OPG's DEEP GEOLOGIC

REPOSITORY

FOR LOW & INTERMEDIATE LEVEL WASTE

T2GGM Version 2: Gas Generation and Transport Code

March 2011

Prepared by: Quintessa Ltd. and Geofirma Engineering Ltd.

NWMO DGR-TR-2011-33

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Quintessa Ltd. and Geofirma Engineering Ltd.[1]			
Prepared by:	P. Suckling, J. Avis, P. Humphreys, F. King		
Reviewed by:	J. Pickens		
Approved by:	R. Little		
Nuclear Waste Management Organization			
Reviewed by:	H. Leung, K. Sedor		
Accepted by:	P. Gierszewski		

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[1] Previously known as Intera Engineering Ltd.

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EXECUTIVE SUMMARY

T2GGM Version 2 is a software package that can be used to analyze the generation and transport of gases in a deep geologic repository. The current version is V2.1. It is specifically intended for assessment of a repository for low and intermediate level waste, in which there can be significant amounts of organic materials and metals.

This report provides the documentation for the T2GGM software. It includes the theory for the gas generation model, the design documentation with descriptions of the software inputs and outputs, and verification and validation documentation.

T2GGM includes the following capabilities:

- Corrosion product and hydrogen gas generation from corrosion of steels and other alloys under aerobic and anaerobic conditions;
- CO_2 and CH_4 gas generation from degradation of organic materials under aerobic and anaerobic conditions;
- H_2 gas reactions, including methanogenesis with CO_2;
- Biomass generation, decay and recycling;
- Exchange of gas and water between the repository and the surrounding geosphere; and
- Two-phase flow of water and gas within the geosphere.

Key results include the gas pressure and water saturation levels within a repository, as well as flow rates of water and gas within the geosphere. T2GGM does not include radionuclide transport and decay.

T2GGM is comprised of two coupled models: a Gas Generation Model (GGM) used to model the generation of gas within a repository due to corrosion and microbial degradation of the various materials present, and a TOUGH2 model for gas-water transport from the repository through the geosphere.

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1. INTRODUCTION

The long-term safety assessment of deep geological repositories may involve the analysis of behaviour of gases within and from the repository. This assessment requires the calculation of the generation and build-up of gas in the repository and the movement of gas from the repository to the surface environment. This may be particularly relevant for deep repositories for low and/or intermediate level waste because of the large amounts of steel and organic materials present as wastes or containers.

T2GGM was developed to undertake these calculations. It is comprised of two coupled models: a Gas Generation Model (GGM) used to model the generation of gas within a repository due to corrosion and microbial degradation of the various materials present, and a TOUGH2 model (Pruess et al. 1999) for gas-water transport from the repository through the geosphere (Figure 1.1). The key outputs from this software are estimates of the peak repository pressure, repository saturation, and total flux of gases from the geosphere to surface.

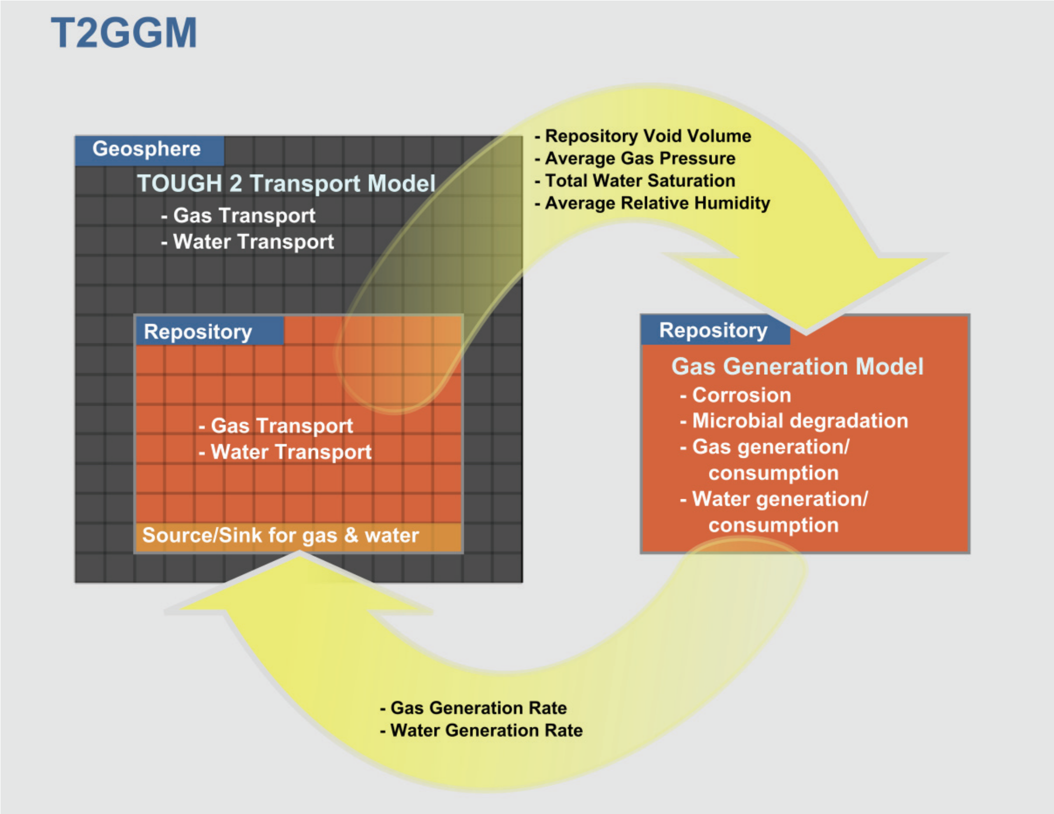

Figure 1.1: Coupling Gas Generation and Transport in T2GGM

The present report includes the following documentation for T2GGM, consistent with Nuclear Waste Management Organization (NWMO) procedure for technical computing software (NWMO 2010):

- Problem Definition (Chapter 2);
- Program Abstract (Chapter 3);
- Theory (Chapter 4 and Chapter 5);
- Requirements Specification (Chapter 6);
- Design Description / Programming Manual (Chapter 7);
- Verification (Chapter 8);
- Validation (Chapter 9); and
- User Manual (Chapter 10).

2. PROBLEM DEFINITION

Ontario Power Generation (OPG) is proposing to build a Deep Geologic Repository (DGR) for Low and Intermediate Level Waste (L&ILW) near the existing Western Waste Management Facility at the Bruce nuclear site in the Municipality of Kincardine, Ontario.

Gas generation within the repository is one of the key factors in the postclosure safety of the proposed facility. Gas will be generated and consumed within the repository by various microbial and corrosion processes. The repository will interact with the geosphere through the fluxes of gas and water into and out of the repository. Following closure, the build-up of gas within the repository could affect the resaturation time and lead to the release of gaseous radionuclides.

T2GGM is the name of the software that has been designed and applied to calculate the generation of gas and consumption of water in the repository and their subsequent transport through the geosphere. The code itself has two components: a custom GGM and a TOUGH2 gas and water transport code. Using site-specific data, T2GGM provides results that inform models used to assess the impact of radionuclides on human and non-human biota and the impact of non-radioactive species on humans and the environment for the safety assessment.

A description of the scenarios to which T2GGM has been applied is given in the DGR safety assessment reports, for example, see GEOFIRMA and QUINTESSA (2011) and supporting reports.

3. COMPUTER PROGRAM ABSTRACT

T2GGM Version 2.1 is comprised of two coupled models: a gas generation model (GGM V2.1) used to model the generation of gas within a repository due to corrosion and microbial degradation of the various materials or waste streams present, and the TOUGH2 V2 model for gas transport from the repository through the geosphere. The key output parameters from this software are estimates of the peak repository pressure, repository saturation, and total flux of gases from or to the geosphere.

GGM Version 2.1 is implemented as a FORTRAN module that is used by TOUGH2 in its own gas generation and repository saturation calculations. GGM includes a kinetic description of the various microbial and corrosion processes that lead to the generation and consumption of various gases. Mass-balance equations are given for each of the species included in the model, including three forms of organic waste (cellulose, ion-exchange (IX) resins, and plastics and rubbers), four metallic waste forms and container materials (carbon and galvanized steel, passivated carbon steel, stainless steel and nickel-based alloys, and zirconium alloys), six different gases (CO_2, N_2, O_2, H_2, H_2S, and CH_4), five terminal electron acceptors (O_2, NO_3^-, Fe(III), SO_4^{2-}, and CO_2), five forms of biomass (aerobes, denitrifiers, iron reducers, sulphate reducers, and methanogens), four types of corrosion product (FeOOH, $FeCO_3$, Fe_3O_4, and FeS), water, and MgO, which could be added to the repository to mitigate the effects of CO_2 generation.

