Gas Generation in Radioactive Wastes - MAGGAS Predictive Life Cycle Model

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ABSTRACT

Gases may form from radioactive waste in quantities posing different potential hazards throughout the waste package life cycle. The latter includes surface storage, transport, placing in an operating repository, storage in the repository prior to backfill, closure and the post-closure stage. Potentially hazardous situations involving gas include fire, flood, dropped packages, blocked package vents and disruption to a sealed repository. The MAGGAS (MAGnox GAS generation) model was developed to assess gas formation for safety assessments during all stages of the waste package lifecycle. This is a requirement of the U.K. regulatory authorities and Nirex and progress in this context is discussed. The processes represented in the model include: Corrosion, microbial degradation, radiolysis, solid-state diffusion, chemico-physical degradation and pressurisation. The calculation was split into three time periods. First the 'aerobic phase' is used to model the periods of surface storage, transport and repository operations including storage in the repository prior to backfill. The second and third periods were designated 'anaerobic phase 1' and 'anaerobic phase 2' and used to model the waste packages in the post-closure phase of the repository. The various significant gas production processes are modeled in each phase. MAGGAS (currently Version 8) is mounted on an Excel spreadsheet for ease of use and speed, has 22 worksheets and is operated routinely for assessing waste packages (e.g. for ventilation of stores and pressurisation of containers). Ten operational and decommissioning generic nuclear power station waste streams were defined as initial inputs, which included ion exchange materials, sludges and concentrates, fuel element debris, graphite debris, activated components, contaminated items, desiccants and catalysts.

INTRODUCTION

In the U.K., the British Nuclear Group operates some Magnox reactors and is decommissioning others, British Energy Generation Ltd is operating AGRs and the Sizewell B PWR, and all reactors will be decommissioned in due course. The operational wastes arising from Magnox and AGR gas-cooled graphite-moderated reactors include ion exchange (IX) materials, sludge and concentrates, AGR fuel element graphite and, from the Magnox reactors, fuel element debris (FED), graphite, stainless and carbon steels (SS & CS respectively), aluminium (Al), nimonic and zirconium (Zr) [1]. In addition there are larger items generally classified under the headings of miscellaneous activated components (MAC), e.g. control rods, and miscellaneous contaminated items (MCI), e.g. filters. A range of desiccants (silica gel, activated alumina, molecular sieve) will also require treatment although these tend to be ILW due solely to tritium. The main PWR wastes requiring consideration of gas production are chemical and volume control system (CVCS) IX resins, primary filters and non-CVCS primary IX resin.

A wide range of materials arise from the decommissioning of a Magnox reactor, in particular metals mainly SS, CS, Magnox, Al and Zircaloy [1]. Also cellulose, oil and grease, organic materials, such as acetic acid, aldehydes,

ketones, citrates, succinic acid and amines used for chemical treatments and decontamination, and organic IX materials. In addition there will be a number of plastic, polymer and rubber based materials spread fairly widely throughout the wastes, and may be present in halogenated or non-halogenated form. Decommissioning wastes from Final Site Clearance (FSC) will consist mainly of concrete, rubble and other construction materials, steel from pipe, ducting, boilers and other large plant items. Some is likely to be decontaminated and some will be LLW.

The current waste management strategy is for the routine packaging and disposal of operational Low Level Waste (LLW) to the U.K. national shallow disposal facility at Drigg in Cumbria. Operational Intermediate Level Waste (ILW) is accumulated on stations in purpose built storage facilities and following shutdown these wastes would be retrieved and packaged for disposal during the period of preparation of the station for long-term care and maintenance (C&M). At the end of the C&M period, the station would move into FSC, where the bulk of the decommissioning waste will arise. At some time during the C&M period, it is expected that a U.K. deep disposal facility will become available and all operational and decommissioning wastes will eventually be disposed of in this way. Some changes to reactor waste management and decommissioning policy may stem from the recent public consultation on Nuclear Decommissioning Authority (NDA) draft Strategy and the current review by The Committee on Radioactive Waste Management (CoRWM) of options for managing those U.K. radioactive wastes for which there is no agreed long-term solution.

APPLICATIONS INVOLVING PROGRESS WITH REGULATORS AND STAKEHOLDERS

Under current national and British Nuclear Group policies, radioactive Magnox reactor ILW will ultimately be encapsulated in cement (or exceptionally polymer) based matrix (wasteform) in metal waste containers (the wasteform and waste container representing a completed waste package). As now planned, this will be followed by interim storage at power station sites, transport to the repository and deep disposal underground. The exact timescale for these stages is under discussion. Waste producers are required to demonstrate that they understand and can control where appropriate, risks resulting from gas generation, including hydrogen gas (H_2) flammability, throughout the whole package life-cycle. The regulatory background includes the Nuclear Installations Inspectorate (NII) covering mainly operational issues such as retrieval, packaging and interim storage and the Environment Agency (EA) and the Scottish Environmental Protection Agency (SEPA) covering discharges to the environment and post-closure repository safety. In addition, Nirex operate a 'Letter of Compliance' process where proposed waste packages are assessed against the Nirex *Waste Package Specifications* to ensure that compliant waste packages do not threaten any aspect of the *Generic Disposal System* transport, operational or post-closure safety cases.

The following potentially hazardous gas-related situations can arise during the lifecycle of a waste package.

- Initial acute corrosion rates of encapsulated metal wastes resulting in high gas production rates at the time of encapsulation and for weeks/months following requiring e.g. monitoring and forced ventilation.
- Degradation of the wasteform resulting in enhanced corrosion of metallic waste and waste container.
- Interim store degradation resulting in enhanced external corrosion of the waste container and possible ingress of water to packages giving enhanced corrosion of metallic wastes and internal waste container corrosion.
- Fire producing a high rate of gas and steam evolution.
- Flood producing very enhanced external corrosion rates for waste containers, enhanced corrosion of metallic wastes and initiation of pitting/crevice corrosion, which may cause long lasting gas generation.
- Dropped packages where internal build-up of H_2 could be ignited in an incident, particularly where the waste container is breached.
- Accumulation of corrosion products within the vent/filter, blocking it and resulting in pressure build-up.
- Post-closure re-saturation of the wasteform in a sealed repository resulting in substantial gas pressure causing fracture of the backfill, so enhancing gas, groundwater and radionuclide movement.
- H_2 permeating to the surface represents a potential hazard in buildings, similar to the evolution of CH_4 from waste disposal sites, subsequently built on.

Gas production from waste packages will therefore have an effect on the design of the encapsulation facility and interim store in terms of ventilation rates, and on the repository performance in terms of the potential risk to the public from certain isotopes. The waste producer, therefore, needs a quantitative knowledge of the gas production propensity of the range of packaged wastes, and this was the original motivation for the development of the

MAGGAS code. Based on these considerations, MAGGAS has been designed to be sufficiently flexible to model gas generation for a wide range of packaged waste types, conditions and time scales (from encapsulation, through storage, transport and repository emplacement, to post closure), so that it can be applied without significant further development to most waste management scenarios. The main gas generating processes incorporated into the model are corrosion, microbial degradation and radiolysis. Release of gases containing H-3, and pressurisation of containers resulting from bulk gas generation can also be modelled.

