemistry interpretation and modelling were identified in terms of the specialist skills required, the size of the team required and the experienced needed. Potential variations in resources for the different host rocks were also identified.

The review identified that hydrochemistry interpretation and modelling can be undertaken by a small team of specialist practitioners. Previous experience of site characterisation within the team would be highly beneficial, particularly so that the team are familiar with the information requirements of end users. It was considered that higher strength host rock is likely to require the greatest resources and evaporites the least.
The lack of availability of hydrochemists to undertake the work is not identified as a high risk, although the experienced senior advisors in this discipline are, and will continue to be, in short supply. However, the availability of resources will depend on the extent and timing of any programme.

10.5 Concluding Remarks

The following concluding remarks arise from the review of hydrochemical interpretation and modelling.

- The case studies illustrate the general importance of data processing as an intermediate stage between site data acquisition and site descriptive models. It is evident that, regardless of the programme and the type of host rock, very little raw data feeds directly into Site Descriptive Models and even less so into the Environmental Safety Case;

- The importance of identifying user needs runs through the whole exercise. From those needs, the requirements for quality control of raw data, data processing techniques and resources, and interpretative models can be identified;

- Data management and QA/QC is critical in ensuring that the data used in interpretation are consistent, reliable and traceable;

- There needs to be an emphasis on the site-specific nature of the interpretative programme and methods, depending not just on the three categories of potential host rock but on the site-specific challenges of hydrochemical data acquisition (testing and sampling);

- The case studies were progressed on the basis of a set of hydrogeochemical data and interpretation methods that are well-established. However, these methods require specialist interpreters and modellers, who are drawn from a small population;

- A review of other sectors has identified exotic isotopic, trace element geochemical methods etc. These are unlikely to offer viable alternative or additional methods in the near future, but RWMD should be alert to future developments especially in coupled flow-transport-reaction modelling and in trace element hydrochemistry;

- The case study programmes have ended up acquiring more data (more types of data, and more of each type) than have been used in interpretation and modelling for site characterisation and for other user needs. With this review and the previous reviews on sampling, analysis, etc, and other aspects of site characterisation methodology, RWMD have the documentation to form the basis of a critical appraisal of what should be included and excluded from their site characterisation and interpretation strategy, so that it is well-focused, cost-effective and efficient, whilst also remaining flexible for site-specific factors;

- Site-specific factors in complex geological conditions will be a major challenge. The interpretation methods and modelling tools should be assembled, and the expertise of an interpretation team should be developed, by dry run projects using case study data, URL projects and other training exercises, to address these factors and challenges.
11. References


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## 12. List of Acronyms and Abbreviations

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>BVG</td>
<td>Borrowdale Volcanic Group</td>
</tr>
<tr>
<td>CCA</td>
<td>Compliance Certificate Application (US)</td>
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<tr>
<td>CEC</td>
<td>Cation exchange capacity</td>
</tr>
<tr>
<td>DO</td>
<td>dissolved oxygen</td>
</tr>
<tr>
<td>DOC</td>
<td>Dissolved organic carbon</td>
</tr>
<tr>
<td>DOE</td>
<td>(United States) Department of Energy</td>
</tr>
<tr>
<td>CRIEPI</td>
<td>Central Research Institute of the Electrical Power Industry (of Japan)</td>
</tr>
<tr>
<td>EA</td>
<td>Environment Agency (for England and Wales)</td>
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<tr>
<td>EBS</td>
<td>engineered barrier system</td>
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<tr>
<td>EC</td>
<td>Electrical conductivity</td>
</tr>
<tr>
<td>Eh</td>
<td>the potential generated between a platinum and a standard hydrogen electrode</td>
</tr>
<tr>
<td>ESC</td>
<td>environmental safety case</td>
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<tr>
<td>EU</td>
<td>European Union</td>
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<tr>
<td>GDB</td>
<td>Geochemical database</td>
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<tr>
<td>GDF</td>
<td>geological disposal facility</td>
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<tr>
<td>GMWL</td>
<td>Global Meteoric Water Line</td>
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<tr>
<td>HLW</td>
<td>high level waste</td>
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<tr>
<td>IAEA</td>
<td>International Atomic Energy Agency</td>
</tr>
<tr>
<td>ILW</td>
<td>intermediate level waste</td>
</tr>
<tr>
<td>KBS-3</td>
<td>Kärnbränslesäkerhet-3 (Nuclear Fuel Safety #3)</td>
</tr>
<tr>
<td>JNES</td>
<td>Japan Nuclear Energy Safety Organisation</td>
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<tr>
<td>JNFL</td>
<td>Japan Nuclear Fuel Limited</td>
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<tr>
<td>LLW</td>
<td>low level waste</td>
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<tr>
<td>NDA</td>
<td>Nuclear Decommissioning Authority</td>
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<tr>
<td>NUMO</td>
<td>Nuclear Waste Management Organisation of Japan</td>
</tr>
<tr>
<td>OBM</td>
<td>Oil based mud (drilling fluid)</td>
</tr>
</tbody>
</table>
OECD  Organisation for Economic Co-operation and Development
ORP  Oxidation-reduction potential
PA  Performance assessment
PCSC  post-closure safety case
pMC  percent modern carbon
pH  The pH scale measures how acidic or basic a substance is
PCA  Principal components analysis
PNC  Power and Nuclear Fuel Development Corporation (of Japan)
PRZ  Potential Repository Zone
R&D  research and development
RCF  Rock characterisation facility
REE  Rare earth element