TOUGH2 is a multi-phase flow and heat transport program for fluid mixtures. TOUGH2 is the collective name for a family of numeric models that simulate multi-phase flow and transport developed and maintained by the Earth Sciences Division of Lawrence Berkeley National Laboratory. TOUGH2 uses different Equations-of-State (EOS) modules to simulate different combinations of liquids and gases. T2GGM Version 2.1 includes TOUGH2 Version 2.0 with the EOS3 V1.01 equation-of-state module (ideal gas - air and water) (Pruess et al. 1999). TOUGH2 was modified to include the modified van Genuchten model provided in iTOUGH2 (Finsterle 1999). This is a set of capillary pressure and relative permeability equations that are widely used in modeling two-phase flow in low-permeability media. Additional modifications were made to allow user specification of gas (air, CH_4, CO_2, H_2, or user-specified). T2GGM-MP Version 2.1 is a version of T2GGM that couples GGM with TOUGH2-MP Version 2.0. TOUGH2-MP uses multiple processors to undertake its calculations in order to improve run times. The majority of this documentation covers both the single and multiple processor versions of T2GGM. Sections that relate to single- or multi-processor functionality only are indicated as such.

3.1 Capabilities

T2GGM Version 2.1 includes the following capabilities:

- Corrosion product and hydrogen gas generation from corrosion of steels and other alloys under aerobic and anaerobic conditions;
- CO_2-enhanced corrosion of carbon steel and passive alloys;
- CO_2 and CH_4 gas generation from degradation of organic materials under aerobic and anaerobic conditions;
- Degradation of cellulose, IX resins, and plastics and rubbers at different rates based on the nature and energy yield of the terminal electron acceptor;
- H_2 gas reactions, including methanogenesis with CO_2;

- Biomass generation, decay and recycling;
- Limitation of both microbial and corrosion reactions by the availability of water;
- Exchange of gas and water between the repository and the surrounding geosphere;
- Calculation of the generation and build-up of gas in the repository;
- Two-phase flow of water and gas within the geosphere; and
- The ability to assess the effect of different gas-mitigation methods and other processes that may lead to the consumption of gas in the repository.

3.2 Limitations

T2GGM Version 2.1 is subject to the following limitations:

- It does not model heat generation;
- It does not model radionuclide transport and decay;
- For the gas generation modelling, the repository is represented as a single compartment with variable saturation;
- Repository corrosion and gas reaction rates are first order in a primary reactant, and in particular are not dependent on the amount of microbial biomass;
- Metal corrosion and organic decomposition is described by a constant corrosion rate for the relevant conditions (aerobic/anaerobic, saturated/unsaturated);
- Organics are modelled as either cellulose or styrene;
- All gas in the geosphere is modelled as a single gas (either air, CH_4, CO_2 or H_2); all gases released from the repository are converted into this gas on an equivalent molar basis (e.g., if GGM calculates a generation rate of 1 mol s^{-1} of H_2 and 2 mol s^{-1} of CH_4, then it is converted into 3 mol s^{-1} of the selected gas, and then converted to a mass rate at the selected gas molecular weight for use by TOUGH2); and
- Groundwater in the geosphere is modelled as freshwater.

4. THEORY – GGM

4.1 Introduction

Gas generation within the repository may be important to both operational and post-closure safety. During the operational phase, when air is still present, care must be taken to avoid the formation of flammable gas mixtures in closed spaces. Following closure and consumption of O_2, the build-up of gas within the sealed repository affects the resaturation time and can lead to the release of gaseous radionuclides. Gas is generated and consumed by various microbial and corrosion processes. For example, microbial degradation of organic components of the waste or other materials left in the repository produces CO_2 and CH_4. Corrosion of metallic waste forms and container materials consumes O_2 and CO_2, and produces H_2 under anaerobic[2] conditions.

This section describes GGM Version 2.1, the gas generation model for the T2GGM Version 2.1. The model incorporates a detailed description of the kinetics of microbial degradation of the organic wastes and accounts for the possible limitation of both microbial and corrosion processes due to the availability of water. In addition, GGM can be used to assess the effect of different gas-mitigation methods and other processes that may lead to the consumption of gas in the repository.

This Theory section provides a detailed specification of all the equations solved by GGM Version 2.1. Microbial processes are described in Section 4.2, corrosion processes in Section 4.3, additional processes (e.g., gas mitigation) in Section 4.4, and general model and coding information is provided in Section 4.5.

A detailed list of the model parameters referenced throughout this section is given in Table 4.1.

4.2 Microbial Gas Generation Processes

4.2.1 Degradation of Organic Waste Components

GGM considers three classes of organic wastes which may be present in a repository, at least for a repository containing low and intermediate level waste:

1. Cellulosic materials;
2. IX resins; and
3. Plastics and rubbers.

All three of these groups represent polymeric organic materials. The microbial degradation of polymeric organics follows a generic sequence of events (Figure 4.1) (Rittmann and McCarty 2001). Firstly the polymer is converted into soluble intermediates, which are then subject to microbial oxidation reactions, the exact nature of which depends on the prevailing geochemical conditions. Microbes either couple the oxidation of these soluble intermediates to the reduction of Terminal Electron Acceptors (TEAs) or subject them to fermentation (Barlaz 1997, Pedersen

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[2] Here, the term anaerobic is used to describe not only the absence of air (oxygen), but also more generally to describe environments in which one or more redox couples control the redox potential at relatively negative values of Eh.

2000, Rittmann and McCarty 2001). Under ideal conditions microbial systems employ a range of TEAs in oxidation-reduction reactions which are consumed in a well-defined order depending on the amount of energy provided by each reaction (Zehnder and Stumm 1988). This order is outlined below:

- Oxygen followed by;
- Nitrate followed by;
- Ferric ion (Fe III) followed by;
- Manganese (Mn IV) followed by;
- Sulphate followed by; and
- Carbon dioxide.

In subsurface environments the simultaneous consumption of terminal electron acceptors does occur due to local heterogeneity and the presence of microbial microsites. However, the general trend of sequential terminal electron consumption is seen in subsurface environments' pollution plumes, for example Williams et al. (2001). Consequently the sequential consumption of terminal electron acceptors within the model is justifiable on the basis of reaction thermodynamics (Zehnder and Stumm 1988) and environmental observations (e.g., Williams et al. 2001).

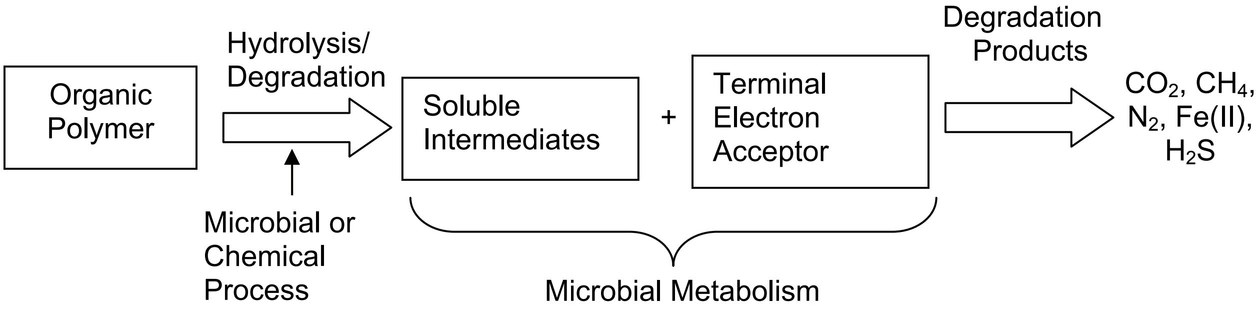

Figure 4.1: Microbial Degradation of Polymeric Substrates

Under oxidizing conditions when oxygen, and to a lesser extent nitrate, is used as a terminal electron acceptor, the degradation of polymeric substrates such as cellulose progresses to completion (Equations (4.1) and (4.2)). When oxygen is depleted and anaerobic conditions are established, polymeric substrates tend to undergo fermentation, with fermentation end products being fully oxidized by TEA processes (Equations (4.3) and (4.4)) (Leschine 1995, Pedersen 2000). Fermentation is carried out by a varied group of microbes and consequently a wide range of fermentation end products (carboxylic acids and alcohols) are possible (Leschine 1995, Barlaz 1997, Rittmann and McCarty 2001), with Equation (4.3) showing the fermentation of glucose to acetic acid. The consumption of these fermentation end products during iron reduction is illustrated in Equation (4.4).

