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Gas generation and migration from a deep geological repository for radioactive waste

A review of Nirex/NDA's work

Issue 1, November 2008.

NWAT/NDA/RWMD/2008/002

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Preface

Any future authorisation to dispose of higher activity solid radioactive waste at a specialised deep geological disposal facility will be granted by the Environment Agency (EA) of England and Wales, subject to the production of an acceptable environmental safety case. Guidance on the development of such a safety case and the expectations of the Environment Agency is outlined in *“Deep geological disposal facilities on land for solid radioactive wastes: Guidance on Requirements for Authorisation”*, draft for public consultation 15 May 2008, issued by the Environment Agency and the Environment & Heritage Service.

Nirex’s mission was “*to provide the UK with safe, environmentally sound and publicly acceptable options for the long-term management of radioactive materials*”. An agreement between Nirex and the Environment Agency was put in place to permit regulatory scrutiny of the work of Nirex in developing these options. Whilst we were producing this review, the Nuclear Decommissioning Authority (NDA) was given responsibility for planning and implementing geological disposal and staff and resources from United Kingdom Nirex Ltd (Nirex) have now transferred to the NDA. This process was completed in March 2007. This report is based on a review of Nirex's work prior to this change and “Nirex” is referred to throughout. However, our recommendations are now directed to the NDA's Radioactive Waste Management Directorate, which now has many of the responsibilities that were formerly associated with Nirex.

Environment Agency

Environment Agency Summary

This work was carried out for us by Quintessa Ltd. Here, we explain briefly why we commissioned this research, the conclusions that are important for us and the next steps.

In 2005, we reviewed a series of 'Context Notes' that Nirex[1] produced to summarise the status of work in various technical areas important to designing and building a geological disposal facility and demonstrating that it could provide a safe place to dispose of radioactive waste. One of these Context Notes dealt with gases that would be generated over time from waste in a repository. During the post-closure phase of a repository, significant quantities of gas would be generated, mainly by metal corrosion and microbial degradation of organic (particularly cellulosic) wastes. The main gases produced are hydrogen, carbon dioxide and methane. It is likely that a small proportion of the generated gas will be radioactive, mainly as a result of the incorporation of tritium and carbon-14 that will be present within the waste. If gas accumulated within a repository, there would be a build-up of pressure. This could have an effect on the engineered structure and host rock, and might lead to a disturbance of the pressure-head gradients and groundwater flows near the repository. On the other hand, if gas were not contained, there could be various other consequences. For example, the gas might have an effect on the local groundwater flow regime.

We were keen to understand the status of research carried out by Nirex (now the NDA RWMD) on gas generation and gas transport over the last 20 years. We, therefore, asked Quintessa to review Nirex's research and assessment work relating to gas evolution and migration to:

- evaluate whether Nirex (now the NDA RWMD) has explored (or identified as future work) all significant issues of concern in relation to gas generation and migration (given the current decision-context of a geological repository);
- review differences in approach to the assessment of gas generation and migration for a selection of overseas repository programmes;
- identify significant uncertainties and any omissions in the Nirex commissioned work.

[1] This report refers primarily to 'Nirex' because the research and assessment work reviewed by Quintessa was effectively performed or commissioned by Nirex. Follow-up actions are being pursued with the successor organisation to Nirex, the Radioactive Waste Management Directorate of the Nuclear Decommissioning Authority (NDA RWMD).

Quintessa produced a draft report in March 2007 and Nirex reviewed this for factual accuracy. At this point, Nirex brought a number of additional (Nirex) studies to our attention. This final report takes account of those additional studies published around the end of 2007.

A review of the gas behaviour processes within the biosphere was outside the scope of the work, although some of the literature considered does include biosphere-specific information.

The Quintessa report concludes that Nirex has taken into account the majority of processes likely to generate gas, and has addressed many of the issues that may affect long-term safety. However, the modelling of gas and its effects continues to present many challenges. The report highlights many technical issues in what is a complex and specialist area, and identifies some key issues that need to be addressed. Our conclusions and recommendations in considering this study are:

- The NDA RWMD should review and evaluate the significance of Quintessa's findings and recommendations. A key challenge is knowing how significant each of the identified technical issues are and what priority the NDA RWMD should give them as part of future research and development, site modelling or any site investigation studies.

- The NDA RWMD should explain the relevance of its current gas research, the questions that are being addressed, and present a strategy for future work on gas, explaining what information is required and why.

- We note that many of the gas transport issues are site-specific. Nirex research on gas focussed on a cementitious repository located in fractured hard rock, overlain by sedimentary layers. Therefore, given the current decision context, continued detailed modelling for any particular geologic formation may not be the best use of resources. We consider that the NDA RWMD should focus on identifying key gas transport questions that need to be addressed to support a site selection and characterisation process.

- There are competing software tools available for modelling gas generation through the lifecycle of a waste package. The NDA RWMD has opted to develop one particular model (SMOGG) but the NDA, more widely, is funding development of similar, but different models for nuclear sites (for example MAGGAS and models adapted specifically for the Low Level Waste Repository near Drigg). There is a role for model inter-comparison studies, but the NDA should also consider rationalising the future use and development of such models.

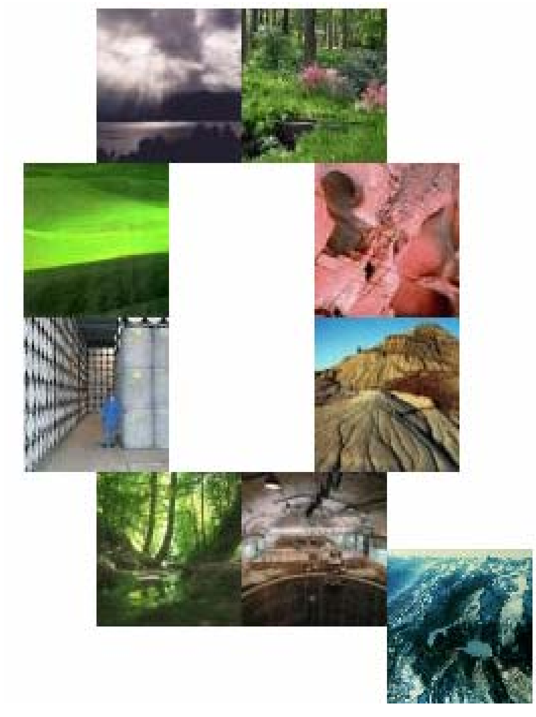
- Metal corrosion is a key mechanism for bulk gas generation. The potential disposal of un-reprocessed spent Magnox fuel could be a significant additional source term that should be evaluated.
- We encourage the NDA RWMD corrosion specialists to work closely with their gas modelling colleagues and share research results.
- A general challenge (that is not just limited to considerations on gas) is the extent to which cautious or conservative assumptions (adopted for the purpose of demonstrating safety) influence decisions in terms of package design, repository design and choice of disposal concept. While using conservative assumptions is a standard approach to demonstrating confidence in meeting safety targets, these same assumptions (some of which are speculative modelling assumptions) can compromise design decisions. The NDA RWMD should review the role of conservatisms in the gas pathway safety assessment and highlight areas of tensions with design decisions.

When we have received the NDA RWMD's response to these recommendations and had any subsequent discussions, we may identify issues to be pursued further through the formal Issue Resolution Process between us and the NDA RWMD.

Providing these comments does not place us under any obligation to approve any future post-closure safety case submitted by any organisation in support of any subsequent application, nor does it bind us in any way to grant an authorisation for any future disposals.

NDA Work on Gas Generation and Migration from a Deep Geological Repository

A review undertaken on behalf of the Nuclear Waste Assessment Team



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Preface

Any future authorisation to dispose of solid radioactive waste at a specialised disposal facility will be granted by the environment agencies, the Environment Agency in England and Wales and the Scottish Environment Protection Agency (SEPA) in Scotland, subject to the production of an acceptable post-closure safety case. Guidance on the development of such safety cases and the expectations of the environment agencies is outlined in RSA 1993, Disposal Facilities on Land for Low and Intermediate Level Radioactive Wastes: Guidance on Requirements for Authorisation (GRA).

This report was produced by Quintessa Limited to inform Environment Agency views on the Nuclear Decommissioning Authority (NDA), and formerly Nirex work on gas from a deep geological repository. It does not necessarily commit the Environment Agency to the recommendations herein, though the findings will be of use in developing a dialogue with the Nuclear Decommissioning Authority (NDA), the organisation now charged with implementing geological disposal.

Summary

This report describes a review of research into gas evolution and migration from a possible future deep geological repository that was completed and/or initiated by Nirex. At the time the review commenced, Nirex was the organisation charged with ensuring the safe long-term management of the UK's Intermediate Level Radioactive Waste (ILW) and some long-lived Low Level Radioactive Waste (LLW). However, the role of implementing geological disposal has now transferred to the Nuclear Decommissioning Authority, with the Radioactive Waste Management Directorate (RWMD) as the delivery organisation. Some of the research into gas that was initiated and substantially completed by Nirex was reported following the RWMD's establishment and is covered by the present review. In consideration of the organisational changes this report attributes on-going work to the NDA, whereas past research is attributed to Nirex for clarity.

The particular focus of the review is research relating to the disposal of Intermediate Level Radioactive Waste (ILW) and some long-lived Low Level Radioactive Waste (LLW) via a cementitious based concept, rather than high level waste and spent fuel and other material, that if declared waste are to be managed through geological disposal. Specific objectives were to:

- evaluate whether Nirex explored (or identified as future work) all significant issues of concern in relation to gas generation and migration;
- review differences in approach to the assessment of gas generation and migration within a selection of overseas repository programmes; and
- identify significant uncertainties and any omissions in the Nirex-commissioned work.

Information against which to evaluate whether or not the work covered by the Nirex reports is complete and relevant was compiled. This information consisted of published overviews of international research in the field and a generic (not geology-specific) list of Features Events and Processes (FEPs) developed by Quintessa and aimed at underground sequestration of carbon dioxide (though based on the NEA FEP database, NEA/OECD 2000).

The review focussed initially on two overview documents, Context Note 3.5 (Nirex, 2006a), and the "Viability Report" (Nirex, 2005a), Geosphere Research Context Notes (Nirex, 2005b, 2006c) and a report on future geosphere research (Nirex 2006c). Subsequently, reports referenced in these documents (and then, in turn, the sources

referenced in them) were evaluated. In this way, a total of 61 reports relating to research undertaken by Nirex were reviewed in their entirety. An additional 43 supporting documents were identified during this review and consulted, though not read completely. It is however acknowledged that the selection of reports considered in this review represents only a subset of the material published by Nirex. This report considers reports published by around the end of 2007. Some of the cited references are unpublished contractor reports and these references may be superseded by (NDA) published material.

These documents were judged against general measures of adequacy including :

- ▲ in the case of the overview documents, the extent to which the information in the supporting documents is appropriately summarised and placed in context;
- ▲ in the case of all documents (i.e. overviews and supporting documents) considered as a whole, the extent to which the work is complete and relevant;
- ▲ in the case of each document considered on an individual basis:
  - the extent to which the drivers/rationale for research are identified;
  - the extent to which the work would impact upon:
    - o repository design;
    - o safety/performance assessment; and
    - o building confidence in the suitability of a repository concept;
  - the extent to which models adopted are relevant and adequate for the purposes for which they are intended;
  - the extent to which outstanding issues and uncertainties have been identified.

The major processes responsible for the majority of generated gas had been taken into account by Nirex. It is clear from the work that the travel times of the gas between the repository and the surface will depend to a large extent upon the nature of the geology and the characteristics of groundwater flow, once a free gas phase has formed. However, travel times will also be influenced by the volumes and pressures of gas developed, which will in turn depend upon the inventory of potentially gas-generating materials (metals and organic matter) and upon the rates of gas generation from these materials. Nirex's previous safety assessments (Nirex, 1997a, Nirex, 2001 and Nirex 2003a,b) aimed to adopt a conservative approach for simulating gas migration in so far as little or no credit is taken for possible retardation and dilution/dispersion processes within the geosphere. The calculations carried out by Nirex are based on parameterisations that were considered to be conservative/pessimistic and suggest that repository generated gas will migrate as a free phase, rather than be dissolved within the groundwater thereby becoming part of the groundwater pathway. During the preparation of this report, the inventory of gas-generating metals and graphite was revised upwards, and therefore greater volumes of free gas are likely to be developed than were estimated previously. Nonetheless, the NDA presently recognises that in reality some of the gas will be dissolved within the groundwater and the extent to which this happens is currently being evaluated.

It is concluded that the work conducted by Nirex addressed most of the issues relevant to performance assessment. Nirex developed an understanding of the processes and issues relevant to a Sellafield-type site that is at a broadly comparable level to that attained by the most developed radioactive waste management programmes in other countries. In some areas, particularly concerning near field evolution and in particular the uptake of carbon dioxide by cementitious materials, the NDA is at the forefront of research. Nirex also used evidence from analogues to confirm the completeness of gas migration FEPs. Conversely, there are other areas, notably in attributing a barrier or retardation function to the geosphere, where the work of the NDA is arguably less advanced than in some other programmes. One field where Nirex did not conduct significant research is gas generation from carbides trapped in metals. However, other major limitations of the research by Nirex are also common to research programmes elsewhere in the world and reflect fundamental technical challenges. An example is research aimed at understanding coupling between physical and chemical processes affecting repository resaturation and gas evolution. This coupling is inherently challenging to investigate and to evaluate in performance assessment.

Nirex identified most of the main areas where future work is required, namely:

- ▲ evaluation of the extent to which carbon dioxide generated by microbial degradation of organic matter or by other mechanisms will be sequestered by carbonation of a cementitious backfill;
- ▲ the possible liberation of ^{14}C by corrosion of metals;
- ▲ the need to consider alternative geological environments besides those with fractured crystalline rocks and argillaceous rocks, and to consider argillaceous host rocks in greater detail; and

- validation[1] of the models for organic degradation (which in practice is likely to mean building confidence in the models by a variety of complimentary approaches, such as comparing model output with experimental and field observations, and demonstrating that modelled processes are understood).

In addition to these issues, it is suggested that additional research needs to consider the following general issues:

- understanding the significance for performance assessment of the heterogeneity of gas generation within the repository;
- consideration of the role of gas generation (and its heterogeneity) in optimising the design of the repository;
- justification of the assertion that estimates of radionuclide doses are in fact conservative if *all* processes influencing gas generation and migration are taken into account;
- evaluation of the degree of pessimism/conservatism associated with parameterisation of individual features and processes, to ensure that future assessments are not unrealistic, as has been the case in the past.

More specific issues that need to be considered by NDA are:

- the coupling between gas generation, groundwater flow and accessibility of water to corroding/degrading waste (which is particularly related to the third bullet point above);
- the coupling of the convergence behaviour of the host rock (tendency of voids to close) to the processes in the previous bullet point (particularly if consideration is to be given to disposal in salt);
- the influence of salinity on gas solubility (and hence transport) is important and could usefully be evaluated theoretically and experimentally for the range of groundwater salinities likely to be encountered during a future site selection programme in the UK;

[1] Here "validation" refers to demonstrating that within its domain of applicability, a model gives results of satisfactory accuracy, consistent with the intended application of the model (Schlesinger et al. 1979).

- the potential importance of any space that might exist between the backfill and the Excavation Disturbed Zone (EDZ) could be evaluated (usefully by theoretical means) for a range of possible host rock lithologies and potential backfills;
- similarly the potential importance of any EDZ as a pathway for enhanced gas migration could be evaluated theoretically for a range of possible host rock lithologies;
- demonstration that upscaling of two phase flow in fractured crystalline rocks is possible such as to capture the key processes relevant to gas migration in the context of a radioactive waste repository; and
- the possibility that there might be future temporal changes in rock properties during glaciation.

The review has also highlighted that, with the possible exception of results from investigations related to LLW, all the key research findings into gas evolution have been utilised by the previous generic performance assessments, GPA01 and GPA03 (Nirex, 2001 and Nirex 2003a,b respectively). However, the ways in which much of the previous work on gas migration has been used in these assessments are less clear. For example, there has been much research that has provided an improved understanding of gas migration processes in fractures. Nevertheless, it is unclear how this work has been used in the generic performance assessment.

Gas migration through the geosphere has been shown to depend on fine details of the geology and hydrogeology of the overlying strata. During site screening and selection the need to demonstrate that the geosphere will retard or disperse gases will need to be considered more than perhaps in the past.

It appears that there may have been considerable overlap between the work carried out by Nirex and work undertaken by BNFL in relation to the LLWR near Drigg, particularly relating to organic matter degradation. It is recommended that a systematic review of this work is undertaken to identify the extent to which results from the BNFL work might help to build confidence in NDA results.

Contents

1 Introduction

This report describes a review carried out by Quintessa on behalf of the Environment Agency. The review covers research concerning gas evolution and migration from a possible future deep geological repository that was completed and/or initiated by Nirex.

The review was started in January 2007 and a first version of this report was completed in March 2007. However, it subsequently became apparent that this initial review had been unable to cover several research projects that were substantially completed, but not yet fully reported by Nirex before the end of the review period. Consequently, in February 2008, the Environment Agency commissioned Quintessa to revise the first version of the report to take into account these later Nirex research results.

At the time the review commenced, Nirex was the organisation charged with ensuring the safe long-term management of the UK's Intermediate Level Radioactive Waste (ILW) and some long-lived Low Level Radioactive Waste (LLW). However, the role of implementing geological disposal has now transferred to the Nuclear Decommissioning Authority, with the Radioactive Waste Management Directorate (RWMD) as the delivery organisation. Some of the research into gas that was initiated and substantially completed by Nirex was reported following the RWMD's establishment and is covered by the present review. In consideration of the organisational changes this report attributes on-going work to the NDA, whereas past research is attributed to Nirex for clarity.

As part of improved regulatory arrangements, the Environment Agency has framed an agreement enabling scrutiny of NDA's programme of work. Part of this scrutiny involved examining Nirex's Phased Geological Repository Concept (PGRC) and how Nirex applied this to the assessment of Intermediate Level Waste (ILW) conditioning proposals through the Letter of Compliance (LoC) process.

Nirex undertook two Generic Post-closure Performance Assessments, GPA01 (Nirex, 2001) and a later GPA03 (Nirex, 2003a,b). The latter is a revision of the earlier assessment that takes into account revised inventory information. The GPA03 (Nirex, 2003a,b) includes assessments of the radiological risk posed by gas following repository closure.

After 2003 Nirex undertook a number of additional calculations relating to the gas pathway. These calculations included an extension of the human intrusion pathway in GPA03 to include gas (Hoch and Thorne, 2007) and a reworking of the Nirex 97 gas pathway calculations using a more sophisticated two phase flow model incorporating groundwater flow (Hoch et al. 2007a). These latest studies were undertaken using a revised inventory of gas generating materials as reported in Nirex's 'Viability Report' (Nirex 2005a).

Depending on the nature of the waste and the ambient conditions, a number of different gases are likely to be produced from ILW, including: hydrogen, carbon dioxide, methane, radon and other minor gases, such as hydrogen sulphide. Some of these gases may have a radiological impact (e.g. ^{14}C-labelled methane and carbon dioxide). Other, non-radioactive 'bulk' gases (e.g. hydrogen from metal corrosion), may have an indirect impact (e.g. by promoting the release of radiologically significant gases from the repository and their subsequent transport). It also needs to be considered whether or not hydrogen and methane could pose a flammability hazard at the ground surface. The overall objective of the current review is to provide an initial critical analysis of the April 2007 NDA position on gas generation and migration, based on work carried out or initiated previously by Nirex.

The initial stage of the work was a review of Nirex Context Note 3.5 ("Gas and its Effects"; Nirex, 2006a) and its key underpinning references. Specific objectives are to:

- Evaluate whether Nirex explored (or identified as future work) all significant issues of concern in relation to gas generation and migration (given the current decision-context of a geological repository). This evaluation includes a review of whether major recommendations and issues identified in key contractor reports were captured in the Context Note[2].
- Review differences in approach to the assessment of gas generation and migration for a selection of overseas repository programmes. This task will need to account for any differences that may exist between a UK repository concept and waste inventory and that of other countries.
- Identify significant uncertainties and any omissions in the work commissioned by Nirex.

[2] It was aimed to evaluate only whether earlier recommendations and issues had been appropriately recorded in the Context Note; it is recognised that other documents, some of which post-date the Context Note, aim to address these recommendations and issues in depth.

2 Approach

Most of the reviewed documents are reports published by Nirex or its contractors (see Appendix 1) relating to ILW disposal. In addition, a small number of documents prepared as a result of international research programmes were also consulted to enable the Nirex work to be put into an international perspective. It should be noted that biosphere issues are outside the scope of the review though some of the literature considered does include biosphere-specific information.

An initial list of reports to be reviewed was prepared by the Environment Agency. This list was then augmented by Quintessa staff, based on their own knowledge of research into gas generation and migration connected with radioactive waste disposal. The Nirex reports were then obtained directly from NDA RWMD and subjected to an initial review by Quintessa. As a result of this review several areas of uncertainty were identified and formed the subject of direct discussions between staff of Nirex and Quintessa. In order to clarify some of the uncertainties, NDA RWMD supplied Quintessa with additional documents for review.

The reviewed Nirex reports consisted of a combination of:

- ▲ overview documents, principally Context Note 3.5 (Nirex, 2006a), the 'Viability Report' (Nirex, 2005a), Geosphere Research Context Notes (Nirex, 2005b, 2006b) and a report on future geosphere research (Nirex 2006c); and
- ▲ supporting documents, which included reports referenced directly in the overviews and reports not directly referenced in the overviews but referenced in other supporting documents.

The general approach to evaluating these Nirex documents had the following main elements:

1. Information against which to evaluate whether or not the work covered by the Nirex reports is complete and relevant was compiled and consisted of:
   - reports, especially containing overviews generated outside Nirex's main research programme, both in the UK and internationally; and
   - Quintessa's FEP list aimed at carbon dioxide sequestration (which is based on the NEA list (NEA/OECD, 2000), but targeted at underground carbon dioxide sequestration and hence relevant to gas migration).

The reports mentioned in the first bullet are described in Section 3.1 below. The FEP database, and its comparison with the research of Nirex are summarised in Appendix 2.

2. General measures of the adequacy of the research by Nirex were identified and include:

- the extent to which the information in the supporting documents is summarised by overviews;
- the extent to which the work is complete and relevant (as judged against the information summarised in 1 above) when all documents (overviews and supporting documents) are considered globally;
- the extent to which each document (overviews and supporting documents) considered individually:
    - identifies the drivers/rationale for research;
    - describes repetition of work;
    - describes work that would impact upon:
        - repository design;
        - safety/Performance Assessment (PA); and
        - building confidence in the suitability of a repository concept (or a particular site in the case of documents produced as part of the Sellafield investigations);
    - extent to which models adopted are relevant and adequate for the purposes for which they are intended;
    - identifies outstanding issues and uncertainties.

3. The overview documents concerning gas research that have been produced by Nirex were checked against the measures of adequacy given in 2, leading to the identification and documentation of:

- issues that have apparently been adequately addressed;
- uncertainties and outstanding questions that have been recognised by Nirex;

- potential future work proposed by Nirex to address the uncertainties and outstanding questions;
- uncertainties and outstanding questions that have not been recognised by Nirex;
- potential future work not proposed by Nirex, but which could be carried out to reduce uncertainties and answer outstanding questions (irrespective of whether these uncertainties and outstanding questions have been recognised by Nirex).

4. Other documents referenced in the overview reports were then evaluated to obtain documentary evidence to support (or refute) the statements made as to the extent to which the measures of adequacy in 2 have been met.

5. A list of outstanding uncertainties and questions arising from the reviews under bullet points 2 and 3 above was prepared and discussed with staff from Nirex.

6. The information obtained during Tasks 1 to 5 above was used to address the questions and issues identified by the Environment Agency as being of particular relevance. The following sections are structured in accordance with these questions and issues.

3 Important Issues Concerning Gas Generation and Migration

3.1 The International Position

3.1.1 International Literature

Summaries of international research into the generation and behaviour of gas in and around radioactive waste repositories can be used to compile issues against which the research that has been carried out by Nirex may be judged. Accordingly, the present review commenced by carrying out on-line literature searches (especially the web-sites of the International Atomic Energy Agency (IAEA), Nuclear Energy Agency (NEA) and EC(CORDIS)). These searches highlighted that in connection with geological repositories for radioactive wastes, international research on the generation and behaviour of gas is less mature than the research on aqueous solutes. The principal reason is that not all wasteforms have been considered to cause gas problems. Research has tended to be undertaken only by those agencies intending to dispose of LLW/ILW, that is Nirex, Andra (France), Nagra (Switzerland), JAEA/JNC and JNFL (Japan) and US DoE (for WIPP).

Consequently, this search revealed very few documents, the most relevant being:

- Rodwell et al. (2003), recording the views of GASNET, a network of researchers concerned with gas issues in safety assessments;
- NEA/OECD (2001), the proceedings of an international workshop covering safety-relevant issues related to gas generation and migration in radioactive waste disposal;
- Rodwell et al. (1999), a review of the status of understanding (in 1999) of gas migration and two-phase flow through engineered and geological barriers in deep repositories for radioactive waste;
- Horseman et al. (1996), a review of the fundamental processes governing water, gas and solute migration through argillaceous media.

Older research summaries were not considered since they reflect different priorities to those of the recent UK research programme, owing to different repository concepts and/or different perceptions and levels of knowledge. In the case of Nirex, the move to the Phased Geological Repository Concept (PGRC) is an example of a change in concept. The realisation that significant ^{14}C gas may be generated from a wide range of wastes, and not just the labelled organic molecules assessed in Nirex 97 (Nirex, 1997a) is an example of changing knowledge and perceptions.

It is pointed out that work by Nirex is included in each of the four documents in the above list. Consequently, these documents should not be viewed as completely independent sources against which to judge Nirex's research.

Each of the above documents considers gas generation in repositories for all the main kinds of radioactive waste (LLW, ILW and High-Level Waste (HLW)/Spent Fuel (SF)) and gas migration from these repositories. The work reported on gas generation in HLW/SF repositories is of only marginal relevance to the present work. The quantities of gas generated in such repositories are expected to be much lower than the amounts that would be generated in an ILW repository, which is the main concern of this report. Additionally, the engineered barrier system in an HLW/SF repository would differ from that envisaged by the PGRC. In particular, in most HLW/SF disposal concepts the barrier system would probably include a compacted bentonite buffer, unlike the PGRC which envisages a porous cementitious backfill. However, some of the research into gas migration through bentonite buffers is also relevant to understanding the migration of gas through compacted plastic clay host rocks. It is conceivable that such host rocks might be considered in future for implementation of the PGRC.

Rodwell et al. (2003) cover the possible impacts of gas migration on PA and safety, providing recommendations for further research covering gas generation, migration and biosphere issues. The focus of Rodwell et al. (1999) is on gas migration topics, although there is a shorter review of gas generation and its modelling. This report makes no formal recommendations for further research, but observations are made at various points in the text and these have been taken into account in the analysis that follows. In contrast to these two documents, the report by Horseman et al. (1996) deals with fundamental physico-chemical processes that control gas migration through clay barrier systems (including engineered bentonite-based systems and natural mudrocks). The main conclusion relating to gas is that further research should be undertaken to understand the mechanism by which gas moves through clays. This recommendation is repeated in the report by Rodwell et al. (2003), and so Horseman et al. (1996) has not been considered further here.

NEA/OECD (2001) comprises an overview and separate papers covering a range of issues relating to gas generation and migration in a variety of host rock lithologies, including non-indurated clays, indurated clays, crystalline rocks and salt.

3.1.2 The International Position Concerning Gas Generation

The main processes and uncertainties concerning gas generation identified by Rodwell et al. (1999, 2003) and NEA/OECD (2001) are very similar. It is apparent that there were few advances in the understanding of gas generation during the reporting period spanned by these documents. The summaries below focus on the main themes of each document, but do not repeat information that is provided in a later document.

Four topics concerning gas generation were identified by GASNET as being targets for future research (Rodwell et al., 2003), and are described below:

- **Long-term corrosion rates**. It is considered important to have available reliable values of long-term corrosion rates of ferrous metals (and Zircaloy) appropriate to the particular conditions expected in the various repository concepts under consideration. In recent years many data concerning corrosion of ferrous metals under conditions relevant to radioactive waste repositories have been collected. However, for any proposed repository environment it is important to show that there are sufficient measurements covering the range of expected conditions, in order to provide confirmation of the corrosion mechanisms and rates.

- **Microbial gas generation rates**. There is considerable uncertainty in the potential quantities of gas that may be generated by microbial degradation and also uncertainty in the rates at which such gas may be evolved. The conventional approach has been to use bounding upper estimates, but improved bounds on both amounts and rates would be helpful.

- **Release of gaseous ^{14}C**. Radioactive waste can contain large quantities of ^{14}C in a variety of materials. Better understanding is required of the potential of these materials, particularly irradiated steels and other metals and graphite, to release ^{14}C in gaseous form. Although not relevant to gas generation in the repository itself, it is possible for methane containing ^{14}C to be converted to ^{14}C-labelled carbon dioxide by bacteria in the near-surface environment. The likelihood of this happening needs to be established, as $^{14}CO_2$ presents a greater radiological hazard than $^{14}CH_4$.

- **Evolution of the near field**. The evolution of the near field involves complex coupled processes. A better understanding of this evolution is required to justify assumptions about near-field conditions during the extended period of gas generation that is expected. For example, it is desirable to develop an improved capability to predict the long-term degradation of cementitious materials (backfill and concrete). The presence of these materials maintains high pH conditions. However, if the pH were to decrease as a result of cement degradation, gas generation rates might also change (if gas-generating materials are still present in the repository).

The GASNET report (Rodwell et al., 2003) also states that generally gas generation in geological repositories for radioactive waste will occur by a combination of three main mechanisms:

- corrosion of metals in the wastes and packaging, producing hydrogen;
- radiolysis of water and some organic molecules in the waste packages, generating mainly hydrogen; and
- microbial degradation of various organic wastes, giving mostly methane and carbon dioxide.

The dominance of these mechanisms will mean that the bulk gas produced within a repository under saturated conditions would be mainly hydrogen and methane.

The report points out that to assess the relative importance of these mechanisms requires information about the disposal site, the disposal concept and the waste characteristics. Usually, radiolysis will be subordinate to gas generation by corrosion, which will be dominant in volume terms, or degradation of organic matter. However, there are some circumstances (e.g. HLW disposal in thin-walled containers) in which radiolysis may become the dominant mechanism. In the case of ILW, which usually contains relatively small volumes of degradable organic material, corrosion is likely to be the dominant gas generation mechanism.

Usually, corrosion rates have been calculated by multiplying the surface area of the metals present by a defined corrosion rate. However, this approach is simplistic and other factors also need to be taken into consideration, including:

- The extent to which corrosion occurs within any time interval will depend upon the availability of water. It is pointed out in Rodwell et al. (2003) that in fractured rock, the volume of available groundwater is likely to be effectively unlimited. Argillaceous host rocks may contain sufficient water to allow corrosion to progress, provided that the water is accessible. In contrast, in salt, corrosion will be limited by the availability of water, provided that the rock remains physically undisturbed.
- Galvanic corrosion may be an issue but needs to be considered on a case-by-case basis. However, this corrosion process may be significant where metals such as Magnox and aluminium are in close proximity to other metals.

- A related issue is that graphite is cathodic to most metals and may therefore promote the galvanic corrosion of steels.
- Microbially-induced localised corrosion may be significant (although this process is anticipated to be more important as an influence on physical containment integrity than as a cause of gas generation).
- It may be appropriate to represent anaerobic corrosion of iron and steel containers as a uniform process. However, there is a possibility that corrosion rates can be affected by the presence of passivating layers. It is necessary to use corrosion rates that have been obtained from experiments in which such layers become well established, because using rates based only on short term measurements could substantially over-estimate overall gas generation rates.
- Uranium corrosion rates are uncertain because available measurements have been made in aqueous solutions not in cementitious grouts.

The GASNET report notes that gas may contribute directly to radiological risk mainly through acting as a carrier of ^{14}C. However, ^{14}C is heterogeneously distributed in the wastes and it may therefore be necessary to represent release of this radionuclide using a spatially variable fractional release function.

Many of the issues that are pointed out in Rodwell et al. (2003) are also presented in NEA/OECD (2001). However, the following additional points are particularly relevant:

- It is recommended that repositories should be designed to minimise gas generation and mitigate its consequences.
- There is stated to be a need for a better understanding of gas generation and evolution during the early phases of repository development, during which resaturation occurs.

In commenting on rates of gas generation obtained using models, Rodwell et al. (1999) note that "attempts should be made to relate the results to observations in comparable situations in nature, experiments or practical experience". This comment stresses the importance of attempting to validate[3] models against data, and doing so over the range

[3] Here "validate" refers to the process of demonstrating that within its domain of applicability, a model gives results of satisfactory accuracy, consistent with the intended application of the model (Schlesinger et al. 1979).

of conditions that waste packages will experience, which include interim storage[4], transport, repository operations and the post-closure period. In the strictest sense, complete validation will not be possible in practice, since all the relevant repository conditions will not be accessible to direct observation and/or experimental replication. However, it should be possible to build confidence that any inaccuracies in the model will not invalidate any conservative assumptions that might be made.

The theme of understanding the chemical properties of the near field that are relevant to gas generation is also mentioned by Rodwell et al. (1999) in relation to both corrosion and microbial processes. Three issues are highlighted as being particularly important:

- ▲ The behaviour of the wastes and the near field more generally will depend to some extent on the time for which the wastes are held within interim storage and the period for which the repository is open between waste emplacement and closure. During these time intervals, organic matter in the wastes will begin to degrade and metals in the wastes and canisters will to some extent corrode. These processes will be facilitated by the presence of an oxygen-rich atmosphere (air) and moisture. The latter will be contained by the wastes initially, but may also be supplied by the air, or the pore space of any backfill that is emplaced during the operational phase. Thus, the effect of extended storage prior to final disposal, and possibly deferring final closure of the repository, can be to alter the nature of the gas-generating inventory at the time of closure. Potentially during such an extended period of storage or deferral of repository closure, there would be a need to treat ventilated gases.

- ▲ The spatial heterogeneity of the near-field can be an important factor in system evolution and its influence should be recognised within PA. Previous approaches have assumed spatially constant conditions throughout the repository, or step-wise temporal changes in conditions. However, in reality on a local scale conditions are unlikely to be uniform, particularly soon after closure when gas generation rates will be greatest. It is pointed out that the spatial scales represented in the PA therefore need to appropriately reflect the actual scales over which gas generation processes vary.

- ▲ It is apparent that carbon dioxide is widely assumed to be trapped by cements and that this trapping process may have a major impact upon predicted repository performance in containing the radionuclide hazard. Additionally, it

[4] "Interim storage" refers storage of wastes at the surface, prior to their acceptance by Nirex or the NDA.

is always assumed that grouts etc will be designed to allow the gas to escape. However, confidence needs to be built in assumptions regarding the properties of the cementitious barrier that facilitate gas escape, especially in ensuring that these will be preserved and that other aspects of barrier performance will not be compromised by the carbonation reactions that trap the carbon dioxide.

3.1.3 The International Position Concerning Gas Migration

General issues

As was the case for gas generation, the investigations concerning gas migration described in Rodwell et al. (1999, 2003) and NEA/OECD (2001) are very similar. In part, the lack of significant changes may reflect a sound understanding of fundamental gas migration processes resulting from the earlier work. However, over the time period covered by these reports approaches for upscaling gas migration models from the typical repository scale to the site scale do not appear to have improved. Upscaling representations of gas migration remains a significant problem when modelling of gas migration. The insignificant advance in this area most probably reflects the inherent difficulty of addressing this issue.

The implications of gas migration for PA

The GASNET report (Rodwell et al., 2003) reviews the state of knowledge concerning gas generation and migration from the point of view of PA. It was concluded that internationally, early safety assessments considered gas to be a secondary pathway for radionuclide migration to the biosphere. Consequently, gas was evaluated separately from the other pathways. Additionally, gas may not have been taken into account when designing repositories, although some design features included for other reasons have turned out to be favourable from the point of view of gas. However, the report notes that gas generation and migration are now typically being considered from the outset of developing a repository concept and an approach to safety assessment. This change in emphasis has resulted in a more consistent approach to the evaluation of all pathways being adopted.

The main potential impacts of gas migration on safety that need to be evaluated are stated to be:

- radiological impacts; and
- a flammability hazard due to the possibility that any gas arriving at the surface will be dominated by hydrogen and methane.

