nagra

National Cooperative for
the Disposal of Radioactive Waste

TECHNICAL REPORT 92-07

Post-Disposal Implications
of Gas Generated from a
Repository for Low and
Intermediate Level Wastes

H. A. Grogan
K. J. Worgan
G. M. Smith
D. P. Hodkinson

INTERA, Environmental Division, Henley-on-Thames, UK

November 1992

nagra

National Cooperative for
the Disposal of Radioactive Waste

TECHNICAL

REPORT 92-07

**Post-Disposal Implications
of Gas Generated from a
Repository for Low and
Intermediate Level Wastes**

H. A. Grogan
K. J. Worgan
G. M. Smith
D. P. Hodkinson

November 1992

INTERA, Environmental Division, Henley-on-Thames, UK

This report was prepared as an account of work sponsored by Nagra. The viewpoints presented and conclusions reached are those of the author(s) and do not necessarily represent those of Nagra.

POST-DISPOSAL IMPLICATIONS OF GAS GENERATED FROM A REPOSITORY FOR LOW AND INTERMEDIATE LEVEL WASTES

SUMMARY

The generation of gases within a deep geological repository for radioactive wastes may have significant post-emplacement implications for repository safety. This report examines this issue in the context of short-lived low and intermediate level waste (L/ILW) disposal in Switzerland, according to the Nagra SMA repository development programme.

The various gases which may be generated are briefly reviewed along with their sources and estimated generation rates. Hydrogen and methane are recognised as the two main gases requiring closer evaluation. Hydrogen is generated primarily during the anaerobic corrosion of metals whereas methane and CO_2 are produced mainly during the chemical and microbiological degradation of organic materials under anaerobic conditions.

The report goes on to identify and investigate three potentially important scenarios related to gas production within a Swiss L/ILW repository. These are:

- radiological consequences arising from ^{14}C and tritium becoming incorporated in methane and hydrogen gas and rapid transfer of this gas to the biosphere,

- flammable or explosive hazards associated with hydrogen and methane gas entering a confined space in the biosphere,

- gas pressure effects, causing expulsion of water from the repository environment and even physical disruption of the cavern lining.

The potential significance of these scenarios has been quantified primarily by way of scoping and bounding calculations for two operational waste streams, BA-1a and BA-5 (Nagra 1984). BA-1a consists of ion exchange resins which contain significant amounts of degradable organic materials, and BA-5 consists of steel and other metallic waste immobilised in a cement matrix, a major potential source of hydrogen. Subsets of these streams and other wastes have also been considered where these contain particularly high levels of relevant radionuclides.

The radiological consequences arising from ^{14}C and tritium substituted methane and hydrogen gas generated from ion exchange resins are extremely small. Using conservative assumptions the maximum annual doses associated with average BA-1a waste are predicted to be of the order of 10^{-11} Sv a^{-1} per metre of repository tunnel and to be dominated by $^{14}CH_4$. Even allowing for the fact that a small proportion

of the wastes may have a higher ^{14}C and organic material content, then the total dose is thought extremely unlikely to exceed about 10^{-8} Sv a^{-1}.

The hydrogen gas production rates do not represent a flammable or explosive hazard on the surface. However, if a single rapid flow path to the surface were connected to the total length of tunnel containing all the BA-5 then the potential source term could be sufficient for the lower explosive limit to be reached in a confined space in a building connected with the flow path. In terms of Swiss performance assessment requirements, such a combination of factors is deemed to be a scenario which cannot be realistically assumed.

Of the scoping and bounding calculations carried out, the major gas scenario of potential significance concerns the effect of the gas pressure on groundwater movement within the repository environment and its structural integrity. Assuming the repository is fully resaturated at repository closure the scoping calculations indicate that initially all the generated gas goes into solution. The repository porewater becomes fully saturated with hydrogen within a few years at which time a free gas phase forms. For waste stream BA-5 this is 25 days if the gas arising from aluminium and zinc corrosion is included, otherwise the time is longer (2.5 years). Assuming that there are no cracks in the liner the scoping calculations indicate that the excess gas pressure would rise rapidly and sufficiently to overcome the capillary pressures in the liner. At this point the gas would enter and move through the liner and/or initiate cracks in the repository liner, allowing the gas to escape through the cracks produced.

These calculations are based on conservative assumptions. In reality gas generation rates can be expected to be at least one order of magnitude smaller. The contribution of aluminium and zinc to the gas volumes generated is probably overestimated recognising that much of the corrosion and hence gas generation is likely to occur prior to emplacement in the repository. The scoping calculations focus on those waste streams expected to generate the greatest quantities of gas and it is assumed that it all is placed together within the repository. The particular distribution of these wastes among others within the caverns would clearly affect the significance of gas generation.

It is unlikely that the repository liner would be of such a uniformly low permeability. The occurrence of small cracks as a result of thermal stresses during curing are inevitable. Such cracks will have lower capillary pressures. For this reason it is considered unlikely that the generated gas pressure effects would result in a loss of structural integrity but rather the expulsion of near field groundwater.

ZUSAMMENFASSUNG

Die Gasentwicklung in einem tiefen geologischen Endlager für radioaktive Abfälle ist nach Abschluss der Einlagerungsphase unter Umständen von ausschlaggebender Bedeutung für die Endlagersicherheit. Im vorliegenden Bericht wird dieser Themenkreis in Bezug auf die Endlagerung von kurzlebigen, schwach- und mittelaktiven Abfällen (SMA) gemäss dem gegenwärtigen Entsorgungskonzept der Nagra untersucht.

Die verschiedenen Gase, die dabei produziert werden können, sowie deren Herkunft werden kurz diskutiert und potentielle Produktionsraten werden rechnerisch abgeschätzt. Wasserstoff und Methan werden als die beiden wichtigsten Gase erkannt und wurden deshalb vertieft untersucht. Wasserstoff wird vor allem bei der anaeroben Korrosion von Metallen entwickelt, Methan und CO_2 hingegen während des chemischen und mikrobiologischen Abbaus von organischen Stoffen unter anaeroben Bedingungen.

Drei Szenarien, die im Zusammenhang mit einer Gasentwicklung von potentieller Bedeutung für ein schweizerisches SMA-Endlager sind, werden identifiziert und näher untersucht:

- die radiologischen Konsequenzen einer Inkorporation von ^{14}C und Tritium in Methan- und Wasserstoffgas und schneller Transport dieser Gase zur Biosphäre

- die Feuer- oder Explosionsgefahr infolge einer Infiltration von Methan und Wasserstoff in geschlossene Räume innerhalb der Biosphäre

- Auswirkungen hoher Gasdrücke, die Wasser aus dem Endlagermilieu zu treiben vermögen und unter Umständen sogar eine zerstörerische Wirkung auf Kavernenbauten haben können.

Die möglichen Auswirkungen im Zusammenhang mit den zwei Betriebsabfallsorten BA-1a und BA-5 (Nagra, 1984) wurden weitgehend unter Annahme von extremsten Bedingungen rechnerisch abgeschätzt. BA-1a enthält Ionenaustauschharze und damit bedeutende Mengen von abbaubaren organischen Stoffen; BA-5 enthält Stahl und andere metallische Abfälle, die in einer Zementmatrix, die potentielle Hauptquelle einer Wasserstoffproduktion, verfestigt sind. Unter-Kategorien dieser Abfallsorten, sowie auch Abfälle mit besonders hohen Gehalten an relevanten Radionukliden, wurden ebenfalls betrachtet.

Die radiologischen Auswirkungen einer Inkorporation von ^{14}C und Tritium, im Zusammenhang mit einer möglichen Methan- oder Wasserstoffproduktion aus Ionenaustauschharzen, sind äusserst gering. Unter konservativen Annahmen wird die maximale Jahresdosis aus dem durchschnittlichen BA-1a Abfall auf etwa 10^{-11} Sv a^{-1} pro Meter Endlagerstollen geschätzt, wobei $^{14}CH_4$ die dominierende chemische Komponente darstellt.

Selbst im Falle der Annahme, dass ein kleiner Teil des Abfalls einen wesentlich höheren Gehalt an organischem Material und ^{14}C aufweisen könnte, ist es äusserst unwahrscheinlich, dass dabei eine Jahresdosis von 10^{-8} Sv a^{-1} überschritten wäre.

Die Produktionsraten für Wasserstoffgas sind zu gering, um an der Erdoberfläche je eine etwaige Feuer- oder Explosionsgefahr verursachen zu können. Würde man aber davon ausgehen, dass ein einziger, schneller Fliesspfad alles (rechnerisch) aus BA-5 Abfällen produzierte Gas in geschlossene Räume an der Erdoberfläche zu transportieren vermöchte, wäre die untere Explosionslimite erreicht. Für die Anforderungen einer schweizerischen Sicherheitsanalyse wird eine solche Verknüpfung von Faktoren als ein Szenarium betrachtet, welches vom realistischen Standpunkt aus nicht anzunehmen ist.

Für sämtliche Gas-Szenarien geht aus den durchgeführten Auslegerechnungen klar hervor, dass die bedeutendsten Störeinflüsse durch hohe Gasdrücke entstehen, welche einerseits die Grundwasserbewegungen im Endlagerbereich, andererseits dessen strukturelle Integrität beeinträchtigen können. Falls sich das Endlager nach Verschluss sofort wieder mit Wasser aufsättigt, zeigen die rechnerischen Abschätzungen, dass alles bereits produzierte Gas sofort in Lösung gehen würde. Innerhalb von wenigen Jahren aber wird das Porenwasser im Endlager vollständig mit Gasen gesättigt sein und eine freie Gasphase kann sich bilden. Für die Abfallsorte BA-5 ist dieser Zeitpunkt nach etwa 2.5 Jahren erreicht; falls jedoch die Korrosion von Zink und Aluminium voll miteinbezogen wird, bereits schon nach 25 Tagen. Falls nun weiter angenommen wird, dass keine Risse in der Stollenauskleidung vorhanden sind, steigt der Gasdruck rasch an, um bald die herrschenden Kapillarkräfte zu überschreiten. Zu diesem Zeitpunkt beginnt das Gas in die Auskleidung zu dringen oder verursacht Risse, wodurch es in der Folge entweichen kann.

Die dargelegten Auslegerechnungen basieren auf konservativen Annahmen. Für realistischere Betrachtungen kann man davon ausgehen, dass die Gas-Produktionsraten mindestens um eine Grössenordnung geringer sind. Der Beitrag zur Gasproduktion durch die Korrosion von Zink und Aluminium wurde möglicherweise überschätzt, da ein wesentlicher Teil des Korrosionsprozesses - und der damit verbundenen Gasentwicklung - bereits schon vor der Einlagerung stattfindet. Die Rechnungen beziehen sich stets auf diejenigen Abfallsorten, die erwartungsgemäss die grössten potentiellen Gasmengen zu produzieren vermögen, und da weiter angenommen wird, dass alle diese Abfälle zusammen eingelagert werden, muss die Bedeutung der Gasproduktion gemäss der jeweils gewählten Verteilung in den Stollen relativiert werden.

Es ist unwahrscheinlich, dass die Stollenauskleidung eine derart geringe Durchlässigkeit hat, dass die Gase nicht entweichen könnten, denn die Bildung feiner Risse beim Abbinden des Betons sind üblich und unvermeidbar. Solche Risse zeichnen sich gegenüber "heilem" Beton durch eine niedrigere Kapillarspannung aus und es ist somit kaum denkbar, dass die aufbauenden Gasdrücke die strukturelle Integrität der Auskleidung beeinträchtigen könnten. Es scheint eher plausibel, dass Wässer aus dem Nahfeld ins Nebengestein getrieben werden.

RESUME

La génération de gaz dans un dépôt final géologique profond pour déchets radioactifs peut avoir des implications significatives pour sa sécurité après entreposage des déchets. Le présent rapport examine cette question dans le contexte du stockage final de déchets de faible et moyenne activité à vie courte (DFMA) en Suisse, dans le cadre du projet de développement d'un tel dépôt par la Cédra.

On passe brièvement en revue les différents gaz qui peuvent être générés en relation avec leurs sources, ainsi qu'une estimation de leur taux de production. L'hydrogène et le méthane sont identifiés comme les deux gaz qui doivent faire l'objet d'une évaluation plus précise. L'hydrogène est essentiellement généré lors de la corrosion anaérobique de métaux alors que le méthane et le CO_2 proviennent essentiellement de la dégradation chimique et microbiologique de matériaux organiques sous conditions anaérobiques.

Le rapport se poursuit par l'identification et l'étude de trois scénarii potentiellement importants liés à la production de gaz à l'intérieur d'un dépôt final suisse pour DFMA. Ce sont:

- conséquences radiologiques dues au ^{14}C et au tritium incorporés dans le méthane et l'hydrogène avec transfert rapide de ces gaz vers la biosphère

- risques de feu ou d'explosion suite à l'introduction d'hydrogène et de méthane dans un espace confiné de la biosphère

- effets dûs à la pression des gaz entraînant l'expulsion d'eau de l'environnement du dépôt, voire même la dislocation physique du revêtement des cavernes.

La signification potentielle de ces scénarii a été quantifiée principalement à l'aide de calculs d'ordres de grandeur pour deux flux de déchets d'exploitation, les types BA-1a et BA-5 (Cédra 1984). BA-1a consiste en résines échangeuses d'ions qui contiennent une quantité significative de matériaux organiques dégradables alors que BA-5 consiste en acier et autres déchets métalliques immobilisés dans une matrice de ciment, sources potentielles majeures d'hydrogène. Des sous-ensembles de ces flux et d'autres déchets ont également été pris en considération lorsque ceux-ci présentent des taux de radionucléides pertinents particulièrement élevés.

Les conséquences radiologiques provenant du ^{14}C et du tritium incorporés dans les gaz méthane et hydrogène, générés à partir de résines échangeuses d'ions, sont extrèmement faibles. Partant d'hypothèses prudentes les doses annuelles maximales associées avec un BA-1a moyen sont estimées devoir être de l'ordre de $10^{-11}Sv\ a^{-1}$ par mètre de galerie de dépôt où le $^{14}CH_4$ domine. Même en considérant qu'une faible partie des déchets pourrait présenter une teneur plus élevée en ^{14}C et en matériaux organiques, on pense qu'il est extrèmement peu probable que la dose totale dépasse $10^{-8}Sv\ a^{-1}$ environ.

Les taux de production d'hydrogène ne présentent pas de risque de feu ou d'explosion en surface. Si toutefois un unique cheminement rapide devait connecter la surface avec toute la longeur des galeries contenant la totalité des BA-5, le terme source potentiel pourrait être suffisant pour que la limite inférieure de déflagration soit atteinte dans un bâtiment présentant un espace confiné relié à ce cheminement de fuite. Une telle combinaison de facteurs doit être vue comme un scénario qui, aux termes des exigences pour les analyses de sûreté en Suisse, ne peut pas être pris en considération d'un point de vue réaliste.

Il ressort de tous les calculs d'ordre de grandeur exécutés que le principal scénario de gaz potentiellement significatif concerne les effets de la pression des gaz sur le mouvement des eaux souterraines dans les environs du dépôt et l'intégrité structurelle de celui-ci. Dans l'hypothèse que le dépôt final est totalement resaturé lors de son scellement, les calculs montrent qu'initialement tous les gaz générés vont aller en solution. L'eau des pores du dépôt se sature totalement en hydrogène en l'espace de quelques années après quoi une phase de gaz libre apparaît. Pour les déchets de type BA-5 cela se produit après 25 jours déjà si le gaz provenant de la corrosion de l'aluminium et du zinc est inclu, sinon la durée est plus longue (2.5 années). En supposant qu'il n'y ait pas de fissures dans le revêtement des cavernes, les calculs d'ordre de grandeur indiquent que la pression excédentaire des gaz augmenterait rapidement et suffisamment pour vaincre les pressions capillaires dans le revêtement des cavernes. A ce moment là le gaz pénétrerait dans le revêtement et le traverserait et/ou provoquerait des fissures dans le revêtement du dépôt qui permettraient au gaz de s'échapper.

Ces calculs reposent sur des hypothèses prudentes. En réalité on doit s'attendre à des taux de production de gaz inférieurs d'au moins un ordre de grandeur. La contribution de l'aluminium et du zinc aux volumes de gaz générés est probablement surestimée, considérant qu'une bonne partie de la corrosion, donc de la génération de gaz, aura lieu avant introduction dans le dépôt final. Les calculs d'ordre de grandeur se concentrent sur les flux de déchets dont on attend une production de gaz maximale et en admettant que tous ces déchets sont entreposés côte à côte dans le dépôt final. Une répartition particulière de ces déchets parmi les autres à l'intérieur des cavernes affecterait bien évidemment l'impact de la génération de gaz.