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow nC_6H_{12}O_6 \qquad \text{cellulose hydrolysis} \qquad (4.1)$$

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \qquad \text{aerobic glucose degradation} \qquad (4.2)$$

$$C_6H_{12}O_6 + 4H_2O \rightarrow CH_3COOH + 8H_2 + 4CO_2$$

glucose fermentation to acetic acid (4.3)

$$CH_3COOH + 8H_2 + 24Fe(III) + 2H_2O \rightarrow 24Fe(II) + 2CO_2 + 24H^+$$

iron reduction of glucose fermentation products (4.4)

4.2.1.1 Modelling Organic Waste Degradation

The microbial degradation of polymeric substrates and the subsequent generation of gas is a complex multistage process involving a large array of microbial species (Pedersen 2000, Grant et al. 1997). However, for modelling purposes, this can be simplified by the fact that the conversion of polymeric substrates such as cellulose to their soluble intermediates is often the rate limiting step in the gas generation process (Rittmann and McCarty 2001). This allows the microbial oxidation of polymeric substrates to be coupled directly to the reduction of the relevant TEA. The degradation of polymeric substrates then becomes a single-stage process with the consumption of TEAs being instantaneous and controlled by the rate of polymer degradation. This partial-equilibrium approach has been applied in other modelling studies (McNab and Narasimhan 1994, Postma and Jakobsen 1996), since it significantly simplifies the modelling of microbially driven systems and reduces the number of kinetic parameters required to run the model. The application of this approach to gas generation modelling can be justified on the basis that it is conservative from a gas generation perspective, since it maximizes gas generation by preventing the accumulation of intermediate products and ensuring gas generating processes proceed to completion.

Balanced reactions coupling the oxidation of organic waste components to the reduction of TEAs can be constructed using the approach outlined by Rittmann and McCarty (2001). Taking cellulose as an example, its hydrolysis to glucose is outlined in Equation (4.1) with its oxidation under aerobic conditions being outlined in Equation (4.2). However, if the rate of glucose oxidation is taken to be instantaneous when compared to the rate of cellulose hydrolysis then the overall reaction can be written as:

$$(C_6H_{10}O_5)_n + 6nO_2 \rightarrow 6nCO_2 + 5nH_2O$$

or complete oxidation of cellulose (4.5)

$$C_6H_{10}O_5 + 6O_2 \rightarrow 6CO_2 + 5H_2O$$

where the controlling reaction rate is that for cellulose hydrolysis, Equation (4.1).

Note that the rate of hydrolysis (and of the degradation of polystyrene into styrene) is redox dependent and so an aerobic rate and an anaerobic rate are considered.

The above approach closely resembles microbial cellulose degradation under oxidizing conditions where the polymer is completely degraded to carbon dioxide and water (Leschine 1995). However, under anaerobic conditions when fermentation occurs, the instantaneous consumption of fermentation end products is not always observed, resulting in the accumulation of carboxylic acids such as acetic acid and butyric acid. This accumulation generally occurs because the microbes responsible for the degradation of these products are inhibited by low pH, a process known as acid souring in landfill sites (EA 2004). In anaerobic hypersaline environment the accumulation of volatile fatty acids has also been observed

(Ollivier et al. 1994). The accumulation of fermentation end products such as acetic acid is not included in the model, allowing the degradation of polymeric organics to be modelled as a series of single-stage processes. As before, this approach is justified on the basis that it is conservative since it maximizes gas generation by preventing the accumulation of soluble organic intermediates.

Employing this approach, the metabolism of cellulose degradation (oxidation) under iron-reducing conditions which is described in Equations (4.1), (4.3), and (4.4) can be simplified to:

$$C_6H_{10}O_5 + 24Fe(III) + 7H_2O \rightarrow 6CO_2 + 24Fe(II) + 24H^+$$

degradation of cellulose under iron-reducing conditions (4.6)

where again the controlling reaction rate is that for cellulose hydrolysis, Equation (4.1).

Origins of Microbes

The model assumes that all microbial groups required to catalyze the processes modelled are present within the repository. This assumption is justified on the basis that it is conservative from a gas generation perspective, since it ensures gas generation processes proceed to completion. In reality, microbes are ubiquitous in terrestrial, man-made and subsurface environments (Pedersen 2000). Microbes will enter the repository during the construction and operational phases on vehicles, materials, people and in the air. In addition the waste will carry its own microbial load. Microbial gas generation in stored and disposed wastes has been reported by a number of authors (Molnar et al. 2006, Molnar et al. 2000, Kannen and Muller 1999). Groundwater entering the repository could also carry a microbial load compatible with the saline conditions at depth.

Terminal Electron Acceptors

The model includes oxygen, nitrate, ferric iron, sulphate, and carbon dioxide as terminal electron acceptors. Oxygen is included, since it will be present in the repository atmosphere post closure. Sources of nitrate are less obvious, but may include blast explosive residue from repository construction, the groundwater, and also a chemical used in the nuclear industry and present in the wastes. Ferric iron is included, since it is a product of aerobic corrosion and sulphate is included since it may be present in the local groundwater. The inclusion of sulphate also allows gas mitigation options involving the precipitation of metal sulphides to be investigated. Finally, carbon dioxide is included since it is a major gaseous product of microbial degradation processes. With the exception of carbon dioxide, any or all of the processes associated with these terminal electron acceptors within the model can be turned off by setting the relevant input concentration to zero.

Terminal electron acceptors are theoretically consumed in a defined sequence (Section 4.2.1) starting with oxygen and finishing with carbon dioxide. This sequence is reflected in the model with a given TEA only being consumed once the previous one has been depleted. Finally, when all the competing TEAs have been depleted, carbon dioxide consumption and methane production will occur. The removal of TEAs is not modelled kinetically, but is controlled by the rate of organic waste degradation and the stoichiometry of the relevant reaction in a partial equilibrium approach similar to that employed by McNab and Narasimhan (1994) and Postma and Jakobsen (1996).

Degradation of Cellulose

The degradation of cellulosic materials has been extensively studied (Leschine 1995) and modelled (Rittmann and McCarty 2001). Consequently the degradation pathways are well established (Leschine 1995, Barlaz 1997). Taking the approach outlined in Section 4.2.1.1, cellulose degradation is modelled via the following equations constructed using the approach outlined by Rittmann and McCarty (2001):

$$C_6H_{10}O_5 + 6O_2 \rightarrow 6CO_2 + 5H_2O \qquad \text{oxidation of cellulose by molecular oxygen} \qquad (4.7)$$

$$5C_6H_{10}O_5 + 24NO_3^- + 24H^+ \rightarrow 30CO_2 + 12N_2 + 37H_2O \qquad \text{oxidation of cellulose by nitrate reduction} \qquad (4.8)$$

$$C_6H_{10}O_5 + 24Fe(III) + 7H_2O \rightarrow 6CO_2 + 24Fe(II) + 24H^+ \qquad \text{oxidation of cellulose by ferric iron reduction} \qquad (4.9)$$

$$C_6H_{10}O_5 + 3SO_4^{2-} + 6H^+ \rightarrow 6CO_2 + 5H_2O + 3H_2S \qquad \text{oxidation of cellulose by sulphate reduction} \qquad (4.10)$$

$$C_6H_{10}O_5 + H_2O \rightarrow 3CO_2 + 3CH_4 \qquad \text{methane generation from cellulose} \qquad (4.11)$$

where the reaction rate for all these is that for cellulose hydrolysis, Equation (4.1).

Degradation of IX Resins

There may be significant amounts of IX resins in the intermediate-level waste inventory, and as such these resins are potentially a significant source of biogenic gases. However, there is disagreement as to the biodegradability of these materials. For example, Grant et al. (1997) listed IX resins as being recalcitrant under repository conditions. However, a number of authors have suggested that these resins are subject to microbial degradation and subsequent gas generation. For example, Bracke et al. (2003, 2004) report gas generation rates from resin wastes in interim storage and attribute a microbial gas generation rate to the degradation of these wastes. Bowerman et al. (1988) investigated the biodegradation of IX media using a mixed microbial culture isolated from resin waste samples, and found microbial growth under various conditions, although it is noted that the work appear to have been carried out under aerobic conditions. EPRI investigated biogas generation from IX resins in the late 1990's, and found that the gas was being generated from cellulose fibres contaminating the resins rather than microbial degradation of the resins themselves (EPRI 1998).

Although the chemical nature of IX resins suggests that they would not be biodegradable, particularly under anaerobic conditions, data from waste resins indicate that degradation is possible. There are a number of scenarios that explain the observed data:

- Organic contaminants adsorbed on the resins and corrosion hydrogen are supporting the gas generation and microbial communities rather than direct biodegradation of the resins;
- Radiolytic and/or chemical degradation is generating soluble intermediates which are subject to biodegradation; and
- The resins are subject to microbial degradation.

There are insufficient data to determine which of these options is correct and it is possible that all three are operating simultaneously. For generality, IX resin degradation is included in the model.

Water coolant IX resins are typically cross-linked polystyrene based, with various functional groups and water attached. The resins are therefore modelled via the degradation of polystyrene with bound water ($(C_8H_8.mH_2O)_n$) to styrene with bound water ($C_8H_8.mH_2O$) as in Figure 4.2, and then to final degradation products. The initial degradation is considered to be the rate-limiting step. This is comparable to the cellulose degradation model. This assumption is justified on the basis that it maximizes the amount of gas generated from this component of the waste inventory and is compatible with a mechanistic approach to the modelling of a water balance.