In terms of application to actual systems, MAGGAS has been used to estimate the gas production rate from (a) Magnox metal encapsulated in cement based matrix as is currently being carried out, (b) IX resin encapsulated in polymer, drums of which are currently in store at Trawsfynnydd power station, and (c) Magnox FED simply containerised for interim storage, which is one current strategy for some stations. Magnox station packaged ILW stores are under construction at Hunterston A and Berkeley and planned for Hinkley A amongst others. Other applications are the prediction of gas production rates with time in a Station storage environment. This allows the potential for H_2 accumulation to be tested against the natural air change rate of the environment for passive storage or highlight the need for forced ventilation during the early period of acute corrosion. The effect of fire conditions on gas generation from waste packages may be assessed. MAGGAS applies also to the process of cement encapsulation where prediction of the high gas production rates is needed to ensure the ventilation system is designed appropriately.

MAGGAS model development and use has been performed under the Nuclear Research Schedule (NRS) of Safety Related R&D work as agreed each year with the Nuclear Installations Inspectorate by the British Nuclear Group, Reactor Sites.
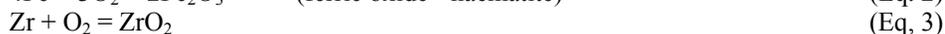
MODELLING GAS GENERATION

Operational wastes are assumed to be encapsulated during the C&M Preparations period. The gas generation rate is highest immediately after encapsulation and for a further 5 years or until a steady state is established under interim storage. The packaged waste could remain at the waste producers' site for 20-30 years before transport to the repository, and aerobic conditions will prevail during this time. Once transported to the repository and still under aerobic conditions, the waste will be emplaced but not backfilled for up to 50 years during operation of the repository. Aerobic conditions will pertain during repository operations and for some time into the backfilling period. During these periods, there is corrosion of Magnox and Al to produce H_2, microbial degradation of cellulose and oil to produce carbon dioxide and radiolysis of cellulose, oil, water, IX resins, plastics and rubber to produce mainly H_2.
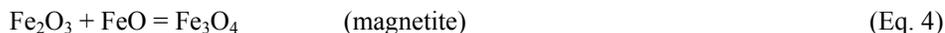
The post-closure period is modelled as anaerobic phase 1, which covers early post-closure, low salinity conditions and anaerobic phase 2 covering late post-closure, high salinity conditions. During these periods, the main processes are corrosion of Magnox, Al, CS and SS to produce H_2 and microbial degradation of cellulose to produce CO_2, CH_4 and H_2. Waste container pressurisation (blocked vent) and tritium release (due to metal corrosion) are modelled for all phases. Design of the MAGGAS code captures more realistic scenarios such as the effect of timing of the groundwater re-saturation on the gas generating mechanisms, taking the overall timescale out to $\geq 1,000$ years for the post-closure situation. When the repository is backfilled, post-closure begins and gas production can be modelled for 100 years plus, though declining dramatically after 20,000 years. Changes in biosphere states over a longer timescale are unlikely to affect gas production. Seismic events could disturb wastes, disrupt passive films on metals and re-start corrosion and gas production if enough metal is still present. This effect has not been modelled. The main gas generating processes modelled in MAGGAS are described below.

Corrosion

Under aerobic conditions steel (CS, SS) and zirconium alloy (mainly Zr) corrode to give oxides and no gas.

$2Fe + O_2 = 2FeO$	(ferrous oxide)	(Eq, 1)
$4Fe + 3O_2 = 2Fe_2O_3$	(ferric oxide - haematite)	(Eq. 2)
$Zr + O_2 = ZrO_2$		(Eq, 3)

Under anaerobic conditions steel (CS/SS) and Zr corrode to give oxides and H_2.

$Fe_2O_3 + FeO = Fe_3O_4$ (magnetite)   (Eq. 4)
$3Fe + 4H_2O = Fe_3O_4 + 4H_2$ (Eq. 5)
$Zr + 2H_2O = ZrO_2 + 2H_2$ (Eq. 6)

Mg and Al corrode to give hydroxides (hydrated oxides) irrespective of the availability of O_2.

$Mg + H_2O = MgO + H_2$ (Eq. 7)
$2Al + 3H_2O = Al_2O_3 + 3H_2$ (Eq. 8)
$Mg + 2H_2O = Mg(OH)_2 + H_2$ (Eq. 9)
$2Al + 6H_2O = 2Al(OH)_3 + 3H_2$ (Eq. 10)

The corrosion rate of carbon steel is greater than for stainless steel and both are increased by temperature and the presence of chloride. The corrosion rate of Al is greater than for steel and is enhanced by Na and K ions and galvanic corrosion in the presence of chloride but decreased by Ca, which forms a protective film. The rate is fairly constant from 30°C - 80°C, a minimum at pH 6 and increases above and below this. The corrosion rate of Magnox is also high and depends upon temperature and aggressive ions with two orders of magnitude increase from 30°C to 80°C. The rate is controlled by buffering to pH ~10.4 by $Mg(OH)_2$ and increases as pH falls from 13.0 to 10.4. Chloride and galvanic corrosion increase the rate as does spalling of the protective oxide film. Cement encapsulation decreases the corrosion rate of metals due to oxide films restricting the movement of H_2O and H_2. However, the corrosion film can represent an increase in volume over the base metal and may cause cracking of the cement matrix, rupture of the protective film and periodic enhancement of the corrosion rate.

For interim storage and the operational phase of the repository, conditions are aerobic at constant pH and about 50°C with the presence of aggressive/passive ions. For the repository post-closure period the conditions will be initially aerobic followed by anaerobic, at about 35°C and re-saturated with groundwater at pH 12, eventually with high Na and Cl ion concentrations. Corrosion of steels, Magnox and Al is of the same functional form producing H_2 with water, where the H_2 generation rate is linearly related to the corrosion rate. Magnox/Al react under aerobic conditions where O_2 is constant and H_2O restricted, and Magnox/Al/steels react under anaerobic conditions where O_2 is restricted and H_2O constant. The characteristic times for acute corrosion rates are set much shorter than for the chronic rates. The acute rate is applied to un-passivated metal surfaces and reduces to the chronic rate as passivation occurs with no account taken of spalling. Corrosion rate data is set for appropriate pH, temperature and Na and Cl ion concentrations, and metals modeled as plates or spheres to achieve the correct surface area/volume ratio.

Microbial degradation

Organic materials (cellulosics, oil products (bitumen) and simple non-polymeric molecules) form substrates for microbial degradation. Cellulosics are long-chain polymers not subject to immediate microbial degradation but are chemically degraded to shorter chain organics and then to glucose which readily undergoes microbial degradation. Oil products and simple organics will degrade directly by microbial action. Aerobic microbial degradation produces CO_2 and anaerobic microbial degradation produces CO_2, H_2 and simple organics which will further degrade to produce CO_2, H_2 and CH_4. Chemical degradation favours high or low pH whereas microbial activity favours neutral pH and the presence of substrates and chemicals may cause enhancement or inhibition.

Under aerobic conditions, cellulose is hydrolysed to glucose that reacts with O_2 to form CO_2 and H_2O.