Il est peu probable que le revêtement des cavernes présente uniformément une très faible perméabilité. L'apparition de petites fissures dans le revêtement est inévitable en raison de contraintes thermiques lors de la prise du béton. Ces fissures présenteront des pressions capillaires plus faibles. On considère par conséquent qu'il est peu probable que la pression des gaz générés conduirait à une perte de l'integrité structurelle du dépôt; elle provoquera bien plutôt l'expulsion d'eaux souterraines du champ proche.

CONTENTS

APPENDICES

LIST OF FIGURES

LIST OF TABLES

1 INTRODUCTION

The Nagra disposal concept for short-lived low- and intermediate-level wastes (L/ILW) is in an SMA[1] repository in a geological formation with a horizontal access tunnel. To demonstrate the safety of this concept Nagra are performing post-emplacement radiological safety assessments backed up by appropriate research (McCombie et al, 1988). A particular issue which has come to the fore in recent years is the impact of gas generation on the design and safety of L/ILW repositories (Wiborgh et al, 1986, Zuidema and Hoglund, 1988, Zuidema et al, 1989). There are two major categories of deleterious effects which need to be considered in this context.

First, gases derived from a repository may be hazardous. For example, a potential radiological hazard could arise from release of tritiated hydrogen (HT), tritiated methane (CH_3T), carbon-14 substituted methane ($^{14}CH_4$) and carbon dioxide ($^{14}CO_2$). Hydrogen (H_2) and methane (CH_4) could present a flammable or explosive hazard, and some trace gases could potentially pose a toxic hazard.

The second area of concern is related to the potential build-up of pressure from bulk gases and its impact on radionuclide migration. For example, gas production and accumulation could result in the expulsion of contaminated water from the repository environment, or even fracturing of repository and geological materials if sufficiently high gas pressures were attained.

A more general reason for assessing the effects of gas concerns the building of confidence in the ability of Nagra to predict, at least in broad terms, the way that a repository will behave over time.

Gas production from landfills for non-nuclear waste has been studied for some time and is increasingly exploited as a source of methane fuel (Emcon Associates, 1980, DoE, 1988). Moreover, gas production in near-surface trenches for LLW has been reported in the USA (Kunz, 1982, Matuszek and Robinson, 1983) where radioactive gaseous compounds such as HTO, HT, CH_3T and other tritiated hydrocarbons, as well as ^{85}Kr, ^{222}Rn, $^{14}CH_4$, and other ^{14}C hydrocarbons have been identified (Francis, 1985). It has been reported that $7.4\ 10^9$ - $2.2\ 10^{11}$ Bq a^{-1} (0.2-6 Ci a^{-1}) of tritiated methane is released from various trenches from West Valley disposal site (Matuszek, 1980) primarily due to microbial activity. At West Valley it has been suggested that radioactive gas migration is the dominant exposure route and that doses could exceed regulatory guidelines (Matuszek and Robinson, 1983).

Wiborgh et al (1986) have carried out an initial assessment of gas formation and transport for a Swiss SMA repository (Wiborgh et al, 1986). The major scenario analysed was gas accumulation in the disturbed zone around a repository and subsequent transport through the geosphere, using simplified gas migration models. This work has been followed up by Pruess (1990) to take account of two-phase divergent flow in two-dimensional vertical cross-section and Mishra and Zuidema (1991) to

---

[1]SMA: German abbreviation for L/ILW

look in closer detail at the near field.

This report provides a more systematic and comprehensive enumeration of gas generation, transport and exposure scenarios. To this end, a number of representative scenarios for performance assessment have been identified and evaluated. Also, an attempt is made to provide qualitative feedback to the Nagra SMA repository development programme. The process of scenario development, performance assessment and concept refinement clearly require a number of iterations in order to converge to a consistent conclusion (Hodgkinson and Sumerling, 1990). It is intended that this document should contribute to this process.

The document is organised as follows. Following this introduction, Section 2 briefly summarises salient features of the repository sites and systems under consideration. Section 3 brings together and discusses factors which influence the generation of gas. Calculation of gas production as a function of waste sort is presented in detail in Appendix 1. In Section 4 a set of representative scenarios for post-closure safety assessment is identified. These scenarios are evaluated in Section 5 and the results discussed. Details of these calculations are given in Appendices 2 – 4. Section 6 draws together the conclusions and recommendations.

It should be noted that all references to dose in this document are to committed effective dose equivalent as defined by the International Commission for Radiation Protection in 1977 (ICRP, 1977). The new definitions and recommendations made in 1990 (ICRP, 1991) do not affect materially the conclusions.

2   REPOSITORY CONCEPTS AND WASTES

In Switzerland the current concept for the disposal of short-lived low and intermediate level waste is in an excavated repository with several hundreds of metres overburden. Four potential sites are under consideration, namely:

1. Oberbauenstock in marl

2. Wellenberg in marl

3. Bois de la Glaive in anhydrite rock

4. Piz Pian Grand in crystalline rock.

A schematic view of an SMA repository layout is given in Figure 1 and Figure 2 provides a schematic view of a cross section through the repository cavern (disposal gallery) containing the waste in drums stacked inside concrete containers.

The waste containers would be stacked into the repository cavern which would probably be lined with reinforced concrete in the host rock, and backfilled with concrete.

From the point of view of potential gas generation within the repository it may be important to ensure that the design allows for the passage of gases without causing pressurisation and disruption to such an extent that repository performance is significantly impaired. Naturally, this must be balanced against the requirement for radionuclide isolation.
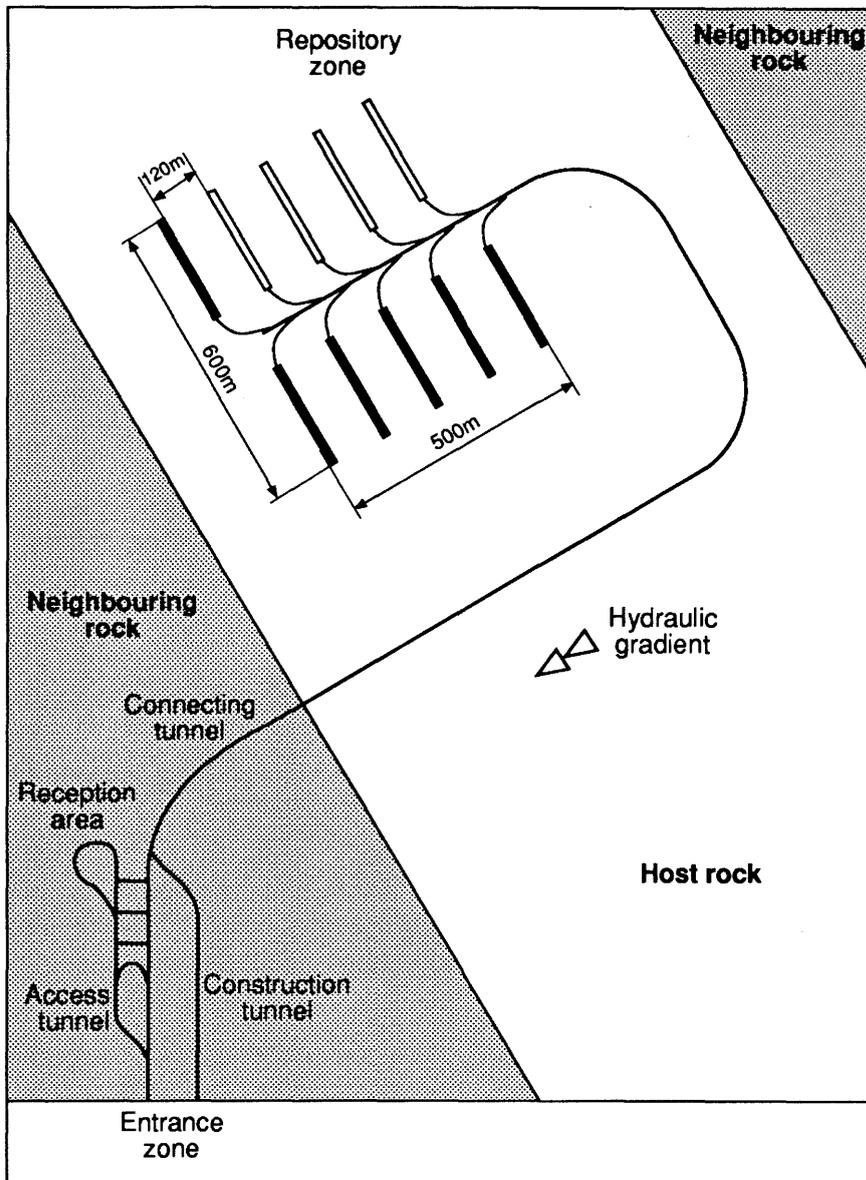
Figure 1: Schematic View of the Layout of an SMA Repository
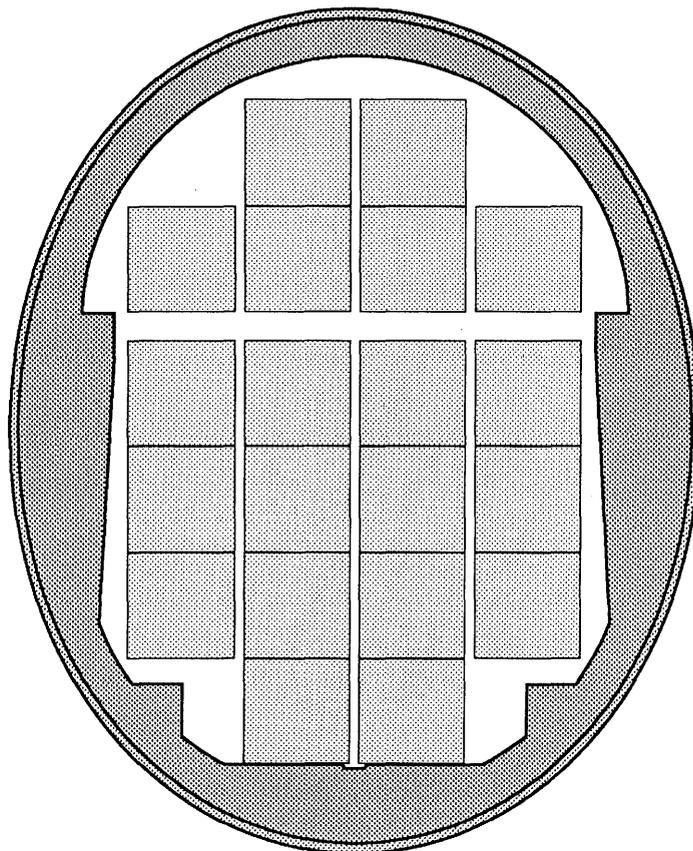
Figure 2: Schematic View of the Layout of a Repository Cavern

Present plans envisage the disposal of solidified L/ILW from plant operation, repro-
cessing and decommissioning arising from a 160^2 GW(e)-year nuclear power pro-
gramme. In addition, an SMA repository would include some wastes from medicine,
industry and research. The main solidification matrix is expected to be cement al-
though some waste streams will be immobilised in bitumen and synthetic resins. The
total quantities of materials to be introduced in an SMA repository are presented
in Table 1. These quantities are less than assumed in previous analyses (Wiborgh
et al 1986, Nagra, 1985) where a 240 GW(e)-year nuclear power programme was
assumed.

The key mechanism for gas generation within the repository is through degradation
of some of the introduced materials. However, some radionuclides in the waste
inventory may decay to radioactive gases, most notably ^{222}Rn and ^{220}Rn from long-
lived radioactive daughters of uranium and thorium. The radioactive gases ^{222}Rn
and ^{220}Rn are too short-lived to reach the biosphere directly from the repository.
However their longer-lived parents may migrate to the biosphere, or near biosphere,

---

[2]Since the time of preparation of this document a 120 GW(e)-year Nuclear Power Programme
is envisaged as the base case.

and then decay to give rise to releases of the radioactive gases. It is not within the scope of this project to consider this pathway which is essentially concerned with groundwater transport. The largest gas production is expected to be associated with the anaerobic corrosion of steel and reactive metals such as aluminium and zinc, producing hydrogen. Further significant gas production is expected from the anaerobic microbiological degradation of organic materials such as cellulose and plastics, producing methane and carbon dioxide. One approach to avoid or limit the effects of gas generation would be to stabilise these materials prior to disposal. This would involve the oxidation of metals and fermentation or combustion of organic materials. This should only be considered however, if significant advantages can be demonstrated and if it appears to be a practical proposition. An inevitable drawback is that processing radioactive waste creates further radioactive waste, in the form of effluents as well as solid wastes. At present, incineration of cellulose is planned, which would significantly reduce the volume of methane gas generated, and may have other benefits in terms of avoiding mobilisation some important long-lived radionuclides (Cross et al, 1989).

In earlier work (Wiborgh et al, 1986) the total quantities of materials introduced into an SMA repository were used to estimate total volumes of gas produced and the duration of gas production. The calculations were based on the assumption that the wastes and materials are homogeneously distributed throughout the repository. The near-field of an SMA repository, however, is heterogeneous in nature containing many waste types and forms. It is therefore not considered appropriate to average gas production rates over the entire repository. Instead, individual waste streams have been examined and the overall implications evaluated taking into account the more likely real distribution of wastes in the disposal galleries.

Two waste streams of potential significance with respect to gas production have been selected for primary consideration. These are the two operational waste streams BA-5 and BA-1a (Nagra, 1984). BA-5 contains significant quantities of steel and other metals and is classified as solid, non-combustible operational waste immobilised in a cement matrix (Nagra, 1984) and could therefore generate significant hydrogen gas. BA-1a consists of ion exchange resins and also has a significant tritium (T) and ^{14}C inventory associated with it. This waste stream therefore not only has the potential for methane gas production but may also give rise to gas containing T and ^{14}C substituted hydrogen and carbon atoms. The half lives of these elements are 12.3 years and 5730 years, respectively.

Assessments of the radiological impact of prompt release of gas to the biosphere require information on the amounts or activities of radionuclides which can exist in a gaseous form, and their precursors. For calculating the radiological consequences of rapid transport of T or ^{14}C substituted gas to the biosphere the initial activity concentrations of radionuclides in a particular waste stream have been taken directly from Nagra (1984) which does provide values for tritium. The KKG sub-set of waste stream BA-1a has also been considered in dose calculations since it has higher than average concentrations of ^{14}C and T, albeit for relatively small volumes of waste.

Table 1: Summary of Total Weight (tonnes) of Waste and Conditioning Material in the SMA Repository recalculated from Nagra (1985) assuming a 160 GW(e)-year nuclear power programme

Conditioning material	Operational Waste	Reprocessing Waste	Decommissioning Waste	Medicine Industry & Research	Whole Repository
concrete	26821	5266	76233	7000	115320
bitumen	332	2096	–	–	2428
plastics	84	–	–	–	84
Waste					
steel	2326	19231	20223	–	41780
Al/Zn	–	439	1355	–	1794
salt concentrates	373	1310	5055	–	6738
ashes	129	–	204	–	333
IEX	5759	47	–	–	5806
concrete	–	–	5764	–	5764
cellulose	–	(3511)†	–	–	(3511)†
plastic	221	439	1589	–	2249
other solids	1107	–	1226	3300	5833

† expected to be incinerated.

3   GAS SOURCES AND GENERATION RATES

The types of gases generated within an SMA repository will depend on the nature of the waste streams disposed of, the packaging, backfill, construction materials, other materials in the near field and the timescales for interaction between them.

Based on previous assessment work (Wiborgh et al. 1986, Zuidema and Hoglund, 1988) the bulk gases generated within such a repository are assumed here to be hydrogen, through the anaerobic corrosion of iron contained in large quantities of steel in the waste and near-field materials, and carbon dioxide and methane, resulting from both chemical and microbiological degradation of organic materials under anaerobic conditions.

Although the cementitious environment will suppress the level of microbial activity, some microorganisms might be able to survive in the hostile environment (Grant and Tindall, 1980). Furthermore microorganisms could be active within microenvironments whose chemistry differs from that of the repository as a whole. Under the initial aerobic conditions carbon dioxide will be the principal gas formed, whilst under anaerobic conditions approximately equal amounts of methane and carbon dioxide would be formed.