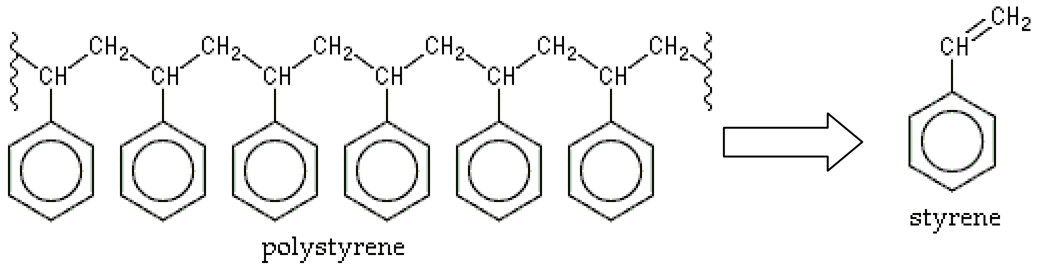

Figure 4.2: Polystyrene Degradation

The degradation of styrene is coupled to the reduction of the relevant TEAs in the same manner as outlined for cellulose. The microbial degradation of styrene under oxidizing conditions has been extensively investigated (Mooney et al. 2006) but there is little information regarding its degradation in reducing environments. The anaerobic degradation of other aromatic compounds has been reported (Lovely 2000, Spormann and Widdel 2000, Karthikeyan and Bhandari 2001) but only where terminal electron acceptors such as ferric iron and sulphate are available.

The degradation of IX resins is modelled using a set of degradation pathways constructed using the approach outlined by Rittmann and McCarty (2001), but with the release of bound water. These pathways are outlined below:

$$C_8H_8.mH_2O + 10O_2 \rightarrow 8CO_2 + (4+m)H_2O$$

oxidation of styrene by molecular oxygen (4.12)

$$C_8H_8.mH_2O + 8NO_3^- + 8H^+ \rightarrow 8CO_2 + 4N_2 + (8+m)H_2O$$

oxidation of styrene by nitrate reduction (4.13)

$$C_8H_8.mH_2O + 40Fe(III) + 16H_2O \rightarrow 8CO_2 + 40Fe(II) + 40H^+ + mH_2O$$

oxidation of styrene by ferric iron reduction (4.14)

$C_8H_8.mH_2O + 5SO_4^{2-} + 10H^+ \rightarrow 8CO_2 + (4+m)H_2O + 5H_2S$

oxidation of styrene by sulphate reduction (4.15)

$C_8H_8.mH_2O + 6H_2O \rightarrow 3CO_2 + 5CH_4 + mH_2O$ methane generation from styrene (4.16)

where the reaction rates for all these are that for polystyrene degradation and m represents the number of moles of bound water per mole of styrene monomer in the initial resin material.

Note that resins typically consist of anion and/or cation functional groups on the polystyrene divinylbenzene backbone, in addition to the bound water. These functional groups comprise a significant fraction of the mass of the resins, but do not usually contain much carbon and therefore do not contribute significantly to potential gas generation. In the GGM model, these mass components are not explicitly treated when modelling the degradation of resins. They are treated as being part of the polystyrene divinylbenzene backbone instead. The total dry resin mass is input (excluding bound water) and the degradation reactions refer to the polystyrene divinylbenzene backbone and associated bound water.

Degradation of Plastics and Rubber

The plastic and rubber components of radioactive waste represent a heterogeneous mix of materials such as PVC, polyethylene, neoprene, nitrile, and latex. The heterogeneous nature of this waste category makes it difficult to model since the degradation of each material would have to be modelled explicitly with an individual inventory and reaction scheme for each component.

A number of authors have suggested that plastic waste components such as polythene, PVC and polyurethane are recalcitrant under repository conditions (Grant et al. 1997, BNFL 2002). British Nuclear Fuels Limited (BNFL 2002) stated in documentation supporting the 2002 Drigg safety case that: "*The current available information would suggest that the majority of the higher molecular weight polymers would remain undegraded for a considerable length of time, particularly addition polymers*." This position is supported by the work of Francis et al. (1997) who found no evidence of biodegradation of electron beam irradiated plastic and rubber.

A more recent review by Cohen (2006) for the Waste Isolation Pilot Plant (WIPP) project concluded that some degradation of plastics and rubbers "*may occur over 10,000 years in the WIPP repository*." This conclusion appears to be based on the fact that oxidation and radiation damage may enhance biodegradation of these materials or generate soluble intermediates amenable to microbial attack. The authors point out that much of the evidence for the microbial degradation of these materials comes from aerobic systems. However, they do not rule out the possibility of anaerobic microbial degradation.

In order to assess the impact of potential plastic and rubber degradation on the overall gas generation in the repository these components are modelled in the same manner as IX resins, but with separate initial inventory and rate constants. This allows their impact to be assessed without the need for detailed degradation pathways for each component.

4.2.1.2 Microbial Hydrogen Metabolism

In radioactive waste disposal sites, significant amounts of hydrogen may be produced via anaerobic corrosion of metals. Hydrogen is also a common product of anaerobic microbial metabolism and consequently there are a large number of microbial processes able to process hydrogen (Grant et al. 1997, Pedersen 2000). The oxidation of hydrogen takes place under anaerobic conditions and is therefore coupled with the reduction of ferric iron, sulphate and carbon dioxide:

$$H_2 + 2Fe(III) \rightarrow 2Fe(II) + 2H^+ \qquad \text{hydrogen oxidation via iron reduction} \quad (4.17)$$

$$4H_2 + SO_4^{2-} + 2H^+ \rightarrow H_2S + 4H_2O \qquad \text{hydrogen oxidation via sulphate reduction} \quad (4.18)$$

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \qquad \text{methane generation from hydrogen oxidation} \quad (4.19)$$

where the corresponding rate constants are expressed in terms of the rate of consumption of H_2.

The ferric ion Fe(III) is assumed primarily present as FeOOH within the saturated region. The sulphate reaction also only occurs in the saturated region. The methane generation can occur anywhere within the system, if there is enough humidity to support microbial processes.

The corrosion hydrogen generation and microbial hydrogen consumption are independent of each other, each having independent rates of reaction. The accumulation of hydrogen within the system is controlled by the relative rates of anaerobic corrosion and microbial hydrogen consumption. If the rate of microbial hydrogen consumption is higher than that of corrosion and associated hydrogen generation, then the rate of corrosion becomes the rate-limiting step in the process. Consequently hydrogen consumption progresses instantaneously as long as sufficient TEA capacity is present. This case reflects the low levels of hydrogen detected in radioactive waste degradation experiments where significant amounts of corrodible metal are present (Beadle et al. 2001, Grey 2002 and Small et al. 2005).

4.2.1.3 Microbial Biomass

<u>Biomass Production</u>

When microbes degrade materials, some of the feed material is used to produce new biomass. Biological systems require more water than that required for the reactions they catalyze, since cells are typically 80 wt% water. Therefore, any attempt to model water within microbially active systems needs to account for the amount of water required to maintain microbial cells. This means that biomass production and degradation has to be modelled since significant amounts of water may be held up in microbial biomass. Consequently, although there may be sufficient water to complete the oxidation-reduction reactions, there may be insufficient water to support the production of microbial cells (Wang and Francis 2005).

The amount of water needed to support microbial biomass can be calculated using an empirical formula for microbial dry biomass such as $C_5H_7O_2N$ (Rittmann and McCarty 2001), which indicates that 1 mole of biomass would weigh 113 g. Since biomass is 80 wt% water then each mole of biomass also requires approximately 25 moles of water[3]. This requirement for water can then be integrated into the biomass generation reactions outlined below (in the model, we conservatively assume that there is always sufficient NH_3 to support these reactions):

$$5C_6H_{10}O_5 + 6NH_3 + 137H_2O \rightarrow 6C_5H_7O_2N\cdot 25H_2O$$

biomass generation from cellulose (4.20)

$$C_8H_8 + 2NH_3 + 2CO_2 + 50H_2O \rightarrow 2C_5H_7O_2N\cdot 25H_2O$$

biomass generation from styrene (4.21)

$$5CO_2 + 10H_2 + NH_3 + 17H_2O \rightarrow C_5H_7O_2N\cdot 25H_2O$$

biomass generation from hydrogen (4.22)

Cellulose degradation will involve both degradation products as outlined in Equations (4.7) to (4.11), as well as production of biomass as per Equation (4.20) using the energy from the degradation reactions (and CO_2 per Equation (4.21)). The overall reaction rate is described by the effective cellulose degradation rate, but with the cellulose mass divided between biomass and degradation products according to an empirical yield coefficient, Y:

$$\text{Cellulose} \rightarrow Y\ (\text{biomass}) + (1\text{-}Y)\ (\text{degradation products})$$

The rate of production of biomass is controlled, as with the degradation products, by the degradation rate of cellulose or styrene, or the rate of the methane-generation reaction Equation (4.19).

<u>Biomass Decay</u>

Microbial biomass is subject to natural turnover since cells have finite lifetimes. Biomass contains a range of compounds, which have different degradabilities. Some microbial cell components are recalcitrant to further degradation and accumulate in the environment. In the present model, two classes of biomass compounds are considered – easily recycled and recalcitrant.

