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An overview of gas research in support of the UK geological disposal programme

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ABSTRACT

Gases will be generated in waste packages during their transport to a geological disposal facility (GDF), this generation will continue during GDF operations and after GDF closure. The range of gases produced will include flammable, radioactive and chemotoxic species. These must be managed to ensure safety during transport and operations, and the post-closure consequences need to be understood. The two primary post-closure gas issues for a GDF are the need for the system pressure to remain below a value at which irreversible damage to the engineered barrier system and host geology could occur, and the need to ensure that any flux of gas (in particular gaseous radionuclides) to the biosphere does not result in unacceptable risk. This paper provides an overview of the research of the Nuclear Decommissioning Authority, Radioactive Waste Management Directorate into gas generation and its migration from a GDF.

KEYWORDS: gas generation, gas migration, geological disposal facility.

Introduction

GASES will be formed from processes occurring in many waste packages that are intended for emplacement in a geological disposal facility (GDF). Thus gases will be generated during transport, operations and after closure of a GDF. In addition, the evolution of some of the other components of the engineered barrier system (EBS) (e.g. any steel reinforcement used in underground construction) will also contribute to gas generation after closure of a GDF. The range of gases produced from these various sources will include flammable, radioactive and chemotoxic species.

In order to be transported, waste packages will have to comply with the International Atomic Energy Agency (IAEA) Regulations for transporting radioactive material (International Atomic Energy Agency, 2005), implemented in the UK via the *Carriage of Dangerous Goods Regulations* (UK Government, 2009). These include limits on the generation rates of both bulk gas and radioactive gases.

During the operational phase of a GDF, the main gas management issues that will need to be addressed are associated with flammable and radioactive gases, similar to those arising during interim surface storage. Ventilation would be used to keep the concentrations of flammable gases below their lower flammability limit in air. Small quantities of radioactive gases will be produced and the concentrations of these in air could also be controlled by ventilation. Subsequent discharge of air containing radioactive gases from a GDF to atmosphere would be controlled to meet regulatory limits.

After the closure of a GDF gases will continue to be generated. The two primary gas issues to be considered are: the need for the system pressure to remain below a value at which irreversible damage to the EBS and host geology could

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occur; and the need to ensure that any flux of gas (in particular gaseous radionuclides) to the biosphere does not result in unacceptable risk. The relative importance of these issues will depend on the geology and geological disposal concept and this can be judged from existing information (Rodwell *et al*., 1999). However, they can only be addressed in detail once a potential site has become available.

Therefore, it is necessary to understand the rates of generation of gases during all phases of a GDF, their effects on the EBS and any migration from the EBS after closure, in order to demonstrate safety. This paper provides an overview of the gas research of Nuclear Decommissioning Authority, Radioactive Waste Management Directorate (NDA RWMD). A fuller description of the NDA RWMD current understanding of gas generation, reaction and migration is given in the NDA *Gas Status Report* (Nuclear Decommissioning Authority, 2010). At this stage in our programme we make some cautious assumptions when considering the potential impact of gas generation and migration. For example, potential reaction and consumption of bulk gases (other than dissolution and the carbonation of cements) in the EBS and the host rock is not considered. It may be possible to take account of such processes as our understanding develops in the future and as possible specific sites are considered.

Gas generation

There is a general consensus that the key bulk gas generation processes applicable to a GDF are the corrosion of metals, microbial degradation of organic materials (mainly cellulose) and radiolysis (Rodwell *et al*., 1999). Calculations have shown that hydrogen will be the predominant gas by volume from the totality of the packaged wastes. Hydrogen is generated mainly from the anaerobic corrosion of steels and also from the corrosion of more reactive metals such as Magnox and aluminium. Lesser amounts of carbon dioxide (and methane under methanogenic conditions) will be formed from the microbial degradation of organic material. In addition, radioactive gases and some chemotoxic species may also be formed. The relative importance of the various generation processes, and hence the rates of gas formation and the gas composition, depend partly on the type of wasteform and also on the geological disposal concept (e.g. through the possible restriction of water in-flow after closure of a GDF by a build up of gas pressure). Any flammable gases (mainly hydrogen, but possibly also methane) that may be generated during the transport of some waste packages and in an operational GDF would be managed through ventilation and engineering control to meet regulatory requirements. After closure of a GDF, gases will continue to be generated.