In addition to the pressure effects and flammable hazard that the bulk gases (hydrogen, methane) may present there is also the radiological hazard if they are radioactive (eg. containing ^{14}C and/or tritium).

Other gases may be produced in trace quantities from chemical, radiolytic and microbiological processes (Biddle et al. 1988).

In the following sections the key gases are discussed along with their potential sources and generation rates within the repository environment.

3.1   Hydrogen

Hydrogen gas generation is associated with steel, aluminium and zinc corrosion. Steel is found throughout the repository comprising the waste drums, certain waste streams, as reinforcement in drums, containers and possibly in the repository lining, depending on the design option. Aluminium and zinc are found in lesser quantities comprising certain waste streams and occurring as coatings to various drums and containers (Nagra, 1985). The major reactions resulting in hydrogen gas formation occur under anoxic conditions and can be summarised as follows:

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \tag{1}$$

$$2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2 \tag{2}$$

$$Zn + H_2O \rightarrow ZnO + H_2 \tag{3}$$
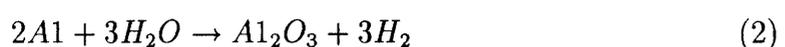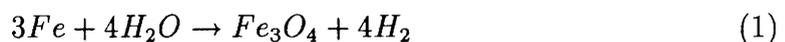
These reactions are described more fully in Wiborgh et al (1986) and Cotton and Wilkinson (1972). On the basis of these reactions it is straightforward to estimate the volumes of hydrogen which would be produced assuming all the metal is consumed in these reactions. The rate at which this occurs will depend amongst other things on the metal, its surface area to mass ratio and the local chemical conditions.

In a cementitious repository environment iron corrosion is expected to be very low and is currently estimated in the range of 0.1 to $0.2\mu m$ per year (Grauer, 1988). It is uncertain to what extent corrosion will be inhibited by the build-up of hydrogen pressure adjacent to the metal surface (Neretnieks, 1985) or by the presence of other corrosion products forming a protective (passive) oxide film under alkaline conditions (Zuidema and Hoglund, 1988, Sharland and Newton, 1989). Corrosion could be catalysed by microbiological action and the rate may vary with the state of saturation.

It is possible that evolution of the near-field aqueous chemical environment could lead to enhancements of the above corrosion rate. For example, it has been suggested that carbon dioxide, produced from microbiological degradation of organic materials in the waste, would make the near-field water highly corrosive for steels and could increase the corrosion rate to about 10^{-3} mm per year (Preece et al, 1981). However, it has been pointed out that these rates would not be achieved in practice for a significant period of time or over a large fraction of the repository, primarily because the corrosion reactions consume carbon dioxide (Dugstad and Videm, 1986, Dugstad, 1987). Furthermore, there are a number of other mechanisms which would consume carbon dioxide and thereby reduce the above effect. The most important of these will be reaction with calcium hydroxide from the cement, precipitating calcium carbonate.

A combination of microbiological and chemical degradation of organic materials could also produce weak acids or complexing agents which could enhance the corrosion rate. Again, the potential for their reaction with other repository materials needs to be considered along with their production rates.

For this assessment a high steel corrosion rate of $1\mu m$ per year is conservatively assumed. This is the maximum value quoted in Wiborgh et al. (1986).

Aluminium is normally protected against corrosion by a layer of oxide, which forms under aerobic conditions. However, at high pH's this oxide is soluble, as indicated in reaction (4), resulting in high corrosion rates (Wiborgh et al, 1986).

$$Al_2O_3 + 2OH^- + 3H_2O \rightarrow 2Al(OH)_4^- \tag{4}$$
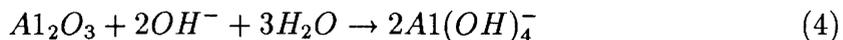
It is possible that the aluminium waste exposed to alkaline water in the waste matrix will have corroded before it is emplaced in the repository. However, since the aluminium embedded in concrete might not be sufficiently wetted to reach sufficiently

high pH until some time after repository closure (Rees and Rodwell, 1988), it is conservatively assumed for assessment purposes that all the aluminium is uncorroded at the time of emplacement. The corrosion rate of 1mm per year which is presented in Wiborgh et al (1986) has been assumed in this study.

Zinc is present as a thin protective layer on waste drums and is rapidly consumed under anaerobic conditions after exposure to the pore water. A conservative corrosion rate of 1mm per year is assumed in this study which is taken from reference Wiborgh et al (1986).

Radiolysis of water in cement and organic materials is another mechanism that could also produce hydrogen. However, other studies (Wiborgh et al, 1986, Biddle et al, 1988) have shown that radiolysis is much less important than corrosion and microbial degradation in the context of a L/ILW repository and is therefore not discussed further here.

3.2   Methane and Carbon Dioxide

Methane gas generation is associated with the microbial degradation of organic materials under anaerobic conditions. In a Swiss SMA repository organics may be present as waste streams, for example, cellulose, plastic materials and ion exchange resins, or as conditioning materials such as bitumen and plastics. They can be divided into four main categories, cellulose, plastics, bitumen and ion exchange resins. Anaerobic conditions will be established once the free oxygen present within the repository environment is consumed. It is anticipated that this will take only a few years (Wiborgh et al 1986) as a consequence of the aerobic degradation of hydrocarbons and the corrosion of metals. In repository sections with a high content of organic material and steel, this phase may last for only a few months. Work by Atkinson et al (1988) for the Nirex repository concept indicates that canister corrosion is sufficient to establish reducing conditions within the repository in approximately 100 years with a lower limit of 50 years and an upper limit of 150 years. In all cases reducing conditions are established very quickly close to the container surface.

Quantitative data exist for the rate of cellulose degradation under a variety of conditions but data concerning the other groups are limited (Wiborgh et al, 1986, Rees and Rodwell, 1988). Earlier work (Wiborgh et al, 1986) has indicated that cellulose degradation would be complete within 200 years. Other more recent experimental evidence Rees and Rodwell (1988) suggests that complete degradation of the cellulose fraction would take much longer, 700 years to 125,000 years. These experiments reported by Rees and Rodwell (1988) were carried out on 200 l drums of simulated LLW waste under a variety of pH and moisture conditions. Increasing moisture content at low pH's (7 and 9) resulted in increased gas production. This effect was not observed at high pH because high pH inhibited gas production.

The ion exchange resin degradation rates used for calculation in Wiborgh et al, (1986) were not based on experimental data but rather on a discussion by Renner-felt (Brandberg and Wiborgh, 1982). Since then, Torstenfelt (1990) has reviewed the chemical degradation of ion exchange resins in a cement matrix and concluded that such a degradation is very unlikely except under extreme environmental conditions eg. temperature and radiation, which will not arise in the repository. Biodegrada-tion of ion exchange resin media has been reported by Bowerman et al (1988) who concluded that a mixed microbial culture can be grown from ion exchange resins wastes when nutrient salts, a secondary carbon source and excess water are added to the waste. They also found that ion exchange resins media are more susceptible to microbial attack after irradiation. West et al (1991) have also conducted ex-periments under simulated repository near-field conditions. Their results indicated that high levels of organic carbon (non polar species) are leached from ion exchange resins. Analysis of the organic species had not, however, been carried out.

Jefferies (1990) reports that the most significant ^{14}C containing waste stream in the UK Nirex disposal programme is $BaCO_3$ sludge derived from reprocessing opera-tions. Degradation of this waste form will give rise to ^{14}C in solution rather than in the gas phase. He considers that the only potential mechanism by which ^{14}C present as dissolved carbonate in the repository porewater may be converted to methane is via the action of autotrophic methanogenic bacteria. Insufficient data are available to determine whether this could be a significant process. This waste stream is not found in a Swiss SMA repository.

For the calculations presented in this report it is assumed that 90% of the ^{14}C associated with ion exchange resins becomes strongly sorbed by the cement during wet processing leaving 10% associated with the ion exchange resins. This 10% is assumed to be released as $^{14}CH_4$ as a result of microbial degradation.

In the absence of any quantitative data it is assumed that plastics and ion exchange resins degrade at the same rate as that measured for bitumen (Wiborgh et al, 1986). This rate is two orders of magnitude less than that observed for cellulose (Wiborgh et al, 1986). In the absence of alternative data it is assumed that the yield of gas per kilogram organic component of waste is the same as the theoretical yield from cellulose which is 37 moles of gas per kg cellulose. This is a conservative assumption because the experimental yield is typically 40–50% of the theoretical yield and contains approximately 60% methane and 40% carbon dioxide. In the modelling described below it is simply assumed that equal volumes of both gases are produced, whereby the carbon dioxide reacts with calcium hydroxide in the cement and is precipitated as calcium carbonate (see section 3.1).

3.3   Trace Gases

In addition to the bulk production of hydrogen, methane and carbon dioxide, it is appropriate to give some consideration to other gases which may be produced in

trace quantities. A comprehensive list of minor active and toxic gases that could be formed from chemical, radiolytic and microbiological processes in the wastes is reproduced in Table 2 from a review carried out by Biddle et al (1988) for Nirex in the UK. The report concluded that many of these gases are expected to be reactive under repository conditions yielding either solids (for example, conversion of hydrogen sulphide to metal sulphides) or species in solution (conversion of iodine to iodides or dissolution of ammonia). Three areas of gas production were selected as first priority for further evaluation. These were helium, krypton-85 and the wide range of organic gases and vapours that could form in trace amounts.

Helium, although neither active nor toxic, was included in the Nirex study because the volumes formed might contribute significantly to overall gas production. This was subsequently found not to be the case (Biddle et al, 1988).

Similarly only small volumes of krypton-85 would be produced and this would dissolve in the pore water and decay before reaching the biosphere, due to its short half-life (10.8 years).

The wide range of organic gases and vapours was shortened by Biddle et al (1988) to a list of 21 by consideration of their toxicity, volatility and extent of formation at a landfill site for non-radioactive wastes. It was considered that some of these gases may be more reactive in a repository environment due to the presence of various cements and high pH water. Some may reach equilibrium solubility in the groundwater due to the greater disposal depths compared with a landfill site. They concluded that further work was required to determine the potential significance of those gases remaining from the list of 21. However, overall it would appear that these trace gases do not present a real problem with regard to SMA repository performance.

Table 2: Minor Active and Toxic Gases that might form in a Repository based on Biddle et al (1988)

Gas	Method of formation [*]	Reactive in Repository?
$CH_3I(^{129}I, T)$	Mainly R (CH_4 or CH_3 + HCl or Cl_2)	May be hydrolysed
$(CH_3)_2Se$ (^{79}Se, T)	R (Se + CH_3)	May be hydrolysed
^{85}Kr	Present in fuel cladding wastes	No
$ClCl(^{36}Cl)$	R	Very reactive
$HCl(^{36}Cl$ T)	R and C (from organic wastes)	Very reactive
$HI(^{129}I, T)$	R and C (from organic wastes)	Very reactive
$SnH_4(^{121}{}_mSn, {}^{126}Sn, T)$	R (Sn + H)	Unstable
PbH_4 (^{210}Pb)	R (Pb + H)	May not exist
SbH_3 (^{125}Sb, T)	R (Sb + H)	Unstable
BiH_3 (T)	R (Bi + H)	Unstable
$Ni(CO)_4$ (^{59}Ni, ^{63}Ni, ^{14}C)	C (Ni + CO)	Unstable
$H_2Se(^{79}Se$, T)	R (Se + H)	Forms metal selenides
H_2S (T)	R (S + H)	Forms metal sulphides
NH_3 (T)	R (reactions involving NH_4, NO_3; trapped N_2; N-containing polymers)	Stable but very soluble
I_2 (^{129}I)	R	Unstable ($\rightarrow I^-$)
$HSeCH_3$ ◊ (^{79}Se, T, ^{14}C)	R (Se, H, CH_3)	Probably unstable
$HSCH_3$ ◊ (T, ^{14}C)	R (S, H, CH_3)	Probably reactive
CH_3SnH_3 ‡ (^{121m}Sn, ^{126}Sn, T, ^{14}C)	R (Sn, H, CH_3)	Probably reactive
CH_3PbH_3 ‡ (^{210}Pb, T, ^{14}C)	R (Pb, H, CH_3)	Probably reactive
He	α-particles; decay of T	Stable
$CO(^{14}C)$	R and M (organics)	Fairly reactive
Organic gases and vapours other than CH_4	R, C and M (organics)	Some are reactive

Notes:

*   R = radiolytic, C = chemical, M = microbial.

◊   And similar compounds containing larger alkyl groups.

‡   And similar compounds containing additional and/or larger alkyl groups.

4   DESCRIPTION OF REPRESENTATIVE SCENARIOS

A number of potentially important scenarios related to gas production within an SMA repository have been identified and are described below. In the following chapter the potential significance of these is quantified using scoping/bounding calculations.

4.1   Scenario 1: Radiological Consequences of Prompt Gas Transfer to the Surface

This scenario concerns the direct radiological consequences of gases generated in an SMA repository which are then assumed to migrate rapidly through the geosphere to the biosphere.

Radioactive gases may arise through the substitution of stable hydrogen and carbon atoms in the gases by tritium and ^{14}C. Significant tritium and ^{14}C inventories are associated with ion exchange resins in reactor operating wastes so the most significant radioactive gas fluxes could be associated with these wastes. The gases produced from the degradation of ion exchange resins are primarily CO_2 and CH_4 and probably lesser amounts of H_2. The proportions will vary with the availability of free oxygen and other factors, which in turn will vary with time. CO_2 generated is expected to react with calcium hydroxide present in the near field and would not therefore be released into the biosphere. (See Section 3.2).

In addition to tritium and ^{14}C substituting into the CH_4 and H_2 gases produced in microbial degradation, tritium may be released from the ion exchange resins and migrate in the water to the site of corrosion in the steel drums becoming converted to gaseous hydrogen during corrosion. For ion exchange resins, steel present in the container drums rather than aluminium corrosion is likely to be the most relevant since aluminium is not associated with ion exchange resin wastes. Nevertheless, since the wastes will be mixed during the emplacement operations, it is hard to be sure about the effects of tritium present in ion exchange resins potentially reaching adjacent aluminium in other waste streams.

Transport of unreactive and low solubility gases from the repository through the geosphere to the surface environment could be rapid compared with the half-lives of tritium and ^{14}C because the Swiss sites in marl may be unsaturated. Studies (Suresh, 1986) indicate also for saturated host-rocks that once gas moves through rock then the migration times to the near-surface environment can be very short in comparison with groundwater travel times, ie. tens of days as opposed to thousands of years. This is because flow will tend to be highest through regions where capillary forces are weakest which correspond to the widest openings in the rock such as fractures. Conversely, gas migration times can also be very long as indicated by the presence of natural gas reservoirs.

If existing pathways are insufficient to transport the gas, then the pressure will build up to such an extent that new routes will be opened up. Once the gas pathway has been established through the rock, it is likely to remain open so long as the gas pressure gradient is maintained. If the pressure falls and then builds up again, the path is likely to re-open, and there may be hysteresis effects. Dilution of radionuclide concentrations by natural gas in the geosphere may occur.

Near the surface, increased weathering may result in subdivision or spreading of channelled flow over a relatively wide area, ie. wider than the channel giving access through the geosphere. As any gas passes through the near surface media a number of interactions may occur, involving for example biological processes in surface soil. Aerobic methane oxidation is a well known process (Mancinelli et al, 1981) and the highest rates reported for this (45g CH_4 m^{-2} day^{-1}) have been observed in top-soil covering a restored landfill near San Francisco, California (Whalen et al, 1990). More recently, the occurrence of anaerobic methane oxidation has been confirmed in terrestrial and marine environments (Alperin and Reeburgh, 1984; Williams and Hitchman, 1989). Similarly, oxidation of gaseous HT to HTO may also occur (Francis 1985). Aerobic oxidation of molecular HT has been observed in the soil column, under laboratory conditions (Murphy et al, 1976). Hydrogenous enzymes were proposed as the catalyst for this oxidation. Methanogenic bacteria produce methane under anaerobic conditions from H_2 and CO_2. In this case, one gas is being replaced by another.