The fraction K_R of dead <u>hydrated</u> biomass that is readily recycled is modelled according to the reverse of Equation (4.20):

$$6C_5H_7O_2N\cdot 25H_2O \rightarrow 5C_6H_{10}O_5 + 6NH_3 + 137H_2O \qquad (4.23)$$

It is assumed that the recycled biomass can be represented as cellulose, with each mole of biomass ($C_5H_7O_2N$) producing 5/6 mol of cellulose ($C_6H_{10}O_5$). The energy to drive this process comes from the oxidation of the organic material itself. This approach to biomass recycling is adopted since it is considered to be conservative with respect to gas generation.

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[3] The molar mass of dry biomass is approximately 113 g mol^{-1}. Since the 113 g represents 20% of the whole, the remaining 80% which is water is equivalent to 452 g, which is 25.1 moles of water.

The remaining fraction of biomass is recalcitrant (1 – K_R) and does not degrade further, except that upon death, the cells will release the water they hold - 25 mol H_2O are released per mol recalcitrant dead biomass.

Threshold for Biomass Activity

Water activity (A_w) is the ratio of the vapour pressure of water in a material to the vapour pressure of pure water at the same temperature. Relative humidity of air is the ratio of the vapour pressure of water in air to the water saturation vapour pressure. When vapour and temperature are at equilibrium, the water activity of a material is equal to the relative humidity of the surrounding air:

$$RH = A_w \qquad (4.24)$$

A_w is important because biological activity ceases at an A_w below 0.6[4] with the lower limit for bacteria being 0.75 (Brown 1976, Wang and Francis 2005). Consequently, to model microbially driven reactions in the repository, it is necessary to check the water activity or RH. Microbial processes should be allowed to proceed within the vapour phase for sufficiently high RH. Rate constants for all the biomass generation reactions and microbial processes that normally occur only under saturated conditions are ramped smoothly down to zero as the RH drops from 0.8 to 0.6. If the rate of water consumption is rapid compared with the rate of water ingress, it is feasible that the relative humidity, or water activity, could fall below that required to sustain microbial activity.

4.2.2 Reaction Kinetics

The degradation of polymeric organic substrates is modelled as being first order with respect to their amounts (Equation (4.25)):

$$-\frac{dQ_i}{dt} = V_{i,j}.Q_i \qquad \text{degradation of polymeric substrates} \qquad (4.25)$$

where Q_i [mol] is the amount of substrate i (i = C, R, P for cellulose, IX resins, and plastics and rubbers, respectively) and $V_{i,j}$ [s^{-1}] is the degradation rate constant for substrate i under conditions j (j = a, b, c, d, e for aerobic respiration, denitrification, iron reduction, sulphate reduction, and methanogenesis, respectively). $V_{i,j} = V_i$ if substrate j is being consumed, and 0 otherwise, where V_i [s^{-1}] is the degradation rate of cellulose, IX resin or plastics and rubbers.

This is an approach commonly applied to the modelling of the degradation of polymeric organic substrates (Pavlostathis and Giraldo-Gomez 1991, Rittmann and McCarty 2001, IWA 2002). The rates of all the microbial reactions modelled are determined by the rate of polymer degradation. This constrains the number of input kinetic parameters required to run the model to an aerobic and an anaerobic rate for each of the three polymeric substrates modelled.

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[4] Note that some fungi can live at an A_w close to 0.6. Fungi are generally considered to be better adapted to low water availability. However fungi are generally aerobic organisms and would not be expected to play an important role in an anaerobic deep geologic environment.

The model is set up to allow the polymer degradation rates to be modified depending on the prevailing environmental conditions. Generally speaking as the system moves from oxidizing to reducing conditions, degradation rates slow down. The model simulates this by having independent polymer degradation rates for when specific TEAs dominate. This is not the same as having the removal of the TEAs being kinetically controlled.

Biomass generation is coupled to polymer degradation via a yield coefficient which determines how organic carbon is partitioned between energy generation and biomass production, Equation (4.26). This yield coefficient depends on the TEA consumed since the yield decreases as the available energy generation decreases.

$$\frac{dX}{dt} = Y_j \frac{dQ_i}{dt} - XD \qquad \text{biomass generation} \qquad (4.26)$$

where X [mol] is the quantity of biomass, Y_j [-] is the biomass yield coefficient for condition j, and D [s^{-1}] is the biomass decay rate.

The production and consumption of gaseous products is also coupled to polymer degradation via the yield coefficient and a stoichiometric coefficient relevant to that product

$$\frac{dQ_k}{dt} = J_{ki}(1 - Y_j)\frac{dQ_i}{dt} \qquad \text{product generation} \qquad (4.27)$$

where Q_k [mol] is the number of moles of product k (k = CO_2, H_2, N_2, H_2S, CH_4) and J_{ki} [-] is the stoichiometric coefficient for product k formed from organic substrate i.

4.2.3 Summary of Microbial Modelling

The modelling of the microbial reactions includes the following features:

1. A mechanistic basis for treatment of microbial processes;
2. The inclusion of different rates of degradation of organic substrates based on either oxidizing or reducing conditions;
3. The possible limitation of microbial processes by the availability of water;
4. Separate treatment of IX resins, and plastics and rubbers;
5. The inclusion of H_2-mediated microbial processes; and
6. The recycling of dead biomass.

4.3 Corrosion Gas Generation Processes

4.3.1 Corrosion Reactions

The various metallic waste forms and container materials considered in the model are: carbon and galvanized steels, passivated carbon steel, stainless steel and nickel alloys, and zirconium alloys.

Corrosion of the metallic wastes and container materials occurs under both aerobic and anaerobic conditions and in unsaturated (i.e., humid) and saturated (i.e., submerged) environments. Under aerobic conditions, corrosion is generally supported by the cathodic reduction of dissolved O_2, although simultaneous reduction of O_2 and H_2O is possible for some materials. Once the initially trapped atmospheric O_2 has been consumed, corrosion is supported by the reduction of H_2O only. The effect of oxidizing radiolysis products is not included, as the radiation fields for the various low and intermediate level waste are insignificant.

Aqueous corrosion processes are possible in humid atmospheres provided the relative humidity is sufficiently high. The relevant vapour phase rate constants are ramped smoothly down to zero between 80% and 60% relative humidity.

4.3.1.1 Carbon and Galvanized Steels

The inventory of carbon and galvanized steels in the repository will comprise various carbon steel wastes, as well as carbon and galvanized steel waste containers. Galvanized and carbon steels are treated as a single metallic source. Although the short-term rate of atmospheric corrosion of galvanized steel is lower than that of carbon steel, the thickness of the zinc layer on galvanized steel represents only a small fraction of the overall container wall thickness. Furthermore, there is little difference in the corrosion rate of these two materials under saturated conditions. Therefore, the corrosion of both materials is represented by the corrosion of Fe as carbon steel (C-steel).

The aerobic corrosion of C-steel under saturated and unsaturated conditions is given by the reaction:

$$4Fe + 2H_2O + 3O_2 \rightarrow 4\ \text{“FeOOH”} \tag{4.28}$$

where “FeOOH” represents an un-specified ferric oxyhydroxide species, which may also contain groundwater species (Cl^-, SO_4^{2-}, CO_3^{2-}) in various forms of green rust (King and Stroes-Gascoyne 2000). Since FeOOH is only an intermediate species, the degree of hydration of the corrosion product need not be specified for the overall water mass-balance calculation (see below).

As the environment becomes anaerobic, the Fe(III) corrosion product is converted to Fe(II) via

$$2FeOOH + Fe + 2H_2O \rightarrow 3Fe(OH)_2 \tag{4.29}$$

Under anaerobic conditions, the corrosion of C-steel is supported by the reduction of H_2O

$$Fe + 2H_2O \rightarrow Fe(OH)_2 + H_2 \tag{4.30}$$

Ferrous hydroxide may also convert to magnetite via the Schikkor reaction (Shreir 1976)

$$3Fe(OH)_2 \rightarrow Fe_3O_4 + 2H_2O + H_2 \tag{4.31}$$

with the formation of additional H_2.

The nature of the long-term stable anaerobic corrosion product, $Fe(OH)_2$ or Fe_3O_4, determines the maximum amount of H_2 that can be produced from the corrosion of carbon steel. If $Fe(OH)_2$ is the stable corrosion product, then 1 mole of H_2 is produced for each mole of Fe corroded. Conversely, if Fe_3O_4 is the stable corrosion product, then 1.33 moles of H_2 are produced for each mole of Fe corroded.

King and Stroes-Gascoyne (2000) reviewed the nature of corrosion products formed during the corrosion of carbon steel in natural waters. Figure 4.3 shows an overall reaction scheme that accounts for the majority of observations reported in the literature[5]. Ferrous hydroxide ($Fe(OH)_2$) is generally an intermediate species in the aerobic and anaerobic oxidation of carbon steel, even at temperatures <80°C where the conversion of $Fe(OH)_2$ to Fe_3O_4 via the Schikkor reaction is generally regarded as slow. There is no evidence in the literature for the formation of $Fe(OH)_2$ as the main end product of the reduction of Fe(III) corrosion products.