RWMD: Radioactive Waste Management Directorate
SDM  Site descriptive model
SEM  scanning electron micrography
SKB  Svensk Kärnbränsleförsörjning (Swedish Nuclear Fuel and Waste Management Company)
SMOW  Standard mean ocean water. Standard for comparison to stable isotopes of O and H.
STZ  Saline transition zone
TDB  Thermodynamic database
TDS  Total dissolved solids
TOC  Total organic carbon
TRAP  Tracer Regression Analysis Programme
URL  Underground rock laboratory
UK  United Kingdom
WIPP  Waste isolation pilot plant
13. Glossary of Terms

**ANDRA**
The organisation responsible for waste management and the development and operation of disposal facilities in France.

**anion**
A negatively charged atom or molecule.

**aquifer**
An underground layer of water-bearing rock.

**backfill**
A material used to fill voids in a GDF. Three types of backfill are recognised:

- local backfill, which is emplaced to fill the free space between and around waste packages;
- peripheral backfill, which is emplaced in disposal modules between waste and local backfill, and the near-field rock or access ways; and
- mass backfill, which is the bulk material used to backfill the excavated volume apart from the disposal areas.

**backfilling**
The refilling of the excavated portions of a disposal facility after emplacement of the waste.

**barrier**
A physical or chemical means of preventing or inhibiting the movement of radionuclides.

**bentonite**
A clay material that swells when saturated with water which is used as a backfill and buffer material in some disposal concepts.

**biosphere**
Regions of the earth’s surface and atmosphere normally inhabited by living organisms.

**British Geological Survey (BGS)**
The BGS provides expert services and impartial advice in all areas of geoscience.

**buffer**
An engineered barrier that protects the waste package and limits the migration of radionuclides following their release from a waste package.
closure
The administrative and technical actions that have to be taken to put a disposal facility in its intended final state after the completion of waste emplacement.

containment
The engineered barriers, including the waste form and packaging, shall be so designed, and a host geological formation shall be selected, as to provide containment of the waste during the period when waste produces heat energy in amounts that could adversely affect the containment, and when radioactive decay has not yet significantly reduced the hazard posed by the waste.

Department of Energy (US)
US government department responsible for disposal of radioactive waste.

disposal
In the context of solid waste, disposal is the emplacement of waste in a suitable facility without intent to retrieve it at a later date; retrieval may be possible but, if intended, the appropriate term is storage. (MRWS)

drift
A sloping underground tunnel.

engineered barrier system
The combination of the man-made engineered components of a disposal facility, including the waste packages/disposal canisters, buffer, backfills and seals.