Such oxidation mechanisms may result in the accumulation and subsequent transfer of the radionuclides into the foodchain via plant uptake (McFarlane et al, 1979). However, there are substantial hydrogen and carbon pools associated with water and organic material in the soil. The more biologically active organic material and water associated with the oxidation processes have relatively short residence times in the soil which implies substantial isotopic dilution and little chance for substantial accumulation. Moreover, there is very considerable uncertainty regarding the transfer of ^{14}C to plants from the soil. Most of the carbon in plants is derived from CO_2 in the air during photosynthesis, so that $^{14}CO_2$ could be the major transfer process from the soil to plants. However dispersion in the air from such a localised release would mean that activity concentrations in crops would be very low.

Much of the repository gas could be transferred directly to the atmosphere without oxidation occurring, and be rapidly dispersed. However, the possibility exists that a proportion of the gas generated will be released into a building eg. through the floor. In this case dispersion would be distinctly less rapid.

Radioactive methane and/or hydrogen in a building would result in radiation exposure primarily through inhalation. ICRP do not offer advice specific on radiomethane dosimetry. However, relevant data are given in Phipps et al (1990). HT is much less radiotoxic than HTO, and so account needs to be taken of the possibility of oxidation prior to inhalation. Dilution of the ion exchange resin generated gas with other less active repository gas or by natural gas might arise in

the geosphere. However, this would not result in reduced equilibrium radionuclide concentrations in the air in a house unless the flow from the ground was large in comparison with the ordinary flow of air through the house.

4.2   Scenario 2:   Explosive Hazards

This scenario concerns the explosive hazards associated with the release of flammable gases from an SMA repository.

Of the gases potentially generated in an SMA repository, methane and hydrogen present a flammable hazard because, when either is mixed in air, flammable mixtures can be produced. If the gas mixture occurs in the open atmosphere, it could ignite whereas an explosion might occur if the mixture is contained within a space, such as a building or underground chamber (HMIP, 1989). Before ignition can occur there must be a flammable gas concentration and the lower flammability limits of both gases are similar for both situations.

Hydrogen has a flammable range in air between 4% and 72% by volume (Howard and Jones, 1952). The lower limit increases from 4% to 9%, however, if ignition develops by downward propagation. Methane has a flammability range of 5% to 15% by volume in air. The presence of carbon dioxide affects both of these ranges, so that if there is more than 25% carbon dioxide in the original atmosphere methane is not flammable; similarly if there is more than 60% by volume in the original atmosphere, hydrogen is not flammable. For the case of a L/ILW repository significant releases of carbon dioxide are not anticipated because any carbon dioxide produced in the repository near field is expected to react with cement, forming calcium carbonate. It should be noted that carbon dioxide can be a hazard to health if present at concentrations exceeding 0.5% by volume as it is involved in the control of respiration in the body.

Dispersion at the surface in the open atmosphere would be rapid, so that it is extremely unlikely that the lower limit of flammability would be obtained. However, if the gas were to be released into a house or underground chamber it could give rise to explosive/flammable concentrations. The highest risks are likely to be associated with the latter, given the relatively low gas release rates anticipated and so the consequences of such a situation are evaluated.

In the scoping calculations the minimum gas generation rate and hence assumed inflow rate necessary to cause an explosive air mixture is calculated. These values are then compared with the gas generation rates calculated for the two waste streams BA-1a and BA-5 assuming a 160 GW (e)-year energy scenario.

4.3 Scenario 3: Gas Pressure Effects

This scenario concerns the impact of gas pressure effects from gas generation within a repository for a range of gas generation rates. Assessment is made of the likelihood that gas may be transported away simply by dissolution and diffusion, and of how gas pressure may build up within a repository lined with concrete.

If gas production proceeds at a sufficiently low rate, then the gas will dissolve in the water of the resaturated repository, and will migrate by diffusion and advection. If the diffusive and advective flux lost through the repository walls is of the same order of magnitude as the gas production rate within the repository, then eventually a steady state will be reached in which the concentration of dissolved gas in the repository pore water and that outside of the repository walls is maintained at constant levels.

For higher rates of gas production, the solubility limit will be exceeded locally and bubbles of gas will be formed. If the permeability of the liner is sufficiently high, gas pressure could be relieved by the expulsion of water through the side-walls and base of the repository. The actual release mechanism would depend upon the relative values of capillary pressure and the liner material permeability to fluid flow. The gas may also escape from the repository through vents or cracks in the liner, and subsequently to the surface via the more permeable pathways such as fracture zones and the backfilled tunnels. If the liner is intact and has a very low permeability, then gas may build up within the repository, forming a larger gas bubble or cushion at the top. Gas could escape in these circumstances either by expelling water from the pores of the repository (if the gas pressure exceeds the capillary pressure) or through cracks and fissures induced in the liner by the excess pressure.

Scoping calculations have been performed to examine the importance of possible transport and release mechanisms of the gas, for a given set of repository parameters and estimates of gas generation rates. The calculations include gas dissolution and diffusion, and the variation of gas pressure and gas saturation within a repository as water is expelled by the gas through the liner, which is assumed to remain intact.

5 EVALUATION OF GAS SCENARIOS

In this section the potential significance of each of the representative gas scenarios has been evaluated using scoping/bounding calculations. Detailed descriptions of these calculations are contained in Appendices 2 to 4 inclusive which correspond to Scenarios 1 to 3, respectively.

5.1   Scenario 1:   Radiological Consequences of Prompt Gas Transfer

In addition to waste stream BA-1a (see page 5), the waste stream BA-KKG-1b has been evaluated as it contains higher than average tritium and ^{14}C inventories. The volume of this waste stream is, however, much smaller (275 m^3) than BA-1a (14,256 m^3). Waste stream BA-5 has not been considered since it is composed of metallic waste which does not generate methane.

The rate of release of ^{14}C in methane from the near field will depend on:

- amounts of ^{14}C in wastes, eg. ion exchange resins,

- the fraction of carbon (and hence, it is assumed, ^{14}C) in waste which is converted to CH_4, and

- the methane generation rate.

Similar considerations apply to tritium in methane, except that since tritium has a half-life of only 12 years compared with 5730 years for ^{14}C, radioactive decay may also be important, during the period of disposal and prior to commencement of degradation.

The rate of release from the near field of tritium in hydrogen produced in corrosion will depend on:

- the rate of release of tritium from wastes, eg. ion exchange resins, and transfer in water to corrosion sites,

- the fraction of hydrogen (in water) converted to gaseous hydrogen during corrosion, and

- the rate of corrosion.

The calculations are presented in detail in Appendix 2, the main assumptions for which can be briefly summarised as follows:

- methane gas production rate associated with ion exchange resin degradation, = 0.025 mol CH_4 kg^{-1} a^{-1}

- corrosion rate for steel in drums, = 1μm a^{-1}

- 10% of carbon and hydrogen in ion exchange resins is converted to CH_4 and hence 10% of ^{14}C and tritium

- tritium goes simultaneously to methane and tritiated hydrogen (double counting). This is conservatively assumed in the absence of data to suggest one reaction would be favoured over the other,

- instantaneous transport through the near field and geosphere,

- release in biosphere to a small house with a low ventilation rate,

- 100% occupancy in house,

- conservative dose conversion factors.

The results are presented in Table 3.

The maximum annual individual doses arising from waste stream BA-1a are very small, in the order of 10^{-11} Sv a^{-1} for each of the gases considered. These calculations assume that all the radioactive gas generated per metre of repository tunnel migrates directly to the biosphere, where it is inhaled by man. The doses from waste stream BA-KKG-1b are approximately 3 orders of magnitude higher ($\sim 10^{-8}$ Sv a^{-1}) reflecting the higher tritium and ^{14}C content in this waste stream. Assuming an emplacement efficiency of 0.3 (Appendix 1) the total waste stream would occupy approximately 7m of tunnel if it were all placed in one location in the repository. If the total volume of gas produced were to migrate directly to a single dwelling the maximum individual dose would be in the order of 10^{-7} Sv a^{-1}. This must be considered as an extremely conservative assumption.

Table 3: Doses Arising from Generation of Radioactive Methane and Hydrogen Gas

Waste Stream		Dose from ^{14}C and Tritium Containing Gases [Sv a^{-1}]		
		CH$_3$T	^{14}CH$_4$	HT
BA-1a	Total	$3.2\ 10^{-9}$	$8.2\ 10^{-9}$	$1.6\ 10^{-9}$
	Per m tunnel	$1.2\ 10^{-11}$	$3.1\ 10^{-11}$	$6.2\ 10^{-12}$
BA-KKG-1b	Total	$4.9\ 10^{-8}$	$1.1\ 10^{-7}$	$2.4\ 10^{-8}$
	Per m tunnel	$7.1\ 10^{-9}$	$1.6\ 10^{-8}$	$3.5\ 10^{-9}$

5.2   Scenario 2:   Explosive Hazards

The potential explosive hazard associated with gases released from an SMA repository will depend on:

- the rate of release from the near field

- transfer pathways to the surface environment

- interaction of gases along pathways eg. sorption, oxidation, dissolution etc.

- presence of voids in the biosphere for accumulation

- accumulation time

- sources of ignition

For these scoping calculations it is assumed that the gas generated in the repository migrates directly through the geosphere along a discrete fracture, fault or similar feature. This is a pessimistic assumption that neglects any possible attenuation processes such as spreading of the channelled flow over a wider area due to increased weathering of the near surface environment, or oxidation on route, (see section 4.1). These conservative assumptions are also made for assessing the radiological hazards arising from these gases migrating to the biosphere (see section 4.1).

Again the calculations for this scenario are presented in detail in Appendix 3. To maintain consistency between the scenarios the same values are used for any parameters common to both scenarios. Hence the gas generation rates which are presented in Appendix 1 and assume maximum degradation/corrosion rates etc are also taken for this scenario. The other main assumptions are summarised briefly below:

- rapid transfer through a fracture to a single dwelling,

- small house and low ventilation rate,

- source of ignition exists.

For comparison the calculations have also been made excluding the contribution from aluminium and zinc. This is because aluminium corrosion occurs very rapidly under alkaline conditions. Consequently the metal may be rapidly consumed after being brought in contact with the concrete immobilisation matrix releasing the hydrogen prior to emplacement and repository closure.

The results are presented in Table 4.

Table 4: Gas Production Rates for Waste Streams Compared to Critical Rates Required for Explosion

Gas	Waste Stream Production Rate [m^3 a^{-1}]		Critical Inflow Rate of Repository Gas to a House [m^3 a^{-1}]
	BA-1a	BA-5	
Hydrogen:			
Total	1400	70000	
Excl. Al, Zn	1400	1900	
			88000
Per m tunnel	5.3	1100	
Excl. Al, Zn	5.3	29.9	
Methane:			
Total	2800	0	110000
Per m tunnel	10.6	0	

The gas generation rate for both waste streams is insufficient to attain the critical inflow rate necessary to achieve a flammable/explosive mixture. The only potentially significant waste stream in this context is BA-5 where the total annual hydrogen production rate is 80% of the required critical inflow rate. If the contribution of aluminium and zinc to the annual hydrogen production is ignored the flammable hazard would appear to be totally negligible.

5.3   Scenario 3:   Gas Pressure Effects

5.3.1   Transport of Gas by Dissolution and Diffusion

To assess the likelihood that gas produced from within a repository by degradation of repository materials could be transported away by dissolution and diffusion, the following quantities were calculated:

- time to reach gas-saturation of the repository pore water, assuming gas is generated at the rates estimated in Appendix 1,

- the maximum gas production rate that could be accommodated by dissolution and diffusion, without formation of a free gas phase,

- the maximum overburden pressure required to dissolve the gas produced at the estimated rates, and

- the effective diffusion coefficient required to accommodate the release of all gas by diffusion, again for the estimated gas production rates.

The following assumptions were made in performing the scoping calculations.

- the repository is fully resaturated.

- the system is assumed to have reached a steady state in which the gas concentration in the repository pore water has reached the solubility limit, and the gas concentration outside the repository liner is zero. This assumption maximises the concentration gradient across the liner and hence the diffusive flux.

- the repository cross-section is assumed to be circular, with a cross-sectional area which matches the true cross-sectional area. This assumption allows the use of a simple analytic solution for flux and concentration variation in the repository liner thickness.

- where applicable, results are compared with the following gas production rates which are reported in Table 6 and the Annex of Appendix 1.

  For waste sort BA-5:

  Production rate per m of repository = 1114.5 m^3 m^{-1} a^{-1} (100.2 kg m^{-1} a^{-1})

  Production rate per m of repository,

  excluding aluminium and zinc = 29.9 m^3 m^{-1} a^{-1} (2.7 kg m^{-1} a^{-1})

  For waste sort BA-1a:

  Production rate per m of repository = 5.32 m^3 m^{-1} a^{-1} (0.48 kg m^{-1} a^{-1})

  These figures are quoted at S.T.P, for which the density of hydrogen gas is 0.08988 g l^{-1} (or kg m^{-3}).

These rates are conservative estimates for gas production rates as they are based on assuming a high steel corrosion rate of 1 μm per year. A more realistic steel corrosion rate is in the range of 0.1 to 0.2 μm per year which would reduce the gas production rates from steel corrosion by about an order of magnitude.

The calculations are presented in full in Appendix 4 and are summarised in Table 5.

Time to saturation of the repository pore water

Saturation of the repository pore water with respect to hydrogen is most rapidly attained for waste stream BA-5 when the gas arising from aluminium and zinc corrosion is included (24.4 days). If this is not accounted for then it would take somewhat longer (2.5 years). In all cases, however, the times are very short compared with repository timescales.

The calculations were made including and excluding the contribution from aluminium and zinc to the total hydrogen production, for the same reasons described in Section 5.2 and Appendix 3. The results of the dissolution and diffusion calculations are described below in Table 5.

Maximum gas production rate without formation of free gas

The maximum hydrogen gas production rate which can be accommodated without the formation of free gas assuming an overpressure of 4MPa (400m overburden) is calculated as $1.89 \ 10^{-2}$ kg m^{-1} a^{-1}. Comparing this figure with the gas production rate estimates for the two waste streams (100.2 or 2.7 kg m^{-1} a^{-1} for BA-5 and 0.48 kg m^{-1} a^{-1} for BA-1a) indicates that even for the lower production rate, diffusion is insufficient to prevent the eventual formation of a gas phase, once the repository pore water becomes saturated with gas.

Minimum overburden pressure permitting release all gas by diffusion

The solubility of hydrogen in water is dependent upon pressure (Equation (8) in Appendix 4). The overburden pressures required to dissolve all the hydrogen gas generated have been calculated and range from 10 MPa (waste stream BA-1a) up to $5.3 \ 10^4$ MPa. These pressures are clearly much higher than the expected hydrostatic pressure of 4 MPa at the Wellenberg site due to 400m overburden.

Diffusion coefficient to release all gas by diffusion

The effective diffusion coefficients required to release all the hydrogen gas produced by diffusion range from $7.6 \ 10^{-1}$ to 159 m^2 a^{-1} for an overburden of 400m. Comparing these results with experimentally measured values of effective diffusion coefficients of hydrogen in water-saturated concrete of less than $3 \ 10^{-2}$ m^2 a^{-1}, it is clearly impossible for the estimated volumes of hydrogen gas which may be generated to be removed by diffusion alone.

Table 5: Results Summary of the Dissolution and Diffusion Scoping Calculations

Parameter	Waste Stream		
	BA-1a	BA-5	
		with Al, Zn	without Al, Zn
Time to saturation of repository pore water [a]	1.4	$6.7 \ 10^{-2}$	2.5
Maximum gas production rate accommodated by diffusion [kg m^{-1} a^{-1}]	$1.89 \ 10^{-2}$	$1.89 \ 10^{-2}$	$1.89 \ 10^{-2}$
Minimum overburden pressure to release gas by diffusion [MPa]	10.1	$5.3 \ 10^{4}$	57
Minimum effective diffusion to release gas [m^2 a^{-1}]	$7.6 \ 10^{-1}$	159	4.3

5.3.2 Expulsion of Water from the Repository

The results presented in the previous section indicate that the repository pore water could become saturated with gas at relatively early times (2.5 years or less) in the estimated total period of gas production of 1000-3000 years (see Appendix 1). Once saturated, bubbles of gas will be formed which will rise to the top of the repository. If there are no vents or cracks in the concrete liner, then the gas will not readily be able to escape to the host rock and will grow to form a larger cushion, or bubble and expel water through the bottom. Eventually the increasing gas pressure will be sufficient to overcome the capillary pressure in the liner pores; or even to cause cracking of the liner.