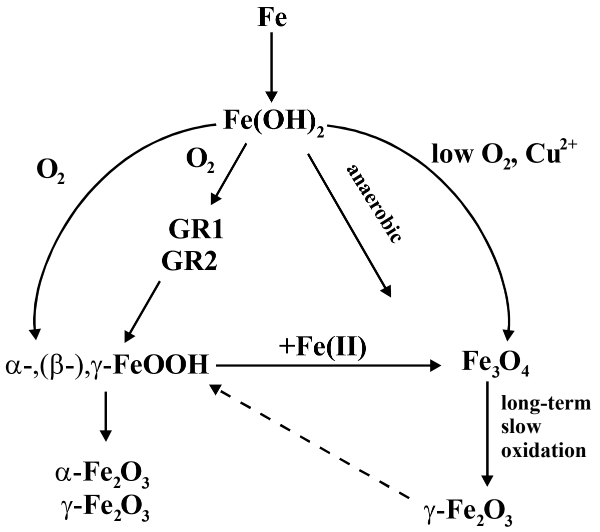

Figure 4.3: Generalized Reaction Scheme for the Formation and Transformation of Corrosion Product Films on C-steel[6]

Therefore, based on the evidence summarized above, the stable product of the corrosion of carbon steel is taken to be Fe_3O_4 rather than $Fe(OH)_2$. The overall reaction for the anaerobic corrosion of C-steel (Equations (4.30) and (4.31)) can, therefore, be written as

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \qquad (4.32)$$

and the overall reduction of FeOOH under anaerobic conditions can be written as

$$2FeOOH + Fe \rightarrow Fe_3O_4 + H_2 \qquad (4.33)$$

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[5] Not all the details in the figure are applicable to corrosion in the DGR, but the entire mechanism is shown for completeness, and to demonstrate the depth of understanding of the corrosion of steels in natural waters.

[6] GR1 and GR2 stand for Green Rust 1 and Green Rust 2, two forms of Fe(III) oxyhydroxide that contain varying amounts of Cl^-, SO_4^{2-}, and CO_3^{2-}. The α, β and γ variants correspond to different crystal structures: α-FeOOH is goethite; β-FeOOH is akaganeite; γ-FeOOH is lepidocrocite; α-Fe_2O_3 is haematite; and γ-Fe_2O_3 is magnetite.

In GGM, the aerobic corrosion of C-steel is represented by Equation (4.28), the conversion of FeOOH under anaerobic conditions by Equation (4.33), and the anaerobic corrosion of C-steel by Equation (4.32).

These latter two processes represent a conservative approach to the calculation of the quantity of H_2 generated since, if $Fe(OH)_2$ rather than Fe_3O_4 is the stable long-term anaerobic corrosion product, less H_2 will be generated.

Carbon steel undergoes accelerated corrosion in the presence of high CO_2 partial pressures (de Waard and Milliams 1976). The enhanced corrosion rate is primarily a consequence of the decrease in pH that accompanies the dissolution of CO_2 in water to form carbonic acid (H_2CO_3). However, because of the high HCO_3^- concentration, the stable corrosion product is $FeCO_3$ rather than Fe_3O_4. The corrosion of carbon steel in CO_2-containing environments is given by

$$Fe + H_2CO_3 \rightarrow FeCO_3 + H_2 \tag{4.34}$$

Because of the importance of this process in the oil and gas industry, there have been a large number of studies to determine the effect of the CO_2 partial pressure, P_{CO2}, on the corrosion rate of carbon steel (ASM 1987, 2003, 2005). Many of these studies have been performed under conditions of high rates of mass transport such as might be encountered in pipelines, and the absolute corrosion rates reported are not relevant to the environmental conditions within the DGR. However, these studies indicate a dependence of the corrosion rate on $(P_{CO2})^q$, where q is typically of the order of 0.66 (de Waard and Milliams 1976; de Waard and Lotz 1993; de Waard et al. 1991, 1995). The empirical model used to derive a value for q was fitted to data for CO_2 partial pressures up to 1 MPa.

In GGM, the corrosion rate of carbon and galvanized steel is taken to be a function of the CO_2 partial pressure, with the overall corrosion reaction given by Equation (4.34). Although the pH of the environment is not specifically calculated within the model, the use of an enhanced corrosion rate in the presence of CO_2 implicitly takes into account the acidification resulting from the dissolution of CO_2 in the aqueous phase. In terms of the model, the rate of reaction given by Equation (4.34) is treated as a multiplier of the anaerobic corrosion rate (see Equation (4.38)). (Under aerobic conditions, the degree of enhancement is minimal as O_2, rather than H^+, is the dominant oxidant). Therefore, depending upon the partial pressure of CO_2, the anaerobic corrosion rate is enhanced by an appropriate factor. If there is no CO_2 present, the factor is 1. The relative amounts of Fe_3O_4 and $FeCO_3$ formed are determined by the values of the respective rate constants and, in the case of $FeCO_3$, by the P_{CO2}.

4.3.1.2 Passivated Carbon Steel

Passivated carbon steel comprises waste forms grouted in cementitious materials and structural steel (rebar, rails, etc.) in contact with concrete. These materials are treated separately from the plain carbon and galvanized steel inventories because of the effect of the cementitious material on the corrosion rate. The high pH environment in the cement results in passivation of the carbon steel and, consequently, a lower corrosion rate.

Although the rate of corrosion of passivated carbon steel is lower, the mechanism is treated in exactly the same fashion as for the plain carbon and galvanized steel. Thus, the aerobic and anaerobic corrosion of passivated carbon steel are given by Equations (4.28) and (4.32), respectively, and the reduction of FeOOH is given by Equation (4.33). In alkaline environments, Fe_3O_4 is more stable than $Fe(OH)_2$ (Pourbaix 1974) and is likely to be the stable long-term corrosion product.

At the elevated pH expected to persist for some time in cementitious materials, Fe_3O_4 is thermodynamically more stable than $FeCO_3$. Therefore, enhanced corrosion of passivated carbon steel due to the presence of elevated CO_2 partial pressures is not included in GGM.

4.3.1.3 Stainless Steels and Nickel Alloys

Stainless steels and nickel alloys are present as container materials and as used reactor components such as from steam generators or pressure tube end fittings. These materials contain Fe, Ni, Cr, Mo, and other minor alloying elements, in amounts dependent on the composition of the particular alloy.

Corrosion of these alloys proceeds with the formation of a protective, or passive, film typically comprising Cr(III) or Ni(II), and possibly small amounts of other alloying elements (ASM 1987, 2003, 2005; Clayton and Olefjord 1995). Over long periods of time, however, other elements within the alloy, notably Fe, must also be oxidized since the amount of Cr in the alloys is limited. There is currently an incomplete understanding of how passive materials corrode over long periods of time, both from the viewpoint of the stability of the Cr-rich passive film that forms initially and from the viewpoint of how the corrosion behaviour evolves as the elements responsible for passivity become consumed.

In the absence of a complete understanding of their long-term corrosion behaviour, the corrosion of the passive materials is treated in GGM in the same manner as carbon steel, and they are assumed to fully oxidize although at a slower rate.

Thus, the aerobic and anaerobic corrosion of stainless steel are assumed to be given by Equations (4.28) and (4.32), respectively, and it is further assumed that oxidized corrosion products formed during the aerobic phase are subsequently reduced by a reaction analogous to Equation (4.33). This is an acceptable assumption for the corrosion of stainless steels, since these materials contain a high percentage of Fe (typically 60-80%, Sedriks 1996). For the Ni-based alloys, the assumption is considered reasonable, even though the aerobic corrosion products formed for these materials, Cr(III) and Ni(II), are not reduced during the aerobic-anaerobic transition in the same manner as Fe(III). However, the degree of aerobic corrosion of the passive materials is minimal, since not only is the inventory of O_2 relatively small compared with the inventory of organic and metallic materials, but the O_2 that is present also tends to be consumed by degradation of cellulose and/or the corrosion of carbon and galvanized steel rather than by the corrosion of the passive materials. Under anaerobic conditions, the Ni-based alloys are assumed to corrode to corrosion products with an average metal to oxygen ratio of 1.33, as with Fe. The predominant valence for Ni corrosion products is +2, compared with a value of 2.67 for Fe in the form of Fe_3O_4. Therefore, this overstates by ~33% the amount of H_2 generated during the anaerobic phase from Ni. This is a sufficient approximation, since these alloys are also not dominant in the waste.

The corrosion rates of passive materials are higher under sour-service conditions, i.e., in the presence of CO_2 and H_2S gases (ASM 1987, 2003, 2005). The pressure of CO_2 developed in a deep repository could approach that typically found in down hole applications in the oil and gas industry. Therefore, the passive alloys undergo accelerated corrosion and the formation of carbonate-containing corrosion products, as for carbon and galvanized steels (Equation (4.34)).