$(C_6H_{10}O_5)_n + nH_2O \rightarrow nC_6H_{12}O_6$ (Eq. 11)
$C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O$ (Eq. 12)

Anaerobic microbial activity hydrolyses organics to produce alcohols, carboxylic acids, CO_2 and H_2. Hydrolysis of alcohols produces H_2.

$C_6H_{12}O_6 + H_2O = C_2H_5OH + CH_3COOH + 2CO_2 + 2H_2$ (Eq. 13)
$C_2H_5OH + H_2O = CH_3COOH + 2H_2$ (Eq. 14)
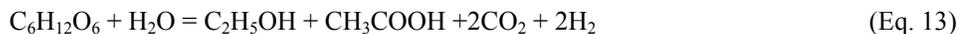
Methanogenic bacteria produce methane from acetic acid, CO_2 and H_2.

$$CH_3COOH = CO_2 + CH_4 \tag{Eq. 15}$$
$$CO_2 + 4H_2 = CH_4 + 2H_2O \tag{Eq. 16}$$

The action of sulphate-reducing and nitrate-reducing bacteria on sulphate and nitrate ions will produce H_2S and N_2 instead of CH_4.

$$(SO4)2\text{-} \rightarrow H2S \tag{Eq. 17}$$
$$(NO3)\text{-} \rightarrow N2 \tag{Eq. 18}$$

In MAGGAS, reactions are divided into aerobic and anaerobic, and reactants represent "pools" of chemicals, which are grouped together. For example, chemical degradation of cellulose is modelled as one process, where cellulose is used to represent all organic substrates and degradation due to $(SO_4)^{2-}$ and $(NO_3)^-$ is neglected. Inclusion of the effect of microbial populations and any enhancing or inhibiting chemicals, not part of the reaction chain, are excluded to avoid non-linearity. The overall mechanism is complex involving aerobic and anaerobic conditions, differing pH values and the presence of inorganic anions and microbial populations. The equations corresponding to the reactions given in equations 11-16 (or approximations) are solved analytically and depend on the initial concentrations of cellulose and water.

Radiolysis

Radiolysis of cement pore water and organics will be a function of the internal and external radiation dose and the nature of the organic material. Radiolysis of plastics, resins and cellulosics produces small molecules which includes H_2. Radiolysis of water produces H_2, H_2O_2 and O_2. In cement, the O_2 is usually absorbed and only H_2 is evolved. Metals do not produce gas under irradiation but products of radiolysis may enhance gas production by enhancing corrosion. Exceptions are the inorganic IX materials such as zeolites (e.g. Na-aluminosilicate) which produce gas from radiolysis of the water contained within their pore structure. Radiolysis of polymers can produce H_2 plus small amounts of CO_2, CO and various hydrocarbons.

The main radionuclides taken into account in MAGGAS are H-3, C-14, Fe-55, Fe-59, Co-60, Ni-59, Ni-63, Sr-90, Nb-94, Tc-99, Ru-106, I-129, Cs-134, Cs-137, Ce-144, Eu-154, U-235, U-238, Pu-238, Pu-239, Pu-240, Pu-241 and Am-241. The energy release rate is derived for these radionuclides for α and β/γ-radiation as the specific product yields differ. The energy deposition rate is examined for each component in the waste stream for the appropriate G-value, i.e. number of molecules of gas produced per 16 aJ (100 eV) energy deposited. About 90% of the γ-radiation generated by a wasteform is assumed to be absorbed internally by the waste package contents and allowance is made for decay and reduction in activity with time. If a component is present at 20 wt% of a waste stream then it is assumed to absorb 20% of the radiation presented. Radiolysis decreases with time and mainly is only significant during the initial 50 or so years, so constant amounts of components are assumed with no removal by corrosion or microbial processes.

OPERATION OF THE MAGGAS MODEL AND WORKSHEETS FOR PACKAGED WASTES

The MAGGAS model has the capability to make the following calculations, while taking account of the effect and timing of temperature variations and groundwater re-saturation of the repository on the gas-producing mechanisms:

- Gas generation from the anaerobic corrosion of mild and stainless steels in waste and waste containers.
- Gas generation from the aerobic and anaerobic corrosion of Magnox and aluminium in waste.
- Non gas-generating aerobic corrosion of uranium in waste, and subsequent gas generation from the anaerobic corrosion of uranium.
- Gas generation from the aerobic and anaerobic microbial degradation of cellulose in the waste.
- Gas generation from the aerobic microbial degradation of oil and grease in the waste.
- Gas generation from the radiolysis of cellulose, oil, other organics, organic ion exchange resins, halogenated plastics, condensation polymers, other non-halogenated plastics, halogenated rubbers, non-halogenated rubbers and water in the waste packages by twenty-three pre-defined (and up to twelve user-defined) radio-nuclides in the waste.
- Release of radioactive tritium as tritiated H_2 and of C-14, during the corrosion of metal waste.

- Release of radioactive tritium as tritiated H_2 by diffusion from metal waste.
- Release of radioactive tritium and C-14 due to the degradation of graphite.
- Pressure rise inside a sealed waste container or a container with a blocked or partially blocked vent.

Version 8, now current, of the MAGGAS model (MAGGASv8.xls) is mounted on an Excel 97 spreadsheet and the main spreadsheet contains the following twenty-two worksheets:

- A header worksheet that includes a version history.
- Three worksheets that contain the user-specified input data.
- Six worksheets that provide additional standard data and data derived from the user input values.
- Nine worksheets containing calculated results. The results of the main calculations of bulk gas generation from corrosion, microbial degradation and radiolysis, of release of tritium and carbon-14 as gases, and of container pressurisation, are reported on seven worksheets, with two more worksheets reporting the combined bulk gas generation and active gas release results.
- A worksheet that provides access to options for plotting the calculated results.
- Two worksheets that verify that the total mass in the system is conserved and that the combined rate of consumption/production of chemicals is zero.

The three worksheets containing the user-specified input divide the data into three categories:

- The first worksheet holds the general input data, including a name or title to identify the calculation, and the time points at which output is required.
- The second worksheet holds the data defining the contents of the waste stream, including the amounts of bulk materials, the inventories of radionuclides, properties of the encapsulation grout, the waste container size and composition, and the temperature profile of the waste over the period of the calculation.
- The third worksheet holds the remaining user-specified data required for the calculations, including metal geometries and initial sizes, rate data for corrosion and microbial degradation, distributions of H-3 and C-14 between wastes, and the container vent properties required to determine pressurisation.

In addition to the main spreadsheet in which the calculations are performed, a secondary spreadsheet, MAGGASPlot(v8).xls, is available for plotting the results. MAGGASPlot can be linked to the results of calculations performed in up to twenty copies of the main MAGGAS spreadsheet. It provides the same functionality as the worksheet for plotting results within the main spreadsheet, but additional plotting functionality is provided allowing straightforward comparison between different calculations. There is also a library file named ODEPack.dll, which uses a standard numerical solution algorithm for efficient solution of ordinary differential equations.