The main radiological impact of gas on safety is stated to be due to ^{14}C released in the form of methane. It appears to be generally assumed that any ^{14}C produced in the form of carbon dioxide will be removed by reaction with components of the engineered barrier, or dissolved in groundwater. Other radionuclides that may be transported in gaseous form include ^{3}H, ^{222}Rn, ^{85}Kr and ^{129}I.

The GASNET report states that the main migration processes by which gas may impact upon safety are:

- migration of gas as a free phase;
- forcing of water from a repository by accumulation of a gas cushion within the repository;
- entrainment of groundwater in streams of gas bubbles;
- induction of groundwater movement as a consequence of instabilities in gas pathways;
- transport of colloids and chemical species by attachment to gas-water interfaces;

Potentially the coupling between gas generation and water movement may be important. While the rate of gas generation could be affected by the availability of water, as noted in Section 3.1.2, conversely gas generation could potentially reduce flow into the repository. The storage of gas within the pore space of the engineered barrier system might act to reduce the access of water to the wastes, thereby diminishing the rate of gas generation.

Rodwell et al. (1999) considered five potential host rocks, four of which are directly relevant to Nirex (saturated fractured crystalline rocks, indurated mudrocks, salt and plastic clay) and unsaturated fractured rock (which the authors of the present report consider irrelevant since no unsaturated rocks in the UK are likely to be suitable, as is implicit in recently published site screening criteria (DEFRA, 2007). The report emphasises the need to consider the consequences for safety of gas release itself and the coupling between this gas release and the development of pathways for radioactive gas migration. Fracturing resulting from over-pressuring was considered to be the most significant process by which gas could influence groundwater flow. This process could lead to the development of migration pathways for both groundwater and gas. It was concluded that this influence of gas on groundwater flow could potentially have a greater impact upon safety than the radiological impact of the gas itself. This conclusion follows from the fact that only a tiny proportion of the generated gas will be radioactive and that, depending upon the groundwater chemistry and the system hydrodynamics a significant proportion of the radioactive gas could dissolve in the groundwater.

It was also concluded by Rodwell et al. (1999) that the level of detail at which gas migration should be represented in a PA may be greater than required for the groundwater pathway. That is, in the case of gas migration it may be necessary to consider heterogeneities at smaller spatial scales and to represent a greater number of migration and retardation processes explicitly. However, research is needed to determine the processes to be included in the PA and to ensure that the resulting representations of gas migration are defensibly bounded.

Rodwell et al. (2003) and Rodwell et al. (1999) point out that repositories can be designed to minimise the quantities of gas produced and the rates at which the gas might be produced. Design measures include using appropriate packaging materials, drying of wastes, using backfills that absorb gas (e.g. cement or magnesium oxide), and designing vaults to facilitate steady gas release. Rodwell et al. (1999) point out that the repository concepts for ILW and LLW usually rely on designing the engineered barriers so as to ensure that gas can escape without damaging the barrier structure. It is also generally assumed that the host rock can easily transmit the released gas. It was considered probable that backfill grout could be designed so as to have a sufficiently high permeability and low enough capillary pressure.

It appears to be a generally made assumption that gas migration in crystalline rocks occurs so readily that there is no need to consider the possibility of over-pressuring and the potential problems that this might cause. In these cases, PA can focus on other potential hazards, principally radiological and flammability hazards. In contrast, gas migration from an ILW repository located within a mudrock will be restricted by the low formation permeability. Hence over-pressuring and fracturing are considered to be potentially important problems in such situations. These processes could potentially generate transient pathways for relatively rapid gas migration through the host rock. Depending upon whether the host rock formation extends to the surface and the characteristics of the rocks overlying the repository, these transient pathways may lead to relatively rapid transport to the surface.

It was considered that in the case of salt host rocks where volumes of available water are small and water fluxes are low, significant over-pressuring by gas would be unlikely (Rodwell et al. 1999). Corrosion and waste degradation would evolve only a relatively small volume of gas at a slow rate owing to the limited water supply. However, there are circumstances in which wastes disposed of in salt might come into contact with significant volumes of brine, potentially causing considerable gas volumes to be produced relatively rapidly. It is noted by Rodwell et al. (1999) that models for gas generation in salt in such cases are at an early stage of development.

The roles of the geosphere

The GASNET report (Rodwell et al. 2003) mentions a number of possible roles of the geosphere. The following roles are particularly important in view of the potential impacts of gas on safety described above:

- The rock may provide a barrier function, if impermeable with respect to gas.
- The geosphere may provide one or more pathways through which gas may travel between the repository and the surface, the lengths of which will be determined by a combination of lithological, structural and hydrogeological characteristics (e.g. head gradients).
- The geosphere may act to disperse the gas (thereby influencing the areal extent of any release to the surface).
- The geosphere may provide a medium within which dilution of gas may occur.
- A gas storage capacity may be provided by the geosphere (that is, the geosphere may act as a gas reservoir).
- The geosphere may act to prevent the development of a continuous gas phase within a potential transport pathway.

It is noted that a further role could be to supply naturally-occurring trace contaminants, most notably radon, to a migrating gas stream. However, according to Rodwell et al. (1999) stripping of natural radon from the rock and its subsequent transport is not considered to be significant contributor to risk.

The precise roles played by the geosphere are highlighted to depend upon site-specific characteristics, which to a large degree will reflect the properties of the rocks present. The extent to which the rock is permeable with respect to gas will partly determine whether a pathway for gas migration will form (the quantities and rates of gas generation are other important factors that influence formation of a gas pathway). Furthermore, the characteristics of the pathway (particularly its length) will influence the time taken for gas to migrate from the repository to the surface.

The longer this travel time, the greater will be the proportion of the transported radionuclides that will undergo radioactive decay. Rodwell et al (2003) noted that, if a pathway to the surface exists, then since the half-life of ^{14}C is so long (5700 years) delays in travel time may have an insignificant effect on the proportions of ^{14}C present in any surface gas releases. However, they point out that the much shorter half-life of tritium (^{3}H; 12.43 years) means that in this case the travel time is more likely to exert a significant influence on the amount (if any) that arrives at the surface. Rodwell et al.

(2003) also considered that none of the ^{222}Rn evolved in a repository will reach the surface, since the half life of this isotope is too short (3.82 days).

In fractured crystalline rocks gas migration will be dominantly by advection through the fracture network. In contrast, in plastic clays, gas migration will be controlled by diffusion, unless pressurization by gas causes migration via microscopic pathways. The report discusses this latter mechanism in some detail and makes clear that it could be transient, with the microscopic pathways resealing once the gas has migrated. However, it is also apparent that this transient mechanism has not been confirmed. It is pointed out that if clay (bentonite) buffers and seals are to be used in a repository, they may need to be designed so as to allow some gas to be released in order to prevent pressurisation leading to fracturing, while at the same time avoiding the development of large-scale fractures that could act as groundwater flow pathways.

The role of an EDZ is also likely to depend upon the characteristics of the host rock (Rodwell et al. 2003). The EDZ may potentially behave as a reservoir for gas, thereby helping to prevent pressures rising excessively due to gas generation. Alternatively, the EDZ may act as a pathway for gas migration. The actual behaviour of the EDZ is likely to depend at least partly upon the characteristics of the host rock. The EDZ in a fractured crystalline rock is likely to exhibit a greater gas reservoir function than the EDZ in a mudrock. However, there appears to be some uncertainty as to the exact role in any particular lithology.

Adequacy of models

From Rodwell et al. (1999) and Rodwell et al. (2003) it is clear that much of the modelling of gas migration that had been undertaken previously adopted a conventional porous medium approach to flow modelling. The approach uses an extended version of Darcy's Law in which relative permeability and pressure functions are used to represent two-phase flow. This method has been applied to all the main potential repository host rocks (water-saturated fractured crystalline rock, unsaturated fractured rock, plastic clay, indurated mudrock and rock salt). However, the details of the models have reflected the specific characteristics of the rock, especially the extent to which flow occurs dominantly through a fracture network or dominantly through the rock matrix. In the former case, dual porosity characteristics may be represented, whereas in the latter case, only matrix porosity is considered.

Other modelling approaches that have been investigated are also mentioned in Rodwell et al. (1999, 2003). Fracture network models, numerical models of two-phase flow in single fractures and simulations of transport processes in salt have all been undertaken. However, it is pointed out that many of these models are more appropriate for developing an underlying understanding of gas transport processes, rather than for PA purposes.

In Rodwell et al. (2003) conventional two-phase flow models are stated to be generally regarded as being adequate for simulating gas transport through cementitious barriers and crystalline rock. However, there are uncertainties concerning the validity of these models for application in cementitious materials. It is pointed out that it may be difficult to obtain parameter values that are sufficiently precise to allow the effects of different transport and retardation processes to be distinguished. Furthermore, it is also apparent that these models may not be appropriate for clay barriers, whether in an engineered barrier system (bentonite) or in the geosphere. In these cases, it is necessary to consider the threshold pressures that must be attained in order for migration to occur.

Rodwell et al. (1999) had previously pointed out that there is uncertainty as to the accuracy of gas migration models when applied to the site scale. They stated that at that time (1999) there was a lack of site-specific or generic large-scale experimental data in order to verify gas migration predictions for crystalline rock. This situation also appears to have been the case in 2003, when the GASNET report was prepared.

Outstanding issues

In summary, the following major outstanding issues identified by Rodwell et al. (2003) are:

- ▲ uncertainties concerning gas migration in cementitious materials (which are of particular relevance to the PGRC), notably in connection with:
  - the gas migration properties of cementitious materials evolve under repository conditions (particularly as a result of cracking and carbonation as a result of reaction with carbon dioxide);
  - a lack of measured relative permeability functions for cementitious materials;
  - a lack of measured capillary pressure functions for cementitious materials; and
  - the validity of two-phase continuum models to simulate gas migration through cementitious materials.
- ▲ uncertainties about gas migration through the geosphere, particularly regarding:

- the appropriate scale at which to represent processes;
- models that upscale microscopic processes to predict large-scale behaviour (in particular determining whether the models are appropriate);
- a lack of data with which to parameterise models for two-phase flow in the geosphere.
- gas migration in argillaceous media, notably:
    - the entry pressure required before gas will pass through clay;
    - uncertain effects of gas migration on the properties of clay;
    - the re-sealing capacity of clay once gas generation has ceased; and
    - the effects of heterogeneities and anisotropy on clay behaviour.

Major uncertainties that were identified by Rodwell et al. (1999) are given below:

▲ It was pointed out that a great deal of uncertainty remains about the chemical and physical interactions between repository engineering materials and repository gases.

▲ The definition of appropriate gas solubilities in saline groundwaters was highlighted as being uncertain. It was also noted that in argillaceous rocks of low hydraulic conductivity, much of the water may be bound to mineral surfaces. Therefore, in these rocks it may be inappropriate to use gas solubilities obtained for free water, although there is some uncertainty as to the actual gas solubilities that should be used.

▲ Generally, migration of a free gas phase will be a temporally fluctuating process that will be affected greatly by small-scale heterogeneities in the rock mass. The characteristics of gas migration will be influenced to a large degree by the inherently unstable character of gas-water interfaces. It is not clear to what level of detail the heterogeneities in the rock mass and fluid dynamic instabilities must be represented in mathematical models. The extent to which all governing processes need to be considered explicitly and the spatial scales over which these processes need to be represented, is not well-known. It was thought to be particularly problematical to ensure that up-scaling is appropriate (and to demonstrate that this is the case). Up-scaling is also a problem of concern when modelling groundwater flow, but the situation for gas flow is complicated by the fact that gas migration will typically involve two phases and different portions of a rock's porosity will be accessible to different degrees by water and gas. The structures of migration pathways in clays are particularly uncertain and in plastic clays may be transient due to repeated dilation and re-sealing. It is unclear how to represent these pathways appropriately in models of site-scale flow.

The present reviewers note that Rodwell et al. (2003) state that in addition to ^{14}C, ^{3}H and ^{222}Rn, ^{85}Kr and ^{129}I could also be transported in gaseous form. However, Rodwell et al. (2003) did not state explicitly what (if any) contribution to risk might be made by ^{85}Kr and ^{129}I. The half-life of ^{85}Kr is short (10.73 years) and therefore it is likely that all of the ^{85}Kr that is evolved in a repository would decay before it could be transported to the surface. However, the half-life of ^{129}I is very long (16 million years). Therefore, any ^{129}I within a gaseous phase would decay insignificantly during a typical PA time frame (generally up to about 1 million years).

3.2 The Position of NDA

3.2.1 Introduction

This section summarises NDA's understanding of gas generation and migration at the end of 2007 based on work carried out by Nirex prior to April 2007, some of which was subsequently reported by NDA between that date and the end of the year. Since the actual work was carried out by Nirex, the text below refers to Nirex; the knowledge and views attributed to Nirex have been inherited by NDA RWMD. Descriptions are given of the main uncertainties that are currently being targeted by NDA's research and assessment methodology development. Comments are given concerning the extent to which the position appears reasonable, possible omissions in the work are not covered. These latter are considered instead in Sections 8 and 10. The ways in which Nirex used its understanding of gas generation and migration to develop numerical models are considered in Section 4.1 and Section 4.2, respectively. The implications of NDA's understanding for PA are given in Section 6.

Up to 1997 Nirex's consideration of gas generation and migration assumed that the then relevant inventory would apply, that the repository would be hosted in fractured crystalline rock (the BVG at Sellafield), and that backfilling of the vaults would take place soon after waste emplacement. These assumptions were captured in the Nirex 97 gas assessment (Nirex 1997a). Following refusal of planning permission for an RCF at Sellafield in 1997, Nirex amended its repository concept in two major ways:

- It considered a range of possible host rocks.

- It adopted a phased approach in which vault backfilling could be delayed for some hundreds of years after emplacement.

In the absence of a specific site Nirex undertook generic performance assessments of the gas pathway in 2001 and 2003 (Nirex 2001, 2003a,b). In 2005 Nirex reviewed all those issues that could impinge on the viability of the phased repository concept (Nirex 2005a) and found that with the publication of a revised waste inventory (Nirex, 2005c) that the annual risk from the gas pathway using generic site geologies could exceed the risk target. The change was due to the inclusion of ^{14}C-bearing graphite and steel wastes. This result led Nirex to increase substantially research and assessment activity in the area of gas generation and migration.

3.2.2 The Position of NDA Concerning Gas Generation

Gas generation by corrosion

It is considered by the NDA that over the million-year time period that is likely to be considered by a PA, corrosion reactions, especially of steel, would be responsible for the bulk of gas generation in a repository (Hoch and Rodwell, 2003a; Hoch et al. 2007b). This gas would therefore dominantly be the corrosion product hydrogen. Subsidiary quantities of this gas would be produced by the corrosion of other metals (principally Magnox, aluminium, uranium, Zircaloy and Inconel). However, there would be relatively short periods during the early evolution of a repository, during which the majority of the hydrogen gas evolved would arise from the corrosion of Magnox and/or aluminium. During the first few tens of years following closure there would be steady hydrogen gas production due to Magnox and aluminium corrosion. Hoch and Rodwell (2003a) calculated that all the Magnox would be consumed after about 100 years. They considered that hydrogen gas would then be generated dominantly by aluminium corrosion during the period of significantly elevated temperature; there would be significant hydrogen production from steel only after all the Magnox had disappeared. However, all the aluminium was calculated to be consumed after about 6000 years. In their modelling Hoch and Rodwell (2003a) treated alloys as if they are composed entirely of the predominant metal (Fe in steel or stainless steel, Mg in Magnox, Zr in Zircaloy, Ni in Inconel). That is, the alloy's corrosion rate was specified, but only the predominant metal was calculated to be reacted. It should also be noted that the timescales calculated will be accurate only if the assumptions concerning the shapes and sizes of reacting metal fragments are accurate.

The temperature dependence of the corrosion rates of these metals leads to maximum gas generation rates soon after backfilling when the vault temperatures are elevated, primarily due to hydration of the cement in the backfill and to a lesser extent to radioactive decay. For the repository design and waste inventory on which the calculations were based, the maximum temperature reached as a result of these processes would be about 80°C (Nirex, 1997b; more recent designs may result in lower peak temperatures). Steel corrosion under anaerobic conditions provides a background of on-going hydrogen production. Uranium corrosion produces only a small addition to the overall quantity of hydrogen evolved, owing to the small amount of uranium present in comparison to the quantities of other metals in the repository. However, uranium is consumed relatively quickly and therefore leads to a small peak in the gas production rate in vaults containing un-shielded ILW (UILW) during an interval of a few years after the vaults become anaerobic. In the calculations of Hoch and Rodwell (2003a) the uranium was completely consumed at around 115 years following closure.

Hoch and Rodwell (2003a) also estimated the release rate of ^3H due to corrosion. Their calculations showed that some ^3H release would take place throughout the interval of operations, but the maximum release rate would occur during the period of increased temperature due to backfilling. A spike in hydrogen release is caused by the elevated temperature. This spike is associated with a smaller peak in ^3H release the later that backfilling takes place, owing to the radioactive decay of ^3H. The release rate is diminished by a factor of about 17 if the release is 50 years later and would become insignificant if backfilling occurs at about 120 years from the start of operations.

The reviewers consider that this view of corrosion is generally reasonable in the light of knowledge concerning the underlying corrosion processes and international practice. However, while in general corrosion rates do increase with temperature, the rate tends to reach a maximum at 60-70 °C in open, aerated systems because of the off-setting effects of increasing temperature on O_2 solubility and the kinetics of thermally-activated processes. In addition, corrosion can decrease with increasing temperature owing to the precipitation of salts with retrograde solubility (e.g. carbonate mineral deposits) on the surface of the metal (e.g. Jullien et al. 2005).

According to the Nirex concept, hydrogen may be produced under aerobic conditions as a result of Magnox and aluminium corrosion. Any gas generated before repository closure would be removed by the vault ventilation system. Whilst this hydrogen production mechanism is correct, it is noted that other corrosion reactions proceeding at the same time, notably aerobic steel corrosion, would cause oxygen consumption. Thus, if ventilation does not effectively replenish the air within parts of the repository where waste is emplaced (because air flow is restricted by the waste), the overall gas volume generated might be less than envisaged within assessments of the Nirex concept. Magnesium will also react directly with oxygen from the air to produce MgO. However, this oxide will tend to form a passivating layer on the surface of the un-reacted metal and will be quantitatively unimportant as a mechanism for consuming oxygen.

Nirex also considers that, under aerobic conditions, steel and uranium may be consumed by reactions that do not produce gas (e.g. Agg et al. 2002; Rodwell et al. 2002). Additionally, as conditions become anaerobic any oxide film that has been formed by aerobic steel corrosion early in the evolution of a repository may decrease by reaction with iron, thereby consuming more steel (e.g. Agg et al. 2002; Rodwell et al. 2002). Nirex also undertook research into the effects of galvanic coupling (Smart and Blackwood, 1998). It was found that galvanic coupling between noble metals (e.g. stainless steel and graphite) and active metals (e.g. Magnox and aluminium) results in accelerated corrosion of the active metal, which may cause enhanced rates of hydrogen generation. However, these experiments were conducted only for cement-grouted wastes in the presence of aerated and fresh water. Under post-closure conditions, the porewaters in the cement would probably be saline and reducing.

Once anaerobic conditions have become established in the repository, hydrogen may be produced by the corrosion of mild and stainless steel, Zircaloy, Magnox, aluminium, and uranium. The potential volume of gas that may be generated under anaerobic conditions will depend on the quantity of metals consumed under aerobic conditions. This position is considered by the reviewers to be reasonable. However, much of the steel inventory is in the form of stainless steel (Table 1, Nirex, 2006a)[5], and the extent to which this is corroded during the aerobic phase could be limited, leaving much of the steel to corrode under anaerobic conditions. Similarly, C-steel that is passivated because of the presence of the cementitious backfill would also tend to corrode slowly. The amount of steel that could be corroded during the aerobic-anaerobic transition by the galvanic coupling of Fe(III) reduction to steel dissolution can be estimated based on the mass-balance of oxygen initially trapped in the repository. Unless there is a large reservoir of trapped oxygen, much of the steel inventory would remain un-corroded at the end of the aerobic phase.

Under anaerobic conditions, uranium corrodes in the presence of water with the production of hydrogen, according to:

$$U + (2+x)H_2O \rightarrow UO_{2+x} + (2+x)H_2 \quad (0.2 < x < 0.4)$$

A value of x = 0.4 was used to avoid underestimating gas production from uranium corrosion. However, it is not expected that in fact $UO_{2.4}$ would be produced under anaerobic conditions. Additionally, in reality there would be reductive dissolution of

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[5] It is now anticipated that a large number of future containers will be produced from Duplex rather than austenitic stainless steel (ASS) It is not clear how well known the corrosion rates of Duplex are under repository conditions, or whether there are any significant differences relative to ASS.

UO_{2+x} formed during the aerobic phase to lower oxides during the anaerobic phase. This process would in turn cause gas generation under anaerobic conditions to be decreased. Considerable oxidation of uranium in historic wastes could also have occurred prior to encapsulation. Following encapsulation there could be additional oxidations before emplacement, owing to interim storage under anaerobic conditions and reactions between the uranium and the porewater in the encapsulating cement.

Recent experimental evidence suggests that a proportion of uranium may react in a reducing cement matrix to form pyrophoric material, possibly uranium hydride (UH_3).

The general representation of passivating reactions by Nirex is somewhat unclear. It is not apparent from the documents reviewed whether the quoted values are rates for material passivated by the presence of cementitious backfill. However, the corrosion rates for mild steel reported in Hoch and Rodwell (2003a) seem rather low for near-neutral pH groundwaters. It is therefore assumed these rates are intended to be appropriate for groundwaters conditioned by alkaline cementitious backfill.

Hoch and Rodwell (2003a) propose corrosion rates of 1 μm y^{-1} for uranium under aerobic storage conditions, and 100 μm y^{-1} at other times. It is uncertain whether the slower rate under aerobic conditions takes into account the formation of a passivating oxide layer. However, if this is the case, then an implication of choosing a higher rate for anaerobic conditions is that this passivating layer subsequently breaks down.

In Hoch and Rodwell (2003a), for both Magnox and aluminium, no account was taken of any effect of the build up of hydroxide layers in reducing the corrosion rate (i.e. the corrosion rate specified in the input is not changed by this inhibition effect). This is potentially a conservative assumption in so far as it will cause the rate gas evolution by corrosion to be over-estimated.

Corrosion of metals within waste containers requires that water is present. In the case of ILW and LLW waste containers there is some uncertainty about the availability of water in the early phase following repository closure. There will initially be some water present in cementitious grout that may participate in initial corrosion. However, it seems likely that this water will be present in insufficient quantities and/or be insufficiently available to allow unrestricted corrosion to take place. Hoch and Rodwell (2003a) quote unpublished data obtained by Nirex that suggests that during waste storage prior to disposal, rates of gas generation by corrosion are lower than would be expected if water is freely available. It is not apparent whether these data were obtained under conditions appropriate for interim waste storage (at the surface, prior to receipt by Nirex) or for underground storage prior to repository sealing. However, it seems likely that corrosion rates would be similarly limited by the availability of water following repository closure, but before saturation by groundwater has been completed. Nirex considers that after this resaturation water will be freely available (both inside and outside the canister). This assumption is thought to be reasonable since the containers will be vented to allow gas release and water will be able to penetrate readily.

The post-resaturation ready availability of water to the ILW and LLW that are the subject of this review can be contrasted with the more restricted supply of water to wastes in a repository for HLW/SF. The containers for these latter wastes would initially contain insignificant quantities of water and would not be vented. In these cases, corrosion of the HLW/SF wastes will be possible only after water has penetrated the containers. This process may take thousands of years to occur. Even following initial water penetration corrosion may proceed only slowly while perforations in the containers are very small. In this case, only small amounts of gas produced by initial corrosion will generate a back pressure that slows down further water ingress (e.g. SKB, 2006).

Nirex have recognised that corrosion of metals may release a significant quantity of ^{14}C-labelled gas. This possibility was reviewed in Rees (2004) and Rodwell et al. (2002). The specific case of ^{14}C release from Magnox wastes was considered in more detail by Rees et al. (2004).

Rees (2004) distinguished between ^{14}C release from the relatively more reactive metals (Magnox, uranium and aluminium) and the relatively less reactive metals (stainless steel and mild steels). However, in both metal groups, the ^{14}C present was formed predominantly by irradiation of the impurity ^{14}N. The specific factors influencing the quantities of ^{14}C that may be released from these metals are:

- the chemical form of the ^{14}C within the metal, principally whether or not it is present as carbon (which is relatively inert and therefore likely to remain within the metal) or as metal carbide (which will be relatively reactive and from which ^{14}C may be released as a consequence of reaction with water);
- the corrosion rates of the metals, which will control the accessibility of water to the metal carbides present;
- the characteristics of the ^{14}C-labelled gas produced (uranium carbides will produce $^{14}CH_4$, magnesium carbides within Magnox will produce acetylene (C_2H_2) , which is expected to react with corrosion-generated hydrogen to yield ethylene (C_2H_4)).

In connection with the ^{14}C-labelled gas that might be evolved from Magnox wastes and the associated uranium, Rees et al. (2004) noted that the following are uncertain:

- the inventory of ^{14}C present in metallic uranium wastes;
- the amounts of uncorroded irradiated uranium waste at repository closure, including any material not associated with Magnox;
- the corrosion rate of uranium and Magnox metal wastes encapsulated in a cementitious grout (under these conditions the rates could be lower than those measured for the metals immersed simply in a high pH solution);
- amounts of ^{14}C in the form of elemental carbon and uranium carbide; and
- the gaseous products of the hydrolysis of uranium carbide.

Rodwell et al. (2002) have also reviewed the mechanisms by which other radionuclides, besides ^{14}C, might be generated in gaseous form. They concluded that Magnox, Zircaloy and stainless steel are likely to be the main sources of tritiated gas (^{3}HH), which could be evolved by the following mechanisms:

- attack of ^{3}HHO on metals in waste and packaging;
- release of embedded ^{3}H by corrosion;
- release of embedded ^{3}H from metals by solid-state diffusion.

Rodwell et al. (2002) note that tritiated methane is not expected to form in significant quantities since ^{3}H and organic substrates for gas production are not present in the same waste streams. They did not however consider the possibility that nearby packages might interact allowing tritium to migrate into packages that contain organic-rich wastes. Also, metal carbides were not considered as a potential source of tritiated methane and other short chain hydrocarbons because these were not included in the potential gas-generating inventory being considered at that time.

They also considered the isotopes ^{85}Kr, ^{81}Kr, ^{39}Ar and ^{42}Ar, which may occur in some waste streams. They identified no quantitative data but considered that probably these isotopes would be liberated over an extended period, due to the slow rates of corrosion of the stainless steel, Zircaloy and any UO_2 fuel, within which they occur. They therefore recommended that these isotopes should be considered for separate detailed assessments only if initial assessments indicate that this is sensible.

The geometry of the metal bodies that undergo corrosion will influence the gas generation rate and hence the rate of radionuclide release from corroding metals. In the Nirex 97 assessment (Nirex, 1997a), metals were assumed to be present in the form of small, solid spheres. Although this assessment did not consider the possibility that ^{14}C would be released from these metals, Rees et al. (2004) made the same geometrical assumptions as Nirex 97 to calculate the peak rate of $^{14}C_2H_2$ (acetylene) generation from irradiated Magnox. However, Hicks et al. (2003) concluded that this approach is overly conservative. They pointed out that this assumption may have resulted in the prediction of pessimistically high generation rates for ^{14}C-labelled gas, and high peak rates of gaseous release to the biosphere after repository closure. This conclusion may be true in view of the fact that a metal sphere of a given volume might be expected to react more rapidly than a metal particle of similar volume, but different shape. However, the conclusion of Hicks et al. (2003) does not appear to take into account the variable sizes of metal particles in actual wastes. Similarly, no consideration seems to have been given to the fact that these particles would in reality have surface irregularities and contain structural defects that might make them more susceptible to reaction. Additionally, Hicks et al. (2003) did not support this assertion of conservatism by an evaluation of the coupling between gas generation, groundwater flow and the accessibility of water to the corroding metal. For these reasons, any assumption of spherical particles being conservative needs justification. This need appears to have been recognised by the RWMD and comparison of models of uranium corrosion in cylinders and spheres has been undertaken using Magnox Electric's code MAGGAS (Hoch et al. 2007c). These calculations have shown that cylindrical geometries corroded more rapidly than spheres where they both started with the same surface areas (Hoch et al. 2007c).

Microbially-mediated gas generation

The examination of microbial processes has been well aligned with the international consensus (Christofi, 1991; Greenfield et al. 1991; West, 1995; Stroes-Gascoyne and West, 1996; Grant et al. 1997). However there may be some potential process omissions and uncertainties:

- Although Nirex generally takes account of the microbial redox cascade (Leschine, 1995) that mediates the transition from aerobic to anaerobic conditions in microbially active environments, microbial iron reduction (Lloyd, 2003) is not considered. Microbial iron reduction would generally occur after nitrate reduction and before sulphate reduction and would consume simple organic compounds at the expense of ferric iron, producing carbon dioxide and ferrous iron. These simple compounds would generally be fermentation and corrosion products such as volatile acids and molecular hydrogen. The magnitude of microbial iron reduction is dependent on the amount of ferric iron available. However, in a repository containing significant amounts of iron and steel it is likely that corrosion during the aerobic phase of the repository would generate ferric corrosion products which would be able to drive microbial iron reduction.

▲ Microbial iron reduction is modelled in the gaseous and aqueous source term model (Humphreys et al., 1997; Beadle et al., 2001) employed in the 2002 Drigg Post Closure Safety Case (BNFL, 2002). The inclusion of iron-reducing bacteria is supported on the basis of the isolation of iron-reducing bacteria from the LLWR near Drigg (Beadle et al., 2001).

▲ Nirex emphasises the role of nitrate reduction and the potential importance of nitrate reduction in inhibiting methanogenesis (Rodwell et al., 2002; Rodwell, 2004). However, the reviewed reports provide no evidence that there is any significant nitrate inventory in the L/ILW. In fact the absence of significant amounts of nitrate in specific wastes is emphasised by Hoch et al. (2004).

▲ One of the key interactions between corrosion and microbiology is the metabolism of hydrogen from metal corrosion. Hydrogen metabolism in microbial ecosystems is well recognised (e.g. Loveley and Goodwin, 1988). Hydrogen-oxidising species are represented amongst the aerobic, denitrifying, iron-reducing, sulphate-reducing and methanogenic species. Under repository conditions the key process is methane generation through the coupling of hydrogen oxidation with carbon dioxide reduction. This process may significantly reduce the overall volume of gas. Recent assessments by Nirex have assumed that this process will not be important because carbon dioxide will react preferentially with cement although there are variant cases where this is not assumed to happen. However, it is not proven that microbial communities are unable to metabolise solid carbonate locked within the cement. If such metabolism is possible, then it may be inappropriate to assume that all the carbon dioxide would be permanently fixed.

▲ Nirex assumes that hydrogen from corrosion will inhibit the organic carbon flow by inhibiting ethanol fermentation. This inhibition can store carbon in the system as ethanol, which can be released rapidly if hydrogen levels drop through hydrogen-utilising methanogenesis. Although it is technically accurate to take this inhibition into account, it must be borne in mind that its recognition originates from studies of acetoclastic methanogenesis. Inhibition of these acetogenic processes is associated with inhibition of methanogens through acidification. Therefore it may be overly conservative to allow corrosion hydrogen to inhibit this step. A consequence of this conservatism is an uneven and unrealistic carbon flow from cellulose hydrolysis. The assumption that ethanol would be produced rather than longer chain volatile fatty acids is unusual and is not explained by the reviewed documents.

▲ Nirex evaluated the possibility that microbial processes may cause ^{14}C to be released from $BaCO_3$ in the form of methane (Holtom, 1997). It was concluded that this process would be insignificant owing to a combination of very low $BaCO_3$ solubility and inhibition of microbial activity under repository conditions. The solubility of $BaCO_3$ would be particularly low under the alkaline conditions due to the presence of cementitious grouts and cementitious backfill. These alkaline conditions would also inhibit microbial activity, which in any case would be suppressed by elevated early post-closure temperature (up to about 80 °C).

- Nirex assumes that only ammonia can be used as a nitrogen source for biomass production and that nitrate can only be used to drive the oxidation of soluble cellulose hydrolysis products. This approach seems to be overly conservative. In reality nitrate can be used as a nitrogen source via assimilatory nitrate reduction; nitrogen fixation is not uncommon in anaerobic cellulose-degrading environments. This focus on ammonia as the only available nitrogen source seems to have contributed to problems with validation experiments where ammonia inhibition of methanogenesis was suspected (Agg et al., 2002).

Overall position on gas generation

The generation and migration of ^{14}C in gaseous form is recognised by NDA to be the most important contributor to potential radiological risks from gas. The mechanisms by which ^{14}C-labelled gases might be generated within a deep geological repository were reviewed by Rees (2004). The specific case of ^{14}C-labelled gas being released by Magnox wastes was evaluated in Rees et al. (2004).

A motivation for the review of Rees (2004) is stated to be the recognition by Nirex that heterogeneities in the waste might result in the heterogeneous evolution of ^{14}C-labelled gas. This recognition stems in turn from the realisation that the previous assessments (Nirex 97 (Nirex, 1997a) and GPA01 (Nirex, 2001)) take into account neither all the ^{14}C-labelled materials in the wastes, nor the heterogeneous distributions of these wastes within the repository. It was pointed out that the earlier assessments had considered only one ^{14}C-labelled waste stream, the Nycomed Amersham (now GE Healthcare) waste stream 1B05. In this waste stream ^{14}C is a label in a range of organic compounds. Although not considered in Rees (2004), the GPA03 (Nirex, 2003a) also took into account only ^{14}C originating in organic wastes. The Reference Case of this latest PA assumed homogeneous waste distributions, but sensitivity calculations were also undertaken to evaluate some heterogeneities in the waste. Heterogeneities in the near field were recognised by Nirex to require further evaluation.

Rees (2004) reviewed the performance assessments and related research projects that had been carried out prior to 2004. Based on the review, it was noted that there is a need to develop an improved understanding of ^{14}C-labelled gas production from graphite wastes, contaminated resins and irradiated steels. It is also stated that in the reviewed assessments Magnox reprocessing wastes give an impact just below the regulatory target. However, the impacts are dependent upon the assumptions made and this conclusion requires validation. Hence, it was recommended that confirmation should be obtained by sensitivity studies and that there should also be assessments of any other wastes containing irradiated uranium metal (e.g. from research reactors).

Rees (2004) also stressed a need to verify the assumption of the earlier Nirex PA (Nirex, 1997a, Nirex, 2001 and Nirex, 2003a) that carbon dioxide generated from organic matter would be immobilised by reactions occurring in the cementitious backfill. Nirex (2006d) reviewed natural analogue evidence for carbonation reactions involving cement-like minerals. This showed that sequestration of carbon dioxide to form carbonate is limited even on geological timescales. A related issue is that microbial activity is expected to convert at least some of the carbon dioxide to methane. The rate at which this process may occur relative to the rate at which the carbon dioxide is able to react with cement could influence the overall mobility of ^{14}C, but is indicated to be uncertain. Consequently, it is recommended that the NDA should carry out additional research into these two processes.

In general, Nirex's work on gas generation is well targeted. Recently, there have been two main emphases:

- The development of the SMOGG model for gas generation as a replacement for GAMMON (Rodwell, 2005a,b). The circumstances that led to the development of SMOGG and an outline of both models are given elsewhere in this review (Section 4.1). This work is essentially complete for the 2004 inventory (Nirex, 2005c) and reflects present Nirex perspectives on potentially important gas generation processes, with the exceptions of gas generation from graphite (see below) and the calibration and validation of SMOGG. Although the need to improve the calibration of SMOGG is acknowledged to be an area for future research (Nirex, 2006a), validation is not included although an inter code comparison exercise between MAGGAS and SMOGG has been undertaken (Hoch et al. 2007c). In this context, "calibration" refers to determining the relationship between model output and input parameter values, and to adjusting the model so that it gives expected output for the specified input. In contrast, "validation" refers to demonstrating that within its domain of applicability, a model gives results of satisfactory accuracy, consistent with the intended application of the model (following Schlesinger et al. 1979). Thus, "validation" has a broader meaning than "calibration" and typically it is impossible to validate a model for the entire range of conditions under which it might be employed. In the present case, it will be impossible to obtain data under all the environmental conditions for which SMOGG will simulate gas generation. Thus, in the strictest sense, "validation" can never be achieved. Instead, a range of complimentary approaches will be needed to build confidence that SMOGG will give acceptably accurate results under the inaccessible conditions at any UK site that might in future be investigated. Such approaches may include showing that the processes represented in SMOGG are well understood and that SMOGG is able to reproduce data obtained from laboratory systems that are designed to represent a repository environment. At the present stage of model calibration such validation might be premature, although a start to this has been reported in Hoch et al. (2007b,c). However, it is recommended that a strategy for building confidence in the prediction of the models produced using SMOGG should be developed. This activity is important, given that gas issues may prove significant in developing the specification for a UK repository. The particular issues that will need to be considered will depend upon the characteristics of any potential repository site that might in future be investigated.