4.3.1.4 Zirconium Alloys

Zirconium alloy waste may comprise fuel sheaths/hulls, pressure tubes and/or other components of the decommissioned reactors. Typically these alloys contain small amounts of Nb, which is approximated as oxidizing similar to Zr.

Under aerobic conditions the corrosion of Zr is given by

$$Zr + O_2 \rightarrow ZrO_2 \tag{4.35}$$

and under anaerobic conditions by

$$Zr + 2H_2O \rightarrow ZrO_2 + 2H_2 \tag{4.36}$$

The oxide film on zirconium alloys is a stable, effective barrier to corrosion. There are few reports of the use of Zr alloys exposed to aqueous environments with high pressures of CO_2. Neither the corrosion rate nor the nature of the corrosion products is affected by the presence of high CO_2 partial pressure.

4.3.2 Reaction Kinetics

The general expression for the consumption of the metallic wastes and container materials is given by

$$-\frac{dQ_\ell}{dt} = h\sum_{m=1,2}\frac{A_{\ell,1}\rho_\ell}{M_\ell}R_{\ell,m,1} + \varepsilon\sum_{m=1,2}\frac{A_{\ell,2}\rho_\ell}{M_\ell}R_{\ell,m,2} \tag{4.37}$$

where Q_ℓ [mol] is the quantity of metallic material ℓ (where ℓ = 1, 2, 3, 4 for carbon and galvanized steel, passivated carbon steel, passive alloys, and Zr alloys, respectively), ρ_ℓ [$kg \cdot m^{-3}$] and M_ℓ [$kg \cdot mol^{-1}$] are the density and equivalent atomic mass of metallic material ℓ, respectively, $A_{\ell,n}$ [m^2] is the surface area of material ℓ exposed to the vapour phase (n = 1) and submerged (n = 2), and $R_{\ell,m,n}$ [$m \cdot s^{-1}$] is the corrosion rate of material ℓ under redox conditions m (m = 1, 2 for aerobic and anaerobic conditions, respectively) and degree of saturation n (n = 1, 2 for unsaturated and saturated conditions, respectively). The fraction of the surface area submerged is taken to be equal to the degree of saturation S, with the fraction exposed to the vapour phase equal to (1 – S). $R_{\ell,m,n}$ is zero if conditions are not in the appropriate redox regime; i.e., $R_{\ell,1,n} = 0$ under anaerobic conditions, and $R_{\ell,2,n} = 0$ under aerobic conditions. h and ε are scaling factors used to model the effects of relative humidity and water-limited conditions, respectively. They are defined in Table 4.1.

Corrosion of carbon and galvanized steels, and the stainless steel and Ni-based passive alloys, is also enhanced by the presence of CO_2. In the repository, CO_2-enhanced corrosion will occur primarily under anaerobic conditions (m = 2) but could be possible under both saturated and unsaturated conditions (n = 1, 2 respectively).

In GGM, the effect of CO_2 on the rate of corrosion (expressed as a rate of consumption in $mol \cdot s^{-1}$) is given by

$$-\frac{dQ_\ell}{dt} = \frac{\rho_\ell}{M_\ell}\left(hA_{\ell,1}R_{\ell,1,1} + h\left(1+\left(\frac{P_{CO2}}{P^{ref}_{CO2}}\right)^{q}\right)A_{\ell,1}R_{\ell,2,1} + \varepsilon A_{\ell,2}R_{\ell,1,2} + \varepsilon\left(1+\left(\frac{P_{CO2}}{P^{ref}_{CO2}}\right)^{q}\right)A_{\ell,2}R_{\ell,2,2}\right) \tag{4.38}$$

where ℓ = 1, 3 (carbon and galvanized steel, and stainless steel and Ni-based alloys, respectively), and P^{ref}_{CO2} [Pa] is a reference CO_2 partial pressure at which the corrosion rate is twice the value in the absence of CO_2.

The consumption and generation of various gases (O_2, CO_2, and H_2), corrosion products (FeOOH, $FeCO_3$, and Fe_3O_4), and of H_2O are estimated from the respective corrosion rates using appropriate stoichiometric coefficients from Equations (4.28) and (4.32)-(4.36).

As noted in Section 4.3.1.3, the long-term corrosion behaviour of stainless steels and Ni-based alloys is described by the same stoichiometric equations used for carbon and galvanized steel.

The same corrosion rates are used for stainless steel and nickel alloys. Based on evidence from the literature, any differences in the corrosion rates for these alloys is within the reproducibility of the reported corrosion rate of approximately half an order of magnitude. Under anaerobic conditions, the amount of H_2 produced by corrosion depends on the metal/oxygen ratio in the respective oxide formed for each metal. As noted above (Section 4.3.1.3), this can result in an approximately 33% variation in the rate of H_2 generation between stainless steels and Ni-based alloys. This variation, however, is again within the reproducibility of the measured corrosion rates and the use of the same corrosion rates for stainless steels and passive Ni alloys is, therefore, justified.

A detailed list of input parameters for GGM is given in Table 4.1.

Table 4.1: List of Model Parameters for the Gas Generation Model Together with Their Internal Units

Symbol	Definition	Units
$A_{\ell,n}$	Surface area of metal ℓ under saturation conditions n	m^2
$A_{1,1}$	Surface area of carbon and galvanized steel exposed to vapour phase	m^2
$A_{1,2}$	Surface area of carbon and galvanized steel exposed to solution phase	m^2
$A_{2,1}$	Surface area of passivated carbon steel exposed to vapour phase	m^2
$A_{2,2}$	Surface area of passivated carbon exposed to solution phase	m^2
$A_{3,1}$	Surface area of stainless steel and Ni-based alloy exposed to vapour phase	m^2
$A_{3,2}$	Surface area of stainless steel and Ni-based alloy exposed to solution phase	m^2
$A_{4,1}$	Surface area of Zr alloy exposed to vapour phase	m^2

Symbol	Definition	Units
$A_{4,2}$	Surface area of Zr alloy exposed to solution phase	m^2
C_k	Concentration of product k in the water	$mol\ m^{-3}$
C_{CO2}	Concentration of dissolved carbon dioxide	$mol\ m^{-3}$
C_{H2}	Concentration of dissolved hydrogen	$mol\ m^{-3}$
C_{H2S}	Concentration of dissolved hydrogen sulphide	$mol\ m^{-3}$
C_{CH4}	Concentration of dissolved methane	$mol\ m^{-3}$
C_{O2}	Concentration of dissolved oxygen	$mol\ m^{-3}$
C_{N2}	Concentration of dissolved nitrogen	$mol\ m^{-3}$
C_{NO3}	Concentration of dissolved nitrate	$mol\ m^{-3}$
C_{SO4}	Concentration of dissolved sulphate	$mol\ m^{-3}$
D	Biomass decay rate	s^{-1}
ε	A constant with value between 0 and 1 chosen to balance the rate of consumption of water due to saturated phase reactions with the rate of ingress of water when at zero saturation. Has the value 1 under partially or fully saturated conditions.	Unitless
g	S+h(1-S). This factor is used to scale processes that are RH dependent in the vapour phase.	Unitless
h	A RH modulation function, varying linearly from 0 to 1 in the range RH_{min} to RH_{max}	Unitless
J_{ki}	Stoichiometric coefficient for product k formed from organic substrate i	Unitless
J_{H2O}	Flux of water into the repository from the geosphere	$mol \cdot s^{-1}$
K_i	Solubility constant for species i	$mol\ m^{-3}\ Pa^{-1}$
K_{CO2}	Solubility constant for carbon dioxide	$mol\ m^{-3}\ Pa^{-1}$
K_{H2}	Solubility constant for hydrogen	$mol\ m^{-3}\ Pa^{-1}$
K_{H2S}	Solubility constant for hydrogen sulphide	$mol\ m^{-3}\ Pa^{-1}$
K_{CH4}	Solubility constant for methane	$mol\ m^{-3}\ Pa^{-1}$
K_{O2}	Solubility constant for oxygen	$mol\ m^{-3}\ Pa^{-1}$
K_{N2}	Solubility constant for nitrogen	$mol\ m^{-3}\ Pa^{-1}$
K_R	Fraction of dead biomass recycled into cellulose	Unitless
m	The number of moles of bound water per mole of styrene monomer	-
M_ℓ	Effective molecular mass of metal ℓ	$kg\ mol^{-1}$