Results of a typical calculation of gas generation from GDF vaults containing unshielded packages of intermediate-level waste (U-ILW) during operations and shortly after closure in a fractured higher strength host rock are shown in Fig. 1 (Hoch *et al*., 2008). Most of these waste packages consist of waste immobilized with a cementitious grout in vented stainless steel containers. The inventory data for this calculation were derived from the 2004 UK radioactive waste inventory (Nuclear Decommissioning Authority, 2011) and the best-estimate values were used for reaction rates. The calculation assumes that the U-ILW packages are placed within the facility from 2040 until 2090 and that the facility is closed at 2150 (for simplicity it is also assumed that all vaults are backfilled and closed instantaneously at this time). All the vaults are expected to resaturate rapidly in a fractured host rock and this is taken to be complete by 2155. In other host rocks (e.g. clays), resaturation may be much slower and coupled with gas generation. The bulk gas consists largely of hydrogen, generated mainly from the corrosion of metals, but there are smaller amounts of carbon dioxide and methane. The assumption of rapid resaturation means that corrosion processes are essentially not limited by water availability and gives rise to the peak in the rate of hydrogen production centred around 2170 due to the rapid corrosion of reactive metals as water enters the vented waste packages. These metals are calculated to have corroded completely by about 2180. The anaerobic corrosion of steels, along with the radiolysis of water and organic materials, then determines the rate of hydrogen generation (which continues and slowly decreases to 100,000, the end of the period considered in the calculation). No net production of gaseous carbon dioxide is calculated because of its reaction with the cementitious backfill and waste encapsulation grouts. The system is not calculated to become methanogenic over the period shown because of the presence of nitrate and sulphate. Methanogenesis is calculated to begin around

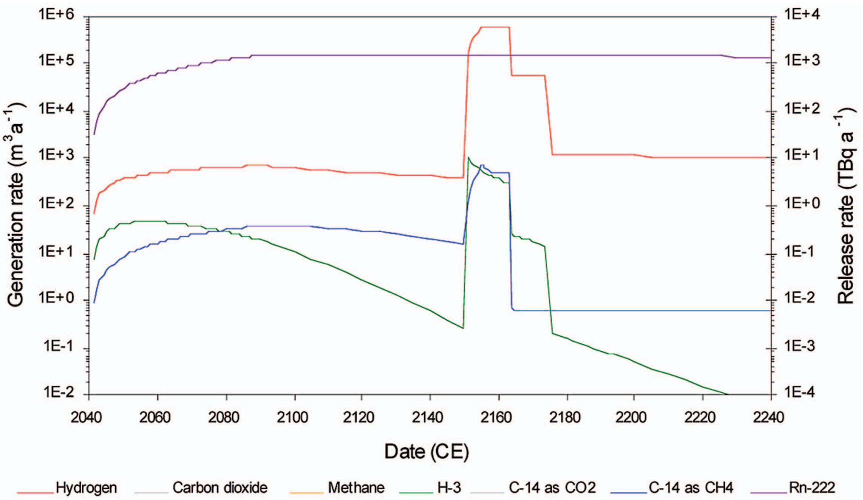

FIG. 1. Illustrative calculated results for net rates of gas generation from UILW in higher strength rocks for the 2004 Inventory with closure at 2150 CE (current era). Figure published with permission of the NDA.

4950, after all the nitrate and sulfate have been consumed.

A very small proportion of the total volume of gas will be radioactive including tritiated hydrogen, tritiated methane, ^{14}C labelled species (e.g. methane and carbon dioxide) and radon. There is uncertainty about the rates at which some of these radioactive gases would be formed, because their formation depends on the release of a radionuclide from the waste matrix, the incorporation of the radionuclide into a gas, and the geological disposal concept example (e.g. the availability of water for metal corrosion). Of the active gases, ^{14}C labelled species may be the most important if free gas migrates from a GDF after closure (see below) because of its relatively long half life (5730 years). In contrast, tritium has a short half life (12.3 years), and so will have decayed significantly within a few hundred years of packaging. Although radon will be formed continually as part of the radioactive decay chain of uranium in the waste packages, it has a very short half life (3.82 days) and is expected to decay within or close to the EBS after closure. However, the stripping of naturally occurring radon from some near-surface host rocks due to migrating bulk gas is considered.

Gas migration and reaction

The generation of bulk gases may affect the performance of the EBS of a GDF through various reactions (e.g. the carbonation of cements may decrease pH). The effects of pressurization, (e.g. the possible formation of cracks and fissures through components of the EBS) may also need to be considered.

The migration of gas from a GDF will be site-specific. Illustrative geological disposal concept examples are being considered at this generic stage in the NDA RWMD programme for three types of host rock: higher strength rocks, lower strength sedimentary rocks and evaporites.