- Assessments of ^{14}C gas generation to include irradiated metals (steels, Zircaloy, uranium, Magnox) alongside the labelled organic models previously assessed. It is acknowledged that a realistic model of irradiated graphite has still to be included in SMOGG, but this will require experimental data that Nirex started to collect only recently (Baston et al., 2006 and Handy, 2006). At present, SMOGG contains a very simple model of ^{14}C gas release from irradiated graphite (Rodwell, 2005a,b). The need to continue to conduct research to improve the reliability of ^{14}C gas assessments is acknowledged by Nirex in the future work outlined in the gas Context Note (Nirex, 2006a).

Nirex has addressed, or is addressing, the key topics identified by GASNET (Rodwell et al., 2003; Section 3.1.2) in the ways described below:

- Regarding long-term corrosion rates, Nirex initiated literature reviews and experimental work in data gathering appropriate to repository environments that has been undertaken over a period of around twenty years. The corrosion data input to the 1997 assessment of Sellafield (Nirex, 1997a) incorporates information for mild steel, stainless steel, aluminium and Magnox relevant to conditions expected for both the operational phase of a repository and the post-closure period. Refinement of these data continued into subsequent assessments. Continued data gathering for hydrogen production from corrosion does not appear to be a current priority for NDA research, with the possible exception of the uranium corrosion which contributes to the production of hydrogen and ^{14}C gas. This process has only been included in gas assessments in recent years. In the Context Note on gas (Nirex, 2006a), one of the main areas defined for future research is to review input data (including corrosion rates) relevant to the assessment of ^{14}C gas production from metals, in order to reduce uncertainties in this aspect of the gas assessment. Given the potential significance of ^{14}C gas for safety, this approach seems sensible.

▲ Nirex has reviewed information concerning the release of ^{14}C from graphite (Marsden et al. 2001). An impetus for this work was the recognition that the GPA01 of 2001 (Nirex 2001) had identified ^{14}C from graphite as being potentially important, but had not considered Stage 3 decommissioning wastes. These latter wastes would potentially account for most of the graphite within any future repository. In addition, Nirex has recently initiated experimental work on the release of ^{14}C from graphite because it has the potential to make a significant contribution to ^{14}C gas production (Baston et al., 2006 and Handy, 2006).

▲ Improving the quality of assessments of microbial gas production has been taken into Nirex's programme through the development of the SMOGG model (see Section 4.1.4). As noted above, more needs to be done to improve its confidence in the model, using data from experiments and operating waste facilities. In the gas Context Note (Nirex, 2006a), it is stated that the potential for gathering gas evolution data from waste stores is a priority for future gas work in the context of calibrating SMOGG. As noted above, this effort could with advantage be extended to building confidence in the model, and aimed ultimately at validation of the model. It is also unclear whether the conditions pertaining in a waste store would be sufficient for calibrating and validating SMOGG over the full scope of a waste package history, particularly for the post-closure period. Data simulating post-closure conditions and used in the exercise to try to validate GAMMON are also available (Agg et al., 2002): initial work appears to show that GAMMON and SMOGG perform similarly, showing different strengths and weaknesses (Rodwell 2005a,b). The Context Note (2006a) also states that it is conservatively assumed that all ^{14}C will remain in the waste until the waste arrives at the repository. However, the consequence of this conservatism for later PA is unclear. It is recommended that gas generation during storage, which was raised as a key area for development several years ago (Rodwell et al., 1999), be given further consideration. There is evidence that Nirex has already started to address these points. Recently there was a review of aluminium, Magnox and uranium corrosion rates under conditions of surface storage, transportation and post-emplacement in an underground repository (Hoch et al. 2007b).

▲ The recommendation in the GASNET report concerning more research into ^{14}C gas evolution is clearly being pursued by Nirex in its forward programme, as noted in its gas Context Note (Nirex, 2006a).

- The GASNET report points out the importance of understanding near-field evolution and states that this should be a priority for research. However, Nirex has been carrying out work on near field evolution over many years, and a considerable understanding has been built up. The 1994 report on current status in near-field research (Chambers et al., 1995) provides a good summary. Areas considered include evolution of temperature, pH, Eh and water composition. Therefore, overall near-field evolution is not believed to be a priority for current Nirex research in the gas context. For most relevant processes there should already be sufficient understanding to support gas generation assessments for waste transport, repository operations (including underground storage) and the post-closure period.

- An exception to the comments in the previous bullet point, where more work is required, is the near-field evolution in response to interactions with migrating gas. In particular, the impact of reactions with carbon dioxide on the evolution of the cementitious backfill requires further research. Nirex has undertaken significant studies into the possible role of carbonation of cementitious materials within the repository, including the backfill (Harris et al. 2001; Harris et al. 2003a,b). However, Nirex also recognises the need for additional confidence-building in this process (e.g. Nirex, 2006a; see below).

- Additionally, to enable variations in gas pressure and gas migration through the near-field to be simulated it will be necessary to predict in particular the evolution of vault temperature, availability of water, backfill porewater pH and salinity, and backfill permeability and porosity. These parameters will depend partly upon the particular design developed for a repository, and partly upon site-specific factors. The latter include host rock permeability and thermal conductivity, natural groundwater head gradients, host rock chemistry and mineralogy and natural groundwater chemistry (particularly salinity).

3.2.3 The Position of NDA Concerning Gas Migration

General issues

Up to 1997 Nirex maintained an active research programme on gas migration. It included aspects of two phase flow in fractured crystalline rocks similar to the BVG, which at that time was being considered as the potential repository host rock at Sellafield. Since 1997 research into gas migration has been reduced because in the absence of a site, or even a preferred host rock type it has been difficult to justify specific research activities.

The general mechanisms by which gas might migrate from a geological repository for radioactive waste were reviewed by Rodwell and Nash (1992). This relatively early review identified most of the main mechanisms that have been recognised subsequently by work carried out internationally (Section 3.1.3), although gas adsorption was not considered. Gas generation within hypothetical repositories sited within relatively permeable fractured crystalline rock and low-permeability sedimentary rocks was evaluated. An important conclusion was that gas dissolution in groundwater followed by diffusion of the dissolved gas or advection of the bulk water would occur too slowly in either kind of host rock to prevent a free gas phase from forming. This issue has been revisited by Hoch (2005), using the simple geology of GPA03. This more recent work confirmed that a free gas phase would form and migrate through a fractured host rock. On encountering overlying sedimentary rocks the gas may either re-dissolve or continue in solution as a free gas phase. Which of these processes dominates will depend on the area over which the gas is released and the rate of groundwater flow in the sedimentary rocks.

Later Nirex research has concentrated on two phase and bubble flow in fractured rocks (Mott and Rodwell, 1998; Nash and Rodwell, 2000; Nash et al., 2000; Goodfield et al., 2000; Goodfield and Rodwell, 2001; McCarthy et al., 2001; Hoch et al., 2001; Hoch et al., 2003). There has been little or no work on gas migration in "tight" rocks such as clays or evaporites. It appears that in part this limitation was due to the site-specific nature of such materials and because extensive research into low-permeability mudrocks has already been undertaken for Nagra and Andra.

Research by Nirex and others has identified that gas migration processes are strongly site-dependent, see for example Bate et al. (2006). Features and processes that influence gas migration in the geosphere are many and varied. It is therefore very difficult to make any meaningful progress in the absence of an actual site, other than to provide a catalogue of factors that should be considered during any future site investigation programme. Nirex has carried out some limited work to understand gas migration in the geosphere and identify features of a site that might be favourable or otherwise but in general the gas migration programme has been in abeyance since there has been no site-specific programme. Recent government policy developments (e.g. the acceptance by the UK government in October 2006 of recommendations by CoWRM) have made deep geological disposal more likely and research into gas-related issues may move forward more rapidly than hitherto. Recent assessments (Nirex, 2001, 2003a) have tended to assume rapid breakthrough of a free gas phase and take little or no credit for the geosphere as a potential barrier to migrating gas. However, Bate et al. (2006) and Hoch et al. (2007a) did investigate the potential importance of low-permeability rock formations overlying a repository. These reports describe two phase calculations using a realistic geological environment. They used the

Nirex 97 2D cross section, with revised parameters for the basal North Head Member (mud-bearing interval). The calculations demonstrated that this member could cause gas to pond and then migrate up-dip, before it leaked through a fault into the overlying aquifers where it dissolved. The work shows conclusively that even quite small details of the geology can have a major effect on gas risk. The studies also showed the importance of selecting an optimum repository footprint.

The role of the geosphere

The work undertaken by Nirex has focussed on the geological environment of Sellafield (e.g. Nirex, 1997a) and a generic geosphere used in GPA01 (Nirex, 2001) and GPA03 (Nirex, 2003a). The parameter values specified for the reference cases of GPA01 and GPA03 were such that the geosphere had some similarities to the geological environment at Sellafield considered by the earlier Nirex 97 assessment (Nirex, 1997a). Namely, the fluxes of gas through the repository and travel times between the repository and the surface were consistent with the rocks having hydrogeological properties within the ranges measured at Sellafield. Additionally, Nirex gave some consideration to gas migration through argillaceous host rocks, although in less detail than for fractured crystalline host rocks (e.g. Rodwell and Nash, 1992; Hoch and Rodwell, 2003b; Nirex, 2003a).

The ways in which gas migration through these geological environments was treated in the various assessments (Nirex, 1997a, 2001, 2003a,b, Bate et al. 2006) are considered in more detail below in Section 6. The present section focuses instead on describing the environments and the assessments of underlying gas migration and retardation processes within them that were made by Nirex to enable a PA to represent gas migration adequately.

The earliest assessment, Nirex 97 (Nirex, 1997a) and subsequent revised calculations (Bate et al. 2006) considered the geological environment at Sellafield, which has the following important characteristics:

- fractured crystalline potential repository host rocks;
- sedimentary rocks that overlie the fractured crystalline rocks and that include relatively low-permeability argillaceous horizons which may act to inhibit and/or deflect gas migration;
- aquifer units within the sedimentary rock sequence;
- fractures and rock matrix in the sedimentary rock sequence that may act as pathways for fluid flow (though the relative importance of fractures and matrix

as fluid flow pathways varies within different sub-divisions of the sedimentary rock sequence);

- a groundwater head gradient causing groundwater to flow from the repository through the host rocks and overlying sedimentary rock sequence.

The generic geosphere of the GPA03 (Nirex, 2003a) consists of a host rock formation and overlying rocks. The host rocks were specified to influence only the flux of groundwater through the repository vaults and not the travel time of radionuclides between the repository and the surface. That is, any radionuclides that leave the repository were assumed to travel through the host rocks instantaneously. Only the rocks overlying the host rocks influence the travel time of these radionuclides from the repository to the surface. These overlying rocks were specified to be divided into a deeper reducing rock sequence and an overlying oxidizing rock sequence. Only redox-sensitive radionuclides, primarily selenium, technetium, uranium and neptunium would be affected by these redox variations.

Nirex has recognised that gas migration depends on fine details of the overlying geology which cannot be represented in the generic geologies used in GPA03. Gas pathway calculations have been undertaken using the geology of the Sellafield site as an example (Bate et al. 2006; Hoch et al. 2007a). Compared to Nirex 97 a more sophisticated model was used. This included, among other enhancements, consideration of both groundwater and gas movement. The study showed that gas moved vertically through the fractured host rock before ponding and then moved updip along the base of the mudrock-rich basal North Head Member and then up a fracture zone into the overlying aquifers where in most scenarios it dissolved. The study confirmed the sensitivity of gas migration to fine details of the overlying geology and the difficulty of capturing the fine details of two phase flow in fracture networks in upscaled equivalent continuum models.

Nirex undertook many other reviews and theoretical studies aimed at developing an improved understanding of gas migration and retardation in the geosphere. The early reviews (pre-1995) were carried out without detailed knowledge of any of the geological environments outlined above. However, the later PA appears to have taken into account the major findings. More recently Nirex published a review of evidence of gas migration from a wide range of analogues (Nirex, 2006d). Whether or not gas will migrate from a repository, and if so the gas flux that will be attained, will depend to a large extent on the degree of over-pressuring that is attained in the repository. A review of the effects of over-pressuring is given in Nash and Rodwell (1990), although this study was relevant only to highly fractured rocks and not deformable mudrocks. This document also presents a simple model for crack opening as a result of over-pressuring. A conclusion was that the over-pressuring and rock permeability are coupled. The response of the rock to pressure increases will depend upon the characteristics of pre-existing fractures. Results obtained indicate that, using the data available in 1990, a repository pore fluid pressure up to 1.4 times the hydrostatic pressure may be sustainable during gas escape from the vaults without causing major disruption of the surrounding geology. However, the permeability of existing fractures may change as a result of dilation caused by over-pressuring. The fracture dilation and consequent increase in permeability will depend upon the fractures' characteristics. Long, thin fractures will show greater proportional dilation and permeability increases than short, thick fractures. However, Nash and Rodwell (1990) ignored any coupling between the dilation and permeability changes occurring in adjacent fractures.

Information about gas leakage from underground gas storage caverns, underground surge chambers, and natural gas accumulations has been reviewed (Rodwell and Nash, 1992; Swift et al. 2003). It was concluded that this information adds little to the understanding of the geosphere around a possible future repository, but the review supported model predictions that overpressurisation is unlikely to occur in fractured crystalline rocks. However, Swift et al. (2003) pointed out that none of the available information contradicts the view that two-phase porous-medium flow calculations provide a better representation of gas migration from repositories than simpler models that include an empirical factor to account for the effect of water on the gas flow rate. Furthermore, they considered that some data concerning gas leakage rates and pressures from storage caverns and surge chambers (which were not available during the review of Rodwell and Nash, 1992), could be useful for validating gas migration models. Swift et al. (2003) matched parameter values in models for gas migration to obtain a fit to such data. They found that the critical ratio of repository gas pressure to host rock water pressure at which gases may enter fractures in the host rock is likely to be significantly below 1.0. This result implies that the geosphere may be less capable of containing gas than was concluded by Rodwell and Nash (1992).

Chemical reactions of gas (principally methane and hydrogen) in the geosphere and biosphere were reviewed by Stenhouse and Grogan (1990). They concluded that the only chemical processes that might potentially attenuate gas fluxes are reactions in near-surface soils. While this study was not targeted at either the Sellafield geological environment or the simplified geological environments considered by the GPA01 and GPA03, the results were used to justify neglecting chemical reactions as a retardation mechanism in the later PA. It should be noted, however, that this study did not consider sorption of CO_2 or CH_4. This process is known to occur in the case of coals and carbonaceous mudrocks (Nirex, 2006d). Again the significance or otherwise of this is highly site specific.

Other gas attenuation mechanisms were reviewed by Rodwell and Goodfield (2000). This study focussed on the following mechanisms:

- the potential for solution in the flowing groundwaters in aquifers lying above the repository; and
- the trapping of gas in geological formations below possible barrier layers. The conditions required for such trapping to occur are reviewed.

It was concluded that in the geological environment of Sellafield, volumes of evolved hydrogen near the minimum end of the possible range (based on the Nirex 97 inventory) could plausibly be dissolved entirely in groundwater. However, if the volume of gas would be towards the upper end of the range, a significant proportion would not be dissolved. Furthermore, estimates of the proportion of gas that might dissolve are sensitive to assumptions concerning the proportion of the gas that might be accessible to the water. If gas migrates dominantly vertically (as a result of its buoyancy), but groundwater flows horizontally, then dissolution will occur too slowly to allow a significant proportion of the gas to be dissolved. This situation is especially likely to occur when gas migrates through fractures in crystalline rocks. It was also concluded that no evidence points to structures at Sellafield that are likely to lead to significant trapping of gas.

Hoch (2005) also presents scoping calculations to determine if gas generated in a repository might migrate to the biosphere in solution. This report assesses whether a free gas phase will form in the repository, whether any free gas that escapes will dissolve in groundwater and whether dispersion etc counteract any decrease in solubility as the groundwater rises. It is concluded that a free phase would form and be unlikely to dissolve in groundwater within a hard fractured host rock. However, the Reference Case GPA geosphere (Nirex, 2003a) is considered to support enough groundwater flow to prevent outgassing of any gas that has dissolved.

The ability of the geosphere to disperse or to localise releases of repository-derived gas at the surface is recognised by Nirex to be a potential contributor to risk (e.g. Thorne and MacKenzie, 2004; Thorne, 2005a,b,c,d). However, it will be inherently difficult to predict accurately the spatial distributions of any gas emissions at the surface at an actual site. Watson et al. (2001) reviewed evidence from natural gas seepages. They suggested a possible alternative approach that might be more likely to be successful when investigating an actual site. In this approach, the general spatial distributions of surface emissions of repository-derived gases are predicted using detailed information about geology, hydrogeology and surface distributions of a range of natural gases, combined with the results of carefully targeted gas injection experiments. Such an experiment was planned to be undertaken at Sellafield but was cancelled following the refusal of planning permission for the Rock Characterisation facility there.

Most recently, Nirex (2006e) summarised the position of Nirex concerning gas migration. The document points out that the extent to which gas would dissolve in groundwater, and thereby migrate via the groundwater pathway, or alternatively migrate to the surface as a free phase, is currently a matter of debate. It is stated that the advance of gas through sedimentary rocks would be slowed by its dissolution into the groundwater, and it is only when the advancing gas has saturated all the water between the repository and the surface that free gas can appear at the surface. Implicit in this statement is the assumption that any migrating gas will dissolve instantaneously in any groundwater and that all the groundwater in the rock will be accessible to the gas. In practice, the most important issue is the volume of water that comes into contact with the gas as the gas migrates. In the case of fracture flow very little gas - water contact will occur. A difficulty is that two phase flow, even for fractured crystalline rocks, tends to be modelled as an equivalent continuum. It is unclear how such a model can ever capture fine details of gas migration through only a small subset of fractures and will only contact a tiny fraction of the water present.

Nirex (2006e) also evaluates the influence of radionuclide travel times through the geosphere on radiological risk. The report considers the only radiologically significant isotopes in the evolved gas to be ^{3}H and ^{14}C. However, the view is that, owing to its very short half-life (12.35 years) ^{3}H will contribute insignificantly to the post-closure radiological risks from any surface emissions of gas originating in the repository. In the case of ^{14}C, the much longer half-life (5700 years) is considered to mean that, should a gas pathway be established, ^{14}C-bearing gas might arrive at the surface before significant radioactive decay can occur. In contrast, the reference case GPA03 calculations (Nirex, 2003a) established that the gas travel time between the repository and the surface could be around 6000 years, which is comparable with the half-life of ^{14}C. It is therefore possible that some decay of ^{14}C will occur during migration. However, to be conservative, Nirex (2006e) considered that the resulting impact on risk would be insignificant. It should be noted, however, (Hoch and Thorne 2007) that there is likely to be no delay in relation to a gas pathway associated with a human intrusion event.

3.2.4 The position of NDA concerning the use of analogues

Nirex has undertaken a number of reviews which have sought to compile evidence from a diverse range of analogue situations relating to gas migration and attenuation in the geosphere. Evidence from the hydrocarbon industry on the migration of methane and the distribution of other naturally-occurring gases (Watson et al. 2001) have been reviewed. Leakages of gases from underground caverns have been considered as an analogue for gas entry into fractured crystalline host rocks (Swift et al. 2003). Possible gas-rock reactions has been included (Stenhouse and Grogan 1991, Bath and Falck 2001) and the implications of altered mineral surface wettability on gas migration based on evidence from the minerals extraction industry was considered in (Swanton 2004). Evidence from landfill sites was used to estimate the likely types and volumes of trace gases (Biddle et al. 1988, Biddle 1989). Recently these have been updated, extended and interpreted in terms of FEPs relevant to a Safety Assessment (Nirex, 2006d)

Some of the analogues also a have a bearing on the assumption that carbon dioxide will be sequestered in the repository by reaction with cement phases to form calcium carbonate. Thus the limited carbonation of naturally-occurring cement-like minerals, the stability of potentially reactive minerals in carbon dioxide reservoirs and during gas floods of hydrocarbon reservoirs all tend to suggest that sequestration is limited in extent even over geological timescales (Nirex, 2006d).

3.3 Presentation of Important Issues in Context Notes 3.3, 3.5 and the Nirex "Viability Report"

The Context Notes (Nirex, 2005b, 2006a, 2006b) summarise the issues, past experience and status of research concerning gas and its effects that are considered relevant to the phased development of a geological repository for intermediate-level and certain low-level radioactive waste in the UK – the PGRC. The notes cover all the key issues identified in Section 3.1 and provide a good summary of Nirex work on gas generation in a repository and on the emergence of ^{14}C–labelled gas as a key issue. Context Note 3.5 gives a largely adequate account of current understanding in relation to ^{14}C. This includes initial estimates of ^{14}C gas production from metals and graphite, showing the potential for significantly above-target radiological impacts to man. However, the issue of the replacement of GAMMON with SMOGG receives less attention. The range of technical references is generally appropriate, and guides the reader to sources of more detailed information. However, limitations in the underlying Nirex work are also reflected in the document.

A key aspect of the presentation is that although the potential problem of ^{14}C-labelled gases is emphasised, comparatively little attention is given to other potential problems associated with gas evolution and migration. In particular, uncertainties surrounding hydrogen generation and its behaviour (e.g. the extent to which it would react with carbon dioxide to generate methane) are not considered. Another related issue is that the report gives considerable attention to the release of ^{14}C in the form of methane, but does not explicitly recognise that this will be significant only if the hydrogen that has been generated causes sufficient over-pressuring to transport the gas away from the repository.

The Context Note implies that the cementitious backfill is designed specifically with regard to gas migration. However, certain aspects of this presentation are open to misunderstanding. The reader could gain the impression that the cementitious barrier was designed to allow carbonation to occur, when in fact this process is simply an incidental consequence of choosing such a barrier for its other properties (high pH to inhibit radionuclide solubility, high surface area for radionuclide sorption, workability etc). The document does, however, note that the extent to which the grout may carbonate is uncertain.

There is relatively little information in the Context Note (Nirex, 2006a) on the details of gas generation by corrosion. The major focus is the consequences of the release of ^{14}C, which can be generated by the corrosion of irradiated steel. The report correctly states that there is currently uncertainty regarding the mechanism for corrosion release of ^{14}C from these materials. Although the respective corrosion rates for different materials are not stated, the discussion on page 11 regarding the most important sources of gas generation at different stages in the repository evolution appears mechanistically reasonable.

The Context Note states that the corrosion of Magnox and aluminium during the aerobic phase will result in hydrogen generation (page 4). An assessment of the fraction of corrosion supported by the cathodic reduction of oxygen and water during the aerobic phase would be appropriate. Such an assessment would establish whether or not other possible oxygen-consuming reactions, such as aerobic organic matter degradation might be more significant

The Geosphere Research Context Notes (Nirex 2005b, 2006b) give details of issues concerning gas migration in the geosphere. They emphasise the highly site-specific nature of gas migration, but note that in the case of very low permeability host rocks over-pressurisation could be an issue. However, it would be valuable to provide some specific details of different gas transport mechanisms. The bounding assumption that ^{14}C could be transported from the repository to the biosphere as methane, with zero retardation or dilution in the geosphere, is conservative. If the risk target is exceeded when these latter processes are neglected, it would be appropriate to assess the degree of conservatism, and particularly the extent to which retardation and dilution processes could plausibly reduce doses. Context Note 3.5 recognises this need. However, it is unclear whether this conservatism would be significant in all geological environments that might be considered as potential hosts for a future repository. The significance of the conservative assumptions needs to be evaluated in the overall context of the various site characteristics and transport processes. For example, there may be circumstances in which there is a short travel time through the geosphere from the repository to the biosphere, compared with the half-life of ^{14}C. In such cases, neglecting retardation and dilution processes might not have a significant effect on the overall dose. Prior to selection of an actual site it would be possible to evaluate the significance of various possible retardation processes in generic alternative geological environments specified to represent possible repository environments in the UK.

The main published source for many of the statements made in Context Note 3.5 is the "Viability Report" (Nirex, 2005a). This document is concerned with the full range of issues that need to be considered in proving a disposal concept. However, the report is written as a high-level review and contains few detailed statements about gas generation. The general statements that are made concerning gas research emphasise ^{14}C–labelled gas, which is described as "a key challenge to the PGRC". There is much less discussion of the generation of bulk gases. The number of references to research on gas generation is small, and overall the reader would not be able to obtain a sound all-round understanding of the subject from the report alone.

Thus there are several cases in Context Note 3.5 where the origins of a statement about the significance of a particular gas issue are either not referenced, or else the "Viability Report" is referenced, but there is no audit trail back to the original source. The most important cases where these omissions occur are:

- ▲ Published work on the latest comprehensive generic performance assessment (GPA03; Nirex, 2003a,b) is referenced but work undertaken since this assessment concerning risks from ^{14}C, though alluded to, is not fully referenced.
- ▲ Recent work showing that ^{14}C can be released from graphite is not referenced.
- ▲ New scoping calculations that assess all potential sources of ^{14}C are mentioned, but only the "Viability Report" is given as the origin of the information presented. Whilst this is an accurate statement, the "Viability Report" itself does not provide references to underpin the statements made concerning ^{14}C generation.

The "Viability Report" (Nirex, 2005a) concludes that, on balance, the generation and migration of gas does not pose a threat to the viability of the PGRC. It is considered that risks are dominated by ^{14}C released in the form of methane; there is thought to be no significant risk from over-pressurisation in the case of hard, fractured host rocks and that there will be no flammability hazard. These conclusions may be justified for this particular host geological environment, but they are based on some bounding assumptions that are likely to be unrealistic in other environments, in particular:

- ▲ The repository is fully saturated only 5 years after repository closure and after this time gas generation is not limited by the availability of water.
- ▲ The geosphere is conservatively assumed not to retard gas migration.

The full significance of these assumptions for overall risk estimates is presently unclear and it needs to be established whether or not they result in significant overestimates of overall risk. There is also a need for additional justification that these assumptions are conservative with respect to all the conclusions reached. Such justification is required to demonstrate that over-pressurisation or flammability risks for this geological environment are insignificant not only for the simulation cases of the GPA, but also under any other circumstances. Subsequently, Hoch and Thorne (2007) have demonstrated a flammability hazard associated with some human intrusion scenarios.

It is recognised in the "Viability Report" that future gas research will be very dependent on the choice of host rock. An implication is that the more recent Nirex programme may not have been well adapted to alternative geological environments. It is also stated that siting requirements may depend upon research into the gas retardation processes in these different environments. This statement implies a scheduling for future work, since it is presently envisaged that site investigations will commence within the next few years. However, it is unclear from the report whether or not this work has commenced.

The report recognises that the GPA didn't consider the potential release of ^{14}C in gaseous form from graphite or irradiated metals, but that future work will include these sources. However, it is unclear why these important sources of ^{14}C were not considered in the past.

For the PGRC, the "Viability Report" correctly states (Sections 4.5.3 and 6.3) that the corrosion rate of stainless steel in a cementitious backfill (and by inference the associated rate of hydrogen generation) will be low.

There is very little discussion in the report about possible gas transport mechanisms in a deep geological repository. This lack of information may be a consequence of the generic nature of the programme and the fact that no specific site or host rock has been identified. The potential impact of gas generation on repository safety should be assessed by comparing the rate of gas generation with the rate of gas removal via various transport mechanisms. Nagra has carried out a thorough study of this issue, which has been considered by Nirex, (e.g. Poppei et al., 2003; Hicks, 2006 and references therein), and has established ranges of gas removal rates for different transport mechanisms: by diffusion of dissolved hydrogen, two-phase flow, transport controlled by the dilation of microfractures, etc. These ranges can then be compared with predicted rates of gas generation to determine whether gas can be removed quickly enough, and via what mechanism.

Although this review focuses on the disposal of ILW and some LLW, it is relevant to comment on how the issues presented in the "Viability Report" differ from issues of relevance to SF/HLW. Since a SF/HLW repository is likely to be more tightly sealed than a L/ILW repository (e.g., more extensive use of clay-based buffer and backfills), it is possible that gas generation and transport could be of more concern for a HLW/SF repository despite the potentially lower rate of gas generation. In this regard, gas generation and transport may be an issue for a reference Cu/cast iron container design due to corrosion of the cast iron insert following breach of the outer Cu shell. A conclusion is that the significance of gas generation and transport should be assessed for each repository design based on a comparison of the generation rate and rate of gas transport out of the repository.

4 Models for Gas Generation and Migration

4.1 Models for Gas Generation

4.1.1 Introduction to Gas Generation Models

For many years, Nirex used a mathematical model called GAMMON to evaluate the rates of generation of a range of flammable, toxic and radioactive gases under repository conditions. Early in this decade, it became apparent that there were a number of drawbacks to continuing to use this model in repository safety assessments, and Nirex developed a new specification for a gas generation model that became known as SMOGG (**S**imple **M**odel **O**f **G**as **G**eneration).

This section explores the reasons for the change, describes SMOGG and the current experience of using it, draws conclusions as to its suitability for use in repository safety assessments, and makes recommendations for further research. These findings are prefaced with a description of GAMMON.

4.1.2 The GAMMON Model

GAMMON was developed to model what were at the time (early 1990s through to about 2001 or so; Nirex, 1994 and references therein) identified as being the most potentially significant sources of gas in a deep UK repository for ILW and that fraction of the LLW that was not acceptable for disposal at the LLWR near Drigg. The inventory considered at that time did not, for example, consider Stage 3 decommissioning wastes, which are now considered in a variant inventory.

The key gas generation processes that are represented in GAMMON were:

- Hydrogen, formed in the corrosion of mild and stainless steels in wastes and their packaging; Magnox metal; aluminium and Zircaloy. Gas formation from steels takes place only after all the oxygen originally in the repository at closure has been consumed in corrosion and microbial processes.

- Methane and carbon dioxide, formed in the microbial degradation of the cellulose component of organic wastes. When oxygen is present, only carbon dioxide is formed, but under anaerobic conditions, approximately equal volumes of methane and carbon dioxide form. Hydrogen formed during corrosion can participate in the web of microbial reactions.

- Hydrogen sulphide, formed as a by-product of the microbial degradation of cellulose and involves the reduction of sulphate ions present in wastes and groundwater.

- Radioactive gases based on the four above gases (H_2, CO_2 , CH_4 and H_2S), in which atoms of inactive hydrogen and carbon are replaced by ^3H and ^{14}C respectively.

Thus GAMMON was able to model the rates of evolution of a range of flammable (H_2, CH_4), toxic (H_2S) and radioactive (containing ^3H and ^{14}C) gases. The contents of a repository were assumed to be homogeneous, as were the conditions (Eh, pH, groundwater composition, although it is understood that GAMMON has the capability to take account of time-varying conditions etc).

The two key sub-models in GAMMON are concerned with corrosion and microbial degradation. GAMMON aimed to be a model that could be justified on a scientific basis; this resulted in a web of microbial reactions that was particularly complex, and contained a large number of intermediate species and a link into the corrosion model (Agg et al., 1996). The model was justified by making use of knowledge of the microbial degradation of cellulosic wastes in landfill sites (Kidby and Rosevear, 1997).

4.1.3 Deficiencies of GAMMON

GAMMON was used in a number of major assessments for about ten years from the early 1990s. In the second half of this period, a number of long-running gas evolution experiments involving simulated wastes were set up to provide data against which GAMMON could be quantitatively validated (Agg et al., 2002). The project produced some predictions of experimental results that were a reasonable fit to the experimental data, particularly when corrosion alone was studied. However, the microbiological processes appeared to be difficult to model quantitatively: this was ascribed to heterogeneities in the gas-producing experiments, in contrast to the homogeneous system assumed in the model. In addition, the detailed nature of the model means that when calibrating[6] it, values would need to be set for a large number of parameters

[6] As noted in Section 3.2.2, calibration typically involves adjusting a model until specified reference input values produce expected output values. In practice calibration is an empirical process, and ranges of input parameter values will not typically represent the full range of conditions within a deep repository. Therefore, multiple approaches are needed to build confidence in the model. This confidence-building is inherently more difficult for models with many parameters representing many processes, than for simpler models with fewer parameters representing fewer processes.

(about 50). Overall, it seemed that GAMMON could not be used with confidence in repository safety assessments. At the same time, Nirex's requirements of a gas generation model were changing in a number of ways (Rodwell et al., 2002):

- A model should be applicable to HLW and spent fuel, as well as to ILW and some LLW.

- This change in emphasis would necessitate modelling a greater range of gas-producing processes, as described below.

- A model should be capable of operating at the waste package or waste stream scale so that gas evolution during the transport of waste packages, the operational phase of a repository and the post-closure period could be modelled on a consistent basis. This extended capability should also help to overcome the problem of GAMMON not taking heterogeneities into account.

It is noteworthy that Rodwell et al (2002) does not consider long-term interim storage, prior to transport to the repository. However, the extent to which gas generation during this storage phase would impact upon safety needs to be determined. The capability of a gas generation model to operate at the waste package or waste stream level would also be necessary for this purpose.

It was also argued by Rodwell et al. (2002) that a new model should be simpler than GAMMON, in line with the more empirical models used by other national disposal agencies. The use of an entirely empirical model (presumably based entirely on observed rates of gas production from wastes) was not recommended because this would not allow the representation of a range of conditions in waste packages. Instead, it was recommended that a simplified kinetic model be produced. This recommendation led to the development of the code SMOGG (see below).

4.1.4 Description of SMOGG

SMOGG has been developed to overcome the deficiencies of GAMMON that are noted in Section 4.1.3. Overall, functionality has been considerably increased to incorporate the following processes (Rodwell 2004):

- Corrosion of relatively unreactive (steels, Zircaloy and uranium) and more reactive (Magnox and aluminium) metals, leading to the formation of hydrogen. Note that uranium, like steels, only yields gas under anaerobic conditions.

- Microbial degradation of cellulosic wastes, producing carbon dioxide and methane. Production of hydrogen sulphide is no longer modelled because, although the gas is highly toxic, it is also very reactive, and would not be expected to escape from the near field (Biddle et al., 1988). It is assumed that this would be the case in the operational phase as well as post-closure.

- ▲ Radiolysis of water and organic wastes to yield hydrogen. Again this is a simplification, as carbon-containing gases are also produced during the radiolysis of organics, but hydrogen is the gas produced in the largest amount (Biddle et al., 1987). There is an exception to this picture: the radiolysis of molecules labelled with ^{14}C leads to the production of ^{14}C gas in SMOGG.

- ▲ Generation of gases containing ^{14}C from irradiated graphite and metals and labelled organic wastes. For metals, release of ^{14}C is assumed to depend on the rate of corrosion. The gas is assumed to be $^{14}CH_4$, although in practice other hydrocarbons would also be generated. For irradiated graphite, the user can choose whether $^{14}CO_2$ or $^{14}CH_4$ is formed. Gas production from labelled organic wastes is considered within the models for microbiological degradation of cellulose and radiolysis.

- ▲ Production of tritiated hydrogen during corrosion of metallic wastes by tritiated water and as a result of solid-state diffusion in metals and metal corrosion products. Tritium release from irradiated graphite is also modelled.

- ▲ Release of a range of radioactive gases in elemental form, including: ^{222}Rn from radium wastes; and ^{81}Kr, ^{85}Kr, ^{39}Ar and ^{42}Ar produced as a result of solid-state diffusion in irradiated metals and metal corrosion products.

Simplified kinetic equations are used (most notably in the model of microbial degradation) compared with GAMMON, and this enabled SMOGG to be implemented in a C++ computer program interfaced with an Excel work book. The model is in principle easier to calibrate than its predecessor, runs faster and is designed to be numerically more stable (run times and obtaining a properly converged solution had on occasion been a problem when using GAMMON).