In this section the results of scoping calculations performed to investigate the evolution of repository gas pressure and gas saturation as water is expelled by the gas, are presented. The calculations assume that no cracks appear in the liner and that capillary pressures are not exceeded at the top of the repository. This approach allows a comparison to be made between the estimated rise in pressure and the excess pressures required to overcome capillary pressures, together with the times at which these mechanisms would come into effect.

Model of Water Expulsion

A simple one-dimensional model has been developed to monitor the changes in gas pressure and gas saturation, assuming gas is produced at a constant rate throughout the repository. As a first approximation, it was assumed that water can escape only through the floor of the repository, permitting a one-dimensional formulation.
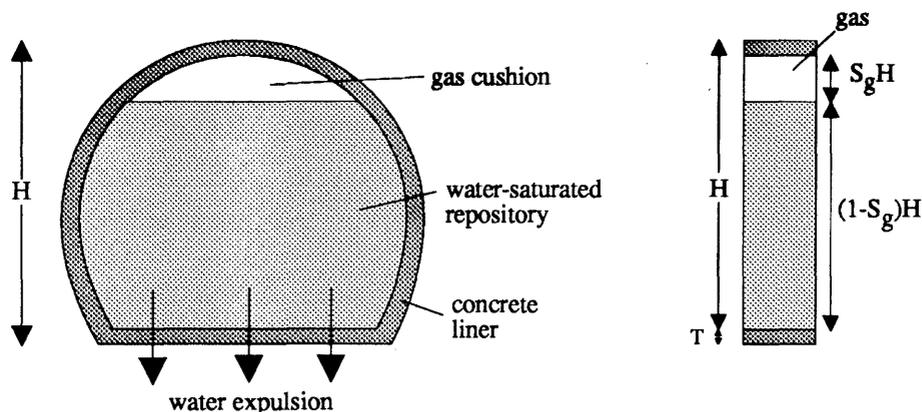
Schematic representation of   1-D Representation
vertical c/s through a repository

The diagrams above illustrate the model. The repository has a height H (14m) and liner thickness T(0.7m). In the 1-D model, the cross-sectional area of the floor is assumed to be unity. The model is described more fully in Appendix 4.

Calculations were performed for gas generation rates corresponding to waste streams BA-5 (including and excluding the aluminium and zinc components) and BA-1a, for repository overburden pressures of 4 and 2 MPa. The repository parameters used in the calculations are the same as those used for the dissolution and diffusion scoping calculations and are summarised in Table 6 for convenience.

The results for waste stream BA-5 at 4 MPa are shown in Figure 3 a), b). The graphs plot the total gas pressure on the left hand axis and gas saturation on the right hand axis, against time. At the higher gas generation rate (Figure 3a) the gas pressure rises very quickly for little increase in gas saturation. This is to be expected, since the gas is highly compressible and the hydraulic conductivity of the liner is low. At the lower gas generation rate (Figure 3b) the gas pressure rises more gradually, but the pressure increases are still considerable. Similar behaviour is displayed in the 2 MPa variation for this waste stream (Figures 4 a), b)).

Table 6: Parameter Values and Input Data for Gas Pressure Scoping Calculations

Repository cross-section (excluding liner)	165 m^2
Repository height	14 m
Backfill porosity	0.66†
Liner thickness	0.7m
Liner porosity	0.154
Liner permeability	3 x 10^{-18} - 10^{-20} m^2
Backfill permeability	10^{-16} -10^{-14} m^2
Repository overburden pressure (hydrostatic)	4 MPa
	2 MPa variation
Gas generation rates per m of repository length:	
Waste stream BA-5 including Al and Zn	1114.5 m^3 a^{-1} at STP
excluding Al and Zn	29.9 m^3 a^{-1} at STP
Waste stream BA-1a	5.32 m^3 a^{-1} at STP

† Could be much lower ie 30%.

In comparison, the pressure increase for waste stream BA-1a occurs much more gradually. Figure 5 a) and b) show the gas pressure and saturation history over a 10 year period for the 4 and 2 MPa overburden pressures, respectively. Although growth is slower, within 2 years the excess pressures have risen to more than 1.6 MPa. The excess pressure required to initiate cracks in the liner is estimated to be in the order of 6 MPa (Estoppey et al, 1992). The lower end of the range of capillary pressures in concrete (Wiborgh et al, 1986) depend on their water content. However, for structures as large as the liner the occurrence of cracks with lower capillary pressures is to be expected. Such cracks are likely to be formed as a result of thermal stresses at the time of production.

The gas generation rate might reasonably be expected to fall as the water saturation decreases. The results indicate however, that significant pressure rises would be obtained with little change in water saturation, so that gas generation rates should not be unduly affected by this parameter.

Figure 3: Gas Pressure & Saturation History for Waste Stream BA-5 with 4 MPa Overburden a) including contribution from aluminium and zinc, b) excluding contribution from aluminium and zinc
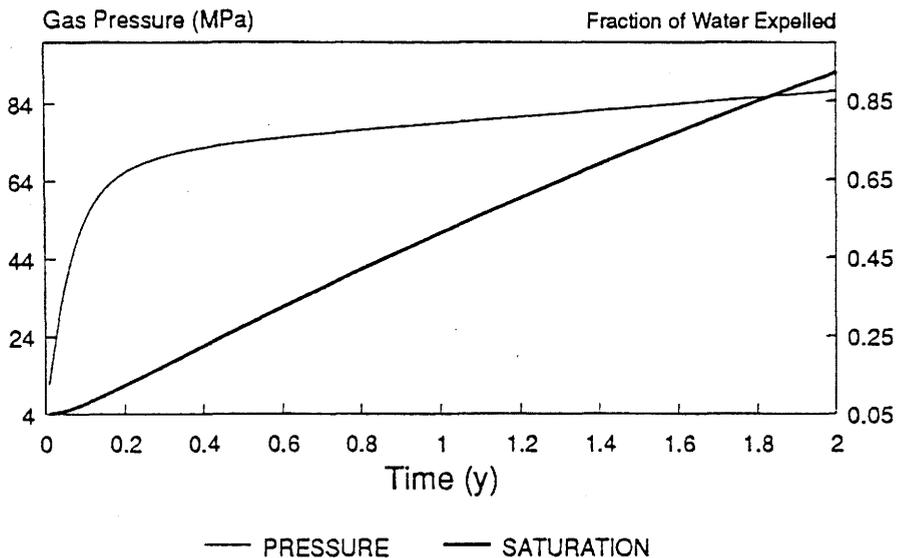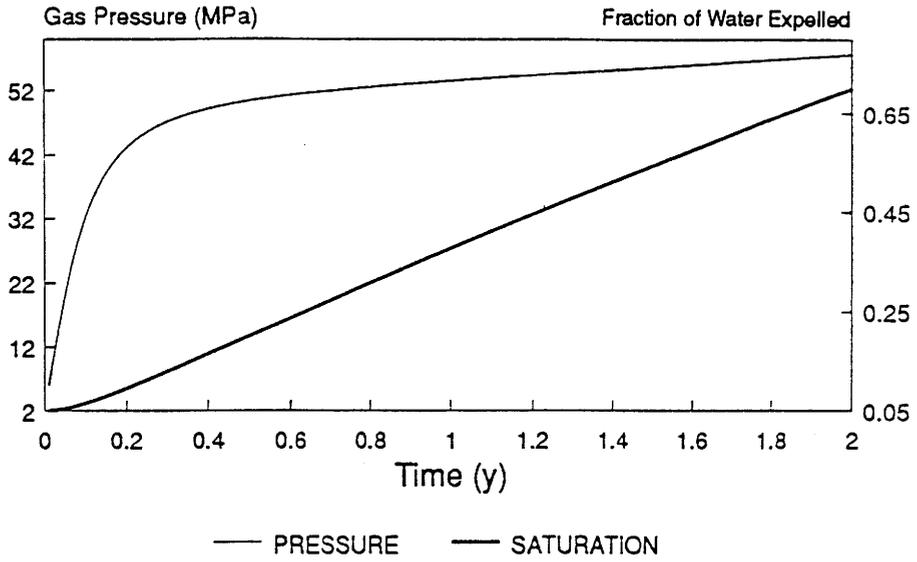
Gas Gen.Rate = 1.114E3 cu.m/y at STP
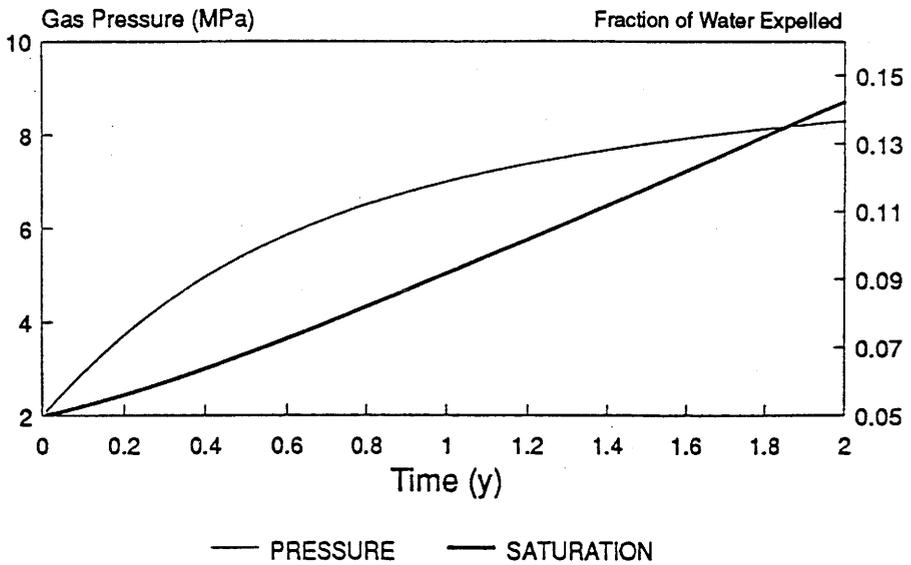
Gas Gen.Rate = 29.9 cu.m/y at STP

Figure 4: Gas Pressure & Saturation History for Waste Stream BA-5 with 2 MPa Overburden a) including contribution from aluminium and zinc, b) excluding contribution from aluminium and zinc
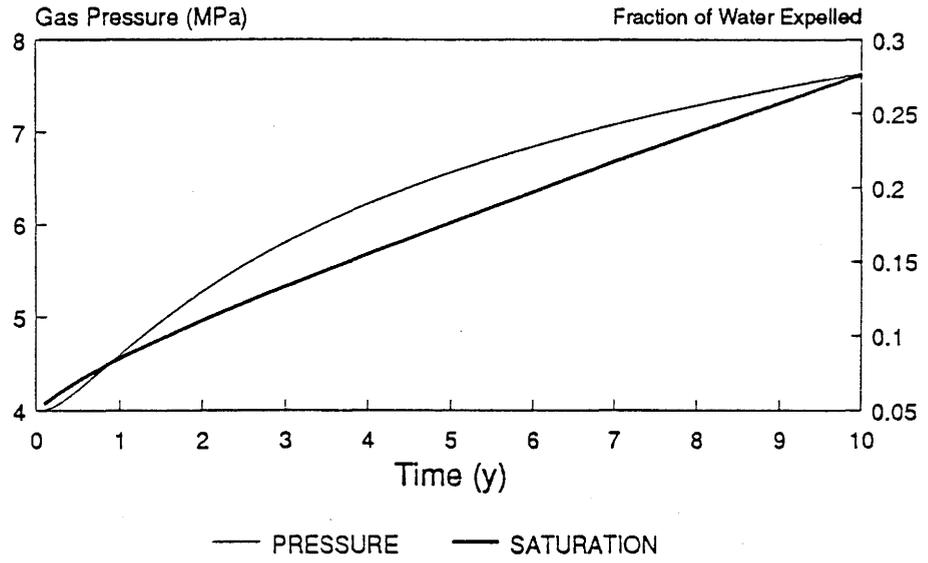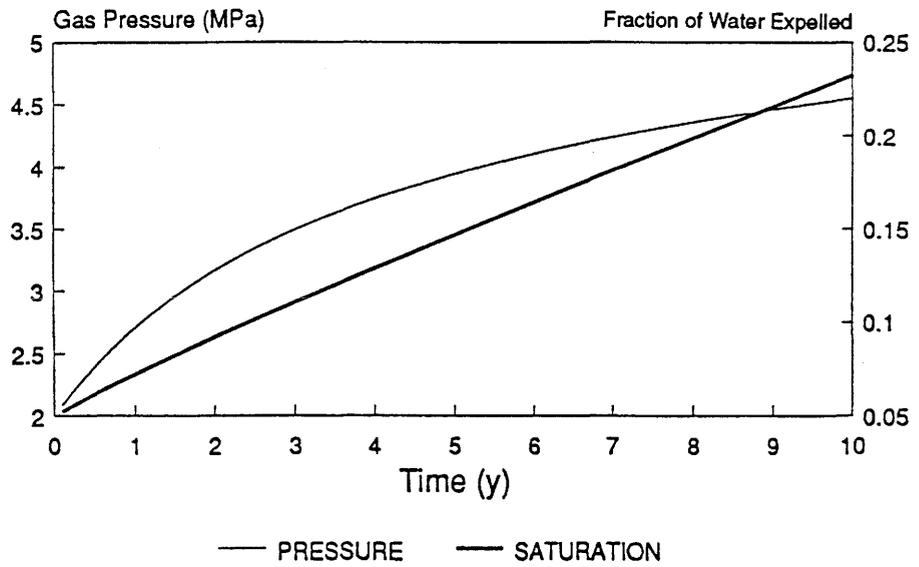
Figure 5: Gas Pressure & Saturation History for Waste Stream BA-1a
a) with 4 MPa Overburden, b) with 2 MPa Overburden

6 DISCUSSION OF CONCLUSIONS

The results from each of the scenarios are discussed in turn before drawing some final conclusions about the potential impact of gas generation on repository performance.

## 6.1 Scenario 1: Radiological Consequences of Prompt Gas Transfer to the Surface

Even with very pessimistic assumptions for release into a home and subsequent inhalation the predicted maximum annual individual dose is considered extremely unlikely to exceed 10^{-8} Sv^{-1}, allowing for all the sources of gas and their distribution among the various wastes. To ensure that the cellulosic contribution to gas generation has not been underestimated, it would be useful to obtain some idea of the cellulose content of critical waste streams. The possibility of methane oxidation in the near surface environment has also been noted. The significance of subsequent incorporation of ^{14}C from methane oxidation into foodchains is very uncertain (Morgan and Beetham, 1990). However, this is unlikely to give rise to individual doses higher than those from inhalation.

6.2 Scenario 2: Explosive Hazards

The results (Table 4) show that the methane gas production rates are too small to pose any flammable/explosive hazard. The total methane production from waste type BA-la is almost two orders of magnitude below the critical inflow rate necessary to attain the lower limit of flammability in the reference house. Similarly the total hydrogen gas production by waste stream BA-1a is significantly below (factor 63) any potentially critical level and can therefore also be ruled out as a flammable/explosive hazard.

Waste stream BA-5 contains significant quantities of corrodible metals and might be expected to pose a flammable hazard due to hydrogen production. The hydrogen production rate **per metre** of tunnel containing this waste is significantly below (factor 80) any potentially critical level. However, if a fracture/gas flow path were connected to a greater length of tunnel then the potential source term could be sufficient for the limit to be reached. Assuming an emplacement efficiency of 33%, waste type BA-5 would occupy approximately 60m of repository tunnel length. Thus even assuming that all the hydrogen generated by this waste type migrates to a single fracture and is transported directly to a house, explosive air concentrations would still not be reached. The resultant inflow rate is still only 80% of that necessary to reach the lower explosive limit, based on a 24h average. At certain times throughout a 24 hour period, gas concentrations could reach higher levels as the ventilation rate will fluctuate about the average value. For example, at night ventilation rates are typically lower by about a factor of two (NRPB, 1990). For the corrosion rates

assumed this level of gas generation would continue for less than ten years. By excluding the contribution of aluminium and zinc to the annual hydrogen production values, the flammable hazard would appear to be non existent. Furthermore, it should be recognised that the calculations are based on pessimistic assumptions which can be briefly summarised as follows:

- corrosion rates are an order of magnitude greater than base case values (Wiborgh et al, 1986).

- reactive metals (aluminium, zinc) do not corrode prior to emplacement, but once emplaced corrode rapidly.