Environment Agency (EA)
The environmental regulator for England and Wales. The Agency’s role is the enforcement of specified laws and regulations aimed at protecting the environment, in the context of sustainable development, predominantly by authorising and controlling radioactive discharges and waste disposal to air, water (surface water, groundwater) and land. The Environment Agency also regulates nuclear sites under the Environmental Permitting Regulations and issues consents for non-radioactive discharges. (MRWS)

environmental safety
The safety of people and the environment both at the time of disposal and in the future. (Definition taken from the GRA.)

Environmental Safety Case (ESC)
The collection of arguments, provided by the developer or operator of a disposal facility, that seeks to demonstrate that the required standard of environmental safety is achieved.

European Union (EU)
The European Union of countries of which the United Kingdom is a member. The EU issues its own legislation which the UK, as a member state, is obliged to follow. (MRWS)
evaporite
The generic term for a geological environment created by the evaporation of water from a salt bearing solution to form a solid structure.

far field
The geosphere surrounding a GDF, comprising the surrounding geological strata, at a distance such that the GDF can be, for modelling purposes, considered a single entity.

footprint
The area of host rock required to accept the inventory which is to be disposed of. The footprint will also be determined by the properties of the host rock, the geometry of the features within it and whether the disposal tunnels or vaults are built on a single or multiple levels within a GDF.

groundwater
Water located beneath the earth’s surface in rock pores and fractures.

higher strength rock
Typically crystalline igneous and metamorphic rocks or geologically older sedimentary rocks where any fluid movement is predominantly through discontinuities.

International Atomic Energy Agency (IAEA)
The IAEA is the world’s centre of cooperation in the nuclear field. It was set up as the world’s Atoms for Peace organization in 1957 within the United Nations family. The Agency works with its Member States and multiple partners worldwide to promote safe, secure and peaceful nuclear technologies.
**isolation**
A GDF shall be sited in a geological formation and at a depth that provide isolation of the waste from the biosphere and from humans over the long term, for at least several thousand years, with account of both the natural evolution of the geological disposal system, and events that could disturb the facility.

**lower strength sedimentary rock**
Typically geologically ‘young’ sedimentary rocks where any fluid movement is predominantly through the rock matrix.

**low level waste (LLW)**
Defined as radioactive waste having a radioactive content not exceeding 4 gigabecquerels per tonne (GBq/te) of alpha or 12 GBq/te of beta/gamma activity. MRWS

**LLWR**
The Low level waste repository at Drigg operated by LLWR Limited.

**NAGRA**
The National Cooperative for the Disposal of Radioactive Waste; the organisation responsible for waste management in Switzerland.

**natural uranium**
Uranium containing the naturally occurring distribution of uranium isotopes (approximately 99.28% uranium-238 and 0.72% uranium-235 by mass).

**near field**
The engineered barrier system (including the wasteform, waste containers, buffer materials, backfill, and seals), as well as the host rock within which the GDF is situated, to whatever distance the properties of the host rock have been affected by the presence of a GDF.

**Nirex (United Kingdom Nirex Limited)**
An organisation previously owned jointly by Department for the Environment, Food and Rural Affairs and the Department for Trade and Industry. Its objectives were, in support of Government policy, to develop and advise on safe, environmentally sound and publicly acceptable options for the long-term management of radioactive materials in the United Kingdom. The Government’s response to Committee on Radioactive Waste Management in October 2006 initiated the incorporation of Nirex functions into the NDA, a process which was completed in March 2007. (MRWS)

**Nuclear Decommissioning Authority (NDA)**
The NDA is the implementing organisation, responsible for planning and delivering the GDF. The NDA was set up on 1 April 2005, under the Energy Act 2004. It is a non-departmental public body with designated responsibility for managing the liabilities at specific sites. These sites are operated under contract by site licensee companies (initially British Nuclear Group Sellafield Limited, Magnox Electric Limited, Springfields Fuels Limited and UK Atomic Energy Authority). The NDA has a statutory requirement under the Energy Act 2004, to
publish and consult on its Strategy and Annual Plans, which have to be agreed by the Secretary of State (currently the Secretary of State for Trade and Industry) and Scottish Ministers. (MRWS)

**nuclear waste**¹
A general term for the radioactive waste produced by those industries involved with nuclear energy and nuclear weapons’ production. (MRWS)

**performance assessment**
Assessment of the performance of a system or sub-system and its implications for protection and safety at an authorised facility. (IAEA)

**permeability**
A measure of the rate at which a gas or a liquid moves under a pressure gradient through a porous material.