The requirement to include spent fuel and HLW in the wastes to be modelled is reflected in new capabilities to model radiolysis and the release of radioactive isotopes of krypton and argon. The treatment of the release of ^{14}C gas is no longer restricted to labelled organic molecules, and now includes irradiated metals and graphite.

The new model can be applied to individual waste packages or waste streams (as required), which makes it suitable for assessments of long-term interim storage, waste transport and the operational period, as well as the post-closure phase.

4.1.5 Experience of Using SMOGG

SMOGG outputs have been compared with those from GAMMON by Rodwell (2005a,b). Both programs gave similar results for the production of corrosion gases, i.e. hydrogen and tritiated hydrogen. The main difference lay in estimates of the production of carbon dioxide and methane from cellulosic wastes. SMOGG avoids giving the spikes in gas production that output from GAMMON sometimes exhibits, which is more realistic in view of the observed behaviour of organic-bearing wastes, for example in landfills. It is, however, not entirely clear why this difference in model outputs should have arisen since the comparison cases assumed homogeneous conditions and the observed results are believed to result from heterogeneity that is not included in the comparison example. In addition, the partitioning of ^{14}C between carbon dioxide and methane in SMOGG output is more in line with expectations than with GAMMON. However, it is noted that with presently-available experimental data, it remains difficult to calibrate and validate either model.

A code intercomparison exercise involving SMOGG and MAGGAS (Magnox Electric Ltd code) has been reported (Hoch et al. 2007c). The comparison involved fifteen test cases at the single package scale. They covered metal corrosion, ^{3}H diffusion in stainless steel, radiolysis, graphite degradation and a combination of these processes.

In most cases the two codes yielded similar results. Differences could be attributed to the resolution of the physical constants used and to known limitations of the models. However, it should be noted that both codes were written by the same contractor.

Perhaps the most important discrepancies involve ^{3}H diffusion, where it was found that the methodology used in SMOGG underestimated the concentration gradient in the metal and hence underestimated the release of ^{3}H. It could also not capture the temperature dependence of the diffusion process. Comparison of uranium corrosion rates using MAGGAS, where the metal is assumed to be in cylinders or spheres, found that corrosion of the spheres was less rapid. This result suggests that the use of a spherical model of metal particles in SMOGG may not always be conservative. It is noted, however, that SMOGG permits the user to alter material geometries.

SMOGG has also been used to assess rates of ^{14}C gas production from metals (Nirex, 2005b,d). This study found that, for the conditions assumed in the GPA, the annual individual risk target of 10^{-6} could be exceeded for considerable periods of time when this source of radioactive gas was taken into account.

A user guide (Swift, 2004) has been published, which also sets out the mathematical verification of the code.

4.1.6 Conclusions and Recommendations

The move from GAMMON to SMOGG to assess rates of gas generation was brought about by a combination of circumstances:

- limited success in validating GAMMON;
- the need to include spent fuel and HLW in future assessments;
- the associated increase in model functionality required (as a result of updating the inventory of potentially gas generating materials and reviewing the potential gas generation processes);
- the need to treat waste transport, repository operations and the post-closure period on a consistent basis from the perspective of gas generation; and
- the need to take into account heterogeneities across a repository (in contrast to the GAMMON assumption of spatially homogeneous composition and conditions).

All the above appear to have been addressed with SMOGG; in addition, the model has been satisfactorily verified, as indicated, for example, by the fact that both SMOGG and GAMMON and SMOGG with MAGGAS give similar results for similar input (e.g. Rodwell, 2005, Hoch et al. 2007c). However, to date, the model appears to have been applied in exactly the same way as the previous GAMMON model and the potential of the new features has not yet been explored. For example, the ability to simulate heterogeneous wastes and conditions does not yet appear to have been used to scope the potential implications of heterogeneity for post-closure safety performance. It would also be desirable to model gas generation during long-term interim storage. However, there does not appear to be any documentation of how SMOGG might be used for this purpose.

The corrosion model in SMOGG gives results very similar to those obtained with GAMMON. Since the latter can be considered to have been validated for the corrosion of steel (Agg et al., 2002), this finding can now be extended to SMOGG. The model of microbial degradation has yet to be validated for either model. In the context of SMOGG, Rodwell (2005b) notes that this could be examined using data from other organisations' programmes of monitoring and research. Given that much may depend on SMOGG in terms of evaluating a future disposal site in the UK (stemming particularly from assessed post-closure radiological impacts to the public associated with ^{14}C gas production; (Nirex, 2006f)), it is recommended that a strategy should be developed for further building confidence in the model and ultimately for completing its validation. Nirex appears to have already started to do obtain the data required for this to be done. Recently there was a review of corrosion rates of Magnox, aluminium and uranium with the aim of obtaining data with which to parameterise the SMOGG model (Hoch et al. 2007b).

Most of the underlying models that are implemented in SMOGG are based on established approaches, thereby helping to build confidence in outputs from the code (Rodwell, 2005a). However, to date it has not been possible to build adequate confidence in some of these models due to lack of appropriate knowledge. Rodwell (2005a) notes that the model for ^{14}C gas generation from irradiated graphite is the most notable example. Nirex has already initiated experimental work on release of this isotope from graphite (Baston et al., 2006; Handy, 2006), and it is recommended that such work should be encouraged to continue, with the aim of improving confidence in the overall assessment. Again, the benefit would lie in helping to develop the specification for a repository at a future disposal site in the UK.

4.2 Models for Gas Migration

Several different modelling codes have been used within the Nirex programme to simulate gas migration:

- PORES (Program for Oil Reservoir-Simulation) is a porous medium multiphase flow simulator (Nirex, 1996; 2000), which was originally developed by the oil industry and used for early simulations of gas migration in the far field;
- GWNet was developed by Nirex to simulate multi-phase flow in a single fracture (Goodfield et al., 2000; Nash et al., 2000);
- FRAC was developed to simulate bubble migration in fractures with rough walls (Hoch et al., 2001);
- *tech*SIM is also an oil industry code, which was used for simulations of gas migration as part of Nirex (1997a) ; and
- TOUGH2 (Pruess, 1987, 1991) has been used for the most recent modelling of far field gas migration (Bate et al. 2006).

However, the relationships between these codes (e.g. how (or whether) models developed with one code have been taken into account when developing a model with another code) is not transparent. It appears that, with the exception of TOUGH2 these codes were used while Nirex was investigating Sellafield. Here two phase flow in the fractured crystalline rock (BVG) was anticipated to be in a fracture network whereas that in the overlying sediments could variously include both flow in the porous matrix and fractures. Two of the codes, GWNet and FRAC, were used specifically to model laboratory-scale experiments of flow in single fractures or simple fracture networks to gain a deeper understanding of the often complex interactions seen at this scale. They were relevant therefore to gas flow in the host rock. The other codes used an equivalent continuum representation of two phase flow and are therefore more appropriate to gas migration in the overlying sedimentary rocks. They were also used to model gas migration in the fractured host rock in performance assessment calculations. This requires the derivation of relevant upscaled values for two phase flow. It had been one of the objectives of the Nirex laboratory programme to better understand how this upscaling could be achieved but this work ceased in 1997 and the issue of how to upscale such phenomena remains unresolved.

The gas generation curves produced by the models of gas generation described in Section 4.1 have been used as inputs to models for gas migration (Bate et al., 2006). However, the precise way in which this has been done is not clearly reported. Bate et al. (2006) make the statement that:

"For Nirex 97, gas generation calculations were carried out using the code GAMMON and the best information then available. Gas generation calculations within the Nirex programme are now carried out using the code SMOGG, which also includes a model for gas generation as a result of radiolysis. The inventory and the corrosion rates have also been revised to reflect information now available."

Precise details of how the gas generation model was interfaced to the gas migration model are unclear. It is not transparent how uncertainties in gas evolution calculations might have propagated uncertainties in the final migration models.

The rationale for changing the preferred code following the completion of the Nirex 97 assessment was stated in Bate et al. (2006) to have been the fact that Serco and Nirex did not have a licence for *tech*SIM at the time of the more recent modelling. It is noteworthy that, prior to 1997, the code PORES was also used to model gas migration and the earlier change to *tech*SIM is also thought to have been motivated by licensing issues.

TOUGH2 (Pruess, 1987, 1991) is a very widely-used code that has been extensively tested internationally. Bate et al. (2006) report that it has been used to repeat some of the simulations carried out with *tech*SIM, with similar results. Consequently, TOUGH2 has been judged to be at least as accurate as *tech*SIM. However, the absolute accuracy of either code when applied to the migration of gas from a geological repository is less certain. A combination of laboratory and field testing would be needed to determine this accuracy.

The migration model set up by Bate et al. (2006) covered a larger cross-sectional area than was considered by the Nirex 97 simulations (Nirex, 1997a). These authors used

TOUGH2 to examine phenomena that were not considered by the earlier *tech*SIM simulations, including:

- ▲ the initial drawdown;
- ▲ the compressibility of the rocks and groundwater;
- ▲ the regional groundwater flow; and
- ▲ the background temperature gradient.

However, it is unclear why these phenomena had not been considered in the *tech*SIM simulations of Nirex 97. The capabilities of TOUGH2 and *tech*SIM appear to be similar, raising the question as to why more realistic models were not produced previously. Presumably the reason is the level of significance attributed to the gas pathway at the time the simulations were carried out, but this is not stated explicitly in any of the reviewed documentation.

The simulations reported in Bate et al. (2006) considered coupling between the gas generation and the rate of resaturation by means of different simulation cases with different gas generation rates. These simulations represented pressure increase in the repository as a result of gas generation, thereby opposing the inflow of water from the surrounding rock. However, the simulations were not fully-coupled in the sense that groundwater fluxes and gas generation rates were not linked dynamically. Thus, continuous variations in gas generation rates as a function of resaturation rates (which are in turn dependent upon gas generation rates) have not been simulated. It would be valuable to evaluate what implications, if any, this lack of direct coupling may have for safety assessments and in particular to establish whether or not the approach adopted is in fact conservative. Depending upon the outcome of such evaluations it might be appropriate to consider development of fully-coupled models of groundwater flow and gas generation.

In the Nirex 97 simulations, carried out using *tech*SIM, breakthrough of gas to the surface occurred after only about 40 years following repository closure. However, among the TOUGH2 simulations, the only case in which breakthrough occurred by the end of the simulation period (1000 years) was one in which the Henry's Law constant was reduced by an order of magnitude. This reduction was carried out to simulate the effects of fingering and bubble formation, which would reduce the volume of water with which the gas would come into contact.

Simulations were carried out to evaluate why there was this significant difference in simulated breakthrough behaviour. The main conclusions were that:

- ▲ The earlier model did not include regional groundwater flow. This flow has the effect of increasing the amount of water with which the gas comes into contact, leading to greater gas dissolution and therefore delaying any gas breakthrough.

- ▲ In cases when there was no regional groundwater flow, the time taken for a critical volume of gas to be produced (in the models based on Sellafield several hundred tonnes) determines whether breakthrough occurs. It is stated that in the TOUGH2 models the gas generation rate as a function of time was different to that in the earlier *tech*SIM models. These latter models simulated a greater total volume of gas being produced at early times. It is unclear to what extent these differences reflect realistic variations in representations of coupling between groundwater flow and gas generation.

- ▲ In cases where there is a regional groundwater flow, the repository design influences the time required for breakthrough to occur. An increase in the length of the repository caused the time to breakthrough to be decreased. The reason for this phenomenon is that the length of the repository influences the rate of pressure increase during re-saturation. This influence occurs because the rock units that are intersected by the repository depend partly upon the geometry of the repository and influence the inflow of groundwater.

Some simulations were carried out to examine the influence of salinity variations. The conclusion was that salinity variations affect the groundwater flow rate, but do not have much effect on gas migration. This result seems to be counter-intuitive, since salinity is a major control on gas solubility, which in turn influences gas migration.

It should be noted that TOUGH2 uses an equivalent continuum representation of the two phase transport properties of each rock unit. For low permeability fractured rocks such as the Borrowdale Volcanic Group it is unclear how well upscaled properties represent the fine details of gas migration in fracture networks. Of particular concern is the extent to which up-scaling accurately reproduces the actual contact area between the gaseous and aqueous phases within the fracture network. The larger this contact area, the greater will be the degree of gas dissolution. To explore the significance of this upscaling the modellers changed the Henry's Law constant which, as noted above, led to gas breakthrough at the surface. This demonstrated the sensitivity of the model to assumptions and the method of deriving upscaled continuum parameters for such fracture networks.

In addition, the chemical speciation and reaction path code HARPHRQ (Brown et al. 1991; Haworth et al. 1995) was used in the Nirex 97 assessment to simulate reactions between gas (carbon dioxide) and the cementitious backfill (Nirex, 1997a). Although not a gas migration model, its output had implications for gas migration through the backfill and subsequently into the geosphere. This output included estimates of the quantities of gas that would be fixed in solid mineral phases as a result of this reaction.

A preliminary analytical model for radon migration was also developed and used during the Nirex 97 assessment (Nirex, 1997a). This model couples the following processes:

- transport of radon from the vaults in the migrating bulk gas;
- the radioactive decay of radon during its passage through the geosphere to the surface; and
- the release of natural radon from the surfaces of fractures (in fractured rock) or capillary pathways (in porous rock).

It is pointed out in Nirex (1997a) that the model does not address the possible leaching of radon precursors from the repository and their subsequent transport in the groundwater, which may lead to generation of radon at locations remote from the repository. It is also noted in Nirex (1997a) that validation of the model is needed.

The preliminary model for radon transport is also described in detail by Hoch et al. (2002). These workers extended the model to take into account transport in the near-surface unsaturated zone. This modification was considered necessary because assessments using the 1997 version showed that typically only natural radon derived from near-surface rocks would reach the surface. These rocks are likely to be largely unsaturated.

5 Influence of Pre-closure Conditions on Post-closure Performance

The conditions of the repository prior to closure may potentially exert a significant effect on the characteristics of the waste, which may then impact upon gas generation following closure. The possibility that extended operations, during which conditions remain aerobic within the repository, was noted at an early stage of the Sellafield investigations (Nirex, 1994). The main processes of relevance are the corrosion of metals and the degradation of organic materials under these aerobic conditions. However, the precise extent to which the pre-closure phase will impact upon post-closure performance is presently uncertain[7].

The period for which aerobic conditions are maintained underground prior to repository closure, may influence the transit time for gas travelling between the repository and the biosphere (Nirex, 2006e). Gas generation during this period will reduce the quantities of material that may potentially evolve gas following closure. Nirex has stated that one reason for the GPA03 assessment (Nirex, 2003a) calculating much longer transit times compared to Nirex 97 (Nirex, 1997a) is that the GPA03 considered a longer period of aerobic conditions prior to repository closure (Nirex, 2006e).

However, several factors would act to limit the effect of pre-closure conditions on post-closure gas generation. Much of the steel inventory is in the form of stainless steel (Table 1 in Nirex, 2006a). The extent to which this metal is corroded during the aerobic phase could be limited, leaving much of the steel to corrode under anaerobic conditions. Similarly, once a cementitious encapsulant is emplaced C-steel will be passivated and would also corrode slowly. The amount of steel that could be corroded during the aerobic-anaerobic transition by the galvanic coupling of Fe(III) reduction to steel dissolution will also be limited by amount of oxygen trapped initially in the repository. Unless there is a large reservoir of trapped oxygen much of the steel inventory would remain un-corroded at the end of the aerobic phase.

For Magnox and aluminium, lower rates of corrosion were specified for the storage period than for the post-closure period in the GPA03 (Nirex, 2003a). This difference was justified using un-published data obtained by Nirex (see Section 3.2.2) that

[7] Nirex staff indicated that it is thought that there would be limited metal corrosion before resaturation of the repository following closure. Additionally, corrosion of Magnox would be limited by water availability in the pores of the cementitious grouts (see Appendix 3)

suggests that corrosion in the grouted wastes was limited locally by water availability once the water in pores close to the waste fragments had been consumed. It has been assumed that, once the wastes are backfilled, water becomes more available, and the faster corrosion rates assumed in previous assessments have therefore been used. However, the question arises as to what extent the gas formed might itself restrict the availability of water, thereby slowing the rate of corrosion even in the post-closure phase.

6 Application of Gas Research in PA

6.1 General Applications of Gas Research

The treatment of gas break through times in Nirex 97 (Nirex, 1997a), GPA01 (Nirex, 2001) and GPA03 (Nirex, 2003a) is summarised in Nirex (2006e).

The GASNET report (Rodwell et al., 2003) lists the following processes that are deemed to be important for safety assessment:

- over-pressurisation;
- impact on groundwater transport (including gas cushion effects, bubbles, unstable pathways);
- release of toxic or radioactive gases, primarily methane;
- transport of radionuclides through attachment of colloids at gas-water interfaces;
- human intrusion into a pressurised repository; and
- flammability.

Nirex currently take into account the first, third and fourth of these issues but apparently considered the second too difficult to treat explicitly in the assessment models. However, Bate et al. (2006) have presented a more realistic evaluation of gas transport by groundwater. Additionally, Hoch and Thorne (2007) have extended the human intrusion calculations in GPA03 to include consideration of the gas pathway. Scenarios involving gas blowout while a well is being drilled and steady state gas emission from an existing well are considered.. The possibility of a flammability hazard arising was assessed within the Nirex 97, GPA01 and GPA03 assessments (Nirex, 1997a, Nirex, 2001 and Nirex 2003a, respectively) and supporting studies (e.g. Hoch and Rodwell, 2003b). During the GPA, simple analytical arguments are presented to support the view that the release of gas at the surface would occur at a rate that is several orders of magnitude lower than that required to support combustion. However, gas flammability is an issue in some human intrusion scenarios (Hoch and Thorne 2007).

The PA work (Nirex 97, GPA01, GPA03 and subsequent studies) appears to draw heavily on the research work in the areas of gas generation and the impact of gas in the biosphere. However, it is less clear from published documents how many of the results from the more detailed research programme in the area of gas migration have been applied in the PA. Similarly, there is evidence that the needs of the safety assessment have driven the research priorities in the gas generation and biosphere areas but much less evidence that the safety assessment has driven the research programme in the area of gas migration. However, the latter is perhaps understandable in view of the fact that the GPA is based on such a simplified geology that the assessment cannot be used to draw meaningful conclusions about gas retardation in the geosphere.

6.2 Application of Research into Gas Generation

In the Nirex 97 (Nirex, 1997a), GPA01 (Nirex, 2001) and GPA03 (Nirex, 2003a) assessments, gas generation was modelled using the GAMMON code (see Sections 4.1.2 and 4.1.3). This code was used to calculate the evolution of gas from wastes that were specified to be homogeneous. Thus, the research into gas generation that was applied by Nirex in its PA is the research used to develop and justify the models that are implemented in GAMMON and to obtain parameter values for the simulations. However, it is clear that significant additional research into gas generation was undertaken at the same time as the GPA01 (Nirex, 2001) and GPA03 (Nirex, 2003a). As a result, this latest research is not fully applied in these PA. For example, there was considerable work that has led to the development of the SMOGG code (Section 4.1.4), that has yet to be used for PA. The work has, however, been used in the calculations presented in Bate et al. (2006), which to all intents and purposes are PA calculations.

The previous PA (Nirex 97, GPA01, GPA03) only consider ^{14}C-labelled gas generation from organic materials in the inventory. However, the GPA03 (Nirex, 2003a) did acknowledge that the other sources of ^{14}C exist and pointed out that more work is needed to understand their behaviour. More recent Nirex work (e.g. Rees, 2004) emphasises in particular, the potential significance of ^{14}C-labelled gas generated from irradiated metals and graphite and this is now captured in Bate et al. (2006).

6.3 Application of Research into Gas Migration

Gas migration calculations to support the PAs have used pre-existing codes developed by and/or for the oil industry, but parameterised as appropriate for the needs of the PA (see Section 4.2). Early work used PORES and research was carried out as part of the Nirex Safety Assessment Research Programme (NSARP) to try and validate this model, but the Nirex 97 calculations used *tech*SIM. In the GPA03 simulations and those reported in Bate et al. (2006), gas migration was simulated using the TOUGH2 code (Pruess, 1987, 1991).

There has been a large amount of detailed work carried out as part of the research programme to assess the migration of gas in fractures via two-phase and bubble flow. A number of numerical models have been developed and field experiments were carried out at Reskajeague. However, it is not clear how (or whether) this work has fed into the gas transport calculations carried out as part of the assessments, or how it has been taken into account in defining future site investigation strategies. In general, the research work carried out in the area of gas migration appears to have been at too detailed a level to allow it to be used directly in the safety assessment. Instead, more pragmatic approaches derived from the oil industry have been used to model fluid flow in the safety assessments. Presumably, the detailed research work was used to determine the suitability of these latter approaches. However, the means by which this was done is not apparent from the reviewed documents, perhaps reflecting the fact that funding for the work ceased in 1997.

Nirex 97 (Nirex, 1997a) was the first Nirex assessment to consider the gas pathway in any detail. The treatment was comprehensive and covered all of the main pathways and processes perceived as being important at the time. The GPA03 (Nirex, 2003a) and subsequent generic calculations have essentially repeated the Nirex 97 analysis for updated inventories of gas-generating materials and the very much simpler GPA geosphere (see Section 3.2.3). Work carried out under the NSARP and by other organisations has shown that gas migration within the geosphere is highly dependent on site specific features. As a result there is only a token treatment of gas migration in the GPA and subsequent calculations. For example, the potential barrier provided by the geosphere is ignored in calculations of the doses due to ^{14}C-labelled gases (methane). These calculations may therefore give an upper bound on the potential doses for the geological conditions considered by the GPA, assuming that all the potential sources of gas have been included and that the gas generation rate used is also an upper bound. However, it is unclear that this treatment would necessarily be conservative for other geological environments. It could be argued, for example, that there may be circumstances where the geosphere could act as a barrier until a certain critical gas pressure had been attained at which time there might be a sudden release of gas, resulting in a transiently high dose. Conversely, even for a Sellafield-like geosphere such as that considered by the GPA03 (Nirex, 2003a, Bate et al. 2006) it is by no means certain that in reality there will be breakthrough of a free gas phase to the surface and therefore it is possible that the assumptions made for this environment are actually overly conservative.

Somewhat inconsistently, the GPA and other calculations take credit for the geosphere when assessing the dose due to ^{3}H (Nirex, 2003a). That is, the travel time between the repository and the surface is 6000 years for the Reference Case and therefore all the ^{3}H arising in the repository is correctly predicted to decay before it can arrive at the surface. However, in contrast, all the ^{14}C leaving the repository in gaseous form is assumed to arrive at the surface. This approach neglects the fact that the travel time is similar to the half-life of ^{14}C (approximately 5700 years), so that around half the ^{14}C originating in the repository can be expected to have decayed before it can arrive at the surface.

The gas breakthrough times predicted within the various assessments were compared in Nirex (2006e). This document points out that the Nirex 97 assessment indicated much more rapid gas transit times between the repository and the biosphere than did the later assessments. In Nirex 97, these times ranged between 26 and 160 years, whereas the GPA03 assessment gave a time of around 6000 years. The difference was due partly to the decreased inventory of gas-generating materials in the wastes considered by GPA03. However, Nirex (2006e) also states that differences in geosphere characteristics between Nirex 97 and the later assessments also partly explain the different gas breakthrough times. The Nirex 97 geosphere was more complex than the one used in the GPA01 and GPA03 assessments (Nirex, 2001, 2003a). These latter assessments lead to the recognition that useful conclusions concerning gas migration could not be made using an unrealistically simplified geology. Therefore, a further assessment was carried out using the same 2D geological cross section as was used in Nirex 97 and TOUGH2 (Bate et al. 2006). This latest modelling showed that the detailed characteristics of the geology could exert a significant effect on gas migration. It was also demonstrated that whether or not gas reached the surface depended on assumptions used to upscale two-phase flow in fracture networks so as to parameterise equivalent porous medium models.

7 Comparison with Overseas Repository Programmes

7.1 European Research

The main issues being considered in Europe are covered by Rodwell et al. (1999), NEA/OECD (2001) and Rodwell et al. (2003), and are described in detail in Section 3.1.

Hicks (2006) has already reviewed work being undertaken by Nagra in Switzerland and Andra in France. An important point is that in both countries, gas research has considered not only ILW, but also HLW and SF.

Nagra's research programme has focussed on gas generation from long-lived ILW, and especially upon possible ILW disposal in the Opalinus Clay of Northern Switzerland (Nagra, 2004). Post-closure gas generation mechanisms have been evaluated and the hydraulic and mechanical impacts of gas generation and migration have been calculated.

Andra has assessed a potential repository for SF, HLW, and long-lived ILW in the Callovo-Oxfordian clay formation of the Meuse/Haute-Marne area of Eastern France (Andra, 2005). The assessment has included post-closure gas generation mechanisms in different parts of the repository.

Compared to Nirex, both Nagra and Andra have given much greater emphasis to the role of the geosphere as a barrier to gas. The difference arises because Nagra and Andra are evaluating sites where mudrocks will act as barriers to gas migration. In contrast, for most of the period during which it conducted gas research, Nirex was concerned predominantly with characterising the Sellafield site. Here, a repository was planned to have been hosted by fractured crystalline rocks which would not have acted as barriers. Nagra envisages that gas will accumulate within a relatively high-permeability confined rock formation that overlies the repository host. During migration into the confining rocks, the gas would dissolve and therefore a free gas phase would not emerge at the ground surface. Similarly, Andra envisages that dissolution of gas would occur. The dissolved gas will then be transported through a confining rock formation by a combination of advection and diffusion. As in the concept of Nagra, there would be no free gas emerging from the ground surface.

Both Nagra and Andra have considered the mechanical effects of gas generation. While Nirex did consider fracturing as a result of overpressuring (e.g. Nash and Rodwell, 1990; Hoch and Rodwell, 2003b), there has not been modelling of dilation effects in plastic lithologies such as argillaceous rocks Among these three organisations, only Nagra has evaluated the effect of gas-induced migration of radionuclides in groundwater.

Like Nirex, Andra and Nagra envisage that the ILW waste packages will be surrounded by cementitious material. However, both Nagra and Andra plan that the waste packages will be emplaced within pre-formed concrete containers. In addition, in the case of Andra's concept, pre-cast concrete will be used to line disposal vaults. The use of pre-formed concrete reduces the amount of cementitous grout that will be needed to backfill vaults in comparison with the quantities that would be needed otherwise. Additionally, the use of pre-formed concrete materials reduces the heat of cement hydration, with the result that temperatures are expected to rise less in the post-closure period. This limitation of the temperature excursion may act to reduce the rate of gas generation from corrosion, but extend its duration.

7.2 Japanese Research

Research that has been done in Japan has some similarities to that being undertaken by the NDA and it is therefore informative to compare the two programmes. The most relevant Japanese research has been undertaken by the Japan Nuclear Cycle Development Institute (JNC) and is being continued by the Japan Atomic Energy Agency (JAEA), which was formed in 2005 when JNC merged with the Japan Atomic Energy Research Institute, JAERI). This research has been described in JAEA (2007) and supports a geological disposal programme for TRU wastes (JAEA, 2007). These latter wastes are ILW containing radionuclides with long half-lives, such as transuranic (TRU) radionuclides, fission products (e.g. ^{129}I) and activation products (e.g. ^{14}C). Key similarities with research that was undertaken by Nirex and that is being continued by the NDA are:

- The investigations are presently generic and a range of host rock types and disposal concepts are being evaluated.
- Phased geological disposal is being considered.
- The wastes include organic materials.
- ^{14}C will be a major contributor to radiological risk.
- There are several possible gas-generating mechanisms, but overall breakdown of organic matter (generating mainly carbon dioxide and methane) and corrosion of carbon steel and stainless steel (evolving mainly hydrogen) will be very important.

- ▲ Like the UK wastes, Japanese wastes include Zircaloy and Inconel which are used for fuel assemblies.

- ▲ Cementitious engineered barriers are being evaluated.

There are, however, several major differences from the Nirex research:

- ▲ Reflecting the wide variety of sources, the Japanese wastes are more heterogeneous and have widely varying activity levels, from intermediate to very low.

- ▲ The Japanese waste is immobilised in various materials including cement, organic substances (e.g. asphalt), metal, etc. Some of the wastes contain large amounts of sodium nitrate, which might reduce the distribution coefficients for iodine and carbon on cement paste.

- ▲ Disposal concepts employing both bentonite and cementitious barriers together have been considered.

- ▲ Co-location of TRU wastes in a HLW repository has been evaluated as a disposal option.

- ▲ Alternative disposal concepts at shallow depths of a few metres and intermediate depths of a few tens of metres have also been considered.

The research reported draws heavily on international experience, in particular that reported in Rodwell et al (2003) and NEA/OECD (2001). Consequently, the overall approach is broadly similar to that of Nirex. As in the Nirex case, corrosion will be the main source of gas (hydrogen) for most of the wastes. However, radiolysis would be the main source of gas generated by one group of Japanese wastes. Consequently, the Japanese research has given greater prominence to this gas source than has been necessary in the UK situation for ILW.

As in the Nirex assessments, preliminary PA for the disposal of Japanese TRU waste (JAEA, 2007) considered that any carbon dioxide evolved from the wastes would be locked up in solid carbonate minerals as a result of reacting with the cementitious backfill. Thus, like Nirex, JAEA consider that ^{14}C-labelled methane would dominate radiological the risk. The Japanese PA work has also considered ^{3}H, ^{222}Rn, ^{129}I and ^{85}Kr, but it was concluded that none of these radionuclides would contribute significantly to risk.

In Japan considerable research has been carried out into the influence of microbiological activity on gas generation. It has been concluded that this activity could generate both carbon dioxide and nitrogen. The latter gas would be produced by denitrification of the nitrate-bearing waste.

An additional effect of the high nitrate content of the TRU waste is that hydrogen generation by corrosion might be inhibited during the early stages of disposal.

These reactions involving nitrate may not be an issue for Nirex, owing to the fact that nitrate is a very small component of the UK inventory. However, this difference between the Japanese and UK situations does illustrate how the characteristics of the inventory exert a significant influence on the nature of gas generation.

Like Nirex, JNC used the TOUGH2 code to simulate gas migration. However, in Japan greater consideration seems to have been given to the coupling between gas generation and resaturation.

Owing to the Japanese programme considering the possible co-location of TRU waste and HLW, considerable effort has been expended on understanding possible interactions between TRU waste and HLW.

JAEA have identified the following as key issues for future research:

- temporal variations in the rate of gas evolution, particularly from corrosion; and
- Coupling between two-phase fluid flow, gas generation and deformation of the engineered barrier (particularly targeted at the clay barrier).

8 Completeness of Research

The research undertaken by Nirex has addressed most of the key issues that have been identified to be important internationally (Section 3.1). However, the following issues don't appear to have been covered in the reviewed reports:

- Although the differences between individual waste streams and packages are taken into account during the LoC process, there has been no systematic evaluation of the impact of heterogeneity on gas generation in a repository environment. However, the potential significance of heterogeneities has been recognised by Nirex (e.g. Rees, 2004). The need to be able to represent heterogeneity has been touched on as one of the drivers for the development of SMOGG. However, it has not yet been realised to any great extent in actual calculations.

- Reviews of research into gas migration (Section 3.2.3 and 4.2) highlighted that very little has been done to investigate the implications of possible preferential gas transport along and through the EDZs of engineered structures.

- The design of the gas vents in the waste packages and how this might impact upon the calculations of gas generation and gas release is an important issue. Gas release via these vents might be expected to influence the design of a repository, since the rate at which release occurs will govern pressures attained within the repository and rates of resaturation by groundwater. However, a review of the characteristics and likely behaviour of these vents under repository conditions is outside the scope of the present work and relevant information was not included in the reviewed documents.

- None of the reviewed documents consider the possible dependence of gas generation rate on the flux of groundwater through the repository or on water chemistry. The flux through the repository and the chemistry of groundwater to be considered will be highly dependent upon the geological environment at an actual repository site. Presently, no site is under consideration and safety assessment studies have been generic and illustrative in character. Thus, the characteristics of the geological environment considered by the GPA03 (Nirex, 2003a) may well be considerably different to those occurring at an actual UK disposal site. It would be valuable to extend the previous generic research to consider the possible nature of gas generation and migration in a repository sited in alternative geological environments so as to understand to what extent gas migration through the geosphere will influence site screening / selection.

9 Future Work Proposed by Nirex/NDA

The Context Notes (Nirex, 2005b, 2006a, 2006b) and the report on future geosphere research (Nirex 2006c) have been used as the primary source of information on Nirex's future gas programme, with reference made to supporting documents where appropriate. Additional information was also obtained from Nirex (2006g). The "Viability Report" (Nirex, 2005a) does not add significantly to the material presented in these other documents. It should be noted that biosphere issues are outside the scope of the review. Not all reports reviewed under this project are referenced in the main part of the report, and additional reports may be included in the appendix 1.

Nirex has been involved in research into gas generation for around 20 years, and during that time has built up considerable knowledge of potential impacts that require knowledge of gas generation, the associated key processes and their modelling. Several potential impacts have been identified by GASNET (Rodwell et al., 2003) and are reproduced in the Context Note (Nirex, 2006a). Nirex work on processes and modelling is described in a number of references, for example Agg et al. (1996).

The Context Note (Nirex 2006a) indicates that Nirex has not yet examined all the potential implications of gas for the long-term safety case. However, it is judged that current knowledge and planned work should put Nirex in a good position to attain an adequate understanding of gas generation. Assessments such as Nirex 97 and the GPA have been able to include quantitative assessments of bulk gas production (hydrogen, carbon dioxide and methane), radioactive gas production (^{14}C and ^{3}H- containing gases and radon) and toxic gas generation (hydrogen sulphide).

The summaries of Nirex reports provided elsewhere in this review (Appendix 1) indicate that work on gas generation in recent years has focused on two main areas:

- The development of the gas generation model SMOGG as a replacement for GAMMON. This development arose initially from a failure to validate GAMMON convincingly against experimental data, but ultimately was also due to changes in the range of wastes that Nirex wished to consider and the need to assess gas generation on a consistent basis during waste transport, repository operations and the post-closure phase.

- ^{14}C-labelled gas generation. In assessments up to and including the GPA, this type of radioactive gas was assumed to arise from the microbial degradation of labelled organic compounds in GE Healthcare wastes. More recently, it has been appreciated that irradiated metals and graphite could also be significant sources of this gas in terms of its impact to man, and Nirex has initiated modelling and experimental work to enable these processes to be included in assessments.

When it comes to research into gas migration NDA have recently taken the view that to a large extent this is a site specific issue. However, Nirex published a report which addresses the potential scope of future research in the area of gas migration (Nirex 2006c). This report identified the following generic and site specific research:

- ▲ Generic research areas:
  - Restart two-phase flow experiments in natural and artificial fractures and fracture networks in order to understand how two phase flow in fracture networks can be upscaled to performance assessment relevant scales.
  - Explore the significance of trace organic contaminants, both natural (humics) and repository derived, on the wetting characteristics of fracture lining minerals. Determine what if any impact this has on two phase behaviour in fractures.
  - Investigate the attachment of colloids to bubble surfaces and explore the stability of the attachment as a function of groundwater chemistry.
  - Undertake laboratory experiments to obtain data to parameterise the radon stripping model.
  - Maintain a watching brief on developments regarding gas migration in mudrocks and evaporites.
- ▲ Once a site was selected the following additional site-specific research activities were identified:
  - Derive two phase saturation functions for each rock unit.
  - Determine the possibility for gas overpressurisation to occur both in the unaltered host rock and in rock altered by reactions between the host rock and the high pH plume.
  - Undertake a full scale gas localisation experiment above a major fracture or fault to determine the extent to which Quaternary sediments and soils will disperse gas.
  - Monitor natural radon flux at the site to parameterise the radon flux model.

The reworking of the Nirex 97 gas calculations using a more sophisticated two phase flow model based on TOUGH2 (Bate et al. 2006) provided a starting point for Nirex to update its gas migration modelling capability. It confirmed the site specific nature of gas migration but also revealed the sensitivity of the results to assumptions about upscaling two phase flow in fracture networks to an equivalent continuum.