- ion exchange resin degradation rates equivalent to maximum rates for bitumen (Wiborgh et al, 1986).

- direct transport of gases generated from a particular waste stream in the near field to a single house assuming no spreading of the channelled flow over a wider area or interaction with the geosphere.

- small house volume and low ventilation rate.

Taking into account the pessimistic assumptions made for these calculations it would appear that hydrogen gas generation does not pose a significant explosive hazard. There is clearly a relationship between flammable gas accumulation rate, void space size and accumulation period. Consequently the gas could collect in smaller voids within a house or underground structure characterised by even lower ventilation rates than those assumed for the house as a whole. Obviously the volume of explosive gas mixture accumulated must be sufficiently large that significant damage would occur on ignition.

6.3 Scenario 3: Gas Pressure Effects

The overall conclusions to be drawn from the scoping calculations on dissolution and diffusion are that these mechanisms of gas transport will be quickly exhausted. The gas generation rate would need to be reduced by a factor of 25 for waste stream BA-1a, and by a factor of between 5000 and 140 for waste stream BA-5, depending whether aluminium and zinc are expected to contribute to gas generation after emplacement, before dissolution and diffusion could cope sufficiently to avoid the formation of a free gas phase. By assuming more realistic corrosion rates these factors would decrease by approximately one order of magnitude.

A similar conclusion was reached by Rodwell (1989) who made a preliminary examination of the factors that are expected to control near field gas migration in a deep geologic repository for the UK Nirex programme. Diffusion of dissolved gas

through the near field pore water would not provide sufficient flux to remove the gas generated within the vault.

The scoping calculations for water expulsion indicate that in the absence of vents or cracks in the repository liner, the excess gas pressure would rise sufficiently to overcome the capillary pressures and/or to initiate cracks in the liner assuming a fully resaturated repository environment. For waste stream BA-5 this would happen almost immediately, but would take between one and two years for a repository containing only waste stream BA-1a. The particular distribution of these wastes among others within the repository caverns would clearly affect the significance of gas generation as will the rate of repository resaturation.

Cox and Rodwell (1989) have investigated post-closure resaturation of a deep radioactive waste repository within the UK Nirex programme. Their calculations indicate that for certain combinations of gas generation rate, overburden and host rock permeability, resaturation of the repository would not be fully achieved owing to the build up of gas pressure and expulsion of water.

6.4   Overall Conclusions and Recommendations

From the scoping and bounding calculations carried out it can be concluded that the major gas scenario of potential significance concerns the effect of the gas pressure on groundwater movement within the repository environment and its structural integrity. Assuming the repository is fully resaturated at repository closure the scoping calculations indicate that initially all the generated gas goes into solution. The repository porewater becomes fully saturated with hydrogen within a few years at which time a free gas phase forms. For waste stream BA-5 this is 25 days if the gas arising from aluminium and zinc corrosion is included, otherwise the time is longer (2.5 years). Assuming that there are no cracks in the liner and that the capillary pressure is not exceeded the scoping calculations indicate that the excess gas pressure would rise rapidly and sufficiently to overcome the capillary pressures in the liner at which point the gas would enter and move through the liner and/or to initiate cracks in the repository liner allowing the gas to escape through the cracks produced.

These calculations are based on conservative assumptions. In reality gas generation rates can be expected to be at least one order of magnitude smaller. The contribution of aluminium and zinc to the gas volumes generated is probably overestimated recognising that much of the corrosion and hence gas generation is likely to occur prior to emplacement in the repository. The scoping calculations have focused on those waste streams expected to generate the greatest quantities of gas and it is assumed that they are all placed together within the repository. The particular distribution of these wastes among others within the caverns would clearly affect the significance of gas generation as well as the rate of repository resaturation.

It is unlikely that the repository liner would be of such a uniformly low permeability. The occurrence of small cracks as a result of thermal stresses during curing are inevitable. Such cracks will have lower capillary pressures. For this reason it is considered unlikely that the generated gas pressure effects would result in a loss of structural integrity but rather the expulsion of near field groundwater.

The significance of groundwater expulsion from the near field under pressure from the gas generated has subsequently been assessed with 2-D calculations (Mishra and Zuidema, 1991). For these calculations it was assumed that the repository liner contains a lower permeability (10^{-15} m^2) gas vent. Parametric analyses indicated that hydraulic properties of the backfill material strongly affect the degree and distribution of repository pressurisation. Only extreme scenarios appear to result in pressure gradients which would enhance the release of water borne solutes significant enough to potentially jeopardize the structural integrity of the repository.

If the gas were to escape directly to the surface environment the associated flammable/explosive hazards from CH_4 and H_2 are calculated to be minimal, as are the radiological consequences of any ^{14}C and/or tritium substituted H_2 and CH_4 gas escaping to the biosphere. The same conservatisms in parameter values were adopted for these calculations as for the gas pressure effect calculations. It is noted, however, that considerable uncertainty exists in the mechanism by which ^{14}C and tritium associated with ion exchange resins may be released in a gaseous form. For the calculations presented in this report it is assumed that only the ^{14}C and tritium which remains associated with ion exchange resins is available to be released as $^{14}CH_4$, CH_3T due to microbial degradation. A significant quantity of ^{14}C may therefore be present as dissolved carbonate in the cement porewater. However even accounting for the uncertainty in this particular value the consequences are negligible. To ensure that the potential significance of microbial gas generation has not been underestimated it is recommended that information concerning the quantities of cellulose associated with critical waste streams is obtained.

REFERENCES

Alperin M J and Reeburgh W S. Geochemical Observations supporting anaerobic methane oxidation. In Microbial Growth on CL compounds, R L Crawford and R S Hanson (eds). American Society for Microbiology pp 282–289, 1984.

Andersson K. Chemical Conditions in the Near Field of a Repository for Low and Intermediate Level Waste. Nagra Internal Document, 1992.

Atkinson A, Ewart F T, Pugh S Y R, Rees J H, Sharland S M, Tasker P W and Wilkins J D. Experimental and Modelling Studies of Near-Field Chemistry for Nirex Repository concepts. Proceedings of an NEA Workshop on Near-Field Assessment of Repositories for Low and Medium Level Radioactive Waste, pp 143–157, OECD, 1988.

Biddle P, Davies A A, McGahan D J, Rees J H, Rushbrook P E. The Evolution of Minor Active and Toxic Gases in Repositories. Nirex Safety Studies NSS/R118. 1988.

Bowerman B S, Clinton J H and Cowdery S R. Biodegradation of Ion – Exchange Media. Topical Report. NUREG/CR-5221. BNL-NUREG-52163 AN, RW, 1988.

Brandberg S and Wiborgh M. Long-term changes. SKBF/KBS Working Report SFR 81-10 (in Swedish) Rennerfelt J, In Appendix. 1982.

Cotton F A and Wilkinson G. Advanced Inorganic Chemistry. 3rd Edition. Interscience Publications, New York, 1972.

Cox I C S and Rodwell W R. Post-Closure Resaturation of a Deep Radioactive Waste Repository. Nirex Safety Studies NSS/R141. 1989.

Cross J E, Ewart F T and Greenfield B F. Modelling the Behaviour of Organic Degradation Products. Nirex Safety Studies, NSS/R151, UKAEA, 1989.

Department of the Environment (DoE). Waste Management Paper No. 26. Landfilling Wastes HMSO, London, 1988.

Dugstad A and Videm K. Evaluation of Hydrogen Production from CO_2 Corrosion of Steel Drums in SFR, Institute for Energy Technology, Norway, Report IFE/KR/F-86/019, 1986.

Dugstad A. Evaluation of Hydrogen Production from CO_2 Corrosion of Steel Drums in SFR: Part 2, Institute for Energy Technology, Norway, Report IFE/KR/F-87/046, 1987.

Emcon Associates. Methane Generation and Recovery from Landfills Consolidated Concrete Ltd and Alberta Environment. Ann Arbor Science, Michigan ISBN 0-250-40360-9, 1980.

Estoppey R, Gerber P and Hufschmied P. Auswirkungen Quellender Abfälle auf ein Endlager für Schwach und Mittelaktive Abfälle im Wellenberg. Nagra Internal Report, 1992.

Francis A J. Low-level Radioactive Wastes in Subsurface Soils. In Soil Reclamation Processes-Microbiological Analysis and Applications, Eds R L Tate III and D A Klein. Marcel Dekker Inc, 1985.

Grant W D and Tindall B J. The Isolation of Alkalophilic Bacteria. In: Microbial Growth and Survival in Extremes of Environment, pp 27–28. Eds G W Gould and J E L Corry. Academic Press, London/New York, 1980.

Grauer R. Zum Korrosionsverhalten von Unlegiertem Stahl in Portlandzement. Nagra Technical Report NTB 88-02, 1988.

Hansson C M. Hydrogen Evolution in Anaerobic Concrete Resulting for Corrosion of Steel Reinforcement. The Danish Corrosion Centre, 1984.

Her Majesty's Inspectorate of Pollution (HMIP). Waste Management Paper No. 27. The Control of Landfill Gas. A technical memorandum on the monitoring and control of landfill gas. HMSO, London, 1989.

Hodgkinson D P and Sumerling T J. A Review of Approaches to Scenario Analysis for Repository Safety Assessment. In NEA/IAEA/CEC, Safety Assessment of Radioactive Waste Repositories, Paris, pp 333-350, 1990.

Howard and Jones. Limits of Flammability and Vaporisation. US Bureau of Mines, Bulletin 503, 1952.

ICRP. Recommendations of the International Commission on Radiological Protection, ICRP Publication 26. Pergamon Press, Oxford, 1977.

ICRP. The 1990 Recommendations of ICRP. ICRP Publication 60. Pergamon Press, Oxford, 1991.

Jefferies N L. The Evolution of Carbon-14 and Tritium Containing Gases in a Radioactive Waste Repository. Nirex Safety Studies. NSS/R198, 1990.

Kemakta Konsult AB. Modelling of Water-flow, Barrier Degradation, Chemistry and Radionuclide Transport in the Near-Field of a Repository for L/ILW. Nagra Technical Report NTB 88–42, 1989.

Kunz C O. Radioactive Gas Production and Venting at Low Level Radioactive Waste Burial Site. Nuclear and Chemical Waste Management, Vol. 3, 185-190, 1982.

Mancinelli R L, Schulls W A, McKay C P. Methanol Oxidizing Bacteria Used as an Index of Soil Methane Content. J. Appl. and Env. Microbiol. Vol. 42, No 1, pp 70–73, 1981.

Matuszek J M. Biochemical and Chemical Processes Leading to Radioactive Transport from Low-Level Waste Burial Sites. Trans. Am. Nucl. Soc. Vol 34, pp 155-156, 1980.

Matuszek J M and Robinson L W. Respiration of Gases from Near-Surface Radioactive Waste Burial Trenches. Waste Management '83, Vol. 1, 423-427, Editor R G Post, 1983.

McCombie C, van Dorp F, Zuidema P. Impact of Performance Assessment on Swiss Projects for a L/ILW Repository. Proceedings of the NEA workshop on Near-Field Assessment of Repositories for Low and Medium Level Radioactive Waste, pp 55-69, OECD 1988.

McFarlane J C, Rogers R D and Bradley D V Jr. Tritium Oxidation in Surface Soils. A Survey of Soils Near Five Nuclear Fuel Reprocessing Plants. Env. Sci & Tech. Vol 13, 5, 1979.

Mishra S and Zuidema P. Modelling Gas Migration from a Low/Intermediate Level Nuclear Waste Repository. Proceedings of an NEA Workshop on Gas Generation and Release from Radioactive Waste Repositories (in press), 1991.

Morgan J E and Beetham C J. Review of Literature for Radium, Protactinium, Tin and Carbon. Nirex Safety Studies, NSS/R220, 1990.

Murphy C E, Boni A L, Tucker S P. The conversion of gaseous molecular tritium to tritiated water in biological systems. E I Du Pont De Nemours and Company, Savannah River Lab. Aiken, S. Carolina, DP-1422, 1976.

Nagra. Inventar und Charakterisierung der Radioaktiven Abfälle in der Schweiz. Nagra Technical Report Series, NTB 84-47. Nagra, Baden. 1984.

Nagra, Project Gewähr 1985: Nuclear Waste Management in Switzerland: Feasibility Studies and Safety Analyses, Project Report NGB 85-09, 1985.

Neretnieks I. Some Aspects of the Use of Iron Canisters in Deep Lying Repositories for Nuclear Waste. Nagra Technical Report NTB 85-35, 1985.

NRPB Bulletin No. 115, p 23, September 1990.

Phipps A W, Kendall G M and Harrison J D. Radiation Protection Dosimetry, Vol. 30, No. 3, pp 191-195, 1990.

Preece C M, Arup H and Gronvold F D. The Influences of Hydrogen and Carbon Dioxide on the Corrosion of Steel in Anaerobic Waste Storage Silos, SKBF/KBS Progress Report for the Swedish Final Repository for Reactor Waste, SFR 81-09, 1981.

Pruess K. Numerical Modelling of Gas Migration at a Potential Repository for Low and Intermediate Level Nuclear Wastes at Oberbauenstock, Switzerland. Nagra Technical Report NTB 89-28, 1990.

Rees J H and Rodwell W R. Gas Evolution and Migration in Repositories – Current status. Nirex Safety Studies NSS/G104, 1988.

Rodwell W R. Near Field Gas Migration – A Preliminary Review. Nirex Safety Series Report NSS/R200, 1989.

Sharland S M and Newton C K. The Long Term Prediction of Corrosion of Stainless Steel Nuclear Waste Canisters. Nirex Safety Series, NSS/R136, UKAEA, 1989.

Suresh B P. Gas Migration in Fractured Rock from a Low-Level Waste Repository Using a Two-Phase Flow Code. INTERA Technologies Report for the Swedish Nuclear Power Inspectorate, 1986.

Torstenfelt B. Chemical Degradation of Ion Exchange Resins in a Cement Matrix - A Review. RVC 89–160, ABB Atom. Nagra Internal Document, 1990

UNSCEAR. Sources, Effects and Risks of Ionizing Radiation. Report of the United Nations Scientific Committee on the Effects of Atomic Radiation, 1988.

West J M, Allen M R, Cave M R, Gardner S, Higgo J, Milodowski A E, Moody P, Pearce J, Reeder S, Ross C A M, Sibley P J. The Effect of Microbial Activity on the Near and Far Fields of a Swiss Type B Repository – a study of gross effects on structures, geochemistry, radionuclide sorption. Nagra Internal Report, 1991.

Whalen S C, Reeburgh W S, Sandbeck K A. Rapid methane Oxidation in a Landfill Cover Soil. Appl. Environ. Microbiol. Vol. 56, No. 11, pp 3405–3411, 1990.

Wiborgh M, Hoglund L O and Pers K. Gas Formation in a L/ILW Repository and Gas Transport in the Host Rock, Nagra Technical Report NTB 85-17, 1986.

Williams G M and Hitchman S P. The Generation and Migration of Gases in the Subsurface. Symposium, Methane – Facing the Problems, E. Midlands Conference Centre, Nottingham, 26–28 September, 1989.

Zuidema P and Hoglund L O. Impact of Production and Release of Gas in a L/ILW Repository: A Summary of the Work Performed within the Nagra Programme, Proceedings of the NEA Workshop on Near-Field Assessment of Repositories for Low and Medium Level Radioactive Waste, 97-114, 1988.

Zuidema P, van Dorp F and Knecht B. Gas Formation and Release in Repositories for Low and Intermediate-Level Wastes: An Issue of Potentially Decisive Importance. Proceedings of an International Symposium on the Safety Assessment of Radioactive Waste Repositories, Paris, 9-13 October, 1989.

APPENDIX 1

Gas Production as a Function of Waste Sort

This appendix describes the spreadsheet database developed for Nagra by Intera to calculate the volumes of the two principal gases, hydrogen and methane, that may be produced within a SMA repository, as a function of waste sort. The spreadsheet is designed to run within LOTUS 123 on an IBM 286 or compatible.

An illustration of the spreadsheet is provided in Annex 1 where it has been used to calculate the gas production for two waste streams BA-1a and BA-5, assuming a 4 GW energy production scenario.

INTRODUCTION

This document describes the spreadsheet database developed to calculate the volumes of gas generated within an SMA repository as a function of waste sort.

The spreadsheet is designed to run within LOTUS 123 on an IBM 286 or compatible. For illustration the Annex contains a copy of the spreadsheet as applied to two waste streams, BA-1a and BA-5. The volumes of waste arising have been calculated assuming a 4 GW energy production scenario.