In the case of fractured higher strength rocks, were a free gas phase to form, it would migrate away from a GDF. In order to determine where the gas would migrate to and if it might be released at the surface, the properties of the host rock (fracture size, density and connectivity) and overlying geological formations are important. In particular, geological features (e.g. cap rocks) may act as barriers to the migration of the gas, whereas fault zones may or may not act as conduits depending on their ability to maintain a free gas pathway. The volume of water that is available for gas to dissolve in is also important and would be determined by flow rate and porosity in the overlying rocks. A typical result for calculated migration of free gas, 240 years after closure, from a GDF in a higher strength rock, and the corresponding dissolved gas plume, is illustrated in Figs 2 and 3 (Hoch and Swift, 2010). The disposal vaults are depicted as the rectangle in the centre of each figure and different rock units are

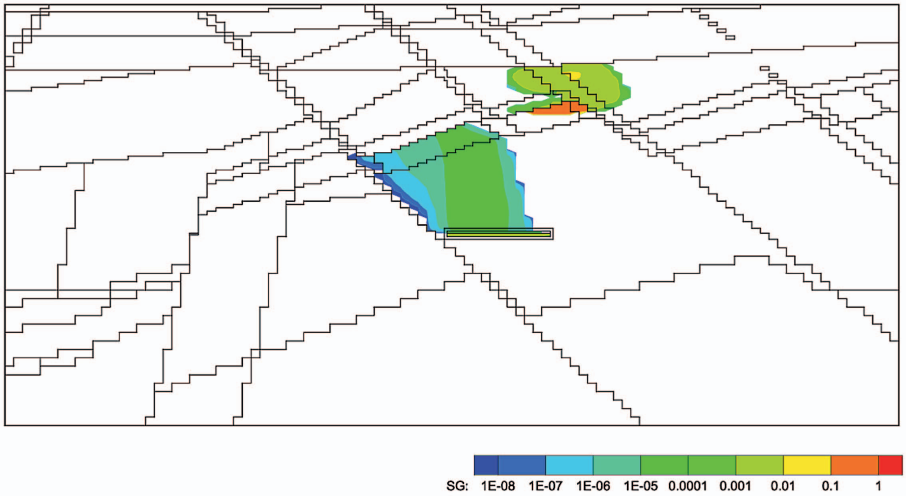

FIG. 2. Contour plot of gas saturation at 240 years after closure for gas migration from a GDF in a higher strength rock. Figure published with permission of the NDA.

defined by the black lines. Fluid flow occurs in fracture or matrix porosity, depending on the rock type. Increasing gas saturation, or mass fraction of dissolved gas, is depicted by changes in the colour spectrum from blue towards red, as shown by the key on each figure. The calculations take no credit for the possible participation of hydrogen (or other gases such as methane) in chemical or microbiological processes as it migrates through the host rock, which could lead to its consumption. Figure 2 shows free gas moving upwards through the host rock and overlying rocks until it reaches a low-permeability formation that acts as a 'cap rock'. The gas then flows towards the right in Fig. 2 until it reaches a place where a fault breaks the continuity of the low-permeability formation. It is then able to continue to move upwards into more permeable near-surface rocks. The free gas reaching these dissolves completely in flowing near-surface ground water and the free gas phase

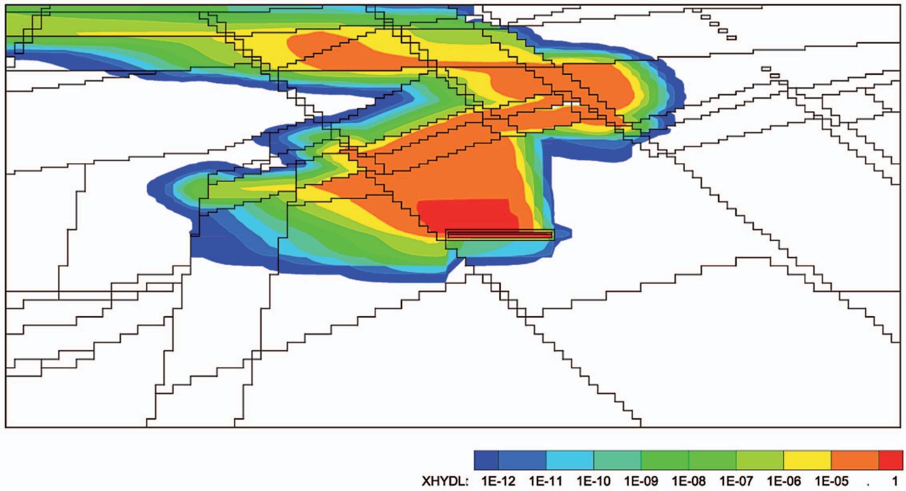

FIG. 3. Contour plot of mass fraction of dissolved gas at 240 years after closure for gas migration from a GDF in a higher strength rock. Figure published with permission of the NDA.