VERIFICATION

The verification procedure was based on the IAEA definition [2]: "A mathematical model, or corresponding computer program, is verified when it is shown that the program behaves as intended, i.e. that it is a proper mathematical representation of the conceptual model and that the equations are correctly encoded and solved." The verification procedure for MAGGAS consisted of three parts:

1. A verification of the analytical form of equations comprising the conceptual model to ensure that the equations and solutions are correct and written as intended.
2. A verification of the correct incorporation of the model equations into the spreadsheet model.
3. A verification that outputs from the spreadsheet are in agreement with results calculated directly from the equations in the analytical model.

Parts 1 and 2 confirm that the equations that represent the conceptual model have been written as intended, solved correctly and encoded correctly into the spreadsheet. Part 3 confirms that the solutions to the equations form a good mathematical representation of the conceptual model. An automated testing procedure has been set up in an additional spreadsheet so that Part 3 can easily be repeated for each new version of the model. Overall, verification has been successfully completed on the correct analytical form of the model equations and their incorporation into the spreadsheet model.

APPLICATION OF MAGGAS TO GENERIC WASTE STREAMS

To simplify overall prediction for single or mixed waste streams, generic categories were identified as organic IX, sludges and concentrates, and Magnox metal FED. In addition Magnox graphite debris, contaminated gravel, MAC, MCI, desiccant and catalyst, high activity IX material and Berkeley Centre waste are identified streams. MAGGAS was used to calculate gas generation rates for these generic waste streams, see Fig 1. Table I shows peak values of predicted gas production rates. From these, wastes are classified into four categories as follows in terms of their gas production propensity: No gas produced; Gas produced but volume, toxicity and flammability unlikely to affect safety; or Volume, toxicity, corrosion or flammability may affect safety; or Volume, toxicity, corrosion or flammability is likely to affect safety.
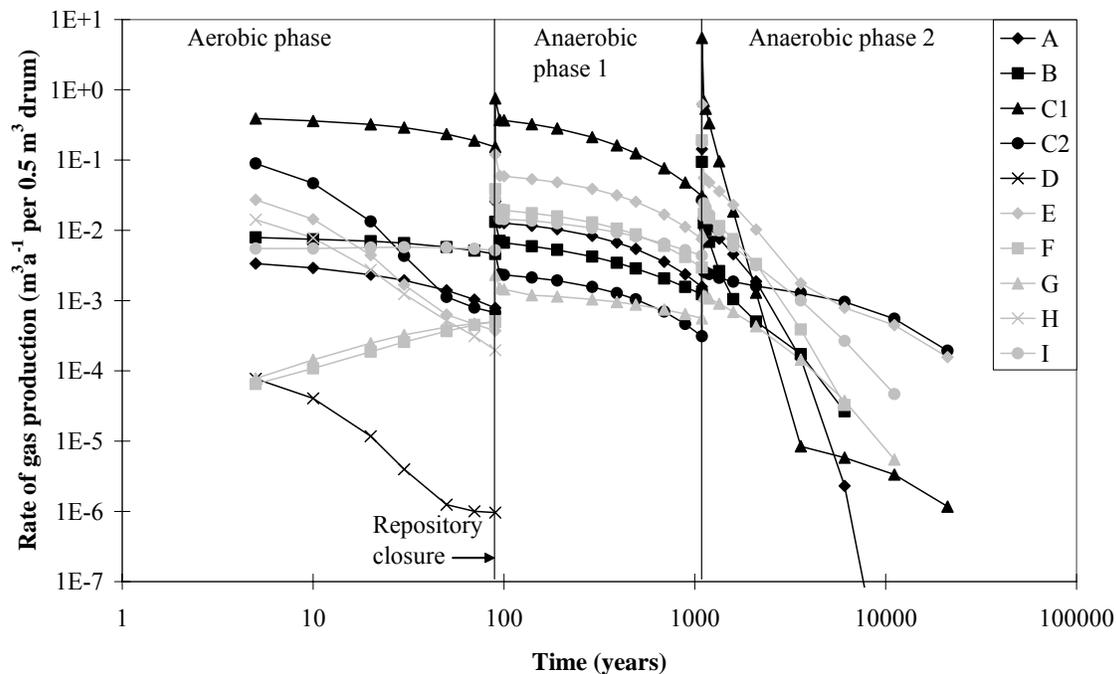

Fig. 1. Predicted gas production rates over the waste package lifecycle for various waste materials

APPLICATION OF MAGGAS TO PARTICULAR WASTE SCENARIOS

The MAGGAS code focuses on various waste streams of interest in terms of gas generation rates, in particular those comprising reactive metals such as Magnox and Al pond skips (fuel containers) in cement. The generation rates were quite high for the aerobic and post-closure anaerobic phases, as expected, particularly when aggressive ions accessed the system. This analytical approach was extended to other waste streams including a typical AGR Pond Water treatment Plant (PWTP) organic IX resin in cement, Magnox (near pure magnesium) in polymer, organic IX resin in polymer and vent size and container pressurisation for Magnox packages under normal and fire conditions. An assessment was also made of the gas production tendency of Magnox stored in steel containers but not encapsulated in cement. These assessments included validation of the corrosion models and a consideration of α-radiolysis and microbial degradation of oils as contaminants.

Magnox fuel element debris (FED) in cement

Two MAGGAS calculations were needed to describe gas generation from cement encapsulated FED in 3 m^3 stainless steel box waste containers, firstly Magnox in direct contact with cement and secondly Magnox in direct contact with moist air in macro-voids within cement. The bulk H$_2$ generation, and the release of both H-3 and C-14, arising from Magnox corrosion are determined using MAGGAS (with minor modifications for C-14). The corrosion rate for the fraction of Magnox in the macro-voids was determined to be 550 x 10^{-6} m a^{-1}, with an uncertainty estimated as an order of magnitude. The rate chosen does not allow for the passivation of the corrosion

reaction with time and is an over-estimate for longer time scales. The maximum gas generation and gaseous radionuclide release rates assuming best estimate wasteform properties were calculated as 84 m^3 a^{-1} for H_2, 2.9 TBq a^{-1} for H-3 and 60 x 10^{-6} TBq a^{-1} for C-14, all per 3 m^3 box. A worse case combination of wasteform properties could increase these rates by factors of 30, 2 and 30 respectively. In a grout with uncorroded Magnox in macro-voids, the gas generation rates remain significantly higher than for a grout with no macro-voids. The Magnox in the macro-voids corrodes completely in 1.4 years if the 'base case' wasteform properties are assumed, but this corrosion could take between 0.1 and 2 years. The Nirex transport requirement for the total gas generation rate generally is met only when Magnox in the macro-voids has completely corroded. The release rates of H-3 and C-14 in combination fall well within the Nirex transport requirement for radiotoxic gases at all times. The study recommended that the uncertainty in the reported gas generation rates could be improved if the large uncertainty in the corrosion rate for Magnox in the macro-voids was reduced. Over short timescales after packaging, it is unlikely that a constant corrosion rate of Magnox in the macro-voids, as used in the calculations, will be appropriate and more detailed profiles of the gas generation rates may be needed.