Future work proposed by Nirex appears to concentrate on the behaviour of ^{14}C. Little mention is made of other gases. One way of mitigating the predicted impact to man of ^{14}C gas generation is to take credit for the dissolution of gas in the groundwater, thereby minimising the amount of gas that migrates to the surface. In the limiting case when all the gas can dissolve, and the subsequent travel time is sufficiently long in relation to the half-life of ^{14}C, the radiological impact of ^{14}C gas falls by many orders of magnitude. Thus, it is important to evaluate the proportion of gas that might dissolve in the groundwater and to consider the potential for siting a repository at a location which maximises the opportunity for this process to occur. Demonstration of significant dissolution in an assessment requires convincing estimates of bulk gas generation, as well as of ^{14}C-labelled gas. The development of SMOGG should therefore have received greater attention in the Context Note (Nirex, 2006a). Based on discussions held with Nirex staff during the course of this review, it is clearly recognised by Nirex that the calibration of SMOGG across the range of conditions to be modelled remains to be completed.

Another key issue in relation to gas generation is stated to be the extent to which $^{14}CO_2$ will be retained in the repository by reaction with the various cements present to give calcium carbonate. A review of evidence from natural analogues of such reactions suggested that they do not proceed to completion even over geological timescales (Nirex, 2006d). Migration of $^{14}CO_2$ to the surface would increase further the radiological impact to man arising from ^{14}C-labelled gas, especially because carbon dioxide is more readily assimilated by living organisms.

The Context Note (Nirex, 2006a) and Nirex (2006g) indicate that the following work will be carried out in future:

- developing and implementing a programme of work to gather data on the release of ^{14}C-labelled gas from irradiated materials, to reduce uncertainties in the rates and quantities of generated ^{14}C-labelled gases;
- ensuring that the source terms of gas (organics, metals, graphite) are more appropriately represented in gas generation software (e.g. SMOGG) than was the case in GPA03;

- reviewing the current understanding of carbonation (including natural analogues) and deciding whether further experimental and or modelling work is required;
- investigating the potential to collect gas generation data from waste stores, for use in model calibration;
- assessing the extent to which gas would dissolve in groundwater;
- assessing the extent to which different geological environments (as measured by the presence of highly impermeable layers in the overlying strata) have the potential to retard gas migration.

More detailed topics for future work are also raised in the Context Note (Nirex, 2005a,b, 2006a,b) and the report on future geosphere research (Nirex 2006c) in connection with the first of these areas:

- Further research is required to determine the mechanisms and rates of the chemical reactions with water affecting ^{14}C release from irradiated metals and graphite to determine whether such wastes do have the potential to contribute significantly to ^{14}C-labelled methane production.
- The accuracy of the inventory of ^{14}C in graphite needs to be reviewed in consultation with waste producers.
- Further research is required to determine the distribution of ^{14}C in irradiated steels and the form in which it is released during corrosion.

The experimental work on the release of ^{14}C from irradiated graphite (Baston et al., 2006; Handy, 2006) is not referenced in any of the Context Notes. The work will presumably be carried forward by NDA under the topic of ^{14}C release from irradiated materials. In doing so, the need for these projects needs to be made clear, as do the overall aims of the work.

Although the Context Note (Nirex, 2006a) on gas does not discuss the validation of SMOGG (see Section 3.2.2) and notwithstanding code intercomparison exercises carried out with SMOGG one of the supporting reports (Rodwell, 2005b) comments that, according to the amount of presently-available experimental data, it is difficult to calibrate and validate either gas generation model. However, the greater complexity of GAMMON makes it harder to carry out these tasks than would be the case with SMOGG. This view supports the finding of this review that development of an approach for building confidence in SMOGG, and ultimately leading to validation of the code, should be included in future research on gas generation. A limited amount of validation work is discussed by Rodwell (2005b), but it is incomplete; some of the results suggest that the performance of SMOGG does not improve on that of GAMMON. Moreover such work is not set in the context of a validation protocol.

10 Outstanding Issues

A number of issues have been identified above that could with advantage be considered by NDA.

General issues

When considered individually most of the features and processes that might influence the radiological impacts of gas generation and migration have apparently been treated pessimistically by Nirex in assessment calculations. For example, it is generally assumed that:

- no ^{14}C will be lost from the waste prior to emplacement;
- water will be freely available to participate in corrosion following re-saturation; and
- oxide layers developed on the surfaces of metals during the aerobic phase will not inhibit corrosion.

However, there is still uncertainty as to whether these (and other) assumptions are indeed pessimistic or even, in some cases, actually optimistic. The uncertainties arise to a large extent from the coupling between the various processes that control gas evolution and migration. In particular, there is a potentially significant coupling between resaturation, gas generation and gas migration. In some cases, these couplings would make it impossible for all the pessimistic parameter values used to describe individual features and processes to occur together. For instance, a pessimistically high rate of gas generation might be inconsistent with a pessimistically rapid rate of resaturation, owing to the gas pressure acting to oppose inflow of water. Conversely, an apparently pessimistic parameter value may actually result in a non-conservative overall result, when non-linear couplings are taken into account. For example, perhaps an apparently conservative disregard for carbonation of the cementitious backfill would result in pressures rising thereby decreasing the rate of resaturation and hence the rate of gas generation. In such a case it might be more conservative to include carbonation. For these reasons, there remains a need to demonstrate that truly conservative assumptions regarding gas generation and migration are made in safety assessments at the appropriate times in the programme.

Given that the calculated public radiological risks associated with the gas pathway (in both Nirex 97 (Nirex, 1997a) and the GPA03 (Nirex, 2003a, Bate et al. 2006, Hoch and Thorne 2007)) are comparatively high, the viability of making a safety case in future would appear to depend on carrying out a review of the current treatment in order to improve understanding and to identify any aspects of the treatment that are unduly pessimistic or optimistic.

Gas Generation

- As noted previously, the calibration of SMOGG is incomplete at present. The intention in the Context Note to collect data from waste stores for this purpose may not permit SMOGG to be calibrated under all the stages of the waste package life cycle, notably the post-closure period. Validation of SMOGG is also currently an outstanding issue, though is possibly premature at the present time, prior to the completion of calibration (see Section 3.2.2).

- SMOGG assumes that corrosion will occur by general corrosion at metallic surfaces. Rodwell et al. (1999) recommend that the potential for microbially-induced and radiation-induced corrosion be examined. This approach is believed to be appropriate in the current context because:

  - (a) SMOGG is intended to cover the stages of waste transport and repository operations, where these mechanisms could be particularly significant.

  - (b) Radiation-induced effects could be important with spent fuel and HLW, wastes types that have been included in Nirex's remit only in recent times.

- Hicks et al. (2003) note that the geometry assumed for evaluating metal corrosion (small solid spheres) may lead to pessimistically high generation rates. It is necessary to establish whether this conclusion is always true and if so to identify alternative more realistic representations that are less pessimistic. It is noteworthy that MAGGAS simulations (Hoch et al. 2007c) contradict the conclusion of Hicks et al. (2003), highlighting uncertainty in this area. The implications of differences in the assumed geometry of metallic wastes need to be understood and appropriately conservative modelling undertaken.

- None of the reports examined during the current review has adequately described work to determine the sensitivity of the gas generation calculations to changes in flow rate (including resaturation time) and variations in porewater chemistry (for example salinity). All of the calculations that underpin the generic PA assume an idealised evolution of chemical conditions and a very short resaturation.

- None of the work reported to date has adequately addressed heterogeneity in the near field. Nirex has not yet demonstrated that the 'homogeneous soup' approximations that underpin the PA calculations are conservative.

- Although the dominant risk arises as a result of ^{14}C-labelled methane, this risk will only arise should the bulk gas generation rate be sufficient to cause gas to reach the surface.

- The assessed risks depend on the extent to which a carbonation reaction occurs within the encapsulation grout and cementitious backfill, and on the overall effects of this process (Nirex, 1997a, 2003a). It is not clear that this reaction would necessarily proceed to completion (Nirex 2006d) or at a rate that is sufficiently rapid to prevent unacceptably large gas pressures to arise. Alternatively, if the rate of carbonation is acceptably rapid, it is uncertain as to whether or not the carbonate minerals produced will compromise the performance of the backfill for the groundwater pathway. The relationships between carbonation, pressurisation and resaturation are also unclear.

Gas Migration

- The material reviewed to date includes little or no treatment of gas migration within the engineered system and the potential for gas to migrate along the engineering damaged/disturbed zone and/or the interfaces between the backfill and the surrounding host rock. Although gas migration through these pathways may not be particularly significant for the geosphere considered in the GPA, it may a relevant consideration for other host rocks (e.g. argillaceous host rocks) or for shafts etc that pass through low permeability strata that might otherwise be expected to trap gas.

- Very little work has been carried out to address gas migration in host rocks other than fractured crystalline rocks. While considerable research was undertaken into the detailed processes of two phase flow in individual fractures and simple fractures more work is needed to develop more appropriate upscaled continuum models of such flow used in performance assessments. Additionally, appropriate models to allow the potential transport of gas in argillaceous rocks and evaporites will need to be developed in order to allow different sites to be assessed (although much can be learned from other programmes, notably those of Andra in France and Nagra in Switzerland).

- The research by Nirex does not consider the effect of temporal changes in rock properties on gas migration. In the UK future glaciation is the main phenomenon that is likely to cause such changes. The possibility that glaciation might affect the groundwater pathway has been considered by Nirex (e.g. Bath et al. 2000). It would be beneficial to discuss also the importance (or otherwise) of this process for gas migration, even though the next glaciation will not occur until long after the peak of gas generation has past. Other assessments elsewhere in the world have at least considered the possibility that gas may accumulate beneath impermeable permafrost and then be released following permafrost melting.

Links to Design

Vents to allow gas generated within waste packages to escape and thereby prevent over-pressuring of the packages are a fundamental part of the Nirex waste package specification. However, in addition to allowing gas generated within the package (as a result of corrosion/degradation resulting from water in the encapsulation matrix) to escape, these vents can also allow water to enter the package, thereby increasing the rate of gas generation. They may also be significant in terms of early release in groundwater of mobile dissolved species. The gas generation calculations that underlie the vent specification do not appear to be documented in the reports reviewed as part of the current contract. In summary, from the reports reviewed there appears to be a missing link between the research and assessment programmes and the waste package specification. Additionally, the implications of alternative repository designs on gas generation and/or gas migration have not been stated explicitly.

11 Recommendations for Further Research

Based on these outstanding issues, the following recommendations for future research can be made:

- ▲ Additional research into the couplings between gas generation, gas migration, groundwater flow and groundwater chemistry is recommended. A major focus should be on developing and demonstrating an understanding of these couplings that may be used to develop defensibly conservative assessment simulations when specific sites and/or geologies are considered in future.

- ▲ If consideration is to be given to disposal in salt, then additional research will be needed into the coupling between convergence (excavated void collapse) and the processes mentioned in the previous bullet point.

- ▲ A related issue is that since the dominant radiological risk from gas originating in a repository arises as a result of ^{14}C-labelled methane, the risk/dose is dependent on the development of a pathway that allows the free release of gas or near-surface dissolution of free gas with subsequent well extraction. The bulk gas generation rate will influence to a large degree whether or not such a pathway forms. Consequently, work to improve understanding of the processes controlling gas generation rates will be of great value. In particular it will be beneficial to develop a better understanding of the coupling between gas generation rates, groundwater flow and the accessibility of groundwater to corroding metals. It will also be important to improve confidence in metal corrosion rates and to understand how the geometries of the wastes and waste packages influence gas generation rates.

- ▲ Regarding the calibration of SMOGG, consideration should be given to defining sources of gas evolution data that will enable this to be carried out over the full range of conditions that waste packages are expected to experience.

- ▲ A strategy for building confidence in SMOGG should be developed, leading eventually to the code's validation (e.g. as set out by Agg et al. (2002)) so that it is demonstrably fit for purpose. Ultimately, this confidence-building process will involve, inter alia, comparison of model outputs against gas evolution data obtained under well defined conditions.

- ▲ It is recommended that the potential for gas generation by radiation-induced and microbially-induced corrosion be assessed, initially in scoping studies, for the main stages of the waste package life cycle and for all waste types of interest to Nirex.

- ▲ Temperature-dependent processes that might slow down the rates of gas generation due to corrosion should be considered for incorporation into future modelling if identified to be significant, notably:
  - effects of increasing temperature on oxygen solubility;
  - the kinetics of thermally activated processes;
  - retrograde solubility of potentially passivating species (e.g. calcareous deposits).
- ▲ Scoping calculations should be carried out to evaluate the importance of corrosion supported by the cathodic reduction of oxygen and water during the aerobic phase.
- ▲ The efficiency of the carbonation reaction in removing ^{14}C- labelled carbon dioxide is central to the safety case in both the operational and post-closure phases. Further work is required to build confidence that this reaction is able to remove carbon dioxide without compromising the other backfill functions.
- ▲ One of the major peaks in gas generation and hence assessed dose occurs at backfilling. This peak could potentially result in a controlled release that could be mitigated by appropriate underground operations (emplacement procedures, ventilation etc). The Nirex research programme identified several ways in which temperatures could be reduced, which could potentially be implemented to reduce gas production rates. However, it would be valuable to investigate other modifications to the disposal concept and repository design to minimise this gas generation. For example, one possibility might be to emplace pre-backfilled packages in a similar manner to that envisaged by the "supercontainer" concept developed by ONDRAF/NIRAS in Belgium (De Preter et al. 2007). In this way, the peak in gas generation associated with conventional backfilling could be avoided, the quality control on the backfilling process would be easier to assure and the repository infrastructure could be simplified.

12 Summary

This report has reviewed work by Nirex concerning predominantly the generation of gas in a deep geological repository for low and intermediate level radioactive wastes and the possible migration of the gas through the geosphere to the biosphere. Specific objectives are to:

- evaluate whether Nirex explored (or identified as future work) all significant issues of concern in relation to gas generation and migration (given the current decision-context of a geological repository);
- review differences in approach to the assessment of gas generation and migration for a selection of overseas repository programmes;
- identify significant uncertainties and any omissions in the Nirex commissioned work.

A review of the processes that occur within the biosphere itself was outside the scope of the work, though some of the literature considered does include biosphere-specific information.

A total of 61 Nirex reports have been reviewed in their entirety. The adequacy of these documents has been judged by comparing the work covered with research that has been conducted internationally. The degree to which the work carried out by Nirex is complete has been judged by comparing the scope of the research with features, events and processes (FEPs) that are covered in Quintessa's online FEP database targeted at carbon dioxide sequestration (which is based partly on the NEA FEP database (NEA/OECD, 2000)). An additional 43 documents supporting documents were identified during this review and consulted, though not read completely.

It is concluded that the work conducted by Nirex has addressed most of the issues relevant to performance assessment. The present understanding of NDA is at a broadly comparable level to that attained by the most developed radioactive waste management programmes in other countries. In some areas, notably concerning near field evolution and in particular the uptake of carbon dioxide by cementitious materials, Nirex is at the forefront of research. Conversely, there are other areas, especially in attributing a barrier or retardation function to low-permeability lithologies, such as argillaceous rocks and evaporites, where the work of Nirex is arguably less advanced than in some other programmes. This limitation is understandable, given the past prominence given by the UK programme to fractured crystalline rocks. However, in future it is possible that future UK programmes will need to give greater emphasis to these low-permeability media.

The major limitations of the research by Nirex are also common to research programmes elsewhere in the world and reflect fundamental technical challenges. An example is research aimed at understanding coupling between physical and chemical processes affecting repository resaturation and gas evolution. This coupling is inherently challenging to investigate.

Nirex has used evidence from analogues to confirm the completeness of gas migration FEPs and has identified the main issues where future work is required, namely:

- evaluation of the extent to which carbon dioxide generated by microbial degradation of organic matter or other mechanisms will be sequestered by carbonation of the cementitious backfill;
- possible liberation of ^{14}C by corrosion of metals and graphite;
- the need to consider alternative geological environments besides fractured crystalline rocks;
- the organic degradation models require validation.

However, the review has identified that in addition to these topics, additional research needs to consider the following general issues:

- justification of the assertion that estimates of radionuclide doses are in fact conservative if *all* processes influencing gas generation and migration are taken into account;
- evaluation of the degree of pessimism/conservatism associated with parameterisation of individual features and processes, to ensure that future assessments are not unrealistic, as has been the case in the past;
- understanding the significance for PA of the heterogeneity of gas generation within the repository;
- a related issue that gas generation (and its heterogeneity) need to be considered when optimizing the design of the repository;

More specific issues that need to be considered by NDA are:

- the coupling between gas generation, groundwater flow and accessibility of water to corroding/degrading waste (which is particularly related to the third bullet point above);

- ▲ the coupling of the convergence behaviour (collapse of excavated voids) of the host rock to the processes in the previous bullet point (particularly if consideration is to be given to disposal in salt);
- ▲ the influence of salinity on gas solubility (and hence transport);
- ▲ the potential importance of any space that might exist between the backfill and the EDZ ;
- ▲ the potential importance of any EDZ as a pathway for enhanced gas migration;
- ▲ demonstration that upscaling of two phase flow in fractured crystalline rocks is possible in such a way as to capture the key processes relevant to gas migration in the context of a radioactive waste repository; and
- ▲ the possibility that there might be future temporal changes in rock properties during glaciation.

The review has also highlighted that all the key research into gas evolution has been utilised by the previous Nirex PA (Nirex, 1997a; Nirex, 2001; and Nirex, 2003a,b). However, the ways in which previous work on gas migration has been used in this PA are less clear. For example, there have been several experimental and theoretical studies directed at the mechanisms of gas transport through fractures and fracture networks. These studies appear to have resulted in a significantly improved understanding of these mechanisms. However, it is not apparent how the information obtained was used within the Nirex 97 and GPA03 assessment studies. A related issue is that several different computer codes have been developed and/or used to simulate gas migration (*tech*SIM, GWNet, Frac, PORES, TOUGH2), but the rationale for choosing these codes for application in particular studies and the relationships between them is not always sufficiently transparent.

For these reasons, it is recommended that the ways in which previous research into gas migration has been used in the PA should be documented more explicitly than has been done previously. Similarly, it would be valuable to review and document the rationale for choosing the migration codes and the reasons why particular protocols were chosen for applying these codes. Such reviews could be used to draw lessons in order to guide future research.

Gas migration through the geosphere has been shown to depend on fine details of the geology and hydrogeology of the overlying strata. During site screening / selection the need to demonstrate that the geosphere will retard or disperse gas needs to be considered more than perhaps in the past.

Finally, it appears that there may have been considerable overlap between the work carried out by Nirex and work undertaken by BNFL for the Low Level Waste Repository (LLWR) near the LLWR near Drigg, particularly relating to organic matter degradation. It is recommended that a systematic review of this work is undertaken to learn relevant lessons.

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Thorne, M.C. 2005b. Development of increased understanding of potential radiological impacts of radioactive gases from a deep geological repository: Interactions of a methane plume with the ground. MTA/P0011b/2005-6: Issue 2.

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Appendix 1 Summaries of Reviewed Documents

The purpose of this appendix is to provide summaries of the Nirex reports on gas generation and migration that are the primary inputs to the present project. The appendix contains details only of those documents that were obtained and reviewed in their entirety. References that were identified during these reviews, but which were not read completely, appear only in the reference list above, in addition to the references described in detail below. The summaries focus on the unique features of each report, thus establishing what each contributes to an understanding of gas generation in a deep repository and subsequent migration of the gas. The reports are categorised into groups, according to their ***main*** focus:

- overview documents;
- ^{14}C-bearing gas;
- gas generation/evolution;
- gas migration/transport;
- gas in the biosphere;
- models of gas evolution and migration; and
- safety and PA.

However, it is noted that usually a particular document will cover issues that span two or more of these topics.

The summaries are given in two forms:

- a table that gives qualitative indications of the value of each document (Table A1 below);
- short précis of the major topics covered.

In the table, the documents are reviewed against the following criteria:

- the extent to which the drivers/rationale for research is identified;
- the degree to which the work is a repeat of research conducted elsewhere;
- the extent to which the work would impact on:

    - repository design;
    - safety/PA;
    - building confidence in the suitability of a repository concept;
- ▲ the extent to which outstanding issues and uncertainties have been identified.

Each of the summary documents and supporting documents prepared by Nirex is assessed against these criteria as low (i.e. criteria met to a low extent), medium and high. The judgments entered into the table reflect the opinions of the reviewers and therefore are inevitably somewhat subjective. These judgements should be used as general pointers towards the types of information in each document, rather than as definitive indications of whether or not a particular document is fit for its intended purpose. For example:

- ▲ A research strategy report may aim to summarise what has gone before (e.g. Nirex, 2006a; Nirex, 2006b), so the designation “High” in the fourth column of Table A1 below (“Degree of repetition of work”) actually indicates that the report meets its objectives.
- ▲ A user guide to an assessment code (e.g. Swift, 2004), does not need to contain a discussion of outstanding issues in order to be fit for its intended purpose. Therefore, the designation “Low” in the final column of Table Al below (“Extent to which outstanding issues have been identified”) does not indicate that the user guide is unsuitable.

Table A1: Qualitative indicators of the value of each document reviewed.

Report	Title	Extent to which research drivers/ rationale are given	Degree of repetition of work	Impact on repository design	Impact on Safety/PA	Impact on building confidence in repository concept	Extent to which outstanding issues have been identified
Agg et al. 2002	AEAT-ERRA-0320 The gas generation program GAMMON: II A blind validation test	High	Low	Low	High: not possible to validate GAMMON	Low	High: need for a replacement identified
Baston et al. 2006	SA/ENV-0654 A preliminary study of the possible release of volatile ^{3}H and carbon-14 from irradiated graphite in contact with alkaline water	Low	High: see Handy, 2006	Low at this early stage of graphite work	Low	Low	High at the detailed experimental level
Bate et al. 2006	SA/ENV-0850 Gas migration calculations: report to Nirex.	High	Medium - it is noted that the work involved building on gas calculations carried out in Nirex 97.	Medium - it is highlighted that repository design could influence gas migration	High - issues identified are directly relevant to safety	Medium	Medium: (1) migration of gas into the rock matrix between the fractures. (2) the effect of stress changes on the hydrogeological

Report	Title	Extent to which research drivers/ rationale are given	Degree of repetition of work	Impact on repository design	Impact on Safety/PA	Impact on building confidence in repository concept	Extent to which outstanding issues have been identified
							properties (3) the effects of fingering and gas bubble flow
Goodfield et al. 2000	AEAT-R-ENV-174 Gas migration through water-saturated fracture networks: modelling studies relevant to the potential localisation of gas release at the surface and the potential inducing of groundwater flow	High	Low - but some overlap with Nash et al. 2000	Low	Medium - general modelling methods	Low	High - simplifications in the modelling approach are discussed
Goodfield and Rodwell, 2001	AEAT-ERRA-0308 Microscopic and macroscopic approaches to understanding gas-water interactions in gas migration through fractured rock	High	Low - but some overlap with Goodfield et al. 2000 and Nash et al. 2000	Low	Medium - general modelling methods	Low	Low - some discussion of the limitations of the models and simplifying assumptions.
Handy, 2006	NNC report 11996/TR/001	Low	High: see Baston et al 2006	Low at this early stage	Low	Low	Low

Report	Title	Extent to which research drivers/ rationale are given	Degree of repetition of work	Impact on repository design	Impact on Safety/PA	Impact on building confidence in repository concept	Extent to which outstanding issues have been identified
	Experimental study of C-14 and H-3 release from irradiated graphite spigot samples in alkaline conditions						
Harris et al. 2003a	SERCO/ERRA-0453 Experimental study of carbon dioxide uptake by NRVB and 3:1 BFS/OPC.	High	Low	Low (though there are implications for repository design)	Low (though there are implications for safety/PA)	Medium	High
Harris et al. 2003b	SERCO/ERRA-0454 Carbonation of Nirex reference vault backfill	High	Low	Low (though there are implications for repository design)	Low (though there are implications for safety/PA)	Medium	Low
Harris et al. 2001	AEAT-R-ENV-0467 The effect of reactive groundwaters on the behaviour of cementitious materials	High	Low	Low (though there are implications for repository design)	Low (though there are implications for safety/PA)	Medium	Medium
Hicks, 2006	Galson 0573-1 Comparison of gas generation and gas	High	Medium: based on a number of gas assessments	High: ^{14}C gas issue	High	Medium/High: could affect specification for a UK repository	High

Report	Title	Extent to which research drivers/ rationale are given	Degree of repetition of work	Impact on repository design	Impact on Safety/PA	Impact on building confidence in repository concept	Extent to which outstanding issues have been identified
	transfer analysis for Nirex PGRC and Nagra and ANDRA ILW/HLW/SF concepts						
Hicks et al. 2003	Galson 0142-1 Carbon-14 in radioactive wastes and mechanisms for its release from a repository as gas	High	High: reviews earlier work	Low	Medium? Work at an early stage	Low	High
Hoch and Thorne, 2007	Report SA/ENV-0966 Gas and human intrusion pathway	High	Low	Low	High	Medium / High (shows that if a house is built over a borehole, death may be caused by Rn inhalation)	Low
Hoch et al. 2007c	Serco Assurance Report SA/ENV-0802 Comparison of the results from the MAGGAS and SMOGG gas generation models	High	Low	Low	Medium/High	Medium	Low/Medium
Hoch, 2005	SA/ENV-0786	Medium	Medium – common areas	Low	High	Medium	Medium

Report	Title	Extent to which research drivers/ rationale are given	Degree of repetition of work	Impact on repository design	Impact on Safety/PA	Impact on building confidence in repository concept	Extent to which outstanding issues have been identified
	Scoping calculations to determine if gas generated in a repository might migrate to the biosphere in solution		with other work				
Hoch and Rodwell, 2003a	SA/ENV-0514v2 Gas generation calculations for generic documents update, 2003	High	Medium - repetition of the many aspects of the models based on the earlier (1994) inventory.	Low	High	High - understanding of the importance of reactions in the backfill and gas generation in different kinds of vaults.	Low - some discussion of the limitations of the models and simplifying assumptions.
Hoch and Rodwell, 2003b	SA/ENV-0542v2 Some consequences of gas generation in a Nirex repository: estimates for generic documents	Medium	Low	Low	High	High	Low
Hoch et al. 2003	Serco-ERRA-0449 Visualisation and modelling of gas migration through simple models of intersecting channels in a fracture under	High	Low - though builds on work indicated in Hoch et al. 2001	Low	Medium - general modelling methods	Low	Low - some discussion of the limitations of the models and simplifying assumptions.

Report	Title	Extent to which research drivers/ rationale are given	Degree of repetition of work	Impact on repository design	Impact on Safety/PA	Impact on building confidence in repository concept	Extent to which outstanding issues have been identified
	liquid-saturated conditions						
Hoch et al. 2002	Serco-ERRA-0446 Modelling of the transport of radon by gas migrating from a radioactive waste repository	High	Medium - much of the report is devoted to a detailed description of earlier work that had not been published	Low	Medium - general modelling methods	Low	Low - some discussion of the limitations of the models and simplifying assumptions.
Hoch et al. 2001	AEAT-ERRA-0323 Gas migration in low-permeability fractured rock: theoretical and experimental studies	High	Low	Low	Medium - general modelling methods	Low	Low - some discussion of the limitationsof the models and simplifying assumptions
Holtom, 1997	Nirex Report NSS/R318 The Biogenesis of ^{14}C-labelled Methane from ^{14}C-labelled barium carbonate in Intermediate Level Waste	High	High (the work is a review of previous studies)	Low	Medium	Medium	High
Marsden et al. 2002	SA/RJCB/RD03612001/R01	Medium	Medium: Particularly regarding	Low: at this early stage	Low	Low	Low

Report	Title	Extent to which research drivers/ rationale are given	Degree of repetition of work	Impact on repository design	Impact on Safety/PA	Impact on building confidence in repository concept	Extent to which outstanding issues have been identified
	The Chemical form of C-14 within graphite		sources of ^{14}C				
McCarthy et al. 2001	EAT/ERRA-0324 Development of single fracture gas migration model	High	Low	Low	Medium - general modelling methods	High	Low
Mott, and Rodwell, 1998	NSS/R349 A review of two-phase flow in fractures	High	Medium - a large part of the work is a review and hence repeats material presented elsewhere	Low	Medium - general modelling methods	Low	High - some indication of the limitations of applying a porous Medium model to simulate two phase flow in a fracture
Nash and Rodwell, 2000	NSS/R377 Modelling of gas migration pathways	High	Low	Low	Medium – concerns general modelling methods	Low	High - Tracking the movement of gas-water interfaces across a 3D network of rough fractures
Nash and Rodwell, 1990	NSS/R208	Medium	High – summarises but	High	Medium	Medium	Low

Report	Title	Extent to which research drivers/ rationale are given	Degree of repetition of work	Impact on repository design	Impact on Safety/PA	Impact on building confidence in repository concept	Extent to which outstanding issues have been identified
	Effects of gas overpressurisation in the geological environment of a deep repository		from unrelated areas				
Nash et al. 2000	AEAT-R-ENV-175 Conceptual studies of the evolution of gas pathways from a radioactive waste repository in fractured rock.	High	Low - but some overlap with Goodfield et al. 2000 (reference above)	Low	Medium - general modelling methods	Low	Medium - some discussion of the limitations of the models and simplifying assumptions
Nirex, 2006a	Context Note 3.5 495714 Gas and its effects	High: summarises earlier work	High	High: due to ^{14}C gas issue	High	Medium/High: could affect specification for a UK repository	High: at a strategic level
Nirex, 2006b	Nirex Report 494944 Context Note. 3.3: Geosphere research - Appendices and Annexes	Medium	High (it was intended to be a review / discussion document)	Low	Medium	Medium	Medium/High
Nirex, 2006c	Nirex Technical Note 494794 Potential areas of future geosphere	High	High (it was intended to be a review / discussion document)	Low	Medium	Medium	Medium / high (issues relating to mudrock and evaporite host rock not

Report	Title	Extent to which research drivers/ rationale are given	Degree of repetition of work	Impact on repository design	Impact on Safety/PA	Impact on building confidence in repository concept	Extent to which outstanding issues have been identified
	research						discussed)
Nirex, 2006d	Nirex Report. N/131 Analogue evidence for the migration of gases and non-aqueous phase liquids in the geosphere	Medium	Low	Low	Medium	Medium/High	Medium
Nirex, 2006e	Note 495194 Summary note for CoRWM on gas breakthrough time issues. Nirex technical note	High - rationale for the document is identified	Medium: no repetition of new work, though a summary of work elsewhere	Low	Low	Low	Low
Nirex, 2006f	TN 498808 C14: How are we addressing the issues?	High: summarises earlier work	High	High: due to ^{14}C gas issue	High	Medium/High: could affect specification for a UK repository	Medium: focuses on ^{14}C strategy
Nirex, 2006g	TN498211v2 Treatment of gas in Nirex post-closure performance assessment – a note for the record on	Medium/High	Medium	Low but there should be some feedback	High – sets out strategy	Medium/High – sets out strategy	Medium

Report	Title	Extent to which research drivers/ rationale are given	Degree of repetition of work	Impact on repository design	Impact on Safety/PA	Impact on building confidence in repository concept	Extent to which outstanding issues have been identified
	forward strategy						
Nirex, 2005a	N/122 The viability of a phased geological repository concept for the long-term management of the UK's radioactive waste	Low	Medium: some summary of earlier gas work "New" work reported seems to be documented in later reports	High: due to ^{14}C gas issue	High	Medium/High: could affect specification for a UK repository	Medium: at a strategic level
Nirex 2005b	Nirex Report 494675 Context Note. 3.3: Geosphere research.	Low	High (it is a high level summary document)	Low	Medium	Medium	Medium/High
Nirex, 2005d	TN 468230v2 Sensitivity studies – carbon-14 bearing gas generation	Low	Low	High: due to ^{14}C gas issue	High	Medium/High: could affect specification for a UK repository	High
Nirex, 2003a	N/080 Generic post-closure performance assessment	Medium	High – summarises work from other reports	Low – but should have feedback	High	High – gave below target results	Medium
Nirex, 2003b	N/079	Low/Medium	Medium	Medium	High	High	Low/Medium

Report	Title	Extent to which research drivers/ rationale are given	Degree of repetition of work	Impact on repository design	Impact on Safety/PA	Impact on building confidence in repository concept	Extent to which outstanding issues have been identified
	Generic operational safety assessment – offsite dose assessment						
Nirex, 2000	NSS/R367 Theoretical modelling of gas injection field experiments	High	Low	Low	Medium - general modelling methods	Low	Low - a comment is made that further experimental data are required to demonstrate that the modelling approaches explain the experimental results, and to test model performance
Nirex, 1997a	S/97/012v4 Nirex 97 Volume 4: the gas pathway	High	Low	Low/Medium – some recommendation s made	High	High – gave below target results	High – comprehensive discussion of bias etc as perceived at that time
Nirex, 1997b	S/97/014 Development of the Nirex reference vault backfill; report on current status in 1994	High	High - the report is largely a summary of other reports	High	High	High	High – the report is largely a summary of other reports

Report	Title	Extent to which research drivers/ rationale are given	Degree of repetition of work	Impact on repository design	Impact on Safety/PA	Impact on building confidence in repository concept	Extent to which outstanding issues have been identified
Nirex, 1996	S/96/002 Nirex gas generation and migration research: Report on current status in 1994	Medium	High – summary report, although much of work not actually published at this time	Low – no feedback	Medium – underpinning research	Low	Medium/High
Nirex, 1994	S.94/003 Post-closure performance assessment: gas generation and migration	Medium	High – summarises programme	Low – no feedback	High – sets out assessment methodology	Medium – sets out strategy	Medium
Rees, 2004	SA/ERRA-0461 Overview of the generation of carbon-14 gas in a deep repository	High	Medium: summarises earlier work	Low	High: due to ^{14}C gas issue	Medium/High: could affect specification for a UK repository	High
Rees et al. 2004	SA/ENV-0528 Risk from ^{14}C-containing gas released from Magnox wastes in a deep repository	Medium	Medium (many reports covering topics)	Medium/High due to ^{14}C gas issue	Medium: explores some routes to ^{14}C gas; – this is a key area but the treatment is pessimistic and simple	Medium	Low/Medium Makes recommendation s
Rodwell, 2005a	SA/ENV-0745	High	Low	Low	Medium: starts to	Low	Low/Medium:

Report	Title	Extent to which research drivers/ rationale are given	Degree of repetition of work	Impact on repository design	Impact on Safety/PA	Impact on building confidence in repository concept	Extent to which outstanding issues have been identified
	SMOGG vs GAMMION output for gas production from radioactive wastes				build confidence in SMOGG		needs more on calibration/validation issues
Rodwell, 2005b	SA/ENV-0781 The use of SMOGG in place of GAMMON in gas generation assessments	High: summarises earlier SMOGG work	High	Low	Medium: overview helps to build confidence in SMOGG	Low	Low: validation against experiment not discussed
Rodwell, 2004	SERCO/ERRA-0452v5 Specification for SMOGG version 4.0: A simplified model of gas generation from radioactive wastes	Medium	Low	Low	High: specification for improved gas generation model	High: improved model, addresses key ^{14}C gas issue	Low
Rodwell et al. 2002	SERCO/ERRA-0422 Comparison of treatments of gas generation from radioactive wastes	High	Low	Low	High: defines form of improved gas generation model	Low	High
Rodwell and Goodfield, 2000	AEAT-ERRA-0084 A review of	Medium - the drivers and rationale are	Low	Low	Medium - general modelling	Low	Low

Report	Title	Extent to which research drivers/ rationale are given	Degree of repetition of work	Impact on repository design	Impact on Safety/PA	Impact on building confidence in repository concept	Extent to which outstanding issues have been identified
	mechanisms that might attenuate the flux at the surface of gas from a deep repository	implicit, though the need for evaluating attenuation mechanisms is not discussed.			methods		
Rodwell and Nash, 1992	NSS/R250 Mechanisms and modelling of gas migration from deep radioactive waste repositories	High	Low - the review of gas migration from underground caverns presented here overlaps with the report "Serco-ERRA-0446"	Medium - it is Highlighted that repository design could influence gas migration	Medium - general modelling methods	Medium - effects of different lithologies on gas migration are considered	High
Smart and Blackwood 1998	AEA Technology Report AEAT-0251 An investigation of the effects of galvanic coupling on the corrosion of container and waste metals in cementitious environments	High	Low	Low	Low	Medium	High
Stenhouse and Grogan, 1991	NSS/R262 Review of reactions of methane and hydrogen in the	High	Medium/High - review	Low	Low	Low	High

Report	Title	Extent to which research drivers/ rationale are given	Degree of repetition of work	Impact on repository design	Impact on Safety/PA	Impact on building confidence in repository concept	Extent to which outstanding issues have been identified
	geosphere and biosphere						
Swift, 2004	SA/ENV-0511v5 SMOGG (Version 4) a simplified model of gas generation from radioactive wastes: User Guide	Low	Medium: describes SMOGG	Low	Low	Medium: user guide enables others to conduct assessments	Low: outside scope of user guide
Swift et al. 2003	Serco/ERRA-0446 A review of leakage of gases from underground caverns	Low	Medium/High - review	Low	Low	Low	Low
Thorne, 2005a	MTA/P0011b/2005-4 Development of increased understanding of potential radiological impacts of radioactive gases from a deep geological repository: Form of release of C-14	Refers back to a review meeting, documentation for which was not reviewed	Medium/High in part that reviews potential sources	Low	High – C-14 is considered to be the major “issue” by Nirex	Medium	Low
Thorne, 2005b	MTA/P0011b/2005-6 Development of increased	Refers back to a review meeting, documentation for which was	Low	Low	Low	Low	Low

Report	Title	Extent to which research drivers/ rationale are given	Degree of repetition of work	Impact on repository design	Impact on Safety/PA	Impact on building confidence in repository concept	Extent to which outstanding issues have been identified
	understanding of potential radiological impacts of radioactive gases from a deep geological repository: interactions of a methane plume with the ground	not reviewed					
Thorne, 2005c	MTA/P0011b/2005-7 Development of increased understanding of potential radiological impacts of radioactive gases from a deep geological repository: dose factors for acetylene and ethylene	Refers back to a review meeting, documentation for which was not reviewed	Low	Low	Medium	Medium	Low
Thorne, 2005d	MTA/P0011b/2005-5i2 Development of an increased understanding of potential radiological impacts of radioactive gases from a deep geological repository: review of FSA and	High	Low	Low	High – biosphere factors	Medium/High	Medium

Report	Title	Extent to which research drivers/ rationale are given	Degree of repetition of work	Impact on repository design	Impact on Safety/PA	Impact on building confidence in repository concept	Extent to which outstanding issues have been identified
	Nirex models and associated scoping calculations						
Thorne and Mackenzie, 2005	Treatment of waste-derived gas in the biosphere in Nirex safety and performance assessments	Low	Low	Low	Medium – looks at consistency	Low	Low
Watson et al. 2001	AEAT-ERRA-0327 A review of observed surface distributions of natural gases	Medium	Medium/High – review	Low	Low	Low/Medium	Medium

Overview documents

Hicks, T. 2006. Comparison of Gas Generation and Gas Transfer Analyses for the Nirex PGRC and the Nagra and Andra ILW/HLW/SF Concepts. Galson Sciences Limited report 0573-1.