ceases to exist. This is illustrated in Fig. 3, which shows the corresponding plume of dissolved gas is more spatially extensive than the free gas after 240 years. The calculations and their parameterization are discussed in more detail in Hoch *et al.* (2008) and Hoch and Swift (2010). The build up of a significant gas overpressure is not expected in a fractured higher strength rock. Possible consequences of gas in this geological context include entrainment of contaminated water by gas and the release of flammable (i.e. hydrogen and methane) and radiotoxic (i.e. ^{14}C labelled methane) gases to the biosphere. Assessments have shown that the flammable gases are of little concern. In contrast, an important area of research is to investigate the rate at which ^{14}C labelled methane might be produced from the wastes, and the radiological consequences associated with this gas were it to migrate to the biosphere.

In the case of lower strength sedimentary rocks (e.g. clays) the rates of gas generation may be limited by the supply of water from the host rock to a GDF. It would be difficult for any free gas phase formed to migrate from a GDF by flow through undisturbed clay because of high gas entry pressure. Depending on the precise combination of gas generation, water inflow and gas migration in solution, the gas may be released through a combination of dilation and microfissuring in the clay. These pathways are then expected to close after the gas pressure has fallen, depending on the properties of the host rock (e.g. the amount of swelling clays in the host rock, the degree of induration and the stress state). The migration of any free gas phase will be much slower in this rock type than in a fractured higher strength rock. Possible consequences of gas in this geology could include overpressurization of a GDF, with potential damage to it and the surrounding clay; and the displacement of contaminated water from a GDF. However, such consequences could be prevented by suitable design of the EBS and associated seals.

In the case of evaporites, the GDF environment may be so dry that gas generation would be very limited due to water availability being restricted to that present in the packaged wastes (e.g. as grout porewater). The possible consequences of gas in an evaporite are similar to the case of clay rocks, although the rock may creep (i.e. move slowly under the influence of the lithostatic pressure) more than some clays and fill voidage.

Coupling of gas generation with other processes is likely in clays and evaporites and would need to be taken into account. The effects of the spatial and temporal evolution of systems (including the thermal impact of higher heat-generating wastes such as spent fuel) on gas generation and migration would also need to be considered as the research programme develops.

As these post-closure issues are site-specific (i.e. their importance depends on the geology and geological disposal concept example), they can only be addressed fully at a site-specific level. However, there is a lot of international experience with different concepts and sites that can be drawn upon to develop the NDA RWMD programme in the absence of a possible site or sites. This gives confidence that a GDF can be shown to be safe with respect to the management of gas as the UK programme develops. In some cases the use of appropriate engineering measures may be necessary to ensure that such requirements can be met.

Research needs for current phase

As noted above, the main mechanisms by which gas could be generated in a GDF are metal corrosion, radiolysis and microbial degradation. For intermediate-level waste (ILW), there is a good process understanding of gas generation from the corrosion of metals and this will need to be developed to include relevant container materials for high-level waste (HLW) and spent fuel under appropriate disposal conditions in the UK. Bulk gas generation from the degradation of organic materials will be studied in order to build confidence in its treatment in safety cases. Studies on the generation of radioactive gases from ILW under disposal conditions have been made and research (national and international) is continuing in this area, focussing particularly on ^{14}C release from graphite and irradiated steel. For spent fuel, radiolysis of water may be an important source of gas and it may be necessary to carry out work to obtain data specific to the UK wastes and disposal concepts.

Understanding the uncertainties in gas generation processes and rates will be important in order that these can be treated in an appropriate manner in safety assessment calculations. There may also be a need to further develop a capability to couple fully gas generation and water availability.

Work on cement-based buffers is continuing, including further work on the reaction of cements with carbon dioxide (carbonation). Work on clay-based buffers is considering possible pressurization followed by release of gas through microfissures in the clay structure. Any microfissures may close (seal) once the gas has been released and the overpressurization reduced; this also has relevance to gas migration through the geosphere in clay-based geologies.