Table I. Maximum Predicted Gas Production Rates for various Waste Materials

#	Waste Stream	Maximum Rate of Gas Production m^3 a^{-1} / 0.5m^3 drum	Rank	Phase of Maximum Rate	Main Contributors to Maximum Predicted Gas Production Rate
A	IX Material	143 x 10^{-3}	6	Anaerobic 2	Corrosion of CS
B	Sludge and concentrate	93.7 x 10^{-3}	7	Anaerobic 2	Corrosion of Magnox
C1	Grouted FED	5.47	1	Anaerobic 2	Corrosion of Magnox
C2	FED treated by Dissolution	179 x 10^{-3}	4	Aerobic	Radiolysis of water
D	Magnox, graphite contaminate gravel	148 x 10^{-6}	10	Aerobic	Radiolysis of water
E	MAC	623 x 10^{-3}	2	Anaerobic 2	Corrosion of steels
F	MCI	191 x 10^{-3}	3	Anaerobic 2	Corrosion of CS
G	Desiccant and catalyst	8.83 x 10^{-3}	9	Anaerobic 2	Corrosion of steels
H	High activity IX Material	27.5 x 10^{-3}	8	Aerobic	Radiolysis of IX materials and water
I	R&D Waste	179 x 10^{-3}	4	Anaerobic 2	Corrosion CS & Magnox

Aluminium pond skips in cement

These are 100% Al pond skips with Cs contaminated corrosion film combined with an adherent layer of sodium silicate from pond water chemical treatment. Each skip weighs 250 kg with an envelope volume of 2.5 m^3 originally coated with an epoxy resin (<<1 wt %). The objective was to review experimental data on Al corrosion, calibrate/validate the MAGGAS model and predict base case gas production rates, see Table II (with comparison of Al and Magnox gas generation rates), and sensitivities. A proposed waste packaging process is that skips are size reduced and packaged in Nirex 4 m ILW stainless steel box waste containers with reinforced concrete shielding with ~2.5 t of Al per box and active surface areas of 52 m^2 per skip and 520 m^2 per box modelled as sheet metal. Each box contained ~20 m^3 concrete and grout and 67.7 kg of CS wire reinforcing. The containers were vented. The G-values for radiolysis of cement pore-water by α and β/γ irradiation are 1.4 and 0.43 molecules per 16 aJ (100 eV). Overall corrosion during the 100 year aerobic period consumes 14% of the water in a container, and all Al corrodes after about 500 years (i.e. during the anaerobic 1 phase). The high corrosion rates during preparation of the wasteform (compaction) and cement curing are likely to be very short-lived.

Table II. Gas Generation Rate at the Start of Each Phase (m^3 a^{-1} per m^3 conditioned waste)

Waste Stream	Aerobic	Anaerobic 1	Anaerobic 2
9J50 – Al skips	1.70 x 10^3	1.81	1.65 x 10^{-3}
9G15 – Magnox	8.91	8.91	85.6

Sensitivity calculations were carried out by varying the number of skips per waste container where gas production rate increases linearly with the number of skips, since Al corrosion dominates. For the base case of 10 skips per container the maximum rate was 36.6 x 10^3 m^3 a^{-1} at the start of the aerobic phase. The surface area of Al per skip

was also varied for changes in size reduction and packing of skips, and doubling or halving the surface area doubles or halves gas production rate as expected. The corrosion rate of Al was varied, also giving a linear increase in gas production rate. The main conclusions are as follows:

- Three sets of experimental data for a range of conditions and for up to several years have been used to calibrate the MAGGAS model and set the acute and chronic corrosion rates.
- Expected trends are increased Al corrosion rate with increased temperature and Na^+ and decreased corrosion with increased Ca^{2+}.
- Acute/chronic corrosion rates and characteristic times gave a good data fit though the chronic characteristic time required longer term data.
- In general, an acute rate was used to model time scales of up to ~0.2 of a year and a chronic rate for longer times.
- During the preparation and curing of the wasteform higher rates were used, with time scales of a few hours and a few days.
- Al is the only significant gas generation source until it is all corroded, with base rates of 36.6 x 10^3 and 39.0 m^3 a^{-1} per 4 m ILW box at the start of the aerobic and anaerobic 1 phases respectively.
- Each waste container will produce 4.7 times its own volume of gas per day at the start of the aerobic phase and 2 times its own volume of gas per year at the start of anaerobic 1 phase.
- After these high rates, the gas production rate decreases significantly due to the short acute characteristic time and a chronic rate that is less than 20% of the acute rate.
- Gas production occurs at a much lower rate after 500 years as the Al has completely corroded.
- Excluding encapsulation, base case gas generation rates per m^3 conditioned waste are less than those for reactive Magnox metal.

AGR fuel storage pond water treatment plant IX resin in cement

This was a proprietary granular organic water treatment IX resin comprising 60% anionic and 40% cationic, with the main activity deriving from Co-60 and Cs-137, to be ultimately encapsulated in 3 m^3 stainless steel drum waste containers. A base case was defined in order to calculate the gas production at the start of each time phase, see Table III, and a number of assumptions were made based upon the best available data:

- G-value for β/γ-radiolysis of pore water = 0.34 molecules per 16 aJ (100 eV).
- G-value for β/γ-radiolysis of organic IX = 0.80 molecules per 16 aJ.
- Only β/γ emitters present, radiolysis only from self-irradiation and G-value for α-emitters zero.
- Radionuclide data from U.K. inventory adjusted for increased arisings and decay.

Table III. Gas Generation Rates at the Start of Each Time Phase (m^3 a^{-1} per $3m^3$ container)

	Aerobic	Anaerobic 1	Anaerobic 2
Corrosion of container		21.3 x 10^{-9}	4.69 x 10^{-3}
Radiolysis of Water	5.28 x 10^{-3}		
Radiolysis of Organic IX	31.8 x 10^{-3}		
Total	37.1 x 10^{-3}	21.3 x 10^{-9}	4.69 x 10^{-3}

Corrosion of the container is the only gas generating mechanism during anaerobic phases. Sensitivity of the gas generation rates to radiolysis, see Table IV, were explored by increasing the G-value for the β/γ irradiation of water from 0.34 to 0.50 molecules per 16 aJ (100eV) and for the β/γ irradiation of organic IX from 0.80 to 1.60 molecules per 16 aJ. The maximum gas generation rate is at the time of encapsulation and increased by a factor of 1.9 mainly due to doubling of the G-value for organic IX.

Table IV. Gas Generation Rates at the Time of Encapsulation for Varying G-values

	m^3 a^{-1} per $3m^3$ drum	Water Radiolysis %	IX Radiolysis %
Base case	37.1 x 10^{-3}	14	86
Higher G-values	71.4 x 10^{-3}	11	89

Sensitivity of gas generation rates to radiation dose, including inter-package effects, was investigated using a specific activity for future arisings of 1.6 times base case, irradiation from Co-60/Cs-137, waste packages placed in storage next to packages with 20 Gy h^{-1} surface dose and 20 Gy h^{-1} from a single high γ-emitting package all absorbed by the waste. Relative to the base case, see Table V, there is an increase of 17% for future waste arising due to Co-60 specific activity and Cs-137 activity increasing, and an increase by factor of 45 for external radiation due to Co-60 which decreases to the base case after 90 years due to $t_{1/2}$ = 5 a.