Analyses of the gas pathway in the post-closure phase have shown that it is not of significant radiological concern for the Nagra and Andra deep geological disposal concepts. However, it is (especially for ^{14}C and ^{3}H-containing gases) for the Nirex Phased Geological Repository System.

The analysis suggests that the volumes of gas generated for the three concepts are of similar magnitude and the differences in predicted consequences cannot be explained solely by differences in inventory. A key difference in the disposal concepts is that Nagra and Andra consider clay host rocks, while Nirex's work focuses on fractured hard rock. The clay rocks have high entry pressures for gas, and gas generated will prefer to expand into the pore space in packages, emplacement containers, backfill and concrete walls and other void spaces. Gas pressure is likely to be only slightly above hydrostatic pressure. Gas will leave the repository dissolved in groundwater and move much more slowly than if remaining in the gas phase.

In fractured hard rock, entry pressures for gas are considerably lower, and gas is more likely to escape rapidly through the fracture system in the gas phase.

Nagra considers that if any free gas does escape the repository, it will subsequently enter a confined formation of relatively high permeability above the host rock. The gas would spread out and dissolve in this confining unit. Andra's results are very similar in this respect. In contrast, Nirex believes that gas escaping from a repository would not dissolve in the near-surface environment.

Much lower doses to man result when gas reaches the biosphere is dissolved form compared with the gas phase.

This work has implications for the host formations used to site a deep repository and the design of the near-field. It is also noted that the ANDRA concept of avoiding the need for a backfilling phase emplacing ILW stillages in preformed concrete casks removes one of the main peaks of gas generation in the Nirex PGRC.

Nirex, 2006a. Gas and its effects. Nirex Context Note 3.5: Number: 495714, January 2006. UK Nirex, Harwell.

Again, there is considerable discussion of the effects of gas containing ^{14}C (again without supporting references for the "new" calculations; simply a reference to report N122, which is then repeated) but no overall summary of the processes that lead to the impact from the ^{14}C (i.e. the generation of very large volumes of inactive "carrier" gases leading to the potential for release of a free gas phase at the surface) and a restatement of the research needs noted in N/122 above. Some additional topics are noted as requiring study:

- If lithologies less permeable than fractured hard rock were to be used (e.g. low permeability mudrocks and evaporites), the potential for gas pressure to lead to fracturing would need to be evaluated.
- Reviewing the current understanding of carbonation of cements to determine whether further experimental and modelling work is needed.
- Investigating the potential for collecting gas generation data from waste stores for use in model calibration (presumably of SMOGG: see section 1.3).

Nirex 2006b. Context Note. 3.3: Geosphere research - Appendices and Annexes. Nirex Report 494944.

This report discusses in detail over one hundred issues raised by third parties that relate to the migration and retention of radionuclides in the geosphere and includes issues raised regarding gas migration. It was intended to be read in conjunction with Context Note 3.3. Geosphere Research (Nirex 2005c).

Issues were considered under the following headings:

- overpressurisation;
- localisation at the ground surface;
- enhanced transport of dissolved radionuclides in groundwater;
- stripping of naturally occurring radon;
- enhanced transport of colloids;
- enhanced transport of light non-aqueous phase liquids (LNAPL); and

- ▲ modelling multi-phase flow.

The report concludes as follows. “Two phase flow in fractured rocks is a complex technical problem that has not been fully addressed in existing Nirex performance assessments. However, it must be borne in mind that the significance of gas release to the geosphere depends on the timing of the gas release. Gas generated and vented from the repository prior to backfilling and sealing the vaults and access routes will bypass the geosphere completely. Similarly gas generated during repository resaturation and the early phases of full resaturation may leave the repository before significant radionuclide dissolution will have occurred. Gas released during these stages will not encounter radionuclide contaminated groundwater, and so issues relating to the entrainment of contaminated groundwater will not be relevant. Even when wastes have deteriorated to such an extent that significant dissolution of radionuclides has occurred, the predominantly vertical buoyancy-driven direction of gas migration could be different from the direction of groundwater flow, which may have a horizontal component, possibly limiting the interaction between the two phases.”

“Overpressurisation remains an important issue especially for repositories hosted in mudrocks and evaporites. Overpressurisation could also occur in fractured crystalline rocks if the fracture permeability to gas is low and / or the fractures become closed by the development of new mineral phases following interaction with the cementitious plume from the repository.”

“In the current context all the issues relating to gas may be classified as detailed site-specific issues but in very low permeability rock gas overpressurisation will have to be considered very carefully.”

It should be noted that this report was prepared before the implications of a revised inventory with increased volumes of ^{14}C bearing steels and graphite on the risk from the gas phase was recognised.

Nirex 2006c. Potential areas of future geosphere research. Nirex Technical Note 494794.

This report reviews the background to processes that affect the migration and retention of radionuclides through the geosphere, including those associated with a gas phase. It details work undertaken by Nirex and other radioactive waste agencies and identifies areas where potential generic and site specific research should be undertaken. It sets out to be the first stage in developing a strategy to prioritise the issues identified.

The report reviews the following processes and models:

- overpressurisation;
- localisation of gas release at the ground surface;
- enhanced transport of dissolved radionuclides in groundwater by gas;
- gas stripping of naturally occurring radon;
- enhanced transport of colloids by gas;
- enhanced transport of light non-aqueous phase liquids (NAPLs) by gas; and
- modelling multi-phase flow.

The review emphasised that the fate of gases in the geosphere depended on fine details of nature and geometry of the repository host rock and overlying rocks. It recommended a number of areas of generic research that should be undertaken. However, it should be noted that these assumed that the repository host rock would be located in a strong fractured crystalline rock. No recommendations were given for a repository hosted in a mudrock or evaporite.

Generic research areas to be pursued in future are:

- restarting two-phase flow experiments in natural and artificial fractures and fracture networks in order to understand how two-phase flow in fracture networks can be upscaled to performance assessment relevant scales;
- exploring the significance of trace organic contaminants, both natural (humics) and repository-derived, on the wetting characteristics of fracture lining minerals;
- determining what if any impact the effects investigated in the previous bullet point have on two phase behaviour in fractures;
- investigating the attachment of colloids to bubble surfaces and exploring the stability of the attachment as a function of groundwater chemistry;
- undertaking laboratory experiments to obtain data to parameterise the radon stripping model; and
- maintaining a watching brief on developments regarding gas migration in mudrocks and evaporites.

Once a site was selected the following site-specific research activities were identified:

- derivation of two-phase saturation functions for each rock unit;
- determination of the possibility for gas overpressurisation to occur both in the unaltered host rock and in rock altered by reactions between the host rock and the high pH plume;
- undertaking a full scale gas localisation experiment above a major fracture or fault to determine the extent to which Quaternary sediments and soils will disperse gas; and
- monitoring natural radon fluxes at the site to parameterise the radon flux model and to gain an insight into gas localisation and speed of gas migration.

Nirex, 2005a. The viability of a phased geological repository concept for the long-term management of the UK's Radioactive waste Nirex Report N/122. UK Nirex, Harwell.

This paper discusses Nirex's Phased Geological Repository Concept in a comprehensive manner, and the treatment of gas issues is therefore brief compared with the other papers summarised here. The main focus is on issues concerned with the impact to man of gases containing ^{14}C, which is described as one of the "key challenges" facing the PGRC, although it is concluded that the ^{14}C issues do not threaten the viability of the concept. This focus is at the expense of providing an adequate summary of the key characteristics of the gas pathway, most notably that the vast majority of the gas generated within the repository will be inactive (mostly hydrogen from metal corrosion) but the volume/rate of generation in a repository constructed in a fractured crystalline host rock leads to likely release of free gas at the surface and the associated risk due to ^{14}C methane.

The results of calculations carried out since the publication of GPA03 that consider additional sources of ^{14}C gas not included in GPA03 are summarised. There is no reference to the underlying report describing this new work, which, although acknowledged to be pessimistic, indicates the possibility that risks associated with the gas pathway may be significantly above the risk target.

The key future developments required are the same as those noted in Nirex Technical Note 498808, summarised in section 1.2:

- The extent to which gas would dissolve in groundwater: dissolved gas would move much more slowly than it would in the gas phase, decreasing considerably the impact to man (see also the summary of the paper by Hicks in this section).

- ▲ The potential for highly impermeable layers in strata overlying the host rock to retard gas migration (also considered in Hicks' report).
- ▲ A reduction in the uncertainties in the rates and quantities of ^{14}C gas generated.

<u>Nirex 2005b. Context Note. 3.3: Geosphere research. Nirex Report 494675.</u>

The objective of this report was to provide a high level analysis of those issues raised by third parties that might impinge on the viability of the Nirex phased disposal concept. Details of the more than one hundred issues raised are discussed in the companion report Context Note. 3.3: Geosphere research - Appendices and Annexes (Nirex 2006b).

The report recognises that gas migration in fractured rocks is a complex technical problem that has not been fully addressed in existing Nirex performance assessments. However, it recognises that many of the issues relating to gas migration depend on detailed aspects of the geology of a specific site and are not such as to impact on the viability of the phased disposal concept. Only repository gas overpressurisation is included in the table of 'potential threats to the successful implementation of the Nirex phased disposal concept'. This was shown to be most significant for very low permeability mudrock and evaporite host rocks. It was considered to be a discriminatory factor against the selection of such rocks as the repository host rock.

It should be noted that this report was prepared before the implications of a revised inventory with increased volumes of ^{14}C bearing steels and graphite on the risk from the gas phase was recognised.

<u>Nirex, 1996. Nirex gas generation and migration research: Report on current status in 1994. Nirex Science Report S/96/002, UK Nirex Ltd, Harwell.</u>

This report provides a fairly comprehensive but high level summary of the relevant work undertaken under the NSARP to the end of 1994. It discusses both the tools that had been developed/were being used (GAMMON for gas generation; PORES and capillary bundle models for migration) and the work undertaken to attempt to validate them, including field experiments.

The report also reviews work in this area carried out by sister organisations.

The report finishes with an assessment of the remaining challenges and uncertainties, which include adequately validating GAMMON and models of gas migration in the Sellafield geosphere.

Nirex, 1994. Post-closure Performance Assessment: Gas generation and migration. Nirex Science Report S/94/003, UK Nirex Ltd, Harwell.

This report provides a summary of the position at the end of 1994 with regard to assessment of the gas pathway. It provides a summary of GAMMON and of the various gas migration processes being investigated and tools under development at the time. It also sets out the proposed assessment methodology for evaluating risks due to repository generated gas.

Swift, B.T., Rees, J.H. and Rodwell, W.R. 2003. A review of the leakage of gases from underground caverns. Serco Assurance Report, Serco-ERRA-0446

This report consists of a literature review following on from work done in 1992 (not reviewed here), which is summarised. The new work concentrates on fracture entry pressures and suggests that leakage pressures are lower than had been assumed in the past. However, the new value is consistent with the values used/derived in the gas modelling in Nirex 97. The report notes that it is not clear how relevant observations from storage and gas surge caverns are to the repository context. The work was done in 1998-1999, although not reported until 2003.

^{14}C-bearing gas

Baston, G.M.N., Chambers, A.V., Cowper, M.M., Fairbrother, H.J., Mather, L.D., Myatt, B.J., Otlet, R.L., Walker, A.J. and Williams, S.J. 2006. A preliminary study of the possible release of volatile tritium and carbon-14 from irradiated graphite in contact with alkaline water. Serco Assurance Report, SA/ENV-0654.

This paper reports the results of a further study in which ^{3}H and ^{14}C gas release from a sample of crushed irradiated graphite was measured. The sample was again in contact with alkaline water. Radioactive species released into the water (notably $^{14}CO_2$ and H^3HO) were not determined. These experiments were preliminary in nature, and it was not possible at this stage to draw conclusions regarding the behaviour of irradiated graphite in a repository.

Handy, B.J. 2006. Experimental study of C-14 and H-3 release from irradiated graphite spigot samples in alkaline solutions. NNC report 11996/TR/001, Issue 1.

Experiments have been set up to monitor the release of ^{3}H and ^{14}C from samples of irradiated graphite in contact with simulated repository water (alkaline aqueous solution). Results indicate that two forms of tritium were released: these are likely to be $H^{3}HO$ and $H^{3}H$, with the latter being released rapidly.

^{14}C was also released in two forms, carbon dioxide and methane. The former may have been adsorbed on to the graphite during reactor operation by radiolytic oxidation.

It was estimated that between 10^{-3} and 1% of the ^{14}C inventory could be released as a gaseous hydrocarbon.

Hicks, T.W., Crawford, M.B. and Bennett, D.G. 2003. Carbon-14 in radioactive wastes and mechanisms for its release from a repository as gas. Galson Sciences Ltd report 0142-1, Version 1.0, Issue 1.

This report examines the sources and forms of ^{14}C in radioactive wastes and how ^{14}C bearing wastes have been treated in the various assessments that have been carried out. One of the objectives was to identify whether or not there were any areas of undue pessimism in the Nirex 97 and GPA analyses. However, the report really succeeds only in highlighting areas of uncertainty. It then goes on to consider how its radiological impact might be reduced. The form of ^{14}C in irradiated metals has not been established conclusively: it could be present either as a carbide or in elemental form. Carbides tend to hydrolyse readily, forming hydrocarbon gases containing ^{14}C (aluminium, Magnox, steels and uranium), although zirconium carbide is stable. Elemental ^{14}C would presumably be relatively stable.

Among the methods considered for reducing the radiological impact of ^{14}C in the post-closure phase are:

- Increasing the period during which the repository remains open. This would result in a greater degree of decomposition of organic materials and metals before closure, reducing the amount of ^{14}C-containing gas that could form in the post-closure phase.
- Including gas sorbers (e.g. zeolites) in the repository.
- Designing the disposal system so as to encourage dissolution of gas and prevent its relatively rapid movement in the gas phase (see also Hicks' paper in section 1.1).

Marsden, B.J., Hopkinson, K.L. and Wickham, A.J. 2002. The chemical form of C-14 within graphite. Serco Assurance Report, SA/RJCB/RD03612001/R01, Issue 4,

This document reviews the routes by which ^{14}C is generated in reactor graphite. Work on the leaching of this isotope under saturated alkaline conditions is reviewed. Leach rates are low (10^{-6} – 10^{-5} cm per day) with ^{14}C possibly being released as carbon dioxide under oxygenated condition. This gas may subsequently be converted to solid calcium carbonate by reaction with cement in the repository.

It is recommended that the availability of oxygen to graphite be restricted by suitable packaging and grouting in order to limit the combustibility of packaged graphite in case of a fire during the operational period of a repository.

Nirex, 2006f. C14: How we are addressing the issues. Nirex Technical Note, Number 498808, UK Nirex, Harwell.

This paper reviews, inter alia, the papers summarised earlier in this section. It lays out the background for why ^{14}C is currently considered to be an issue whereas in Nirex 97 and GPA the risks due to the gas pathway were considered to be below target. The document may be the underlying reference for the new calculations presented in N/122 and the Context note. Essentially, Nirex has now recognised that the inventory and range of gas generation processes used in previous assessments were not comprehensive.

The main areas identified for further work are:

- The extent to which gas would dissolve in groundwater: dissolved gas would move much more slowly than it would in the gas phase, decreasing considerably the impact to man (see also the summary of the paper by Hicks in section 1.1).
- The potential for highly impermeable layers in strata overlying the host rock to retard gas migration (also considered in Hicks' paper).
- A reduction in the uncertainties in the rates and quantities of ^{14}C gas generated.

Nirex, 2005d. Sensitivity studies – carbon-14 bearing gas generation. Nirex technical note, Number 468230v2, Work in progress.

This document records assessments using the SMOGG program of ^{14}C gas generation from wastes containing irradiated metals (steels, Magnox, uranium, aluminium and Zircaloy) and the associated risk to man from these radioactive hydrocarbons. First, the GAMMON calculations that were used in GPA03 were repeated, then a range of sensitivity calculations were carried out, which included some additional sources of ^{14}C that could not be included in GAMMON. The assessments spanned the operational and post-closure phases of a deep repository.

The work was continuing from the GPA03 assessment, where degradation of a waste stream containing organics labelled with ^{14}C was the only ^{14}C waste stream considered.

All of the calculations showed that the annual individual risk target of 10^{-6} would be exceeded over considerable periods of time. A thorough review of input data (especially corrosion rates and ^{14}C inventories) and assumed chemical processes was recommended. This review formed the basis for the proposed work programme for 2005.

Rees, J.H., Fitzgerald, P.L. and Thorne, M.C. 2004. Risk from ^{14}C-containing gas released from Magnox wastes in a deep repository. Serco Assurance Report, SA/ENV-0528.

The report investigates whether the conversion of the C-14 activation products in Magnox wastes might pose a risk to man. The study uses the methodology developed in Nirex 97. It is assumed that any acetylene reacts to form ethylene and that any methane is metabolised to carbon dioxide in the soils. Calculated peak doses from methane derived from uranium carbide are close to or above target and doses from Magnox are well below target. The report finishes with a series of recommendations for further work to address these sources of gas.

Rees, J.H. 2004. Overview of the generation of carbon-14 gas in a deep repository. Serco Assurance Report, Serco/ERRA-0461.

This review was based on assessments showing that the largest impact to man from gas was due to gases containing ^{14}C. This conclusion stemmed from assessments of a single waste stream that contained simple organic molecules labelled with this isotope.

Outstanding issues in this field were identified and recommendations made for developing them:

- Other wastes containing ^{14}C and from which gases could form include irradiated graphite and steels, Magnox reprocessing wastes, and contaminated resins. Scoping calculations suggested that the graphite, steels and resins could give above-target risks to man from the ^{14}C content. Magnox wastes were just below target. These wastes should be considered for inclusion in future assessments.

- Heterogeneities in the waste can affect the ratio of methane to carbon dioxide labelled with ^{14}C. While methane is unreactive, and is likely to reach the biosphere, carbon dioxide would be expected to largely react with the cementitious material present in the near field and be removed from the gas phase. This area should be considered in future work.

- The efficiency of carbonation of cement as a process for removing ^{14}C from the gas phase should continue to be investigated.

- The relative effectiveness of carbonation of cement, migration of carbon dioxide along cracks in cement, and microbial conversion of carbon dioxide to methane should be established.

It is suggested that priority should be given to confirming the efficacy of the carbonation reactions and the potential for waste-derived carbon dioxide to be converted to methane.

Thorne, M.C. 2005a. Development of increased understanding of potential radiological impacts of radioactive gases from a deep geological repository: Form of release of C-14. MTA/P0011b/2005-4: Issue 2.

This report is one of a series addressing topics agreed at a review meeting in January 2005. This report covers the first topic, the development of a coherent account of the form of C-14 release.

This report reviews 2001 inventory to determine the likely sources of gases containing C-14. It identifies the Amersham waste stream 1B05 (labelled organic wastes) as the most significant during the transport and operational stages. It assesses that the doses to the public during transport and surface storage are likely to be very low but if very pessimistic assumptions are made this waste stream could lead to unacceptable doses during the operational phase, post emplacement.

The report then considers the post-closure phase where the key C-14 bearing gases of concern are methane, acetylene, ethylene and ethane (carbon dioxide is assumed to react with the backfill). The report considers the behaviour of each of these gases in the biosphere and identifies that the prior Nirex assumption that methane released to the soil zone will all be metabolised to carbon dioxide may be incorrect. It is concluded that the doses due to acetylene, ethylene and ethane are likely to be below the ICRP recommended value for methane and recommended that for simplicity these gases are considered to be methane for assessment purposes. Consideration of methane releases, in particular from waste stream 1B05, suggest that the doses are sensitive to the combination of gas flux, rate of metabolism in the soil zone and specific activity meaning that reference calculations may not all be conservative.

Thorne, M.C. 2005b. Development of increased understanding of potential radiological impacts of radioactive gases from a deep geological repository: Interactions of a methane plume with the ground. MTA/P0011b/2005-6: Issue 2.

This report is one of a series addressing topics agreed at a review meeting in January 2005. This report covers the third topic, the calculation of the interaction of a methane plume with the ground.

The report considers the degree to which a methane plume might interact with the ground surface and thereby calculates the concentration that might be available to methanogenic microbes. A standard Gaussian plume approach was adopted. The typical effective doses per Bq of released methane were then calculated for typical UK conditions. By combining the calculations in this report with others presented elsewhere a methodology for assessing the radiological impact of chronic and acute radiological releases of methane was developed. The release rate corresponding to the risk target was calculated.

Thorne, M.C. 2005c. Development of increased understanding of potential radiological impacts of radioactive gases from a deep geological repository: Dose factors for acetylene and ethylene. MTA/P0011b/2005-7: Issue 2.

This report is one of a series addressing topics agreed at a review meeting in January 2005. This report covers the fourth topic, the evaluation of the need for and an approach for calculating the doses associated with labelled acetylene and ethylene.

This report assesses potential doses from C-14 labelled acetylene, ethylene and ethane. These gases are likely to be generated by corrosion of metals, notably Magnox and steel, containing carbides. There appears to be considerable uncertainty surrounding the generation of these gases and on how they might behave once they reach the biosphere. Pessimistic calculations indicated doses that might be close to the risk target so the report recommends further work to understand how these gases might be produced and interact in the biosphere. It is recommended that these gases are aggregated with methane in future work since this will be cautious.

Gas Generation/Evolution

Harris, A.W., Boult, K.A., Manning, M.C. and Tearle, W.M. 2003a. Experimental study of carbon dioxide uptake by NRVB and 3:1 BFS/OPC. Serco Assurance Report, SERCO/ERRA-0453.

A study of the carbonation of the Nirex Reference Vault Backfill (NRVB) and 3:1 Blast Furnace Slag/Ordinary Portland Cement (OPC) is described. The latter material is used to encapsulate the waste. The work was preliminary in nature and aimed to develop an experimental method and provide an initial characterisation of the cementitious materials used.

Every cementitious sample was pre-conditioned at a relative humiditiy of either 75% or 100% for at least 74 days. Each sample was then transferred to a diffusion cell, to which a carbon dioxide atmosphere was introduced. The method then involved measuring the decreases in the pressures of carbon dioxide as a function of time. The pressure was cycled during some of the experiments. It is noteworthy that the cycling would inevitably have caused some drying of the samples, so that the relative humidities would not have been constant. Additionally, the water present was not representative of groundwater.

The characteristics of the materials and the degree of water saturation were found to affect strongly the rate of carbon dioxide uptake. At a relative humidity of 75%, 80% of the NRVB was carbonated, but only a maximum of 4% of the material used for encapsulation was carbonated. A simple model in which the rate of carbon dioxide uptake is determined by the thickness of the carbonated layer was found to explain the major features of the results.

It was concluded that the likely behaviour of the materials had been demonstrated, but all the factors that control the rates of carbonation had not been determined. It was recommended that additional experiments should be done to investigate a wider range of water saturations and higher pressures. These experiments should also be carried out over longer durations than those investigated in this study. Additionally, it was noted that models of reactions involving flowing carbon dioxide would be more realistic.

The reviewers here note that it would be valuable to investigate the effect of different porewater compositions on the carbonation rates. Additionally, the study did not directly examine the solid materials used in the experiments or the solid reaction products. Such examinations would help greatly to improve knowledge of the reaction mechanisms. The reviewers also note that this report does not reference the earlier work of Harris et al. (2001).

Harris, A.W., Manning, M.C. and Tearle, W.M. 2003b. Carbonation of Nirex reference vault backfill. Serco Assurance Report, SERCO/ERRA-0454.

This document describes experiments to investigate the carbonation by carbon dioxide of NRVB. Like Harris et al. (2003a), these experiments involved imposing a carbon dioxide-rich atmosphere within a number of diffusion cells. Each cell contained a sample of cementitious material.

The chief differences from the work reported in Harris et al. (2003a) are that:

- The cementitious materials examined were all NRVB samples and were relatively fresh; the work of Harris et al. (2003a) used samples of NRVB and encapsulating cement that had been stored under water for several years.
- Four different humidities (75%, 85%, 95% and 100%) were used to condition the samples; Harris et al. (2003a) report experiments with relative humidities of 75% or 100%. Addition.
- Prior to each experiment, three sides of the sample had been sealed with epoxy resin.
- Each samples was conditioned at fixed humidity for a period of 69 days.
- Staining of the reacted samples with phenolphthalein indicator was used to determine the characteristics of the carbonated layer.
- Some samples that had been conditioned at 75% and 100% relative humidities were examined by scanning electron microscopy (SEM) following carbonation.

It was found that the kinetics of carbonation depends upon the degree of water saturation. In the cases of samples that had been conditioned at humidities of less than about 90%, the kinetics could be described by a parabolic law. However, at greater humidities, carbonation was slower and could not be described by this rate law.

The carbonated layer was found to be approximately uniform in the samples that had been conditioned at lower humidities. In contrast, the samples that had been conditioned at higher humidities showed irregular carbonation. On the basis of these results it is suggested in the report that carbonation proceeded according to different mechanisms at different humidities. Observations of the solid reaction products suggested that in the carbonated zone, calcium hydroxide has been completely consumed.

As for Harris et al. (2003a) the reviewers here note that it would be valuable to investigate the effect of different porewater compositions on the carbonation rates. Additionally, the study did not directly examine the solid materials used in the experiments or the solid reaction products. Such examinations would help greatly to improve knowledge of the reaction mechanisms. The reviewers also note that this report does not reference the earlier work of Harris et al. (2001).

Harris, A.W., Hearne, J.A. and Nickerson, A.K. 2001. The effect of reactive groundwaters on the behaviour of cementitious materials. AEA Technology Report, AEAT-R-ENV-0467.

Preliminary experimental leaching of structural concrete and high-porosity cementitious grouts and backfills is reported. This work was carried out mostly ten years or more before this report was written, mainly between 1988 and 1992.

The experiments used tap water and synthetic Na-Cl dominated groundwater. There were two kinds of groundwater, one a saline water (simulated sea water) and the other brine. The tap water had a pH of 7, whereas the saline water and brine had pH of 8.25 and 12.11 respectively. It is noted that the latter pH is too high to represent realistically a groundwater brine from the UK. It is unclear from the report why such a high pH was specified. Monoliths of cementitious material were leached by these waters under static conditions. Four kinds of experiments were performed:

- static experiments open to the air;
- static sealed experiments at ambient temperature;
- static sealed experiments at 80 °C; and
- sequential leaching experiments, open to the air at ambient temperature.

It was found that formation of carbonate precipitates on grain surfaces, caused by carbonation, affected the ability of the cementitious materials to buffer pH. The ability of these materials to sorb radionuclides was also diminished by the surface precipitates. The main effect was a reduction in the rate of sorbtion, rather than a decrease in the overall sorption capacity. The structural concrete was found to be a relatively poor pH buffer, partly as a result of these precipitates forming. An important conclusion is that the results do not support including structural concrete in calculations of the pH conditioning capacity of a repository.

Hoch, A.R. and Rodwell, W.R. 2003a. Gas generation calculations for generic documents update Serco Assurance Report, SA/ENV-0514, Version 2.

This report presents up-dated calculations of gas generation that are based upon the revised waste inventory of 2001. A major aim is stated to be to contribute to the up-dating of generic Nirex documents that are used, among other things, to prepare advice to waste producers concerning packaging. Prior to the reported work, these documents have been based upon a previous inventory produced in 1994.

Most of the calculations presented were carried out using the code GAMMON. Calculations address a range of possible operational regimes and alternative assumptions that explore variations in the timing of backfilling of the vaults and of closure of the repository.

The following general features of the results obtained from GAMMON simulations were identified:

- Hydrogen generation, predominantly from metal corrosion, dominated the cumulative gas production, and, at most times, the rate of gas production.

- Peaks in the gas production rate were determined by the corrosion of Magnox and to a lesser extent aluminium.

- The temperature dependence of the corrosion rates of these metals leads to maximum gas generation rates during periods, particularly of backfilling, when the vault temperatures are elevated. Steel corrosion under anaerobic conditions provides a background of ongoing hydrogen production.

- Uranium corrosion produces a small addition to the hydrogen production rate in the UILW vaults after the vaults become anaerobic. The uranium is consumed relatively quickly.

An important aspect of the calculations was that one case considered that carbon dioxide would not react with the cementitious backfill allowing the carbon dioxide to react with hydrogen generated by corrosion. In the other cases this reaction did occur, thereby preventing this reaction. There were significant differences in the results of these simulations. Significant ^{14}C release was almost entirely confined to the variant scenario in which carbon dioxide and hydrogen were allowed to react in the UILW vaults. When no reaction of carbon dioxide with the backfill occurred, there was a significant drop in the cumulative gas generation for the UILW vaults, since conversion of hydrogen to methane halves the gas volume.

Holtom, G.J. 1997. The Biogenesis of 14C-labelled Methane from 14C-labelled barium carbonate in Intermediate Level Waste. Nirex Report NSS/R318.

Microbial mediation is required for the production of $^{14}CH_4$ from $Ba^{14}CO_3$ under the conditions that are expected to occur in an underground repository for IWL. Hence, the potential for this process to occur was assessed, based on a literature survey that was carried out in 1992. The UK radioactive waste inventory that was current at the time of the work (the 1989 inventory) indicated that about 20% of the total ^{14}C to be emplaced within the then-planned ILW repository would be in the form of $Ba^{14}CO_3$ originating in THORP reprocessing wastes.

It was concluded that pH is the single most important parameter affecting the contribution of $^{14}CH_4$ by $Ba^{14}CO_3$. This latter compound has very low solubility under typical natural low-temperature groundwater conditions. The solubility would be even lower under the very alkaline conditions caused by the presence of cementitious waste grouts and cementitious repository backfill. These alkaline conditions ensure that dissolved inorganic carbon is predominantly in the form of CO_3^{2-}, thereby suppressing dissociation of $BaCO_3$. Additionally, under these high-pH conditions, methanogenic bacterial activity would be reduced. Early in the post-closure evolution of the repository, temperatures may also rise to about 80 °C, thereby restricting microbial activity.

An overall conclusion from an appraisal of all these factors is that the biological production of $^{14}CH_4$ from $Ba^{14}CO_3$ is extremely unlikely to be significant in a cementitious repository.

Nirex, 1997b. Development of the Nirex reference vault backfill; report on current status in 1994. Nirex Science Report S/97/014.

The physical and chemical specifications of the NRVB, as developed in 1994, are summarised by this document. The main specified properties of the NRVB that are relevant to gas migration through the near field are relatively high permeability and porosity. It is stated in the report that the purpose of specifying these characteristics is to ensure both homogeneous chemical conditions and to permit the escape of gas generated by chemical reactions within the repository. It is noteworthy that the document does not give carbonation (thereby removing any carbon dioxide gas that might be evolved from the waste) as a purpose of the specification. It is recognised in the report that carbonation may be caused by carbon dioxide in the air that comes into contact with backfill before final closure of the repository is completed, and also by carbon dioxide produced by degradation of organic matter. However, the report focuses on the consequences of this carbonation for the temporal evolution of permeability, porosity and chemical buffering capacity. In particular it is noted that carbonation is expected to result in some shrinkage, and hence cracking, of the cement but that in practice sealing of fractures seems to occur. The possibility of cracking due to carbonation is indicated to be a topic requiring further investigation. However, the main consequence of carbonation is stated to be a reduction in buffering capacity due to the consumption of calcium hydroxide. When considering the production of carbon dioxide from the degradation of organic wasteforms, this effect is taken into account in the calculation of the required vault buffering capacity.

Smart, N.R. and Blackwood D.J. 1998. An investigation of the effects of galvanic coupling on the corrosion of container and waste metals in cementitious environments. AEA Technology Report AEAT-0251.

Galvanic coupling between metals, and between metals and graphite (which though not a metal has some metallic properties) was investigated experimentally. The coupling was investigated for metals in 3:1 PFA/OPC grout, under aerobic, fresh water conditions. It is noted that the results would not be applicable to the post-closure environment when Cl-rich groundwater is present.

A galvanic series was developed under these conditions. The results are relevant to other cementitious systems, such as BFS/OPC grouts or NRVB, although account should be taken of the possible effect of impurities (e.g. thiosulphate) or differences in porewater pH which may apply in other cementitious materials of interest to Nirex.

In considering galvanic coupling, stainless steel has been confirmed as a suitable material for the manufacture of containers for radioactive waste. With the exception of graphite, stainless steel has been found to be more noble than all other materials tested. The lifetime of stainless steel containers could be significantly reduced if galvanic coupling to graphite occurs.

Galvanic coupling to any of the other metals likely to be found in a repository should not reduce the lifetime of stainless steel containers.

At 30 °C, uranium behaved as a passive metal. However, at 80°C uranium behaved as an active metal and corroded rapidly when coupled to carbon steel. This led to the formation of a large volume of corrosion product.

Galvanic coupling between noble metals (e.g. stainless steel and graphite) and active metals (e.g. Magnox and aluminium) results in accelerated corrosion of the active metal. This corrosion is sustained in cementitious environments (in contrast to the behaviour of noncoupled active metals where passivation occurs). This may be of concern for waste containing aluminium, aluminium alloys or Magnox wastes, if it leads to a significant increase in the rate at which hydrogen evolves from the waste.

Gas Migration/Transport

Bate, F., Hoch, A.R. and Jackson, C.P. 2006. Gas migration calculations: report to Nirex. Serco Assurance Report, SA/ENV-0850.

The report presents the results of calculations using the TOUGH2 code and data from the Nirex investigations at Sellafield during the 1990's. The Sellafield dataset was used because it represents the only real geoscientific dataset covering a depth range appropriate for a deep geological repository.

The calculations were carried out to improve understanding of the factors affecting gas migration in the geosphere. In particular, the aims are stated to have been to evaluate the period of care and maintenance prior to repository closure, and the significance of improvements to the gas migration model made since the completion of Nirex 1997. The new model considered a larger area than was considered in the Nirex 97 assessment model and explored the following phenomena that were not included in the this model:

- the initial drawdown;
- the compressibility of the rocks and groundwater;

- ▲ the regional groundwater flow;
- ▲ the background temperature gradient.