In the current phase of RWMD preparatory studies, before any specific sites have been selected, the main direction of research on gas migration through the geosphere is to develop tools and techniques for modelling gas migration in different geologies. This will continue to draw upon relevant international experience and involve collaboration with overseas organizations. In the longer term, these would be applied to possible site, or sites, and GDF concepts.

The NDA RWMD gas research studies over the next few years can thus be divided into two broad work sub-topics: studies of gas generation and release from wasteforms and waste packages; and studies of gas migration and reaction within the EBS and in the host rock. The planned research and development programme to address currently identified knowledge gaps is shown in Fig. 4.

The research on gas generation can be broken down into five work areas:

(1) Irradiated graphite provides the largest inventory of ^{14}C associated with irradiated material in ILW. The possibility of ^{14}C in free gas reaching the biosphere depends, amongst other factors, on the rate of generation and the form in which it is released. Limited experimental data on the release of volatile ^{14}C from irradiated graphite under disposal conditions have been obtained to date (Baston *et al.*, 2004; Handy, 2005). In the near term the work programme will extend this work to investigate release of ^{14}C from irradiated graphite from a Magnox station under a range of experimental conditions to reflect possible conditions during packaging and disposal and to understand any impact on speciation of released gaseous ^{14}C.

(2) After graphite, steels provide the largest inventory of ^{14}C associated with irradiated material in ILW. There is little information on the form of ^{14}C released from irradiated steels and the rate of release. Carbon-14 may be present in the form of carbides and the reaction of some

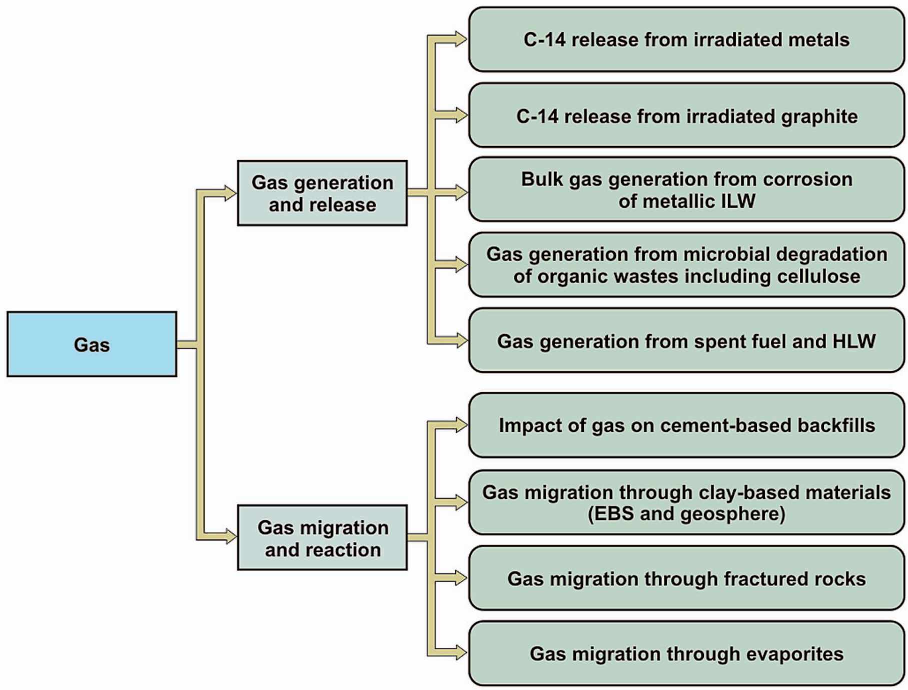

FIG. 4. Structure of the NDA RWMD gas research and development programme. Figure published with permission of the NDA.

carbides with water forms a range of volatile species. An experimental study to determine the rate and chemical form of ^{14}C release from irradiated stainless steel under alkaline conditions to allow improved treatment in post-closure safety assessments is underway and a similar study for irradiated mild steel is planned. It is also intended to examine the release of ^{14}C from more reactive irradiated metals, such as Magnox and uranium, which could contribute to the gaseous release of ^{14}C during operations and shortly after closure of a GDF.

(3) Bulk gas generation is of interest in all phases of a GDF with the relative importance of some of the issues dependent on the concept (e.g. potential pressurization of a GDF). Corrosion of metals in ILW packages (whether as waste or containers) is a significant contributor to gas generation. The mechanisms and rates of corrosion (and hence hydrogen generation) from steels, Zircaloy, Magnox, uranium and aluminium have been reviewed for high pH conditions and these data are used as input to gas-generation modelling. Periodic reviews of data and mechanisms will be made to ensure that these remain up-to-date and applicable to concepts and GDF designs under consideration.