Table V. Gas Generation Rates at the Time of Encapsulation for varying Radiation Levels

	m^3 a^{-1} per 3m^3 drum	Water Radiolysis %	IX Radiolysis %
Base Case	37.1 x 10^{-3}	14	86
Future Waste Arising	43.4 x 10^{-3}	14	86
External Radiation Source	1.69	14	86

Sensitivity studies on the ratio of organic IX to cement assumed the conditioning factor for the waste stream decreased from 2 to 1.5 (ratio of resin to cement increased from 1:1 to 2:1) and that there was an upper limit of waste loading for product stability. This resulted in the same number of waste packages required for the conditioned waste (3 x 3m^3) and therefore same volume of resin but less cement, with a larger void space filled with capping grout and a small decrease in gas generation rate (6% relative to the base case) per waste package due to less cement pore water, see Table VI.

Table VI. Gas Generation Rates at the Time of Encapsulation for varying Organic IX to Cement Ratio

	m^3 a^{-1} per 3m^3 drum	Water Radiolysis %	IX Radiolysis %
Base Case	37.1 x 10^{-3}	14	86
Higher Organic IX / Cement	34.8 x 10^{-3}	9	91

Sensitivity to a combination of factors was explored. G-values for the β/γ irradiation of water and IX were 0.5 and 1.6 molecules per 16 aJ respectively. The waste included future arisings and waste packages placed in an external radiation source of 20 Gy h^{-1}. The cumulative effect was an increase in gas generation rate at the time of encapsulation by 88 times relative to the base case, see Table VII.

Table VII. Gas Generation at Encapsulation for increased G-values, Future Arising & External Radiation

	m^3 a^{-1} per 3m^3 drum	Water Radiolysis %	IX Radiolysis %
Base Case	37.1 x 10^{-3}	14	86
Higher G-values, Future Arisings and External Radiation	3.27	11	89

In summary, from a base case gas generation rate of 37.1 x 10^{-3} m^3 a^{-1} per 3m^3 box, this study established, for the separate cases of 1) G-values x2 best estimates, 2) IX/cement ratio varied, and 3) future arisings considered, the initial (maximum) gas generation rate is <0.10 m^3 a^{-1} per 3m^3 drum. The external radiation sources significantly increase the gas generation rate and the maximum predicted is ~3 m^3 a^{-1} per 3m^3 drum, which is below best estimates for containers of encapsulated Magnox.

Magnox FED in polymer

Some Magnox FED is currently stored compacted in 0.5 m^3 drum waste containers without encapsulation. Immobilisation with a polymer matrix covered with a cement cap is being assessed due to lack of an approved super-plasticised grout. Gas may be generated in such a package by corrosion of the Magnox waste and waste container, and by radiolysis of polymer and any water present. The gas comprises mainly H$_2$, with some CO, CO$_2$, etc from polymer radiolysis. As part of a safety assessment, gas generation has been examined for the whole life cycle from packaging, through storage and emplacement in a repository to post-closure. A review of the corrosion processes was followed by a series of MAGGAS calculations to examine sensitivities.

If Magnox is adequately submerged by polymer, the corrosion rate will be negligible during storage. The polymer is essentially a non-aqueous environment and, due to its slow diffusion rate in polymer, little water will be able to access the Magnox. If Magnox is near the top surface of the polymer, corrosion of a thin layer of Magnox will occur, even while the polymer remains intact. This corrosion could be rapid (~20 x 10^{-6} m a^{-1}), and will stress the

polymer, probably resulting in cracking within a few years. This could give water access to additional parts of the waste, allowing the process to continue further. During the storage period, assuming the waste is packaged so corrosion of Magnox is negligible, the only source of gas generation will be radiolysis of the polymer and water in the grout cap. The best estimate of the maximum gas generation due to radiolysis is only 2.0×10^{-3} m^3 a^{-1} per container (upper bound rate is 3.5×10^{-3} m^3 a^{-1}). This rate occurs at the time of packaging and falls rapidly. Most of the gas generated during storage is due to radiolysis of the polymer. Gas must diffuse through the polymer before it is released from the container. Taking diffusion into account, the maximum gas release rate is $<1 \times 10^{-3}$ m^3 a^{-1}, and occurs after ~5 years.

At the time of repository closure it is (conservatively) assumed that the polymer becomes sufficiently degraded and cracked that water can access the Magnox, so that Magnox corrosion will occur at the standard rate for high pH conditions. Therefore, the post-closure gas generation rate will be predominantly due to Magnox corrosion until all the Magnox has been corroded. There are brief ($<<$ 1 year) peaks per 0.5 m^3 container in the gas generation rate at repository closure, $3 - 28$ m^3 a^{-1}, and at re-saturation, $7 - 105$ m^3 a^{-1}, due to acute Magnox corrosion. In practice, such corrosion is unlikely to occur, or at least the elevated rate will occur at different times in different packages. So, these high rates are not considered significant.

The best estimate for the gas generation rate over most of the post-closure period before re-saturation is 70×10^{-3} m^3 a^{-1} per waste container, but, allowing for uncertainty in the corrosion rate and surface area of the Magnox, may be $\leq$ 1 m^3 a^{-1}. Similarly, the best estimate for the gas generation rate over the post-closure period after re-saturation, while some Magnox remains uncorroded, is 0.7 m^3 a^{-1}, but may be as high as 1 m^3 a^{-1}. These rates are likely to be conservative, particularly for the period soon after repository closure, since the corrosion could be limited by water availability (until the repository re-saturates) and access to the waste due to polymer degradation is likely to be gradual. It will take between 400 and 3,500 years (best estimate 845 a) for all the Magnox to be corroded. Once corrosion of the Magnox ceases, the gas generation rate will reduce to $<1 \times 10^{-3}$ m^3 a^{-1}. The integrity of the wasteform relies on preventing waste corrosion within the polymer matrix, which depends on the time taken by water to diffuse to the waste nearest the surface of the polymer. To prevent waste corrosion for the storage period, the necessary polymer thickness above the FED is estimated to be ~0.1 m depending on the diffusion coefficient of water.

Organic ion exchange resin in polymer

These wastes were packaged in 1985 with the intention of sea disposal, which was not carried out. The packages contain organic IX resin (with some sand) 5.7 %, iron grit 0.5%, polymer (a vinyl ester) 6.1%, water 2.4%, mild steel 1.7%, iron shot 74.8%, cement paste and grout 8.8%; all % by weight. This waste package was chosen for study because of the possible implications of polymer on gas generation. However, the base case calculation demonstrates that the gas generation in the aerobic phase would not be of concern and is assessed as low, being due to radiolysis of polymer, water and IX resins. The average rate of gas production is around 30×10^{-6} m^3 a^{-1} per package, equivalent to about 12×10^{-3} m^3 a^{-1} for the whole waste stream. These rates are low, and suggest the packages are unlikely to pose safety problems regarding gas formation. Sealing is provided by rubber gaskets designed to prevent the ingress of water, but uncharacterised for retention of gas. Assessments of pressurisation without venting suggest that very low overpressures would be generated during the aerobic phase at worst, apparently presenting no safety issues.