**porewater**
Groundwater held within a space or pore in rock.

**porosity**
The ratio of the aggregate volume of interstices or porous media to total volume of a body.

**Posiva**
The organisation responsible for waste management and the development and operation of disposal facilities in Finland.

**quality management system (QMS)**
A quality management system is the overall system by which an organisation determines, implements and ensures quality.

**radioactive decay**
The process by which radioactive material loses activity, e.g. alpha activity naturally. The rate at which atoms disintegrate is measured in becquerels. (MRWS)

**radioactive material**
Material designated in national law or by a regulatory body as being subject to regulatory control because of its radioactivity. (MRWS)

**radioactive waste**
Any material contaminated by or incorporating radioactivity above certain thresholds defined in legislation, and for which no further use is envisaged, is known as radioactive waste. (MRWS)

¹ Whilst the term ‘nuclear waste’ is defined in the MRWS White Paper it is not generally used and the term ‘radioactive waste’ is preferred in all cases.
**Radioactive Waste Management Directorate (RWMD)**
The NDA Directorate established to design and build an effective delivery organisation to implement a safe, sustainable, publicly acceptable geological disposal programme. It is envisaged that this directorate will become a wholly owned subsidiary company of the NDA. Ultimately, it will evolve under the NDA into the organisation responsible for the delivery of the GDF. Ownership of this organisation can then be opened up to competition, in due course, in line with other NDA sites. (MRWS)

**radioactivity**
Atoms undergoing spontaneous random disintegration, usually accompanied by the emission of radiation. (MRWS)

**radionuclide**
A radioactive form of an element, for example carbon-14 or caesium-137. (MRWS)

**retardation**
A feature of a component of a GDF that contributes to safety. The engineered barriers and host geological environment provide retardation of radionuclides through physical and chemical processes that reduce the concentration of contaminants or their rate of release from the barrier. Retardation processes may result in effective containment of the radionuclides if they would only be released through the barriers after the time at which they and their daughters have decayed to negligible levels.

**safety cases**
A ‘safety case’ is the written documentation demonstrating that risks associated with a site, a plant, part of a plant or a plant modification are as low as reasonably practicable and that the relevant standards have been met. Safety cases for licensable activities at nuclear sites are required as license conditions under NIA65. (MRWS)

**shaft**
A vertical or near-vertical tunnel extending underground from the surface.

**site characterisation**
Detailed surface and subsurface investigations and activities at a site to determine the radiological conditions at the site or to evaluate candidate disposal sites to obtain information to determine the suitability of the site for a GDF and to evaluate the long term performance of a GDF at the site. (IAEA)

**sorption**
The interaction of an atom, molecule or particle with the solid surface at a solid–solution or a solid–gas interface. Used in the context of radionuclide migration to describe the interaction of radionuclides in pore- or groundwater with soil or host rock, and of radionuclides in surface water bodies with suspended and bed sediments. (IAEA)

**storage**
The emplacement of waste in a suitable facility with the intent to retrieve it at a later date. (MRWS)

**Svensk Kärnbränsleförsörjning (SKB)**
The organisation responsible for waste management and the development and operation of disposal facilities in Sweden.
uncertainty
A state of limited knowledge that precludes an exact or complete description of past, present or future.

underground rock laboratory (URL)
An underground facility developed for research and testing purposes at a site that may eventually be used for waste disposal and may be a precursor to the development of a GDF at the site

uranium (U)
A heavy, naturally occurring and weakly radioactive element, commercially extracted from uranium ores. By nuclear fission (the nucleus splitting into two or more nuclei and releasing energy) it is used as a fuel in nuclear reactors to generate heat. (MRWS)

Uranium is often categorised by way of the proportion of the radionuclide uranium-235 it contains (see natural uranium, depleted uranium, low enriched uranium and highly enriched uranium).

WIPP
Waste isolation pilot plant.