(4) Gas generation from the microbial degradation of cellulose is an important contributor to the overall gas generation from ILW. However, there are uncertainties in the viability, activity and distribution of microbial activity at high pH and hence gas generation. It is possible that the current modelling treatment used by NDA RWMD may overestimate the rate of gas production from cellulosic wastes under high pH conditions. Therefore, it is proposed to undertake experiments and modelling on rates of gas generation from microbial degradation of cellulose and organic wastes under a range of conditions following the conclusions of a peer preview workshop. These will be underpinned by more fundamental studies of the viability and activity of microbial populations under simulated storage and post-closure conditions.

(5) The rates and mechanisms of gas generation for overseas spent fuel disposal programmes are well understood and a large body of data already exists. Some data also exist for gas evolution from radiolysis of water and container corrosion for HLW. However, applicability of these data to UK environments needs to be assessed and a review of the generation rates and composition of gases released from UK spent fuel and HLW waste packages under a range of conditions relevant to UK environments is underway. The outcome of the review will be used to identify the requirements for any further work to fill knowledge and data gaps.

The planned research on gas migration and reaction can be broken down into four work areas:

(1) One contribution of cement-based backfills (and grouts) to post-closure safety is to remove carbon dioxide from gas and solution and prevent conversion to methane. However, carbonation of backfill leads to different physical and chemical properties. The process of carbonation of cementitious materials continues to be studied [e.g. through participation in collaborative projects such as FORGE (Norris, 2010)]. This area of work will interact with work in the near-field evolution area to ensure that the consequences of carbonation on chemical and physical performance of the EBS are captured. Gas pressurization (e.g. by bulk hydrogen) could lead to disruption of backfill above package vents. Increase in porosity or absence of backfill above vents offers possible preferential pathways to radionuclide release. The impact of high gas flows on cement properties during curing is not yet understood fully. It is also possible that gas pressurization could lead to cracking although, in the case of the vault backfill, the backfill may crack after placement and curing due to a number of other processes.

(2) In a salt-based environment (e.g. evaporite host rock), water availability (which will determine gas generation rates) will be low. A review of the current understanding of gas generation, pressurization and migration relevant to a GDF located in an evaporite is underway. In the longer-term the need for research would depend on the site and concept under consideration and, once site(s) and preferred concepts are available, would be re-evaluated.

(3) Clays typically have very small intergranular pores and so gas will find it difficult to migrate. The possible consequences of gas in this environment include overpressurization with potential damage to the clay. Pressurization can lead to formation of transient preferential pathways through the EBS or a clay-based geosphere and could in theory move contaminated groundwater from the EBS. The mechanisms of microfissuring and self−sealing of clay require additional understanding. In the current phase of preparatory studies, a programme of experiments and modelling of gas migration in clays, including

the effect of overpressurization on clay barrier performance, will continue in order to maintain an enhanced capability in this area. Much of the work will involve participation in international collaborative projects such as the Lasgit experiment at the Äspö Hard Rock Laboratory in Sweden (Cuss *et al*., 2010).

(4) The NDA RWMD research programme has an established capability for modelling gas migration in fractured rock, recognizing that this issue is strongly site-specific (dependent on host geology). The impact of engineering design on migration from EBS and migration through the excavation disturbed zone (EDZ) needs to be understood. In the near term it is proposed to review and, as appropriate, continue to develop models to build capability to model gas transport in fractured rocks, including the ability to treat processes such as rock matrix diffusion and radon stripping from host rocks. In the longer term the direction of this work will depend on the concept under consideration and, once site(s) and preferred concepts are available, will be re-evaluated. For example, if a potential site was located in a fractured hard rock host geology, it would be necessary to undertake experiments and modelling of effects of gas on performance and on gas migration through the EBS and the EDZ.

Conclusions

There is a good understanding of gas generation processes relevant to cement-based ILW conditions, and this will need to be developed to include materials relevant to HLW and spent fuel under appropriate UK disposal conditions. Studies on the generation of radioactive gases from ILW under disposal conditions have been made and research will continue, particularly on ^{14}C release from graphite and irradiated metals. Understanding the uncertainties in gas generation processes and rates will be important in order that these can be included safety assessment calculations. The NDA RWMD research programme has an established capability for modelling gas migration in fractured rock and we have developed a capability to consider gas migration in other potential host rocks.

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