When conditions become anaerobic, however, H_2 production from the iron shot starts, which dominates gas production. In the base case, 0.237 and 1.26 m^3 a^{-1} per container are predicted to be produced at the start of the first and second anaerobic phases respectively. These relatively large rates arise because of the large amount of iron shot that is present that has a large specific surface area. The average rate in the first anaerobic phase is about 50×10^{-3} m^3 a^{-1} for a single package, indicating about 20 m^3 a^{-1} for the whole waste stream. The Magnox wastes still generate more gas than this for a few hundred years into the first anaerobic phase, but later, the IX packages containing iron shot yield gas at a greater rate. The key time periods in terms of gas generation during the first 100 years for this waste stream have been identified as 0–5 years, 5–20 years and 20–100 years. These results may not be relevant to plant ventilation assessments if the containers remain sealed so that no gas escapes during this time. These findings suggest that the effects of gas evolution in the post-closure period on repository performance be examined with this waste package.

Vent size and container pressurisation for Magnox waste packages under normal and fire conditions.

This study concerned the needs for venting a container to prevent significant pressurization, which was defined as an overpressure of >30% above atmospheric. Initial calculations used gas generation under normal conditions and the design performance of the vent. Additional scenarios considered changes to the gas generation rate or the vent behaviour. All cases used the venting requirements of a waste package of greatest gas generation rate, i.e. Magnox metal in cement matrix. Under normal conditions, using the MAGGAS drum pressurisation model, only a small fraction (10^{-5}) of the area of a standard vent is required to prevent significant pressurisation of a waste container. A fire, corrosion of the vent filter and manufacturing defects were considered as potentially important scenarios likely to affect container venting. Steam is likely to be the main product from a container under fire conditions and the generation rate from a container of waste is estimated as $\leq 400 \times 10^{-3}$ m^3 s^{-1}. Rapid steam generation could require up to 69% of the area of a standard vent to be available to prevent significant pressurisation of a container. During a fire, trapping of particulates could also significantly reduce the vent permeability and increase vent requirements.

For FED wastes under fire conditions, Magnox corrosion may be important in determining the total gas generation rate. Corrosion rates and products should be determined for the whole range of temperatures experienced during a fire. Particulates could have a significant effect on venting requirements during a fire and the potential for blocking of the vent should be assessed. The permeability of a corroded vent will be affected by the form of the corrosion product. A fully realistic value for acceptable container pressurisation should be determined since this could be particularly important for the fire scenario, where the current assessment indicates that the container pressurisation may reach close to the 30% overpressure.

Magnox FED stored in steel containers but not encapsulated in cement

An option considered was the consignment of Magnox (FED) to surface storage in carbon steel galvanised containers without grouting. An assessment of H$_2$ release during storage examined the consequences for storage. Work consisted of two main parts, a review of Magnox corrosion rate and MAGGAS calculations to estimate gas generation rates for various parameter values. The review of Magnox corrosion rates focused principally on corrosion in liquid water at pH 10.4, the pH of water equilibrated with Brucite mineral, (Mg(OH)$_2$), and in a humid atmosphere of 80% relative humidity (RH). A corrosion rate of 12.5×10^{-6} m a^{-1} is the best estimate for Magnox immersed in water in the absence of galvanic effects and with no chloride present. The corrosion rate in a humid atmosphere is more uncertain due to the lack of data specific to corrosion in a vented container, but a range of ~13 – 22×10^{-6} m a^{-1} is suggested that demonstrates no clear difference between immersion in liquid water and exposure to 80% RH. Galvanic coupling with either the zinc galvanising or the mild steel of the container could increase the corrosion rate of the Magnox. The effect is expected to be small for zinc but could be larger in the case of coupling with mild steel. In both cases, it is expected that only a small proportion of the Magnox could be subject to accelerated corrosion due to galvanic effects because of the limited contact and the build up of corrosion product inhibiting coupling. Given the estimated corrosion rate of zinc and its much smaller surface area compared to Magnox, zinc only provides an insignificant contribution to the total gas generation rate. No directly relevant data was found on crevice corrosion between the FED and the container walls.

MAGGAS calculations have been undertaken for gas generation from Magnox FED placed in containers, assuming that corrosion takes place in a humid atmosphere in the absence of free liquid water. An average constant rate of Magnox corrosion of 19×10^{-6} m a^{-1} was adopted from data described above, including the possibility of some limited galvanic effects, but higher and lower rates of 125×10^{-6} m a^{-1} and 4×10^{-6} m a^{-1} were assumed in sensitivity calculations to explore the potential range of rates. Gas generation from radiolysis of water possibly carried into the packages with Magnox FED was addressed, and gas generation was completely insignificant compared to that from Magnox corrosion. The best estimate of the gas generation rate per package from Magnox corrosion is about 12.2 m^3 a^{-1} at STP, but the higher and lower corrosion rates considered give rates of 80.2 m^3 a^{-1} and 2.6 m^3 a^{-1} per package, respectively. These use an assumed bulk density of the Magnox FED in the containers of 870 kg m^{-3}, cf. 450 kg m^{-3} for their current location [1]. Estimates were made of the water vapour flow rate through the vents of packages. Diffusion may prevent corrosion occurring at the higher variant rate (125×10^{-6} m a^{-1}), and the maximum rate of gas production from Magnox corrosion is likely to be limited to 4 times more than the base case.

ADDITIONAL MODELLING

As the development and application of MAGGAS proceeded it became necessary to add particular mechanisms for particular wastes. These were most successful where a verified database was available and the option was built in of activating these additional mechanisms if required.

Carbon – 14 release

Various operational and decommissioning wastes from U.K. nuclear power stations will contain graphite from fuel sleeves, core, etc. [1]. Detailed consideration was made of the factors likely to be involved in C-14 release from graphite during the package lifecycle. For the interim storage period, these included:

- At low radiation /temperature, CO_2 will be from air containing naturally occurring level of the gas.
- Graphite attack by CO_2, O_2 or H_2O therefore likely to be very small but relevant to the storage of waste packages containing graphite.
- Carbonaceous deposits on graphite are more reactive to air than graphite but quantities and reactivity are not significant.
- Nitric acid may form by the radiolysis of moist air but low formation rate and storage at ambient temperature make degradation of the graphite by this route insignificant.
- Discharges from typical operating Magnox stations are in the range 0.2 - 4 TBq a^{-1}, the majority due to ^{14}C from radiolytic oxidation of the moderator. For Berkeley and Trawsfynydd, discharges were about 10^{-3} - 10^{-4} TBq a^{-1} constituting ~0.03% of the C-14 discharge limits for the decommissioning sites.
- Some materials are known to lower the graphite/CO_2 reaction temperature by catalysis; however the lowered temperatures are still above 500°C.

In the post-closure repository situation, conditions are more benign with respect to C-14 release. It was concluded that for Magnox reactor wastes there is no need for detailed modeling and an empirical model incorporated into MAGGAS would suffice.

Chlorine – 36 release

Cl-36 is produced by activation of the Cl impurity in graphite, and K and S present in reactor materials also contribute. Some of this might diffuse away from the point of origin and into graphite moderator at reactor operating temperatures. Cl-36 is a β-emitter with a long half-life of 302 x 10^3 years and so will not decay significantly during storage. No data for the release of Cl-36 are quoted in gaseous discharges from Magnox reactors in operation or decommissioning. Cl is expected to be held within the layered structure of graphite, forming a lamellar compound. Release of the Cl-36 isotope is likely to be extremely slow during storage and essentially non-existent during final disposal. If released as a gas, Cl-36 is likely to form either $^{36}ClCl$ or $H^{36}Cl$. Both are soluble in water and reactive towards packaging materials and any cementitious grout in the containers. Overall, significant release of both forms as gases from waste packages is considered unlikely and it was concluded that models should not be incorporated into MAGGAS for the release of gas containing Cl-36 whether packaging of graphite is with or without a cementitious grout.