The results highlighted that the factors controlling gas migration are very site specific. Gas migration paths depend upon the rock properties. The dissolution of free gas and the magnitudes of groundwater flow in more permeable (aquifer units) were found to be important factors that control whether gas breaks through to the surface. The amount and rate of gas generation and the repository design were also stated to be possible controls on breakthrough. Among the phenomena listed above, only the regional groundwater flow was found to have a large affect.

Goodfield, M. and Rodwell, W.R. 2001. Microscopic and macroscopic approaches to understanding gas-water interactions in gas migration through fractured rock AEA Technology Report, AEAT-ERRA-0308.

This report explores further the phenomenon of cyclic flushing considered in Goodfield et al. (2000) and Nash et al. (2000) above. The aim was to determine whether the process is a real physical phenomenon. The work considered both small-scale and large-scale cycling.

Small-scale cycling is caused by the alternate development of water and gas slugs at fracture intersections. In the case of the GWNet simulations presented in Goodfield et al. (2000) and Nash et al. (2000), this cycling process was inevitably caused by the underlying assumptions.

Also evaluated was large-scale cycling caused by repeated water expulsion from a fracture by gas, followed by backflow of water into the fracture. An analytical model was developed to evaluate whether gas streams might be unstable. The results showed that stable gas pathways could form in an idealised variable-aperture fracture channel. However, there was also some indication that the resulting gas streams could be sensitive to small perturbations, so that in real systems at any particular time the gas-filled region would tend either to expand or contract.

The gas-lift models are also presented. These models assume that mixture of groundwater and gas act as a single fluid with a volume-averaged density, which is only valid for low gas volume fractions when the gas is dispersed. The calculated induced upwards groundwater flow varied over several orders of magnitude. This range spanned the magnitude of the regional groundwater flow.

The induced groundwater flows were also simulated using the groundwater flow simulator NAMMU. Gas effects were taken into account by reducing the groundwater density in the region directly above the repository. When the density was equivalent to a free gas volume greater than 1% there were significant perturbations to the shape of the contaminant plume. It was commented that the formation of a gas cushion at the top of the repository may prevent dissolved contaminants from flowing out of the vault ceiling. The migrating gas would therefore flow through uncontaminated water.

Goodfield, M., Nash, P.J., Tate, M.J., Wikramaratna, R.S. and Rodwell, W.R. 2000. Gas migration through water-saturated fracture networks: modelling studies relevant to the potential localisation of gas release at the surface and the potential inducing of groundwater flow. AEA Technology Report, AEAT-R-ENV-174.

The report reviews the processes that might control gas migration through fractured rock. The review is supported by simple calculations. The motivation for the work was stated to be that any safety case for a potential deep repository must consider possible localisation of gas release at the surface, and the potential effects of gas migration on groundwater movement and hence on water-borne contaminant transport.

Two main processes were evaluated:

- The contribution that major fracture features may make to overall gas migration relative to that of lesser conducting features;
- Mechanisms that might lead to intermittent gas release at the surface as a consequence of changing patterns of gas flow through the fracture network.

Simple fracture networks were also used to evaluate the potential for cyclic flushing of water from fractures as a mechanism for inducing groundwater. Simple 2D analytical models and the 3D gas-water fracture network modelling program, GWNet were used. The latter program was improved as part of the work.

The results demonstrated that the mass flow rate of water induced by density reduction due to the addition of a small proportion of gas, would be far higher than the gas flow rate. It was concluded that in systems with a few major fractures and many minor fractures, the major fractures will support most of the gas flow. Flow through a network of interconnected major and minor fractures was found to be unstable, but it was unclear whether the system would evolve to a steady state over time, or whether release of gases to the surface would oscillate.

Hoch, A.R. 2005. Scoping calculations to determine if gas generated in a repository might migrate to the biosphere in solution. Serco Assurance Report, SA/ENV-0786

This report assesses whether a free gas phase will form in the repository, whether any free gas that escapes from the repository will dissolve in the geosphere and whether dispersion etc outweigh the decrease in solubility as water rises. It concludes that a free phase is formed and it is unlikely to dissolve in the hard fractured host rock but the GPA geosphere has enough flow to prevent outgassing of any gas that has dissolved.

This report appears to provide the justification for the very short resaturation time used in the GPA calculations. However, the hydraulic conductivity assumed for the host rock (taken from N/080) appears to be unreasonably high for a candidate host rock.

Hoch, A.R., Myatt, B.J., Rodwell, W.R., Swanton, S.W. and Swift, B.T. 2003. Visualisation and modelling of gas migration through simple models of intersecting channels in a fracture under liquid-saturated conditions. Serco Assurance Report, Serco-ERRA-0449.

The report describes an experimental study of gas migration and induced water flows in a simple physical model of a fracture intersection. A major aim of the work was to evaluate the processes that could cause cyclical movement of gas along a fracture. This cyclical movement would be caused by the fall in pressure that occurs once gas has ascended along a fracture to the surface. The gas pressure drops all along the fracture, allowing water to flow back into the void space. Apart from disrupting flow to the surface, the process can lead to pumping of gas and water from one part of the fracture network to another. The motivation for the work was the need to understand the way in which gas migrates through individual water-saturated fractures. This migration is an important component in the development of approaches for numerical modelling of flow through a network of fractures in a crystalline repository host rock.

The design of the experiments was guided by simulations using the codes GWNet (a program to track the movement of gas-water interfaces through an arbitrary two-dimensional network of fractures, which is saturated initially with water) and FRAC (a program to model the invasion of an initially water saturated rough fracture by gas). Both these codes were also used to predict the outcomes of the experiments.

GWNet reproduced the overall alternation of gas and liquid migration. However, the code does not reproduce the mechanism that controls the movement of fluid between the two fractures. FRAC is not well-suited to this kind of problem because it models movement of fluid through the fracture using a saturation function and cannot represent bubbles of gas and drops of liquid. The code does, however, represent cyclical behaviour.

Hoch, A.R., Jackson, C.P. and Rodwell. W.R. 2002. Modelling of the transport of radon by gas migrating from a radioactive waste repository. Serco Assurance Report, Serco-ERRA-0446.

The half-life of ^{222}Rn is too short (3.82 days) to allow Rn from a deep repository for radioactive waste to reach the surface unless it is transported very rapidly. The report assesses the extent to which such rapid transport might be caused by Rn being carried by the dominantly non-radioactive gas that will also originate in the repository. An additional important issue is the possibility that this migrating gas might also transport Rn produced naturally in the rocks. The rate of emanation of the Rn into a gaseous phase would be greater than the rate of emanation of this Rn into an aqueous phase.

An earlier model for Rn transport beneath the water table is described in detail. Modifications to the model that enable it in addition to explain radon transport above the water table are then presented. The model is implemented in a code termed “radon_90, Version 1.1”, which is a modification of a code that implemented the earlier model.

It is pointed out that Rn produced within the rock originates in the decay of ^{226}Ra close to the surfaces of micro-pores, including microfractures. Since ^{226}Rn has a half-life of 1600 years, much of this Rn must have been deposited near to these surfaces within the last 20,000 to 50,000 years and probably mostly since the peak of the last glaciation. Some of this Ra has been co-precipitated with Mn- and Fe-oxyhydroxides that line pore spaces in the shallower rocks.

The report also points out that safety assessments in future should consider the evolution of ^{222}Rn from the decay of radionuclides that have been transported from the repository. However, it is also stated that such migration is expected to occur dominantly long after the release of bulk gas from a repository has stopped.

As a result of the short half life of Rn, processes occurring in unsaturated zone above the water table may determine the flux of radon to the surface. Most of the radon that reaches the water table from deeper in the geosphere may decay before reaching the surface.

Hoch, A.R., Swanton, S.W., Manning, M.C., Rodwell, W.R., Swift, B.T. and Duddridge, G.A. 2001. Gas migration in low-permeability fractured rock: theoretical and experimental studies. AEA Technology Report, AEAT-ERRA-0323.

This report describes an experimental study of gas migration in transparent artificial fractures, and theoretical evaluations of the data produced.

Aims were to:

- determine whether stable gas pathways are able to form in either smooth or 'real' rough fractures; and
- show that gas bubbles could form, and hence to measure the migration speeds of differently sised and shaped bubbles through a fracture.

Fluid flow through smooth and rough fractures was investigated experimentally. The code FRAC was used to simulate bubble migration in the rough fractures and was able to reproduce the experimental results qualitatively.

The extent to which the fluid in the fracture wets the fracture surfaces influences whether continuous gas migration can occur. If the fluid does not wet the fracture surface, then it is possible for the gas phase to migrate through a stable pathway. However, the pathway is unstable if the fracture surfaces are wetted. The existing theory explains the migration speeds of Hele-Shaw bubbles (those which fill the fracture completely) when the fracture surface is wetted, but not otherwise. It proved impossible to produce microbubbles reliably. However, it was concluded on theoretical grounds that these bubbles are not likely to contribute significantly to contaminant migration.

McCarthy, R.F., Swift, B.T. and Rodwell, W.R. 2001. Development of single fracture gas migration model, AEA Technology Report, EAT/ERRA-0324.

This report described improvements to the fracture flow modelling code FRACv1, giving rise to the FRACv2 code. The motivation for the work was to provide a better understanding of gas migration in fractures. A particular goal was to facilitate an evaluation the extent to which gas migration might enhance contaminant migration from a repository. The report also highlights that characterisation of two-phase flow in fractures forms a theoretical basis for deriving relative permeability curves and capillary pressure functions that are needed to carry out large-scale two-phase flow simulations.

It was found that FRACv2 could accurately simulate flow in a realistic, rough fracture. However, the extent to which it would be valid for simulating flow in fractures of constant aperture is less certain. Inclusion of the in-plane capillary pressure had the effect of eliminating snap-off and "fingering" of the gas as it invaded the fracture. In rough fractures, inclusion of the in-plane capillary pressure had little or no effect on the overall fluid-fluid interface shape.

Mott, R.E. and Rodwell, W.R. 1998. A review of two-phase flow in fractures. Nirex Report NSS/R349, UK Nirex Ltd, Harwell.

The report describes a theoretical study of two-phase flow in a single fracture, aimed at recommending relative permeability curves to be used in modelling gas migration from a radioactive waste repository. The work is stated to have been necessary owing to a lack of published relative permeability or capillary pressure measurements in fractured crystalline rocks or other low-permeability media.

The report quotes work by Preuss and Tsang (1990) that questions the conventional approach to calculating theoretical relative permeability curves in fractured rock. This approach assumes that relative permeabilities are linear functions of the phase saturations, and that critical saturations (the lowest fractional volumes of the phases that can flow) are zero. For these assumptions to be correct the gaseous and aqueous phases must flow without mutual interference and show no tendency to occupy the smaller or larger aperture fractures preferentially. However, both these requirements are unrealistic. Consequently the reported work modified the method proposed by Preuss and Tsang (1990) for estimating relative permeability curves while taking these processes into account. The modified method considers the distributions of the gas and water in a fracture to depend on both the local capillary pressure and on the occurrence of connected flow channels within the fracture. Based on this treatment relative permeability curves were calculated from single-phase flow simulations, using a discretised model of the fracture. These calculations were based on Darcy's Law and used the finite-difference porous medium flow simulator PORES to calculate both single-phase and two-phase flow in fractures. Geostatistical methods were used to generate two different models of fractures with variable apertures. In one, the parameter values were based on published observations from the Stripa Granite. In the other model, parameter values were based on measurements made on Cornish slate using positron emission tomography (PET) . The two-phase simulations were based only on the second fracture model. The use of a porous medium simulator for modelling flow in a fracture required several approximations (notably the choice of relative permeability curves) which may affect the validity of the results. Models based on tracking the position of fronts may give a more reliable method of simulating two-phase flow within a fracture.

Nash, P.J. and Rodwell, W.R. 2000. Modelling of gas migration pathways. Nirex Report NSS/R377, UK Nirex, Harwell.

The reported work aimed to developing a fundamental understanding of the way that gas from a repository may travel through fractured rock to the surface. The single-phase code NAPSAC was used to examine the influences of variable fracture apertures on water flow. It was considered that gas would tend to migrate through the same conductive fractures that support water flow, provided that the gas entry pressures of the fractures are exceeded.

The simulations considered the effect on the effective flow properties of removing from the network those fractures that are considered unlikely to contribute to the gas migration pathways. These latter fractures have narrow apertures and therefore have high capillary entry pressures, so that they would remain fully water-saturated. Particle tracking in the single-phase flow model was used to explore the variations in fracture aperture along different possible flow paths.

Results indicate that continuous connected pathways across the network for gas may be lost at fracture densities which are only just beyond the critical percolation density. However, it was pointed out that most real rocks have fracture densities well above the percolation threshold.

A numerical model was developed for calculating gas and water flow in a single variable-aperture fracture and was implemented in the code "GWNet", written in C++. This code was used to track the movement of a single gas-water interface, displacing water from the bottom of an initially water-saturated variable-aperture fracture. A comparison was made between gas pathways in models with fixed-aperture and variable-aperture pathways, but with the same effective single-phase permeability. It was found that using variable-aperture pathways increases transit times for the gas breakthrough at the surface, and reduces gas flow rates at a given repository pressure.

Nash, P.J., Goodfield, M., Sullivan, N.A. and Rodwell, W.R. 2000. Conceptual studies of the evolution of gas pathways from a radioactive waste repository in fractured rock. AEA Technology Report, AEAT-R-ENV-175.

The objectives of the work presented in this report were the same as those of the previous reference (Goodfield et al. 2000), namely to understand the mechanisms of gas migration in fractures. The work addressed the potential effect of migrating gas on groundwater movement, and the nature any gas release at the surface (notably whether or not localised and whether or not episodic).

The GWNet program was developed as a tool for exploring the mechanisms of gas pathway formation and maintenance in a fracture network. The program simulates gas invasion of simple water-saturated fracture networks by explicitly tracking the position of gas-water fronts as they move through the fracture network. For this work, the program was modified so that the boundary condition representing gas release from the repository could be varied.

The calculations showed that the most important factor in determining which fractures form the gas migration pathway is the fracture transmissivity or aperture. Fractures with a large aperture allow the gas to migrate more easily with a lower pressure gradient and have a lower capillary entry pressure. Only a small proportion of the fracture network had been invaded by gas at the time when gas breakthrough occurred at the top of the modelled region. These observations suggest that, the release of gas at the top of the fracture network could be localised to the positions of a few gas pathways.

The objective of these calculations was to consider the stability of gas pathways after breakthrough. Results indicated that when gas generation rates were high, once gas had broken through at the surface, flow was continuous. However, at low gas generation rates the release of pressure following breakthrough to the surface allowed water to flow back into the major fracture network from interconnecting minor fractures (or rock matrix) and shut off the gas flow. Pressures in the repository then increased until the entry pressure for the fracture was exceeded once more, thereby allowing flow to resume. Under these circumstances, gas breakthrough occurs in short episodes separated by prolonged periods with no gas release at the surface.

Nirex, 2006d. Summary note for CoRWM on gas breakthrough time issues. Nirex technical note, Number: 495194, UK Nirex, Harwell.

This summary note records a response to a query regarding gas release from a repository into the environment up to 300 years after repository closure, that was received at a CoRWM Safety Workshop (20-22 September 05). The note deals with differences between the times of gas breakthrough to the surface calculated in the Nirex 97 assessment and in the GPA03. These assessments calculated breakthrough times of around 40 years and 6000 years respectively. The main reasons for the difference are stated to be:

- The waste inventory used in the GPA03 was revised from that used in Nirex 97, resulting in less gas being produced; and
- In the GPA03 there was a longer phase of repository operation before closure, which resulted in less gas being generated following repository sealing.

It is highlighted that the actual timing of gas breakthrough will depend on geological factors at a particular site. The main radiological risk from any gas that did arrive at the surface would be due to ^{14}C. However, it is stated to be unlikely that gas would reach the surface during the first 300 years following closure and that if such breakthrough did occur, institutional control of the site would ensure that doses received, if any, would be minimal.

Nirex 2006g. Analogue evidence for the migration of gases and non-aqueous phase liquids in the geosphere. Nirex Report. N/131.

This report summarises the historical and current precedence that may be utilised to understand better the migration and attenuation of gases and non-aqueous phase liquids (NAPLs) in the geosphere and the extent to which their release is likely to be localised at the ground surface. It draws examples from a diverse range of sources including the oil and gas, coal mining, environmental remediation industries, and research then current into carbon dioxide sequestration. The report is organised using a FEP approach. The more important observations are summarised below.

Overpressurisation in crystalline rocks: Evidence from gas injection experiments, leakage from hydroelectric power station surge chambers, underground natural gas storage caverns all show that gas leakage can occur into fractured crystalline rocks at pressures less than hydrostatic water pressure. This would suggest that gas overpressurisation is unlikely to occur in such repository host rocks.

Overpressurisation in mudrocks: Mudrocks are known to form the cap rocks to natural gas accumulations. The hydrocarbon industry has developed various rules of thumb to determine the extent of gas seepage through the caprocks but these tend to be region specific. Evidence from the gas fields in the North Sea, which are known from seismic evidence to be leaking, probably by capillary flow, are 0.4-1.0 $m^3m^{-1}y^{-1}$. This may provide a clue to the flux rates that may occur without causing gas fracs in repository host rock.

Gas migration in the geosphere: Analogue evidence from gas seeps and soil-gas anomalies demonstrates the ephemeral and localised nature of natural and man-made gas emissions. Many are localised directly above the source and this is generally interpreted as evidence for rapid migration as a free gas phase rather than due to moving in solution.

Gas attenuation in the geosphere: There is ample evidence for the attenuation of methane and carbon dioxide in the geosphere provided that they are trapped beneath a suitably configured mudstone cap rock. There is also evidence for the sorption of methane and carbon dioxide onto coals and carbonaceous mudrocks. These both depend on the presence of suitable rocks and structural features in the rocks overlying the repository. Evidence from the limited carbonation of naturally-occurring cement-like minerals, the stability of potentially reactive minerals in carbon dioxide reservoirs and during gas floods all tend to suggest that the sequestration of carbon dioxide to form carbonate is limited even on geological timescales. This could have implications for Nirex's current assumptions regarding the extent of in-drum and backfill carbonation.

Co-transport of a gas phase: The movement of a bulk gas phase is used to induce the movement of trace gases in the environmental remediation industry to remove gaseous, volatile and colloid contaminant species. It is also believed to be the reason why deep seated radon gas anomalies can be detected in soil gas surveys. It therefore appears possible that repository-derived gas could induce similar co-transport of gaseous (radon) and colloid species.

Co-transport of solids and liquids: The attachment of LNAPL films and radioactive solute species to gas bubbles is known and there is often a spatial association between carbon dioxide rich springs and oil seeps. These suggest that the co-transport of solutes and oils with gas is possible.

Co-transport of solids: Transport of solid particles attached to the surfaces of bubbles through a water column is used in the froth flotation industry to separate mineral phases. The operation of this process within fractures in the geosphere remains controversial and unproven.

Gas induced redox changes: The bleaching of red sandstones and the formation of magnetic anomalies above hydrocarbon accumulations and landfill sites has been attributed to reduction of iron minerals in the presence of methane or hydrogen sulphide. The spatial association between uranium orebodies and hydrocarbon accumulations has also been attributed to the reduction of soluble uranium species by the presence of hydrocarbons. Conservatively Nirex have not included such processes in their models of radionuclide solute migration.

Nirex, 2000. Theoretical modelling of gas injection field experiments. Nirex Report NSS/R367, UK Nirex, Harwell.

The report presents modelling of two types of He gas injection experiment carried out at the Reskajeage Farm Nirex test site in Cornwall. In both cases the gas was injected into fractured slate below the water table. Data from obtained by Atomic Energy of Canada Limited (AECL) by testing in the the Lac du Bonnet Batholith of Manitoba were also modelled. The work was carried out in order to understand how gas migrates through fractured rock.

In the first kind of test, gas was injected into an inclined borehole and recovered from a nearby parallel borehole. The gas flow in a single plane fracture between the boreholes was modelled using the porous medium multi-phase flow simulator PORES. It is stated that this code can be used in safety assessments to quantify gas migration.

The second kind of test involved helium injection in a borehole and subsequent soil-gas monitoring to identify and quantify gas reaching the surface. A radial model of gas flow displacing water from a fixed-width fracture was used to analyse the injection and allowed the gas flow rate into the zone to be predicted from the injection pressure.

Rodwell, W.R. and Goodfield, M. 2000. A review of mechanisms that might attenuate the flux at the surface of gas from a deep repository. AEA Technology Report, AEAT-ERRA-0084.

This report reviews key processes within the geosphere that could have attenuated the gas flux originating in the repository that Nirex proposed to construct at Sellafield. Simple calculations are presented that aimed to scope the magnitudes of these processes. The details of the work are specific to Sellafield, but the processes considered would apply at any site. The work was based on information available prior to 1994 and consequently does not take into account later geological observations, particularly concerning the possible presence of barriers to gas migration.

Two basic attenuation mechanisms are discussed:

▲ solution in the water flowing through aquifers that lie between the repository and the surface; and

- trapping in formations below geological barriers to gas flow.

Chemical attenuation processes were not considered because it was thought that they could occur only in near-surface soils.

Dissolution models provided upper bounds on the capacity of the flowing water to dissolve the gas, since they assumed that the gas would contact all of the flowing groundwater and reach solution equilibrium. It is stated that these assumptions are probably unrealistic in rocks like those at Sellafield where gas is likely to migrate through fractures. Additionally, methane dissolution would be controlled by the presence of the bulk hydrogen gas. Therefore, in reality the groundwater would not become fully methane-saturated, effectively diminishing its capacity to transport away methane.

It was also considered that there are no geological barriers to gas flow in the area of Sellafield around the proposed repository.

A conclusion from the work was that gas generated within a deep radioactive waste repository at Sellafield is unlikely to be significantly attenuated by dispersion during migration towards the surface.

Rodwell, W.R. and Nash, P.J. 1992. Mechanisms and modelling of gas migration from deep radioactive waste repositories, June 1992. Nirex report NSS/R250, UK Nirex, Harwell.

This report evaluates the mechanisms by which gas might escape through the far field of a radioactive waste repository. The results of the evaluation are then used to determine the circumstances under which excessive pressures would not develop in the repository. This issue is important because excessive pressures could compromise the functioning of the barrier system and accelerate the transport of water-borne radionuclides to the biosphere. The report also considers whether any lessons relevant to gas migration from deep waste repositories can be learned from studies of underground gas migration in other contexts.

It is stated that gas will migrate through the far-field by:

- dissolution in groundwater which then moves by diffusion or advection;
- diffusion or advection of a free gas phase in the form of either bubbles or a continuous stream.

Three approaches were used to evaluate these migration processes:

- ▲ application of Darcy's law with an effective permeability to gas;
- ▲ modelling the far-field rock as a bundle of capillaries with a suitable distribution of radii; and
- ▲ use of a numerical model of two-phase flow in porous media.

The third of these approaches used the PORES (Program for Oil Reservoir-Simulation) oil reservoir simulation code.

Illustrative calculations suggested that gas escape from a repository in unfractured low-permeability sedimentary rocks would require a substantial pressure rise, but would occur relatively easily through fractured hard rocks. In this latter case any substantial pressure rise could occur only soon after closure. Gas fluxes were influenced by repository design factors, in turn reflecting lithological characteristics. Fluxes were 9-19 times larger for a hard rock site than for a soft rock site because the former would have a greater waste concentration. It was concluded that only migration of a continuous free gas phase would prevent pressure from building excessively; the other mechanisms would allow an insufficiently large flux.

It is recommended that further work should consider the how the characteristics of the gas pathways, particularly in fractured rocks, might influence gas migration. The proposed modelling approaches are stated to require validation and it is suggested that this should be done against the results of Nirex's gas injection field project.

Stenhouse, M.J. and Grogan, H. 1991. Review of reactions of methane and hydrogen in the geosphere and biosphere. Nirex Report NSS/R262.

The potential reactions of methane and hydrogen in the geosphere and biosphere are reviewed. The report focuses particularly upon the possible role of these reactions in attenuating fluxes of the gases that would emanate from a deep geological repository for ILW and LLW. Based purely on thermodynamic criteria, both hydrogen and methane may be oxidised by a range of aqueous species and minerals (e.g. those bearing NO_3, Fe(III) and SO_4). However, it is pointed out that kinetic data are lacking and both hydrogen and methane are known to be relatively unreactive under shallow crustal conditions. Consequently there is doubt as to whether reactions of hydrogen and methane would actually occur sufficiently rapidly to consume the gas emitted from the repository before it could arrive at the surface. The extent to which such reactions could occur is likely to depend upon the time taken to make this transit. Both hydrogen and methane may be consumed by microbially mediated reactions within the biosphere.

These authors found little evidence that hydrogen and methane would sorb to mineral surfaces significantly. It was pointed out that these gases would not be expected to show strong sorption owing to their short bond lengths and non-polar characters.

Neither hydrogen nor methane are very soluble compared to polar gases such as carbon dioxide or sulphur dioxide. However, for a given temperature and pressure, methane is about three times more soluble than hydrogen. The solubilities of both gases will decrease with increasing salinity and temperature.

In the biosphere various microbially mediated reactions are capable of oxidizing methane. Similarly one of the sinks postulated for hydrogen is microbial oxidation to form water in soil. However, this latter hydrogen sink is thought to be less significant than the microbial production of methane from hydrogen and carbon dioxide.

It is noted that those anaerobic oxidation reactions which involve hydrogen consumption and methane production convert one gaseous hazard into another. Therefore, methanogenesis involving hydrogen cannot be regarded as an effective attenuation mechanism.

Other potential gas sinks considered included methane hydrates. It was concluded, however, that these solids would not form under the pressure and temperature conditions that might occur in the environs of a deep geological repository for radioactive wastes.

Gas in the Biosphere

Thorne, M.C. 2005d. Development of an increased understanding of potential radiological impacts of radioactive gases from a deep geological repository: Review of FSA and Nirex models and associated scoping calculations. Mike Thorne Associates, MTA/P0011b/2005-5: Issue 2.

This work builds on previous work to compare Nirex and FSA approaches for transport of hydrogen in near surface. For hydrogen Nirex uses a simple specific activity model that agrees well with the FSA compartment model. For ^{14}C both use compartment models but RIMERS (the Nirex model) give much lower specific activities for chronic releases to the soil zone. The report documents RIMERS (not previously documented fully in the public domain), describes its re-implementation in GoldSim and correction of various errors. It then describes enhancements to the GoldSim version of RIMERS to treat exchanges with the canopy differently, so that it is consistent with the FSA model, which was judged to be the more appropriate assessment model.

Thorne, M.C. and McKenzie, J. 2005. Treatment of waste-derived gas in the biosphere in Nirex safety and performance assessments. Quintessa report QRS-1248A-1, version 2.0.

The report reviews appropriate treatments of waste-derived gas for which there is currently no specific legislation or guidance. A review of the international situation did not reveal any useful guidance. The report then reviews the treatment of each of the various Nirex assessments (transport, operational etc). It reveals some inconsistencies between the different assessments, although most are probably cautious. It notes potential issues associated with the use of PC-CREAM. Finally the report notes that the analysis of pathways and processes seems somewhat ad hoc in many cases and needs to be properly laid out and documented.

Watson, S.P., Swift, B.T. and Rodwell, W.R. 2001. A review of observed surface distribution of natural gases. AEA Technology Report, AEAT-ERRA-0327.

The report reviews recent (late 1990s) literature on observed distributions of soil gases, including Nirex surveying done at Sellafield, and gas injection experiments. Discharges are localised and are controlled by the locations of faults in the bedrock and minor features in the cover sequence, which act as pathways for gas migration, or barriers that impede the flow of gas. Soil gas discharges are often not vertically above the gas source owing to the influence of these geosphere structures and advection of groundwater followed by outgassing. The report concludes that for the volumes of gas anticipated in a repository with a free gas phase, only experiments are really useful as pointers to likely behaviour. It also notes that a very detailed characterisation of the potential discharge zone will be required to provide reliable data.

Models of gas evolution and migration

Agg, P.J., Arcus, A., Blackwood, D., FitzGerald, P.L., Holtom, G.J., Lineham, T., Rosevear, A., Smart, N.R. 2002. The gas generation program, GAMMON: II, A blind validation test. AEA Technology Report, AEAT-ERRA-0320.

This report is concerned with the blind validation against experimental data of the gas generation model GAMMON, which takes into account gas formation during corrosion of the metals present in waste packages and the microbiological degradation of certain organic wastes, particularly those containing cellulose. The project produced some predictions that were a reasonable fit to experimental data, particularly where corrosion alone was studied. However, overall the agreement was inadequate to permit GAMMON to be used with confidence in repository safety assessments. It appeared that microbiological processes are particularly difficult to model quantitatively, and may be strongly influenced by heterogeneities in the gas-producing system. In contrast, GAMMON assumes that the system is homogeneous. It is concluded that a simpler, more empirical model may be more appropriate for assessment purposes. This study led to the development of the SMOGG program for modelling gas evolution, as discussed in accompanying summaries below.

Hoch A.R., Norris S., Swift B.T., Askarieh M.M. 2007c. Comparison of the results from the MAGGAS and SMOGG gas generation models. Serco Assurance Report SA/ENV-0802.

SMOGG, developed by Serco Assurance for Nirex and MAGGAS, developed by Magnox Electric Ltd are computer codes to calculate gas generation from radioactive wastes. This report gives the results of a code comparison exercise between SMOGG Version 4.1 (Swift 2005) and MAGGAS version 8 (Swift 2004) with the objectives of better understanding the differences between the codes and building confidence in the methodology to determine gas generation rates.

The comparison involved fifteen test cases at the single package scale as follows. Seven related to metal corrosion, three to tritium diffusion in stainless steel, two to radiolysis, one to graphite degradation and one to a combination of processes. In addition, there was one test case involving gas production during organic degradation. This differed from the other test cases because it was known that the two codes treated organic degradation differently so that a direct comparison was not possible. Instead the codes were used to match the results from an existing experiment.

Corrosion test cases involved the modelling of the corrosion of Magnox, stainless steel and uranium, alone or in combination. Minor differences between the results could be attributed in the simpler test cases to differences in the values of physical constants used in the two models. Other differences were attributed to known limitations in the models. For example, MAGGAS does not model corrosion of the exterior of the waste drum whereas SMOGG did and MAGGAS had a less sophisticated water inventory tracking than SMOGG. SMOGG models uranium corrosion as spheres or plates whereas MAGGAS can also model them as infinitely long cylinders. It was found that the cylindrical model led to more rapid uranium corrosion than the spherical model.

Test cases involving tritium diffusion in stainless steel differed substantially between the two codes. This was attributed to the different models of diffusion used. MAGGAS assumes that the tritium is uniformly distributed, whereas SMOGG estimates a concentration gradient within the metal. It appeared that for the particular choice of dimensions of spherical metal particles used in the test cases that SMOGG underestimated the concentration gradient and hence underestimated the rate of release of tritium. Unlike MAGGAS, SMOGG cannot model the temperature dependence of diffusion rates. This can lead to an underestimate of tritium release by up to an order of magnitude. On the other hand only SMOGG could model tritium diffusion in corroding stainless steel. Despite the known underestimation of tritium diffusion in this model (see above), it was found that tritium release in corroding stainless steel was dominated by diffusion rather than corrosion.

In the case of the radiolysis test case gas generation predicted by MAGGAS was found to be substantially larger in SMOGG. This was attributed to the larger range of radionuclides considered by MAGGAS including their daughters, and a more realistic adjustment of gas generation with water inventory. Only the SMOGG code could include radiolysis of water in grout surrounding the container.

The graphite degradation test case showed that under aerobic conditions both codes yielded very similar results differing only due to the values of physical constants used. However, MAGGAS does not model graphite degradation under aerobic conditions.

The most complex test case considered the simultaneous corrosion of mild steel, stainless steel, Zircaloy, aluminium, Magnox and uranium waste, water radiolysis, tritium release from mild steel, stainless steel, Magnox and waste water. the differences, which were mostly small, could be attributed to a range of known differences between the two codes.

Lastly, the comparison of the output of the two codes for the organic degradation test case provided similar quality fits to the experimental data. The authors considered however that the MAGGAS code was not as theoretically well founded in its representation of microbial processes as the SMOGG code.

Key references referred to as sources in the report are:

1. Swift B.T. 2005. SMOGG (Version 4.0): a simplified model of gas generation from radioactive wastes: User guide. Serco Assurance Report SA/ENV-0511.

2. Swift B.T. 2004. Development of a calculational model for the estimation of gas generation rates from cement encapsulated wastes. Part 18; Overview of the MAGGAS model. Serco Assurance Report SA/ENV-0618.

Rodwell, W.R. 2005a. SMOGG vs GAMMON output for gas production from radioactive wastes. Serco Assurance Report, SA/ENV-0745.

This paper examines the differences in gas generation outputs between the GAMMON program and its replacement, SMOGG. The point of comparison was some of the calculations performed using GAMMON for the GPA(03) assessment.

Both programs gave similar results for the production of hydrogen and tritiated hydrogen by the corrosion of metals. The main differences lay in estimates of the production of carbon dioxide and methane from cellulosic wastes. SMOGG avoids the spikes in gas production that GAMMON can sometimes exhibit, and the former is more realistic in terms of the known behaviour of landfills. In addition, the partitioning of ^{14}C between carbon dioxide and methane is more in line with expectations with SMOGG than with GAMMON. It is however emphasised that with presently-available experimental data, it is difficult to calibrate and validate either model. However, the greater complexity of GAMMON makes it harder to carry out these tasks than with SMOGG.

Rodwell, W.R. 2005b. The use of SMOGG in place of GAMMON in gas generation assessments. Serco Assurance Report, SA/ENV-0781

This report essentially summarises the findings of the reports summarised earlier in this section. In doing so, it makes the case for using SMOGG in safety assessments in place of GAMMON.

Rodwell, W.R., 2004. Specification for SMOGG Version 4.0: A simplified model of gas generation from radioactive wastes. Serco Assurance Report, SERCO/ERRA-0452, Version 5.

This report builds on the conclusions of SERCO/ERRA-0422 (see above) by presenting a detailed specification of a gas generation model to replace the use of GAMMON in assessments. The model focuses on the waste package, or waste stream, scale, with overall repository gas production being obtained by summing over all packages or waste streams. The model is applicable to spent fuel and HLW, as well as to ILW.

The main gas-generating processes included are:

- Corrosion of unreactive (steels, Zircaloy and uranium) and reactive (Magnox and aluminium) metals to produce hydrogen.
- Microbial degradation of cellulose, producing carbon dioxide and methane.
- Radiolysis of water and organic wastes to give mainly hydrogen.
- Gases containing ^{14}C, produced from irradiated metals and graphite and labelled organic wastes.
- Tritiated hydrogen, produced from metallic wastes, graphite and tritiated water.
- ^{222}Rn generated from radium wastes, and ^{81}Kr, ^{85}Kr, ^{39}Ar and ^{42}Ar produced from metals.

The resulting **S**imple **M**odel **O**f **G**as **G**eneration (SMOGG) was implemented in a C++ computer program and interfaced with an Excel work book.

Rodwell, W.R., Rees, J.H., Chambers, A.V., and Hoch, A.R., 2002. Comparison of treatments of gas generation from radioactive wastes. Serco Assurance Report, SERCO/ERRA-0422.

This paper considers how best to move on from the detailed and mechanistic GAMMON model for assessing gas generation rates in the light of the disappointing attempt to validate it (see summary of AEAT-ERRA-0320 above). It was concluded that a greater degree of commonality in modelling gas generation was needed across the stages of waste transport, the operational phase of a repository and the post-closure period. In addition, a greater number of processes should be modelled compared with GAMMON (e.g. hydrogen formation from uranium metal and radiolysis).

Other waste disposal agencies were found to use more empirical models than GAMMON. However, the use of purely empirical models was not recommended because this would not allow the representation of a range of conditions in the waste. Instead, it was recommended that a simplified kinetic model be produced. Calculations using it should focus on characteristic waste streams, rather than the homogeneous vaults that had been assumed to date. This is because the validation work with GAMMON had suggested that heterogeneity had a significant impact on gas generation.

Swift, B.T. 2004. SMOGG (version 4.0), a simplified model of gas generation from radioactive wastes: User guide. Serco Assurance Report, SA/ENV-0511, Version 5.

Following on from the specification for SMOGG contained in SERCO/ERRA-0452 and summarised above, this report describes how to install the program, the structure of its spreadsheet/user interface, its various worksheets, and how to run a typical calculation. Verification of the model is also set out.