DATABASE LAYOUT

The database is organised with the input data presented first followed by the calculated values (see Annex 1). Three main areas of data requirement can be identified for calculating the volumes of gas generated. These are:

- process specific,

- repository design specific,

- waste specific.

The input data are organised into three separate blocks accordingly. This allows changes in the associated parameters to be easily implemented and their impact on the results directly assessed.

The origin of the input data and the calculations used to determine the volumes of gas generated are fully documented in the following sections of this report. Within the database the major data sources are briefly summarised at the start and referenced using lower case letters in parentheses.

PROCESS SPECIFIC DATA

The following process specific data are required for the spreadsheet database.

Volume of Hydrogen Produced on Oxidising 10^6g of Metal [m^3]

In a repository environment hydrogen gas generation is associated with the corrosion of three main metals, namely steel, aluminium and zinc, under anoxic conditions. The key reactions can be summarised as follows:

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \tag{5}$$

$$2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2 \tag{6}$$

$$Zn + H_2O \rightarrow ZnO + H_2 \tag{7}$$
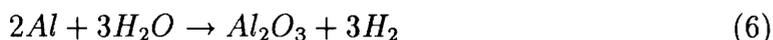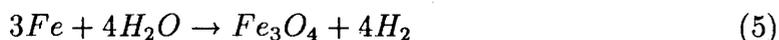
Assuming all the metal is consumed in these reactions, the volume of hydrogen gas produced can be calculated as follows:

$$\frac{M_H V m}{M_m A} ,$$

where

M_H is the number of moles H_2 produced [mols],

V is the molar volume of an ideal gas at STP [m^3 mol^{-1}],

M_m is the number of moles of metal consumed [mols],

A is the atomic mass of the metal [kg mol^{-1}], and

m is the total mass of metal [kg].

Thus 10^6g Fe produces 534 m^3 H$_2$,

10^6g Al produces 1245 m^3 H$_2$, and

10^6 Zn produces 345 m^3 H$_2$.

The spreadsheet database also requires input data for the rate at which gas is produced during anoxic metal oxidation.

The volume of metal equivalent to 1 mol of the metal is first calculated as,

$$\frac{A}{P_m} ,$$

where

P_m [kg m^{-3}] is the density of metal.

Then the volume of hydrogen generated from this volume of metal is determined based on the molar ratio of gas produced to metal consumed, as defined earlier (ie. equations (1), (2) or (3)) and accounting for the volume occupied by one mole of gas at STP.

The hydrogen production rate, per unit surface area of metal, R_H [m^3 m^{-2} a^{-1}] is given by:

$$R_H = \frac{V_H c}{V_m} ,$$

where

V_H is the volume of H$_2$ arising from 1 mole of metal [m^3 mol $^{-1}$],

c is the metal corrosion rate [m^3 m^{-2} a^{-1}], and

V_m is the volume occupied by 1 mole of metal [m^3 mol $^{-1}$].

The metal corrosion rates assumed are presented in Table 1 and are taken from reference Wiborgh et al (1986).

The resultant hydrogen production rates [m^3 m^{-2} a^{-1}] calculated for the three metals are summarised below.

Fe (steel)   =   4.19 x 10^{-3}

Al   =   3.36

Zn   =   7.39 x 10^{-2}.

Table A1.1 : Input Data and Parameter Values

Parameter	Fe (steel)	Al	Zn
atomic mass [kg mol^{-1}] density [kg m^{-3}] corrosion rate [m a^{-1}]	56 7.85×10^3 10^{-6}	27 2.7×10^3 10^{-3}	65 4.14×10^3 3×10^{-5}
molar vol. of ideal gas [m^3 mol^{-1}]	0.022414		

WASTE SPECIFIC DATA

The number of containers n per metre of tunnel is given by:

$$n = \frac{V_T E}{V_c L} ,$$

where

V_T is the tunnel volume [m^3],

E is the waste emplacement efficiency [-],

V_c is the volume of a single container [m^3], and

L is the tunnel length [m].

The length of tunnel with a particular waste type is given by:

$$\frac{N_w}{n} ,$$

where

N_w is the number of containers of a particular waste type.

The surface area of corrodible material [m²] is given by:

$$rm \, ,$$

where

    r is the ratio of surface area to mass [m³ kg⁻¹], and

    m is the total mass of metal [kg].

CALCULATED VALUES

The annual rate of hydrogen production [m³ a⁻¹] is given by:

$$R_H S_A \, ,$$

where

    S_A is the metal surface area [m²].

The total hydrogen production in one year is the sum of all sources, ie. steel, aluminium, zinc.

Microbial degradation of organic material under anoxic conditions results in both methane and carbon dioxide production. It is assumed that these gases are generated in equal volumes. Thus the annual methane production [m³ a⁻¹] is given by:

$$\frac{F M_o V}{2} \, ,$$

where

    F is the total gas formation rate per unit mass of organic material [mol kg⁻¹ a⁻¹]

    M_o is the total mass of organic material [kg], and

    V is the molar volume of an ideal gas at STP [m³ mol⁻¹].

The factor of 2 appears in the above expression because F represents the total gas production rate for both methane and carbon dioxide.

The total methane production in one year is the sum of all sources, ie. bitumen, plastics, ion exchange resins, cellulose.

The time to exhaust hydrogen from a particular metal source is given by:

$$\frac{V_{tot}m}{R_H S_A} ,$$

where

V_{tot} is the total volume of H_2 produced per unit mass of a particular metal [m^3 kg^{-1}],

m is the total mass of metal [kg],

R_H is the H_2 production rate per unit surface area [m^3 m^{-2} a^{-1}],

S_A is the metal surface area [m^2].

Finally, the time to exhaust methane sources is given by:

$$\frac{M_g M_o}{F M_o} ,$$

where

M_g is the number of moles of gas produced per unit mass of organic material [mols kg^{-1}],

M_o is the total mass of organic material [kg], and

F is the gas production rate per unit mass [mols kg^{-1} a^{-1}].

ANNEX

GAS PRODUCTION AS FUNCTION OF WASTE SORT   October 1992

PROCESS SPECIFIC DATA

Volume of H2 Produced on Oxidising 1Mg of Metal [m3]			Gas Production Rates for Metal Oxidation [m3/m2.a]		
1Mg Fe =	534	(c)	Fe (steel)	0.00419	(c)
1Mg Al =	1245	(c)	Al (aluminium)	3.36	(c)
1Mg Zn =	345	(f)	Zn (zinc)	0.0739	(c)

Amount of CO2+CH4 produced on Degradation of Organics [mols/kg]			Gas (CO2+CH4) Formation Rates for Anaerobic Degradation of Organics [mol gas/kg.a]		
Cellulose	37	(c)	Cellulose	0.7	(c)
Bitumen	37	(c)	Bitumen	0.05	(c)
Plastics	37	(c)	Plastics	0.05	(c)
IonExchangeResin	37	(c)	IonExchangeResin	0.05	(c)

DESIGN SPECIFIC DATA

Tunnel Xsectn	[m2]	165	(d)
Waste Emplacement Efficiency	[-]	0.33	(f)
Steel reinforcement in Liner	[Mg/m]	0.5	(f)

WASTE SPECIFIC DATA

Waste Sort	BA-1a	BA-5
1 Number of cont. [-]	66000 (a)	15752 (a)
2 Volume of cont. [m3]	0.216 (a)	0.216 (a)
3 Number of cont. per m tunnel [-]	252.0833	252.0833
4 Metres tunnel with waste [m]	261.8182	62.48727

CONTAINER COMPOSITION BY WEIGHT (Mg, i.e 1000Kg)

		BA-1a	BA-5
5	Container steel (b)	0.045	0.045
6	Container zinc (b)	0	0.004
7	Container reinforce (b)	0	0
8	Waste steel (b)	0	0.2115
9	Waste zinc (b)	0	0
10	Waste aluminium (b)	0	0.0235
11	Plastics (b)	0	0
12	Cellulose (b)	0	0
13	Bitumen (b)	0	0
14	Ion Exchange Resin (b)	0.075	0
15	Miscellaneous	0	0

SURFACE AREA TO WEIGHT RATIO FOR CORRODABLE [m2/Mg]

16	Container steel (b)	110	110
17	Container zinc (b)	1200	1200
18	Container reinforc (c)	43	43
19	Waste steel (b)	110	110
20	Waste zinc (b)	170	170
21	Waste aluminium (b)	50	50
22	Steel in liner (c)	43	43

CALCULATED VALUES

SURFACE AREA OF CORRODABLE MATERIALS [m2/Mg]
(Container comp. by weight * surf area to weight ratio)

23	Container steel	4.95	4.95
24	Container zinc	0	4.8
25	Container reinforc	0	0
26	Waste steel	0	23.265
27	Waste zinc	0	0
28	Waste aluminium	0	1.175
29	Steel in liner	21.5	21.5

HYDROGEN GAS PRODUCTION [m3/a]

30a	Per container Steel only	0.020741	0.118221
30b	Per container Zinc only	0	0.35472
30c	Per container Aluminium only	0	3.948
30d	Per container Total	0.020741	4.420941
31a	Per m3 waste Steel only	0.096021	0.547319
31b	Per m3 waste Zinc only	0	1.642222
31c	Per m3 waste Aluminium only	0	18.27778
31d	Per m3 waste Total	0.096021	20.46732
32a	Per m tunnel Steel only Excl. liner	5.228334	29.80151
32b	Per m tunnel Liner only	0.090085	0.090085
32c	Per m tunnel Steel only Incl. liner	5.318419	29.89159
32d	Per m tunnel Zinc only	0	89.419
32e	Per m tunnel Aluminium only	0	995.225
33	Per m tunnel Total incl. liner	5.318419	1114.536
34	Per m tunnel Total excl. liner	5.228334	1114.446

```
35 Total
   incl. liner        1392.459              69644.29
36 Total
   excl. liner        1368.873              69638.66


   METHANE GAS PRODUCTION [m3/a]

37 per container      0.042026                    0
38 per m3 waste       0.194566                    0
39 per m tunnel       10.59412                    0
40 Total              2773.733                    0


   CARBON DIOXIDE GAS PRODUCTION [m3/a]

41 per container      0.042026                    0
42 per m3 waste       0.194566                    0
43 per m tunnel       10.59412                    0
44 Total              2773.733                    0


   TOTAL H2&CH4 GAS PRODUCTION [m3/a]

45 Per container      0.062767              4.420941
46 Per container
   excl. Al&Zn        0.062767              0.118221
47 Per m3 waste       0.290587              20.46732
48 Per m3 waste
   excl. Al&Zn        0.290587              0.547319
49 Per m tunnel
       Total
   excl. liner        15.82245              1114.446
50 Per m tunnel
       Total
   incl. liner        15.91254              1114.536
51 Per m tunnel
   Steel only
   incl. liner        15.91254              29.89159
52 Total Repository
   incl. liner        4166.191              69644.29
53 Total Repository
   excl. Al&Zn        4166.191              1867.844


   TIME TO EXHAUST HYDROGEN SOURCES [a]
   (ERR indicates no source material for gas production)

54 Container steel         1158.603            1158.603
55 Container zinc          zero                3.890392
56 Container reinforcing   zero                zero
57 Waste steel             zero                1158.603
58 Waste zinc              zero                zero
59 Waste aluminium         zero                7.410714
60 Steel in liner          2963.867            2963.867


   TIME TO EXHAUST METHANE/CARBON DIOXIDE SOURCES [a]

61 Plastics                zero                zero
62 Cellulose               zero                zero
63 Bitumen                 zero                zero
64 Ion Exchange Resin       740                zero
65 Miscellaneous           zero                zero
```

OPERATIONAL WASTE (BA):Comprising mainly steel, bitumen, resin.

```
   DATA      a) NTB 84-47          d) NTB 88-55
   SOURCES   b) J.C. Alder (memo)  e) Cotton & Wilkinson
             c) NTB 85-17          f) estimate/assumption
```

APPENDIX 2   Determination of Radiological Consequences

The maximum annual individual dose to man arising from CH_3T, $^{14}CH_4$ and HT gases released from waste stream BA-1a has been calculated. The waste stream BA-KKG-1b has also been evaluated because it contains higher than average tritium and ^{14}C concentrations. The volume of this waste stream is however fairly small. The dose calculated is the committed effective dose equivalent as defined by ICRP (1977).

The relevant inventory data is given in Table A2.1.

Table A2.1: Tritium and ^{14}C Inventories for Two Waste Streams

Waste Stream	Volume of Waste [m^3]	Activity Conc. [Ci m^{-3}] T	^{14}C	Total Activity [Bq] T	^{14}C
BA-1a	14256	$2.3\ 10^{-5}$	$1.5\ 10^{-5}$	$1.2\ 10^{10}$	$8.1\ 10^{9}$
BA-KKG-1b	375	$1.3\ 10^{-2}$	$8.0\ 10^{-3}$	$1.8\ 10^{11}$	$1.1\ 10^{11}$

The volumes are taken from the waste specific data presented in Appendix 1 and the average activity concentrations are taken from Nagra (1984).

Methane Generation

The maximum gas production rate associated with ion exchange resin degradation suggested in Wiborgh et al (1986) and used for calculations in Appendix 1 is 0.05 mols of total gas ($CH_4 + CO_2$) per year per kg. This implies a maximum production rate (λ_p) for CH_4 of 0.025 mol per year per kg $\times$ 0.016 kg per mol = $4\ 10^{-4}$ per year assuming CH_4 comprises 50% of the total gas volume and the molar mass of CH_4 is 16g per mol.

Hydrogen Generation

It is assumed that only steel corrosion of the drums is relevant for this waste stream. The steel drums are 1.5mm thick (Nagra, 1984) and assuming a corrosion rate of 10^{-3} mm per year as in Appendix 1 implies $6.7\ 10^{-4}$ per year consumption of steel (Fe).

Radiomethane Release Rate (CH_3T; $^{14}CH_4$)

CH_4 could contain $^{14}CH_4$ or tritium. It is assumed that only 10% of carbon in ion exchange resins is converted to methane therefore only 10% of ^{14}C but that 100% of tritium in ion exchange resins goes to methane (see discussion in Section 3.2).

The release rate, R, (Bq a^{-1}) is given by:

$$R = f \, \lambda_p \, I$$

where f is the fraction of the Inventory converted to CH_4 (–)

λ_p is the fractional production rate (a^{-1})

I is the Inventory (Bq)

The total production rates (Bq a^{-1}) and production rate per metre of repository tunnel are summarised below. The data concerning waste emplacement efficiency and containers per metre of tunnel are documented in Annex 1.

Table A2.2: Radiomethane Production Rates

Waste Stream		Radiomethane Release Rate [Bq a^{-1}]	
		CH_3T	$^{14}CH_4$
BA-1a	Total	4.8 10^6	3.2 10^5
	Per m tunnel	1.8 10^4	1.2 10^3
BA-KKG-1b	Total	7.2 10^7	4.4 10^6
	Per m tunnel	1.0 10^7	6.4 10^5

Tritiated Hydrogen Release Rate (HT)

All tritium in the ion exchange resins is assumed to be rapidly lost to HTO in the (resaturated) near field, and transported to the steel drum corrosion sites. A single drum contains 45kg of steel (Annex 1) which if consumed at a rate of 6.7 10^{-4} per year is equivalent to 30g Fe per year. The corrosion equation ((2) Section 3.1) shows that 4 moles of water are required for every 3 moles of iron consumed. Thus corrosion of a single drum consumes $30 \times 72/168$ g of water, ie. 13g water per year (W_{cons}). Assuming a 30% porosity each drum contains:

$0.216 \text{ m}^3 \times 0.3 = 6.48 \ 10^{-2} \text{ m}^3$ water ie. $6.48 \ 10^4$ g of water (W$_{tot}$).

Thus assuming corrosion of the steel is fed only by water which has come from inside the drum and which has already taken up all the tritium in the waste, it follows that the total tritiated hydrogen production, P_{TOT} (Bq a^{-1}), is given by,

$$P_{TOT} = \frac{W_{cons} \ I_{tot}}{W_{tot}}$$

and the tritiated hydrogen production per metre tunnel, P_m (Bq a^{-1} m^{-1}) by,

$$P_m = \frac{W_{cons} \ I_m}{W_{tot}}$$

where W_{cons} is the annual weight of water consumed per drum [g a^{-1}]

W_{tot} is the total weight of water in drum [g]

I_{tot} is the total tritium inventory [Bq] reported in Table A2.1.