Uranium corrosion

Fragments of Magnox fuel (natural U) could be retrieved with power station FED and encapsulated in cement, with other non-power station wastes potentially containing more significant amounts. The time periods and conditions relevant to U corrosion are:

- Interim storage at power stations and the repository, aerobic conditions, low Cl⁻ in available water, pH 7 (un-grouted wastes), pH 12 (grouted wastes), 35-50˚C, temperature transients to 80˚C due to backfill.
- Post-repository closure and before re-saturation, anaerobic conditions, low Cl⁻ in available water, pH 7 (un-grouted wastes), pH 12 (grouted wastes), 35-50˚C.
- Post-repository closure and re-saturation, anaerobic, high Cl⁻ in available water (10, 100 ppm or 3%), pH 12 (all wastes), 15-25˚C.

From an extensive literature search, the following U corrosion rates were identified. Under aerobic conditions a rate of 23 x 10^{-6} m a^{-1} at 50°C and 60 x 10^{-6} m a^{-1} at 80°C initially falling to 12 x 10^{-6} m a^{-1} in 2 months. Under anaerobic conditions the U corrosion rate at 30°C was taken as 69 x 10^{-6} m a^{-1}. Most U corrosion data was for single point measurements after a few hours, and the only time dependent data was for aerobic conditions in 3:1 BFS/OPC at 80°C. U corrosion in aerated conditions is 30-100 times less than in de-aerated conditions with a weak dependence on pH for aerobic and anaerobic conditions (e.g. a 50% reduction in de-aerated water from pH 6 to pH 11.5 at 90°C). As expected, salinity increases the corrosion rate by an order of magnitude. This is from 4.6 x 10^{-6} m a^{-1} in distilled water at 35°C to 60 x 10^{-6} m a^{-1} in synthetic seawater at 25°C. In de-aerated water Cl^- and Na^+ have little effect on corrosion rate.

With the identified U corrosion rates and U modeled as plates and spheres, MAGGAS predicted complete U corrosion between 0-50 years and 250-300 years respectively into the anaerobic phase 1. MAGGAS was calibrated against a time dependent experimental model for aerobic conditions at 80°C, although data for comparable anaerobic conditions were not available. Based on this, the acute rate was set as 150 x 10^{-6} m a^{-1} with a characteristic time of 0.01 years and the chronic rate at 15 x 10^{-6} m a^{-1}. The chronic rate was scaled for other conditions using the ratio of the short-term rates. The gas generation issue is probably less significant than the expansive oxide formation issue which could cause the cemented wasteform to fracture.

Tritium release

H-3 is produced in graphite by the activation of the Li impurity, and can also be absorbed by the graphite from the coolant, whereas H-3 produced during fission of the U fuel is subsequently released by diffusion into the fuel cladding and coolant at reactor operating temperature. Each operating Magnox reactor has discharges to atmosphere of about 0.6 - 6 TBq a^{-1}, and by contrast where operations have ceased reactor discharges fell to 0.005 - 0.18 TBq a^{-1} or 0.2 - 1.8% of the authorised discharge limits for decommissioning sites. These proportions are expected to fall considerably before Stage 3 decommissioning due to isotope decay and the decreasing ease of tritium release from graphite. However, some operational wastes containing graphite may be packaged before significant decay of H-3 so modelling its release may be appropriate. Therefore a sub-model analogous to that for C-14 was developed within MAGGAS to assess the rate of formation of tritiated gas from packages containing graphite. Tritium is released from a metal as a result of corrosion or diffusion. The relative importance of the two mechanisms was investigated for tritium in stainless steels where diffusion coefficient data is available. A single source of data was found on the diffusion coefficient for tritium in an alloy of uranium (U/Nb/Zr), but no data found for tritium diffusing in Magnox. A dimensionless parameter is constructed from the physical variables (i.e. length/ corrosion rate/diffusion coefficient), and used to compare the relative significance of corrosive and diffusive processes. Diffusion usually will dominate as the mechanism for release and in general, it is not possible to find an analytical solution to the coupled problem of corrosion and diffusion. The equations for the diffusive release of tritium from metallic wastes have been implemented in an Excel spreadsheet, and verified. The user of MAGGAS is able to set a "switch" for each metal, allowing selection of either the corrosive or the diffusive release model.

SUPPORTING AND FUTURE WORKS

Periodically, new experimental data has been obtained in order to improve the accuracy and capabilities of MAGGAS. This has included a re-evaluation of the Magnox corrosion database, longer term measurement of Al corrosion and the measurement of G-values for oily sludge. For the latter, experimental studies have provided data for overall $G(H_2)$ values for oily waste streams using a γ-radiation source and inactive simulants with various solids and oil concentrations, cements, water/cement ratios and controls without oil.

Also, the MAGGAS code is being continuously improved by work in the following areas:

- Maintenance of the code, periodic QA audit and issue of overview and user guidance documents.
- Response to particular gas generation scenarios.
- Continuous review of corrosion, radiolysis and microbial activity databases.
- Comparison with the Nirex SMOGG gas generation code in relevant areas with an agreed input database and combination of mechanisms. Comparison with other established codes.

CONCLUSIONS

Overall the MAGGAS model is considered fit for purpose and the main conclusions are as follows:

1. Application of the MAGGAS code in support of reactor waste management and decommissioning is demonstrated in response to U.K. regulatory requirement for safety processes concerning facility construction and operation, and regulatory and Nirex approval for waste packaging.
2. Gas generation was calculated for a wide range of reactor wastes with assumptions regarding waste package, storage and repository conditions. The sensitivity of predicted gas generation rate and waste container pressure values to the input model parameters was extensively studied. This scoped the issue of gas generation, identifying wastes of likely greatest rate and those where safety significance is unlikely.
3. Five well-defined package specifications were assessed to assist waste management planning and studies were performed in more detail on several waste package types, including cemented Magnox fuel element debris and IX in polymer, at opposite ends of the gas production scale ($\sim 10^5$ factor difference in rate during the aerobic phase), including calculation of waste container pressurisation.
4. Metal corrosion is considered the most important mechanism for gas generation, both in terms of the number of waste streams producing significant amounts of gas, and the existence of waste streams producing gas likely to affect the safety of each stage of the waste management and disposal life cycle. The corrosion of mild steel, Magnox (Mg) and Al was modelled in some detail.
5. The main approximation in the MAGGAS model relates to sudden changes in conditions (e.g. oxygen and water) at certain points. In reality, these would take a finite time and result in somewhat smoother gas generation profiles. Peak generation rates calculated using MAGGAS are conservatively high.
6. The development plan for the MAGGAS model complies with the Quality Assurance standard ISO 9001. Development included mathematical verification of the code and validation against experimental data. The way in which stages were executed conforms to the IAEA definitions.

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