Safety and Performance Assessment

Hoch M.R. and Thorne M.C. 2007. Gas and human intrusion pathway. Serco Arssurance Report SA/ENV-0966.

The objective of this report was to extend the analysis of the human intrusion pathway in the GPA03 Generic Post-closure Performance Assessment to include calculations of the radiological and flammability risks associated with gas release should a well accidentally encounter repository-derived gas. The gas generation rates were the same as those used in the 2007 update of the GPA03 (Hoch et al. 2007) which were based on the 2004 UK radioactive waste inventory (Nirex 2005) using SMOGG Version 5.0 (Swift and Rodwell 2006).

Six scenarios were investigated. They all assumed that a well had been drilled accidentally into the repository, or through overlying strata, in which a free gas phase was present. Two cases were envisaged, 1) slow gas release up an abandoned borehole, 2) a 'blowout' in which gas under pressure was encountered during drilling of the well. A third case was mentioned in which water containing dissolved gases was extracted from a well and subsequently utilised. This case was not considered because it was argued that the radiological impacts of the gases would be no worse than in the gas pathway assessment in GPA03.

Five of the six scenarios assumed that the repository was hosted in fractured crystalline rock overlain by a sedimentary sequence, the sixth assumed the repository hosted in a mudrock again overlain by a sedimentary sequence. The six scenarios were:

1. crystalline host rock: well drilled into an unlined repository during resaturation;
2. crystalline host rock: well drilled into an unlined repository after resaturation;
3. crystalline host rock: well drilled into a repository with an intact low-permeability liner;
4. crystalline host rock: well drilled into gas trapped under a 'cap rock' in the overlying sedimentary sequence;
5. crystalline host rock: well drilled into a plume of dissolved gas; and
6. mudrock host rock: well drilled into the repository.

Steady state gas release was associated with scenarios 1, 2, 5 and was assumed to be directly to a domestic dwelling. Blowouts, scenarios 3, 4, 6, were assumed to take place in the open air.

In the steady state case hydrogen was found not to be a flammability hazard. Annual risk from tritium was calculated to be about 7.5 10^{-6}, but this assumed conservatively that ^{3}HH gas was converted to ^{3}HHO on passing up the well. The annual risk associated with $^{14}CH_4$ was estimated to be 1.3 x 10^{-6}. The dose from ^{222}Rn, assuming no decay within the well, was such as to be fatal over much of the repository lifetime. A transit time of 127.4 days would be required to reduce the annual risk to 1 x 10^{-6} from this gas.

Were a blow-out to occur in the open air, it is expected that the flammability threshold for hydrogen close to the well head would be exceeded. However, the radiological impact is likely to be substantially less than in the case of steady state release to an enclosed dwelling. In some instances the radiological impact of $^{14}CH_4$ through inhalation and ingestion pathways may need to be considered.

Key sources referred to above are:

1. Hoch A.R., Thorne M.C., Swift B.T., Bate F. 2007. Update of the GPA(03) assessment of the consequences of gas. Serco Assurance Report SA/ENV-0948.
2. Nirex. 2005. The 2004 UK Radioactive Waste Inventory. Main Report. Nirex Report N/090.

3. Swift B.T., Rodwell W.R. 2006. Specification for SMOGG Version 5.0: a simplified model of gas generation from radioactive wastes. Serco Assurance Report SA/ENV-0452.

<u>Hoch, A.R. and Rodwell, W.R. 2003b. Some consequences of gas generation in a Nirex repository: estimates for the generic documents update. Serco Assurance Report, SA/ENV-0542, Version 2.</u>

This is one of the underlying reports for GPA03 (N/080) which is summarised there, although it is not referenced there. The report considers the potential for overpressure, which is not an issue for a fractured host rock but would be an important issue for an argillaceous host rock, and the impacts of surface releases. It describes the TOUGH2 migration calculations and explains that the main reason for the increase in geosphere travel time compared with Nirex 97 and GPA01 is the significantly decreased bulk gas volumes resulting from the update to the 2001 inventory. Surface impacts are acceptable for the base case but not for the “no carbonation” variant considered.

<u>Nash, P.J. and Rodwell, W.R. 1990. Effects of gas overpressurisation on the geological environment of a deep repository. Nirex Report NSS/R208.</u>

This relatively early (1990) review concluded that an over pressure of 1.4 times hydrostatic pressure is required before a hard crystalline rock that might be considered as a repository host rock would fracture. An overpressure of 1.1 times hydrostatic may be sufficient to re-open existing fractures.

<u>Nirex, 2006f. Treatment of gas in Nirex post-closure assessment – a note for the record on forward strategy. Technical Note Number 498211v2.</u>

This short note sets out the Nirex strategy for moving from GPA03 to the Environmental Safety Case planned for 2009. It identifies the major change as being the use of SMOGG instead of GAMMON for gas generation calculations. The note identifies a need to reduce the estimated gas generation rates but does n’t really discuss the degree of pessimism and/or uncertainty in the GPA and subsequent estimates. The strategy concentrates on addressing gas generation issues and recognises the site-specific nature of gas migration, which will make it difficult to progress this area in the absence of a site.

Nirex, 2003b. Generic Operational Safety Assessment, Part 6 – Off-site dose assessment. Nirex Report No. N/079, UK Nirex, Harwell.

This report summarises the consequences of airborne releases during the operational period for the base case and an early backfilling variant. The gas generation calculations (GAMMON) are summarised in a separate report (SA/ENV-0514). The doses are dominated by ^{3}H release and exceed the target in the variant case. It is assumed that all of the carbon dioxide reacts with the backfill.

Nirex, 2003a. Generic Post-closure Performance Assessment. Nirex Report N/080, UK Nirex, Harwell.

A section of this report deals with gas issues and summarises the results of calculations undertaken to assess risks due to the gas pathway, which are reported separately (SA/ENV-0514 etc but not all referenced in this report). The gas generation calculations used GAMMON supplemented by some analytical calculations for processes not included in GAMMON. The gas migration calculations used TOUGH2 and predicted a breakthrough time of 6000 years (an order of magnitude greater than Nirex 97 or GPA01). The assessment of the risk due to ^{3}H took the geosphere travel time into account whereas the assessment of ^{14}C methane assumed direct release to the biosphere. The calculated risks were below target for the base case but the variant calculations demonstrated that acceptable performance depended on the assumption that carbonation reactions remove carbon dioxide before it can be metabolised into methane.

There is a brief consideration of the implications of an argillaceous host rock. The human intrusion calculations do not consider the case of a borehole striking a pressurised repository.

Nirex, 1997a. Nirex 97: An assessment of the post-closure performance of a deep waste repository at Sellafield, Volume 4: The gas pathway. Nirex Report S/97/012. UK Nirex, Harwell.

This report provides the first comprehensive assessment of the post-closure risks associated with the gas pathway (Nirex 95 did not consider gas). The report sets out the processes considered and provides some justification for including or excluding processes and pathways, discusses the models used (GAMMON for gas generation, *tech*SIM for gas migration and RIMERS for biosphere factors) and the results. Both radiological risks and the potential flammability hazard are assessed quantitatively.

All of the calculated risks are below target. The report also discusses uncertainties and the potential for bias in the results presented.

Appendix 2 Evaluation of Nirex Research Against Quintessa's CO_2 FEP Database

It is beyond the scope of this review to carry out a rigorous analysis of Features, Events and Processes (FEPs) that are relevant to the generation and migration of gases in a deep geological repository for radioactive wastes. Instead this appendix presents, an initial comparison between FEPs in a generic database developed by Quintessa (Savage et al. 2004) and the issues concerning gas that have been addressed by Nirex. This comparison aims to identify whether or not there are any obvious omissions from Nirex's work. The database was inspired by the OECD/Nuclear Energy Agency FEP database for radioactive waste (NEA/OECD, 2000), and was developed for safety assessments of the geological storage of carbon dioxide. The database may be accessed freely via the web page of the International Energy Agency's (IEA) Greenhouse Gas Programme, at the following URL:

http://www.co2captureandstorage.info/riskscenarios/riskscenarios.htm)

It should be noted that because the database was designed for application in carbon dioxide storage projects, it does not include *all* the FEPs that are needed to describe gas *generation* in a geological repository for radioactive wastes. However, the database does contain many FEPs that are relevant to gas generation and all the key FEPs that are relevant to gas migration through the geosphere. Thus, a finding that Nirex has not considered a FEP in the database would highlight an omission in Nirex's research. However, conversely a demonstration that Nirex has evaluated all the relevant FEPs in the database should not be taken to indicate that there are definitely no omissions.

It is also pointed out that this comparison considers not only FEPs that have been investigated explicitly by Nirex, but also those that have been evaluated implicitly. Here a FEP is considered to have been evaluated explicitly by Nirex, if the reviewed documentation clearly describes the FEP. A FEP that has been treated implicitly is one that has not been described, but the existence and influences of which are implied by the occurrence of a FEP for which there is a description. For example, FEP "2.2.4 Reversibility" is mentioned explicitly in the reviewed documents, as part of the specification of the PGRC. However, FEP "2.2.5 Remedial actions" is not described, although it is implicit in the phased character of the PGRC that the possibility of remedial actions being taken has been considered. Judgments as to whether or not a FEP has been considered explicitly or implicitly are often subjective.

An indication is given where a FEP in the generic database is clearly irrelevant to the UK context, or to geological disposal of radioactive wastes, even in cases where there is no documentary evidence that Nirex has considered the FEP (either explicitly or implicitly). Similarly, FEPs that fall outside the scope of the present review are noted.

It is stressed that the initial comparison given here does not take into account the extent to which a particular FEP is important. Additionally, no consideration is given to the ways in which Nirex has treated the FEP. Instead, the aim is simply to assess whether or not Nirex has considered each FEP to some extent.

Finally, in some cases, the title of the FEP includes carbon dioxide. Where relevant, such mentions of carbon dioxide have been treated as references to gas in general. This treatment is indicated in the table below by an entry of "gas" in parentheses following the reference to "CO_2".

FEPs in Quintessa's Generic Database		**Whether/How Considered**
1 External Factors		
	1.1 Geological factors	Considered explicitly
	1.1.1 Neotectonics	Not considered
	1.1.2 Volcanic and magmatic activity	Not relevant to UK
	1.1.3 Seismicity	Not considered
	1.1.4 Hydrothermal activity	Not considered
	1.1.5 Hydrological and hydrogeological response to geological changes	Considered implicitly
	1.1.6 Large scale erosion	Not considered
	1.1.7 Bolide impact	Would be screened out as a low-probability event
	1.2 Climatic factors	Not considered
	1.2.1 Global climate change	Not considered
	1.2.2 Regional and local climate change	Not considered
	1.2.3 Sea level change	Not considered
	1.2.4 Periglacial effects	Not considered
	1.2.5 Glacial and ice sheet effects	Not considered
	1.2.6 Warm climate effects	Not considered
	1.2.7 Hydrological and hydrogeological response to climate change	Not considered
	1.2.8 Responses to climate change	Not considered
	1.3 Future human actions	Not considered
	1.3.1 Human influences on climate	Not considered
	1.3.2 Motivation and knowledge issues	Not considered
	1.3.3 Social and institutional developments	Not considered
	1.3.4 Technological developments	Not considered
	1.3.5 Drilling activities	Considered (human intrusion scenario)
	1.3.6 Mining and other underground activities	Not considered
	1.3.7 Human activities in the surface environment	Not considered
	1.3.8 Water management	Considered (human intrusion scenario)
	1.3.9 CO_2 (gas) presence influencing future operations	Considered (human intrusion scenario)
	1.3.10 Explosions and crashes	Not considered

FEPs in Quintessa's Generic Database		Whether/How Considered
2 CO_2 (gas) Storage		
	2.1 Pre-closure	Considered explicitly
	2.1.1 Storage concept	Considered explicitly
	2.1.2 CO_2 (gas) quantities, injection rate	Not relevant to geological disposal of radioactive waste
	2.1.3 CO_2 (gas) composition	Considered explicitly
	2.1.4 Microbiological contamination	Considered explicitly
	2.1.5 Schedule and planning	Considered explicitly
	2.1.6 Pre-closure administrative control	Considered explicitly
	2.1.7 Pre-closure monitoring of storage	Considered explicitly
	2.1.8 Quality control	Considered explicitly
	2.1.9 Accidents and unplanned events	Considered explicitly
	2.1.10 Overpressuring	Considered explicitly
	2.2 Post-closure	Considered implicitly
	2.2.1 Post-closure administrative control	Considered implicitly
	2.2.2 Post-closure monitoring of storage	Considered implicitly
	2.2.3 Records and markers	Considered implicitly
	2.2.4 Reversibility	Considered explicitly
	2.2.5 Remedial actions	Considered implicitly
3 CO_2 Properties, Interactions & Transport		
	3.1 CO_2 (gas) properties	Considered explicitly
	3.1.1 Physical properties of CO_2 (gas)	Considered explicitly
	3.1.2 CO_2 (gas) phase behaviour	Considered explicitly (but specific case of possible existence of supercritical CO_2 has not been considered)
	3.1.3 CO_2 (gas) solubility and aqueous speciation	Considered explicitly
	3.2 CO_2 (gas) interactions	Considered explicitly
	3.2.1 Effects of pressurisation of reservoir on cap rock	Considered explicitly
	3.2.2 Effects of pressurisation on reservoir fluids	Considered explicitly
	3.2.3 Interaction with hydrocarbons	Considered explicitly
	3.2.4 Displacement of saline formation fluids	Considered explicitly
	3.2.5 Mechanical processes and conditions	Considered explicitly
	3.2.6 Induced seismicity	Not considered
	3.2.7 Subsidence or uplift	Not considered
	3.2.8 Thermal effects on the injection point	Not relevant to geological disposal of radioactive waste
	3.2.9 Water chemistry	Considered explicitly
	3.2.10 Interaction of CO_2 (gas) with chemical barriers	Considered explicitly
	3.2.11 Sorption and desorption of CO_2 (gas)	Considered explicitly
	3.2.12 Heavy metal release	Not considered
	3.2.13 Mineral phase	Considered explicitly
	3.2.13.1 Mineral dissolution and precipitation	Considered explicitly

FEPs in Quintessa's Generic Database		Whether/How Considered
	3.2.13.2 Ion exchange	Not considered
	3.2.13.3 Desiccation of clay	Not considered
	3.2.14 Gas chemistry	Considered explicitly
	3.2.15 Gas stripping	Considered explicitly
	3.2.16 Gas hydrates	Considered explicitly
	3.2.17 Biogeochemistry	Considered explicitly
	3.2.18 Microbial processes	Considered explicitly
	3.2.19 Biomass uptake of CO_2 (gas)	Considered explicitly
	3.3 CO_2 (gas) transport	Considered explicitly
	3.3.1 Advection of free CO_2 (gas)	Considered explicitly
	3.3.1.1 Fault valving	Considered implicitly
	3.3.2 Buoyancy-driven flow	Considered explicitly
	3.3.3 Displacement of formation fluids	Considered explicitly
	3.3.4 Dissolution in formation fluids	Considered explicitly
	3.3.5 Water mediated transport	Considered explicitly
	3.3.6 CO_2 (gas) release processes	Considered explicitly
	3.3.6.1 Limnic eruption	Not considered
	3.3.7 Co-migration of other gases	Considered explicitly
4 Geosphere		Considered explicitly
	4.1 Geology	Considered explicitly
	4.1.1 Geographical location	Not considered
	4.1.2 Natural resources	Considered explicitly
	4.1.3 Reservoir type	Not relevant to geological disposal of radioactive waste
	4.1.4 Reservoir geometry	Not relevant to geological disposal of radioactive waste
	4.1.5 Reservoir exploitation	Not relevant to geological disposal of radioactive waste
	4.1.6 Cap rock or sealing formation	Considered explicitly
	4.1.7 Additional seals	Considered implicitly
	4.1.8 Lithology	Considered explicitly
	4.1.8.1 Lithification/diagenesis	Considered explicitly
	4.1.8.2 Pore architecture	Considered explicitly
	4.1.9 Unconformities	Considered implicitly
	4.1.10 Heterogeneities	Considered explicitly
	4.1.11 Fractures and faults	Considered explicitly
	4.1.12 Undetected features	Considered implicitly
	4.1.13 Vertical geothermal gradient	Considered explicitly
	4.1.14 Formation pressure	Considered explicitly
	4.1.15 Stress and mechanical properties	Considered explicitly
	4.1.16 Petrophysical properties	Considered explicitly
	4.2 Fluids	Considered explicitly
	4.2.1 Fluid properties	Considered explicitly
	4.2.2 Hydrogeology	Considered explicitly
	4.2.3 Hydrocarbons	Not relevant to geological disposal of radioactive waste
5 Boreholes		
	5.1 Drilling and completion	Considered implicitly
	5.1.1 Formation damage	Considered implicitly
	5.1.2 Well lining and completion	Considered implicitly
	5.1.3 Workover	Considered implicitly

FEPs in Quintessa's Generic Database		Whether/How Considered
	5.1.4 Monitoring wells	Considered implicitly
	5.1.5 Well records	Considered implicitly
	5.2 Borehole seals and abandonment	Considered implicitly
	5.2.1 Closure and sealing of boreholes	Considered implicitly
	5.2.2 Seal failure	Considered implicitly
	5.2.3 Blowouts	Considered implicitly
	5.2.4 Orphan wells	Considered implicitly
	5.2.5 Soil creep around boreholes	Not considered
6 Near-Surface Environment		
	6.1 Terrestrial environment	Outside the scope of the present review
	6.1.1 Topography and morphology	Outside the scope of the present review
	6.1.2 Soils and sediments	Considered explicitly
	6.1.3 Erosion and deposition	Outside the scope of the present review
	6.1.4 Atmosphere and meteorology	Outside the scope of the present review
	6.1.5 Hydrological regime and water balance	Considered implicitly
	6.1.6 Near-surface aquifers and surface water bodies	Not considered
	6.1.7 Terrestrial flora and fauna	Outside the scope of the present review
	6.1.8 Terrestrial ecological systems	Outside the scope of the present review
	6.2 Marine environment	Not considered
	6.2.1 Coastal features	Outside the scope of the present review
	6.2.2 Local oceanography	Outside the scope of the present review
	6.2.3 Marine sediments	Outside the scope of the present review
	6.2.4 Marine flora and fauna	Outside the scope of the present review
	6.2.5 Marine ecological systems	Outside the scope of the present review
	6.3 Human behaviour	Outside the scope of the present review
	6.3.1 Human characteristics	Outside the scope of the present review
	6.3.2 Diet and food processing	Outside the scope of the present review
	6.3.3 Lifestyles	Outside the scope of the present review
	6.3.4 Land and water use	Outside the scope of the present review
	6.3.5 Community characteristics	Outside the scope of the present review
	6.3.6 Buildings	Outside the scope of the present review
7 Impacts		Considered explicitly
	7.1 System performance	Considered explicitly
	7.1.1 Loss of containment	Considered explicitly

FEPs in Quintessa's Generic Database		Whether/How Considered
	7.2 Impacts on the physical environment	Considered implicitly
	7.2.1 Contamination of groundwater	Considered explicitly
	7.2.2 Impacts on soils and sediments	Outside the scope of the present review
	7.2.3 Release to the atmosphere	Considered explicitly
	7.2.4 Impacts on exploitation of natural resources	Outside the scope of the present review
	7.2.5 Modified hydrology and hydrogeology	Considered explicitly
	7.2.6 Modified geochemistry	Considered explicitly
	7.2.7 Modified seismicity	Not considered
	7.2.8 Modified surface topography	Not relevant to geological disposal of radioactive waste
	7.2.8.1 Sinkhole formation	Not considered
	7.3 Impacts on flora and fauna	Outside the scope of the present review
	7.3.1 Asphyxiation effects	Outside the scope of the present review
	7.3.2 Effect of CO_2 on plants and algae	Outside the scope of the present review
	7.3.3 Ecotoxicology of contaminants	Outside the scope of the present review
	7.3.4 Ecological effects	Outside the scope of the present review
	7.3.5 Modification of microbiological systems	Outside the scope of the present review
	7.4 Impacts on humans	Outside the scope of the present review
	7.4.1 Health effects of CO_2	Outside the scope of the present review
	7.4.2 Toxicity of contaminants	Outside the scope of the present review
	7.4.3 Impacts from physical disruption	Outside the scope of the present review
	7.4.4 Impacts from ecological modification	Outside the scope of the present review

Appendix 3 Questions Presented to Nirex and Responses Made by Nirex

This appendix records questions put to Nirex by Quintessa, and dictated by the project timescales, the responses to these questions made verbally by Nirex during a meeting between Quintessa staff (R. Metcalfe) and Nirex staff (P. Lock and S. Norris) held on 1st March 2007. This record was prepared by Quintessa (R. Metcalfe).

Q1: What level of external (including international) peer review of Nirex work in the gas generation and migration area has been carried out?

Ans 1: Research reports are all reviewed internally by Nirex as a minimum, external review is also frequently undertaken. "High-level" documents (such as the Nirex 97 reports) are also reviewed externally.

Q2: In the Context Note and Viability Report it is assumed that ^{14}C-labelled carbon dioxide reacts with the cementitous backfill and so is not available for release. Can you point us to any reports that support this assumption; the justification in Nirex 97 seems to be based on general engineering texts with nothing to demonstrate that the process would be efficient at removing all of the carbon dioxide on the required timescales?

Ans 2: Some research into this issue has been reported by Nirex. Additionally, the reactivity of the cementitious backfill with respect to carbon dioxide is recognised by Nirex to be an important issue for future work. Three documents were received (Harris et al. 2001; Harris et al. 2003a; Harris et al. 2003b; see Section 13 above). Cracking of the cementitious backfill as a result of these reactions is seen as a particularly important research target. Research into interactions between carbon dioxide and cement that has been carried out by the oil industry (for example in connection with the effect of carbon dioxide used in enhanced oil recovery on borehole seals) has not been assessed. Similarly, there has been no assessment of the results obtained from research carried out internationally into underground carbon dioxide storage.

Q3: A related question follows from SA/ENV-0745, which states that "In many Nirex assessment calculations, the development of microbe 6 (hydrogen-utilising methanogenesis) has been suppressed because of the assumption that any carbon dioxide produced will react with cementitious materials present before it can be consumed by microbial processes (to as to produce methane by combination with hydrogen). This is a reasonable a priori assumption given the known reactivity of carbon dioxide with cementitious materials, but it does need to be confirmed." Has any work been done, or is any work being done, to confirm or refute the validity of this assumption?

Ans 3: The response to Q2 also covers much of the present state of knowledge and research relevant to Q3. In the GPA03 (Nirex, 2003a) the significance of carbonation of the backfill was evaluated by turning this process off in some variant simulations. The results indicated that carbonation has only a secondary influence on risk. Furthermore, past safety assessments have considered ^{14}C to occur in a significant amount only in one waste stream from Amersham. This waste stream was calculated to contribute only a small proportion of the carbon dioxide that is evolved.

Q4: What investigations of gas generation by degradation of non-cellulosic materials have been carried out?

Ans 4: Degradation of non-cellulosic material is not considered to be a great significance. However, work by Nirex in the past has considered this issue and concluded that it would not be important. Three reports were supplied that describe research concerning this topic (Nirex, 1987; Nirex, 1995; Nirex, 1997; see below for full bibliographical details). Among these references, Nirex (1997) focussed dominantly on LLW. It is argued that if non-cellulosic materials are found to be unimportant for this kind of waste then these materials would be even more insignificant for ILW.

Q5: The "Viability Report" states that the applicability of the PGRC to four different rock types (igneous/metamorphic, strong sedimentary, weak sedimentary, and evaporites) has been considered. However, the report also implies that the gas pathway has only been considered in the case of hard/fractured host rocks. Is this in fact the case? Has consideration been given to the gas pathway in other environments?

Ans 5: Nirex recognises the need to extend its safety assessment work to consider alternative geological environments, besides those evaluated primarily to date. There are plans to do undertake this work in the near future. Previous assessments have made considerable use of the dataset obtained from Sellafield. In addition GPA03 (Nirex, 2003a, Section 13 above) also considered mudrocks. However, other geological environments also need to be considered. Evaporite host rocks may be considered in future overseas work will be utilised as appropriate.

Q6: Has there been any comparison between work done by BNFL (e.g. on the LLWR near Drigg) and work done by Nirex, to ensure no duplication of effort and/or consistency of results?

Ans 6: There has been no systematic comparison between the work undertaken by Nirex and the work carried out at the LLWR near Drigg. However, recently assessments at the LLWR near Drigg have been using the gas generation modelling code MAG GAS. There has been a comparison between this code and SMOGG that has been reported in two draft reports prepared jointly by Nirex and Serco.

Q7: Has Nirex considered any Natural Analogue studies for gas migration studies (there have been natural analogue studies as part of research aimed at CO_2 sequestration)?

Ans 7: Analogue studies are being undertaken and there is a report on the work carried out until 2006 (Nirex, 2006 in reference list below). However, the work is on-going. The BP Institute for Multiphase Flow, which is affiliated to the University of Cambridge, is being funded to contribute to this work looking at gas migration with prime experience in hydro-carbon studies.

Q8: How is gas generation treated in evaluations of human intrusion?

Ans 8: The GPA03 (Nirex 2003a) simulations are being revised to incorporate the latest understanding regarding gas evolution and migration. This work is considering both the Sellafield geological data and a generic geological environment. However, the biosphere being evaluated has been revised. Assessment of human intrusion will be included. One aspect is to consider the impact on risk of human intrusion into a gas plume. This kind of assessment has not been undertaken before. There are presently no reports available.

Q9: How is research on gas evolution and migration captured within the scenario and conceptual model development processes?

Ans 9: Nirex recognises a need to capture gas issues within scenario and model development more thoroughly and systematically than has been done hitherto. The previous assessments included analyses of Features Events and Processes (FEPs) and also development of Master Directed Diagrams (MDDs). However, neither the FEP analyses nor the MDDs were oriented towards gas issues (though it has been confirmed that most of these issues were captured by comparing the Nirex and NEA FEP databases).

Q10: Has any consideration been given to pre-treating ILW waste so that it could be placed in containers similar to those envisaged for HLW/SF? In particular, has any consideration been given to reducing the amounts of potentially gas-generating materials from the ILW?

Ans 10: Waste producers propose packaging designs to Nirex. In evaluating a proposal, Nirex considers whether or not the packaging might need to be improved. Depending upon the outcome of its evaluation, Nirex might request the producer to change the design. Packaging will only tend to commence once Nirex and the waste producer have agreed upon a design. Thus, the packaging employed for presently packaged waste has been designed with the initial agreement of Nirex. It is not possible to change this packaging without significant consequences. Therefore any new thinking concerning gas generation will need to be reflected by the repository design rather than by the packaging of existing packaged wastes. For wastes to be packaged in future there is some prospect that alternative encapsulants might be recommended (e.g. polymer encapsulants). However, there are presently no research projects specifically examining how the waste might be treated to reduce gas evolution.

Q11: It is also stated in the "Viability Report" that the release of ^{14}C in the gaseous phase without retardation has not been researched as extensively as the groundwater pathway. Is such research being undertaken?

Ans 11: There is a Technical Note by Nirex concerning ^{14}C (Technical Note 498808), which gives an overview of all the research that is being undertaken on this topic. There are on-going research projects investigating ^{14}C release from graphite and from carbides in metals.

Q12: The GPA assumed that resaturation of the repository would occur within 5 years. Has the coupling between gas generation and resaturation rates been investigated?

Ans 12 Coupling has been evaluated using the Sellafield dataset. This work is described in the report on gas migration. Nirex plan that the waste vaults will be well ventilated and that consequently conditions in the vaults will not be humid. Therefore, it is thought that there would be little metal corrosion before resaturation of the repository following closure. Additionally, corrosion of Magnox may use up most of the water in the pores of the cementitious grouts. Radiolysis would not consume all the water present in the grouts. Once this porewater had been depleted, there would be no significant further corrosion until after back filling or resaturation of the vaults. These conclusions are based on work carried out under Nirex's "waste package aging" programme. The research is not covered by the reports in the initial list supplied to Nirex for consideration in this review. Nirex Technical Note 468230 v 2 should be consulted for more details.

Q13: What work is being undertaken to evaluate the solubility of gases, especially in saline water?

Ans 13: No basic research into this topic is being undertaken. The effect of salinity on gas solubility is taken into account, but literature solubility values are used.

Q14: Page 72 of the "Viability Report" lists Nirex research programme studies and gives a bibliographical reference for each one EXCEPT for the gas generation section. What are the key documents?

Ans 14: Nirex supplied the key documents.

Q15: It is noted that "In parallel, further research is required to determine the rates and quantities of gaseous carbon-14 generation.". What research is being done/has been done?

Ans 15: This issue will be addressed in future. Some waste producers do monitor the gas that is evolved from the wastes. Nirex Technical Note 498808 covers this topic.

Q16: The "Viability Report" mentions that "Experiments show that 0.001% to 1% of the carbon-14 in graphite could be released as methane and that this is likely to be a short-term release; however, a lower but longer-term release rate has not been ruled out and has been assumed in these calculations." Where are these experiments reported?

Ans 16: These experiments are reported in the NCC report 11996/TR/007. Nirex recognises that graphite itself is heterogeneous and is therefore presently examining three different kinds.

Q17: In SA/ENV-0514 it is stated that "During the emplacement period, it is assumed that the total mass of uranium metal waste is added at a constant rate over the emplacement period". What is the justification for this assumption? Have other rates of emplacement been considered?

Ans 17: Nirex actually uses an average annual rate of uranium emplacement, which is obtained by dividing the total uranium inventory by assumed duration of emplacement in years. However, the rate of addition of uranium is seen as a secondary issue since it will not begin to evolve gas by corrosion until conditions become reducing following repository closure. It is actually considered to be a higher priority to obtain a more accurate inventory. Up to now it has been assumed that all the uranium present is in the form of metal. However, this assumption is clearly conservative.

Q18: In SA/ENV-0514 it is stated that "For Magnox and aluminium, it was the Nirex view that unpublished data on gas release from grouted wastes in storage showed lower rates than indicated by experiments with the metals in contact with aqueous solutions.". Are these unpublished data to be published in future? What kinds of data are they?

Ans 18: Nirex holds data for Magnox and aluminium corrosion in free solutions. These data are considered to be highly conservative. However, they were not produced by Nirex, but were obtained commercially and cannot be quoted by Nirex. Presently, two reports are being prepared by Nirex: (a) a report on the corrosion of Magnox and uranium; and (2) a report on the corrosion of steel, Zircalloy and Aluminium. The data in these reports have been obtained from various sources.

Q19: In SA/ENV-0514 it is stated that "Storage refers to emplacement and care and maintenance times prior to backfilling when the canisters are in an aerobic environment at 35ºC. During this storage period it is believed that for uranium, as for Magnox and aluminium, corrosion is limited by local restrictions in water availability. It is also implicit in the assumption of a rate of 100 µm a^{-1} under anaerobic conditions that the waste conditioning will inhibit corrosion.." What is the basis for this "belief"?

Ans 19: The basis for these statements is the results presented in the reports mentioned in the answer to Q18.

Q20: How were codes for gas migration calculations chosen? What were the criteria applied? Older calculations of gas migration used the program *tech*SIM. The calculations presented in 2006 (Serco report SA/ENV-850) were undertaken using the program TOUGH2. Why was TOUGH2 chosen?

Ans 20: The modelling presented in Nirex 97 (Nirex, 1997a) was undertaken by Serco. At that time, this organisation had a license for *tech*SIM. However, by the time that the GPA was undertaken, this license had lapsed. As a result, TOUGH2 was used. However, a comparison between the two codes was undertaken to establish that they would give comparable results and the question was asked is the code adequate.

Q21: Hoch et al. (2004) state that: "However, the graphite is expected to be inert, and has been assumed in this study not to provide a source of gas or, therefore, to contribute to the generation of gaseous forms containing ^{14}C (although this assumption needs further investigation).". Has any work been done to test this assumption? What was the justification for this assumption?

Ans 21: Since the work reported in Hoch et al. (2004) was undertaken, additional experiments have been carried out that identified graphite as a potential source for ^{14}C-labelled gas. Additional experiments are being carried out to address this issue further.

Q22: SA/ENV-0781 states that a major problem with GAMMON was that reliable values for the multitude of parameters describing organic matter degradation and microbial activity could not be obtained. However, the similarity of results obtained by using GAMMON and the more recent, simplified code SMOGG, is used as a justification of the validity of SMOGG. Is there independent evidence for the validity of the parameter values used in the SMOGG model?

Ans 22: Neither GAMMON nor SMOGG has been validated. It is not considered possible to fully validate these codes since the wastes are very heterogeneous. It is also necessary to recognise that in the case of SMOGG the underlying organic model is not as well validated as the corrosion model. However, this difference is not seen as being a significant problem, since corrosion will be the dominant gas generation mechanism. The report SAE/ENV/0542 should be consulted for more information concerning the status of SMOGG.

Q23: SA/ENV-0781 and SA/ENV-0745 indicate that the SMOGG model produces more realistic gas evolution versus time curves than does GAMMON. In particular, the latter code predicts spikes in gas production due to microbially mediated degradation of organic material that are not observed in experiments. In contrast, SMOGG produces more realistic smoother curves. However, it is stated in SA/ENV-0745 that "The SMOGG model does not exhibit the spikes in gas production seen in GAMMON results, having been designed to mimic the more smoothly changing gas generation rates that seem typical of experimental data.". What is the evidence that the SMOGG model represents a more realistic understanding of gas generation mechanisms, rather than simply being made to fit the experimental results empirically?

Ans 23: The answer to Q22 applies.

Q24: SA/ENV-0745 states that "There does not appear to be the experimental data available to properly calibrate or validate the organic degradation model in either SMOGG or GAMMON." What actions are being taken to obtain such data?

Ans 24: The answer to Q22 applies.

Q25: SA/ENV-0745 also points out that a simple empirical scheme for allowing for the effects of temperature on microbial activity has been used, but that there has been no experimental justification for the effect of temperature assumed for the particular representative microbe populations involved. Is any action being taken to obtain better information?

Ans 25: The answer to Q22 applies.

Q26: Similarly, the same report notes that "In the Nirex GPA03 assessment, the generation of bulk gas was dominated by hydrogen formed as a result of either metal corrosion or radiolysis. For the parameters chosen, microbial degradation of organic materials was a less important process. It remains to be shown that the model parameters used are plausible." What action is being taken/has been take to demonstrate that the parameters used were plausible or to obtain new parameter values if necessary?

Ans 26: The answer to Q22 applies.

Q27: Has any action been taken to explore the consequences of the approximations in the GAMMON models for simulating the degradation of non-cellulosic organic sources of ^{14}C? Alternatively, are these models now considered redundant in view of the simplifications introduced into SMOGG.?

Ans 27: The answer to Q22 applies.

Q28: SERCO/ERRA-0452 states that "However, in the modelling a distinction is not made between different ^{14}C-substituted hydrocarbons and they are all treated as $^{14}CH_4$. This is because the nature and hydrolysis behaviour of the carbides produced as activation products in the metals present in the various waste streams is not well understood at present." Has any work been done to establish whether different results would be obtained if the different ^{14}C-substituted hydrocarbons don't all behave like $^{14}CH_4$?

Ans 28: Attention is presently being given to the possible generation of ^{14}C-labelled methane from carbides. Additional research is planned. This work should shed light on whether it has been justified, so far, to assume that the carbides would behave like ^{14}C within methane. The report MTA/P0011b/2005-7 also considers this issue.

Q29: The same report also states that nitrogen gas production is an issue that should be kept under review. Is this being done? If so, what actions are being taken?

Ans 29: It is possible that nitrate could prevent or diminish methanogenesis. However, generation of nitrogen is not known to be significant. These issues are currently views as being of secondary importance, but may be revisited in future.

Additional references supplied by Nirex

Biddle, P. and Moreton, A.D. 1995. A review of the results and understanding achieved by the Nirex research programme to September 1991 on gas generation in a repository for radioactive wastes. Nirex Report NSS/R210.

Biddle, P., McGahan, D., Rees, J.H. and Rushbrook, P.E. 1987. Gas generation in repositories. AEA Technology Report AERE R 12291.

Macdonald, C., Ambrose, D. Brewer, A.J., Campbell, D.J.V., James, L. and Sopp, C. 1997. Investigations into the potential rate, composition and cumulative amount of gas generated from the biodegradation of simulated low-level waste. Nirex Report NSS/R322.

Nirex, 2006. Analogue evidence for the migration of gases and non-aqueous phase liquids in the geosphere. Nirex Report N/131.