I_m is the tritium inventory per metre tunnel [Bq m^{-1}]

The tritiated hydrogen production rates are summarised in Table A2.3 for both waste streams. The inventory per metre of repository tunnel is calculated using the data presented in Annex 1 concerning the waste emplacement efficiency and number of drums per metre etc.

Table A2.3: Tritiated Hydrogen Production Rates

Waste Stream	Tritiated Hydrogen Production Rate [Bq a^{-1}]	
	Total	Per m tunnel
BA-1a	$2.4 \ 10^6$	$9.2 \ 10^3$
BA-KKG-1b	$3.6 \ 10^7$	$5.2 \ 10^6$

Maximum Annual Dose to Man

It is assumed that the gases travel rapidly through fractures/fissures into a single dwelling. The equilibrium concentration of radionuclides in the house, C (Bq m^{-3}), is given by:

$$C = \frac{A}{\lambda_v V}$$

where A is the release rate (Bq a^{-1})

λ_v is the house ventilation rate (8,800 a^{-1})

V is the house volume (250 m^3)

The maximum dose D (Sv a^{-1}) is given by:

$$D = O \, I \, C \, B$$

where O is the occupancy, assumed constant (8,760 h a^{-1})

I is the dose per unit inhalation (Sv Bq^{-1})

B is the breathing rate (1 m^3 h^{-1})

The ICRP do not offer advice specific to inhalation of methane containing tritium or C-14. However advice from NRPB (Phipps et al, 1990) suggests that using the same value as for CO_2, ie. 6.4 10^{-12} Sv Bq^{-1}, is pessimistic. This value is cautiously adopted here.

Tritium as HT gives a dose per unit intake four orders of magnitude lower than for HTO (Phipps et al, 1990). CH_3T also probably gives rise to a much lower dose than HTO (Phipps et al, 1990). Dose is probably determined by the fraction of HT or CH_3T which is converted to HTO before or during inhalation. Here a 1% fraction is assumed, which is thought to be pessimistic. The HTO dose per unit intake is 1.7 10^{-11} Sv Bq^{-1}. Therefore the inhalation dose conversion factor for the inhaled tritium in this scenario is 1.7 10^{-13} Sv Bq^{-1}.

The maximum doses arising from the ^{14}C or tritium substituted gases are summarised below. The doses have been calculated in two ways: first assuming that all the gas generated in a metre length repository travels rapidly to a house via a single fracture; and secondly, that all the gases from the waste stream travel to a single house. This situation is extremely improbable for BA-1a because in the unlikely event of it all being disposed of together it would occupy over 260 m of repository tunnel. The volume of BA-KKG-1b is much less and would occupy about 7 m of repository tunnel if it were all disposed of together. However, this appears extremely unlikely.

Table A2.4: Maximum Doses to Man from ^{14}C and Tritium Substituted Gases Derived from Specific Waste Streams

Waste Stream		Dose from ^{14}C and Tritium Containing Gases [Sv a^{-1}]		
		CH_3T	$^{14}CH_4$	HT
BA-1a	Total	$3.2\ 10^{-9}$	$8.2\ 10^{-9}$	$1.6\ 10^{-9}$
	Per m tunnel	$1.2\ 10^{-11}$	$3.1\ 10^{-11}$	$6.2\ 10^{-12}$
BA-KKG-1b	Total	$4.9\ 10^{-8}$	$1.1\ 10^{-7}$	$2.4\ 10^{-8}$
	Per m tunnel	$7.1\ 10^{-9}$	$1.6\ 10^{-8}$	$3.5\ 10^{-9}$

APPENDIX 3   Determination of Explosive Hazards

It is assumed that the gases travel rapidly through fractures/fissures into a single dwelling. The critical equilibrium inflow or generation rate, R_i, of a flammable gas for a house or void is given by:

$$R_i = f\lambda_v V$$

Where R_i is the critical inflow rate of gas to the house $(m^3\ a^{-1})$

> f is the lower explosive limit (LEL) expressed as the fractional volume of the original atmosphere (-), = 0.04 for hydrogen and 0.05 for methane, and

> λ_v is the house ventilation rate $(8,800\ a^{-1})$, and

> V is the house volume $(250\ m^3)$.

The values for λ_v and V are taken from UNSCEAR (1988) and are conservative values which assume a low ventilation rate $(1\ hr^{-1})$ and small house.

Hence for hydrogen gas R $= 8.8 \times 10^4\ m^3\ a^{-1}$, and
for methane gas R $= 1.1 \times 10^5\ m^3\ a^{-1}$.

The generation rates for hydrogen and methane are calculated in Appendix 1 for both waste streams. BA-5 contains no organic material thus no methane is produced. The volume of hydrogen gas evolved by this waste stream has also been calculated excluding the contribution from aluminium and zinc because there is considerable uncertainty concerning the timescales for its production via this process. Corrosion of aluminium and zinc is very rapid under alkaline conditions, thus the metal may be consumed shortly after being brought into contact with the concrete so that the hydrogen is released prior to emplacement and repository closure.

APPENDIX 4   Determination of Gas Pressure Effects

Time to saturation of the repository pore water

This calculation assumes no loss of gas through the walls of the repository, so that time to saturation, T_{sat}, is given by:

$$T_{sat} = \frac{C_{sol}}{R} \qquad (8)$$

Where C_{sol} is the solubility of hydrogen at a repository pressure of 4 MPa, and R is the gas production rate per cubic metre of repository pore volume.

The solubility of hydrogen at 25°C and 10^5 Pa is 1.54 x 10^{-3} g l^{-1} (kg m^{-3}). Henry's Law gives the solubility at 4 MPa and 25°C as:

$$C_{sol} = 0.0616 \text{ g } l^{-1} \text{ (kg m}^{-3})$$

The gas production rates (R) per cubic metre of repository pore volume can be obtained from the figures above by dividing by the repository cross-sectional area (165 m^2) and repository porosity (0.66) which gives:

$$R = \quad 0.92 \text{ kg m}^{-3} \text{ a}^{-1} \text{ for waste sort BA-5,or}$$
$$R = \quad 0.025 \text{ kg m}^{-3} \text{ a}^{-1}, \text{ if AL and Zn are excluded, and}$$
$$R = \quad 4.4 \text{ x } 10^{-3} \text{ kg m}^{-3} \text{ a}^{-1} \text{ for waste sort BA-1a}$$

Substituting the above values into equation (1) gives for waste sort BA-5:

$$T_{sat} = 24.4 \text{days}$$

including aluminium and zinc, and

$$T_{sat} = 2.5\text{a}$$

excluding aluminium and zinc. For waste sort BA-1a,

$$T_{sat} = 1.4\text{a}.$$

Maximum gas production rate without formation of free gas

In this calculation, the repository is assumed to have a circular cross-sectional area of 165 m^2, with an inner radius r_o of 7.25 m, and outer radius of 7.95 m. The concentration of dissolved gas inside the repository is assumed to be maintained at a constant value equal to the solubility limit. If free gas is not to be formed, the gas production rate must be balanced by the diffusive flux through the liner walls. The steady state analytical solution for the concentration $C(r)$ at radius r from the centre of the cylinder, with concentration maintained at C_{sol} at an inner radius of r_o is given by:

$$C(r) = C_{sol} + \frac{R}{2\pi D\phi}\ln(r_o/r) \qquad (9)$$

where

R is the gas production rate (100.2 or 2.7, 0.48 kg m^{-1} a^{-1}),

D is the effective diffusivity of hydrogen in water (3 x 10^{-2} m^2 a^{-1}),

ϕ is the porosity of the liner (0.15) and

C_{sol} is the solubility of hydrogen (6.16 10^{-2} kg m^{-3}) at a repository pressure of 4MPa.

If it is assumed that gas can be transported away from the repository sufficiently quickly (by a combination of advection and diffusion) to maintain a zero concentration level outside the liner of the repository (where r = 7.95 m) then equation (2) can be rearranged to give an expression for R:

$$R = -\frac{2\pi D\phi C_{sol}}{\ln(r_o/r)} \qquad (10)$$

Substituting the above values into (3) gives:

$$R = 1.89 \text{ x } 10^{-2} \text{ kg m}^{-1} \text{ a}^{-1}$$

This is an estimate of the maximum gas production rate which can be accommodated without the formation of free gas. Comparing this figure with the gas production rate estimates for the two waste streams (100.2 or 2.7 kg m^{-1} a^{-1} for BA-5 and 0.48 kg m^{-1} a^{-1} for BA-1a) indicates that even for the lower production rate, diffusion is insufficient to prevent the eventual formation of a gas phase, once the repository porewater becomes saturated. If a more realistic corrosion rate is assumed the gas production rates would decrease by at least a factor of 5-10, which is still insufficient to prevent the eventual formation of a gas phase.

Maximum overburden pressure to release all gas by diffusion

The solubility of hydrogen is assumed to increase linearly with pressure according to Henry's Law. It is therefore possible to calculate the pressure at which the solubility limit would be sufficient to maintain a diffusive flux through the liner. The solubility limit required for a given gas generation rate can be obtained by rearranging equation (3):

$$C_{sol} = -\frac{G}{2\pi D\phi}\ln\left(r_o/r\right) \tag{11}$$

Substituting the data values gives a range of solubilities of between 0.156 g l^{-1} for waste sort BA-1a, and (0.88 - 32.7) g l^{-1} for waste sort BA-5. Henry's Law gives the following expression for the equivalent pressure (P) required to obtain a higher solubility:

$$P = \frac{C_{sol}}{C_o}P_o, \tag{12}$$

where C_o, P_o denote solubility and pressure at STP. For waste sort BA-5,

$$P = (5.3 \text{ x } 10^4 \text{ or } 57) \text{ MPa}$$

and for waste sort BA-1a,

$$P = 10.1 \text{ MPa}$$

These pressures are clearly much higher than the expected repository overpressure of 4 MPa.

Diffusion coefficient required to release all gas by diffusion

Equation (4) may be rearranged to give an expression for the effective diffusivity of hydrogen in water:

$$D = \frac{G}{2\pi C_{sol}}\ln\left(r_o/r\right) \tag{13}$$

For waste sort BA-5, the required effective diffusivity is:

$$D = (159 \text{ or } 4.29) \text{ m}^2 \text{ a}^{-1}$$

and for waste sort BA-1a,

$$D = 7.6 \text{x} 10^{-1} \text{m}^2 \text{ a}^{-1}$$

Expulsion of Water from the Repository

Model of Water Expulsion

A simple one-dimensional model has been developed to monitor the changes in gas pressure and the fraction of water expelled (fractional gas saturation), as gas is produced at a constant rate throughout the repository. As a first approximation, it was assumed that water can escape only through the floor of the repository, permitting a one-dimensional formulation.

Schematic representation of   1-D Representation
vertical c/s through a repository
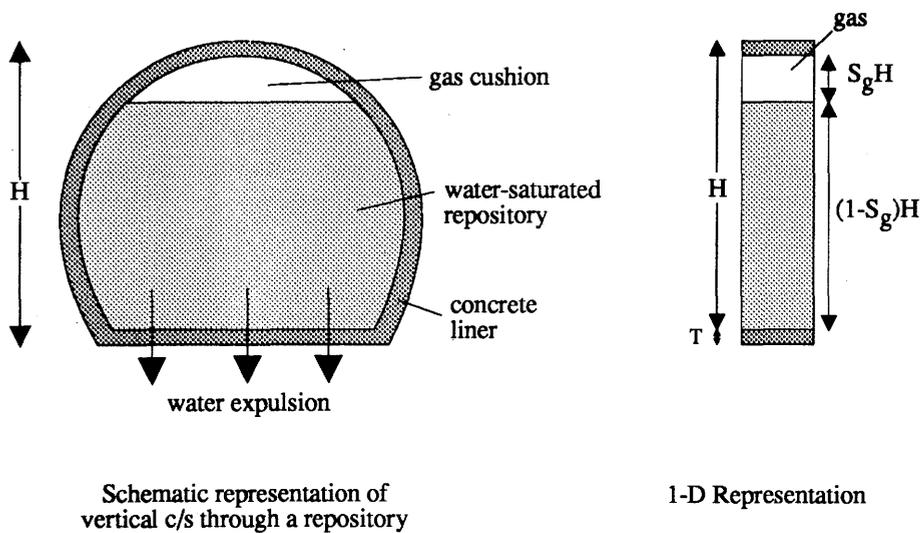
The diagrams above illustrate the model. The repository has a height H (14 m) and liner thickness T(0.7 m). In the 1-D model, the cross-sectional area of the floor is assumed to be unity.

A distinct gas phase is formed once the gas saturation, S_g, has exceeded its irreducible level, S_g^o. A value of 0.05 (5%) has been assumed for S_g^o. The overburden pressure on the outside of the liner at the repository roof is assumed to be 4 MPa (2 MPa variation) which is also the initial gas pressure, P_g^o. Hydrostatic pressure at the base of the repository, P_o is assumed to remain constant throughout, since the permeability of the backfill is several orders of magnitude larger than that of the liner. Hence P_o will be given by:

$$P_o = P_g^o + \rho_w g(H + T) \tag{14}$$

Where ρ_w is the density of water and g is the gravitational acceleration.

The rate at which water is expelled from the repository will be governed by the hydraulic conductivity of the liner, which can be expressed using Darcy's Law for the specific discharge, Q/A:

$$\frac{Q}{A} = -\frac{k}{\mu}\left(\frac{dP}{dz} + \rho_w g\right) \tag{15}$$

where k is the liner permeability and μ is the water viscosity. In the model, the pressure gradient across the liner is assumed to be linear:

$$\frac{Q}{A} = -\frac{k}{\mu} \left(\frac{P - P_o}{T} + \rho_w g \right) \tag{16}$$

where

$$P = P_g + \rho_w g H (1 - S_g) \tag{17}$$

is the pressure at the repository base, inside the liner.

The rate of water expulsion is also equal to the rate of change of water saturation in the repository, and consequently to the rate of increase of gas saturation:

$$\begin{aligned} \frac{Q}{A} &= \frac{d}{dt}(H\phi A S_w) \\ &= H\phi A \frac{d}{dt}(1 - S_g) \\ &= -H\phi A \frac{dS_g}{dt} \end{aligned} \tag{18}$$

where S_w is water saturation, ϕ is repository porosity, and A is the area of the repository floor.

Equating (16) and (18) and setting A to unity gives an expression for the rate of change in gas saturation, which depends on the gas pressure and the gas saturation:

$$\phi \frac{dS_g}{dt} = \frac{k}{\mu H} \left(\frac{P_g + \rho_w g H(1 - S_g) - P_o}{T} + \rho_w g \right) \tag{19}$$

Substituting for P_o, (19) becomes

$$\phi \frac{dS_g}{dt} = \frac{k}{\mu H} \left(P_g - P_g^o - \rho_w g H S_g \right) \tag{20}$$

The gas pressure is governed by the equation of state for the gas. If there are M moles of gas per unit volume (at STP) initially in the repository and gas is generated at a rate of G moles per second, then at time t, the total number of moles is given by

$$\begin{aligned} M S_g^o V_s + Gt &= M S_g^o V_s + \frac{V_s M G t}{V_s M} \\ &= M V_s (S_g^o + gt) \end{aligned} \tag{21}$$

where g $(G/V_s M)$ is the gas volume generation rate per unit void space (m^3 m^{-3} s^{-1} at STP) and V_s is the repository void space.

The gas equation at constant temperature may be written as:

$$\frac{pV}{m} = constant \tag{22}$$

where m is the number of moles of gas at pressure, p and volume V. The gas pressure P_g at time t is therefore related to the initial pressure, gas saturation S_g and generation rate g by the following:

$$\frac{P_g^o S_g^o V_s}{M S_g^o V_s} = \frac{P_g S_g V_s}{M V_s (S_g^o + gt)} \tag{23}$$

Hence the gas pressure at time t is given by:

$$P_g = \frac{P_g^o}{S_g}(S_g^o + gt) \tag{24}$$

This expression may be substituted into (20) to form a first-order non-linear differential equation, which may be solved numerically. This was achieved using a fourth-order Runge-Kutta method (1980), programmed on a PC. Calculated values of gas saturation and gas pressure were output to a file at each time-step. The results could then be displayed using a proprietary graphics software package.