Symbol	Definition	Units
M_1	Effective molecular mass of carbon and galvanized steel	kg mol^{-1}
M_2	Effective molecular mass of passivated carbon steel	kg mol^{-1}
M_3	Effective molecular mass of stainless steel and Ni-based alloys	kg mol^{-1}
M_4	Effective molecular mass of Zr alloys	kg mol^{-1}
P_i	Partial pressure of gaseous species i	Pa
P_{CO2}	Partial pressure of carbon dioxide	Pa
P_{CO2}^{ref}	Reference partial pressure of CO_2 for enhancement of corrosion	Pa
P_{H2}	Partial pressure of hydrogen	Pa
P_{H2S}	Partial pressure of hydrogen sulphide	Pa
P_{CH4}	Partial pressure of methane	Pa
P_{O2}	Partial pressure of oxygen	Pa
P_{N2}	Partial pressure of nitrogen	Pa
q	Exponent for enhancement of corrosion rate by CO_2	Unitless
q_{CO2}	Amount of gaseous carbon dioxide in the repository	mol
q_{H2}	Amount of gaseous hydrogen in the repository	mol
q_{H2S}	Amount of gaseous hydrogen sulphide in the repository	mol
q_{CH4}	Amount of gaseous methane in the repository	mol
q_{O2}	Amount of gaseous oxygen in the repository	mol
q_{N2}	Amount of gaseous nitrogen in the repository	mol
Q_ℓ	Quantity of metallic material ℓ	mol
Q_1	Quantity of carbon and galvanized steel	mol
Q_2	Quantity of passivated carbon steel	mol
Q_3	Quantity of stainless steel and Ni-based alloys	mol
Q_4	Quantity of Zr alloys	mol
Q_{FeOOH}	Quantity of iron oxyhydroxide	mol
Q_{FeCO3}	Quantity of iron carbonate	mol
Q_{Fe3O4}	Quantity of magnetite	mol
Q_{FeS}	Quantity of iron sulphide	mol
Q_{H2O}	Quantity of water	mol
Q_{MgO}	Quantity of magnesium oxide	mol
Q_C	Quantity of (dry) cellulose monomer	mol

Symbol	Definition	Units
Q_R	Quantity of styrene monomer from (dry) IX resin waste	mol
Q_P	Quantity of styrene monomer from (dry) plastics and rubbers	mol
Q_{CO2}	Total amount of carbon dioxide in the repository	mol
Q_{H2}	Total amount of hydrogen in the repository	mol
Q_{H2S}	Total amount of hydrogen sulphide in the repository	mol
Q_{CH4}	Total amount of methane in the repository	mol
Q_{O2}	Total amount of oxygen in the repository	mol
Q_{N2}	Total amount of nitrogen in the repository	mol
$R_{\ell,m,n}$	Corrosion rate of metal ℓ under redox conditions m and degree of saturation n	$m\ s^{-1}$
$R_{1,1,1}$	Corrosion rate of carbon and galvanized steel under aerobic unsaturated conditions	$m\ s^{-1}$
$R_{1,2,1}$	Corrosion rate of carbon and galvanized steel under anaerobic unsaturated conditions	$m\ s^{-1}$
$R_{1,1,2}$	Corrosion rate of carbon and galvanized steel under aerobic saturated conditions	$m\ s^{-1}$
$R_{1,2,2}$	Corrosion rate of carbon and galvanized steel under anaerobic saturated conditions	$m\ s^{-1}$
$R_{2,1,1}$	Corrosion rate of passivated carbon steel under aerobic unsaturated conditions	$m\ s^{-1}$
$R_{2,2,1}$	Corrosion rate of passivated carbon steel under anaerobic unsaturated conditions	$m\ s^{-1}$
$R_{2,1,2}$	Corrosion rate of passivated carbon steel under aerobic saturated conditions	$m \cdot s^{-1}$
$R_{2,2,2}$	Corrosion rate of passivated carbon steel under anaerobic saturated conditions	$m\ s^{-1}$
$R_{3,1,1}$	Corrosion rate of stainless steel and Ni-based alloys under aerobic unsaturated conditions	$m\ s^{-1}$
$R_{3,2,1}$	Corrosion rate of stainless steel and Ni-based alloys under anaerobic unsaturated conditions	$m\ s^{-1}$
$R_{3,1,2}$	Corrosion rate of stainless steel and Ni-based alloys under aerobic saturated conditions	$m\ s^{-1}$
$R_{3,2,2}$	Corrosion rate of stainless steel and Ni-based alloys under anaerobic saturated conditions	$m\ s^{-1}$
$R_{4,1,1}$	Corrosion rate of Zr alloys under aerobic unsaturated conditions	$m\ s^{-1}$
$R_{4,2,1}$	Corrosion rate of Zr alloys under anaerobic unsaturated conditions	$m\ s^{-1}$

Symbol	Definition	Units
$R_{4,1,2}$	Corrosion rate of Zr alloys under aerobic saturated conditions	m s^{-1}
$R_{4,2,2}$	Corrosion rate of Zr alloys under anaerobic saturated conditions	m s^{-1}
RH_{min}	A Relative Humidity value (fractional) below which all vapour phase corrosion and microbial reactions are modelled to have ceased.	Unitless
RH_{max}	A Relative Humidity value (fractional) above which all vapour phase corrosion and microbial reactions are modelled as fully active.	Unitless
ρ_{ℓ}	Density of metal ℓ	kg m^{-3}
ρ_1	Density of carbon and galvanized steel	kg m^{-3}
ρ_2	Density of passivated carbon steel	kg m^{-3}
ρ_3	Density of stainless steel and Ni-based alloys	kg m^{-3}
ρ_4	Density of Zr alloys	kg m^{-3}
S	Degree of saturation. Ratio of volume of free water within repository (excludes bound water) and repository void volume.	Unitless
t	time	s
$V_{i,j}$	Rate constant for the degradation or organic substrate i under microbial condition j	s^{-1}
$V_{C,a}$	Rate constant for the aerobic degradation of cellulose	s^{-1}
$V_{C,b}$	Rate constant for the oxidation of cellulose by nitrate reduction	s^{-1}
$V_{C,c}$	Rate constant for the oxidation of cellulose by ferric ion reduction	s^{-1}
$V_{C,d}$	Rate constant for the oxidation of cellulose by sulphate reduction	s^{-1}
$V_{C,e}$	Rate constant for the generation of methane from cellulose	s^{-1}
$V_{R,a}$	Rate constant for the aerobic degradation of IX resins	s^{-1}
$V_{R,b}$	Rate constant for the oxidation of IX resins by nitrate reduction	s^{-1}
$V_{R,c}$	Rate constant for the oxidation of IX resins by ferric ion reduction	s^{-1}
$V_{R,d}$	Rate constant for the oxidation of IX resins by sulphate reduction	s^{-1}
$V_{R,e}$	Rate constant for the generation of methane from IX resins	s^{-1}
$V_{P,a}$	Rate constant for the aerobic degradation of plastics and rubbers	s^{-1}
$V_{P,b}$	Rate constant for the oxidation of plastics and rubbers by nitrate reduction	s^{-1}
$V_{P,c}$	Rate constant for the oxidation of plastics and rubbers by ferric ion reduction	s^{-1}
$V_{P,d}$	Rate constant for the oxidation of plastics and rubbers by sulphate reduction	s^{-1}

Symbol	Definition	Units
$V_{P,e}$	Rate constant for the generation of methane from plastics and rubbers	s^{-1}
V_{FeS}	Rate constant for the precipitation of FeS	s^{-1}
V_{FeOOH}	Rate constant for the reductive dissolution of FeOOH	s^{-1}
V_{MgO}	Rate constant for the conversion of magnesium oxide to magnesium carbonate	s^{-1}
V_{H1}	Rate constant for the microbial oxidation of H_2 via iron reduction	s^{-1}
V_{H2}	Rate constant for the microbial oxidation of H_2 via sulphate reduction	s^{-1}
V_{H3}	Rate constant for the microbial generation of methane from H_2 oxidation	s^{-1}
V_v	Void volume in the repository	m^3
X	Biomass	mol
X_a	Biomass of aerobes	mol
X_b	Biomass of denitrifiers	mol
X_c	Biomass of iron reducers	mol
X_d	Biomass of sulphate reducers	mol
X_e	Biomass of methanogens	mol
X_{dead}	Dead and non-recyclable biomass	mol
X_{tot}	Live (hydrated) biomass	mol
Y_j	Biomass yield coefficient for microbial condition j	Unitless
Y_a	Biomass yield coefficient for aerobes	Unitless
Y_b	Biomass yield coefficient for denitrifiers	Unitless
Y_c	Biomass yield coefficient for iron reducers	Unitless
Y_d	Biomass yield coefficient for sulphate reducers	Unitless
Y_e	Biomass yield coefficient for methanogens	Unitless

4.3.3 Summary of Corrosion Modelling

The basic corrosion model includes:

1. Aerobic and anaerobic corrosion of carbon and galvanized steel, passivated carbon steel, stainless steel and nickel alloys, and zirconium alloys;
2. Corrosion under saturated and unsaturated conditions;
3. Consumption of O_2 and CO_2 and, under anaerobic conditions, the generation of H_2;
4. The reductive dissolution of Fe(III) formed during the aerobic period;

5. Treatment of the corrosion of carbon and galvanized steel and passive alloys in the presence of CO_2, leading to enhanced corrosion rates and the formation of $FeCO_3$, and in the absence of CO_2 leading to the formation of Fe_3O_4; and
6. Rationalization for the formation of Fe_3O_4 as a long-term, stable corrosion product.

4.4 Additional Processes

4.4.1 Gas Mitigation Processes

There are a number of processes by which the impact of gas production in the repository could be mitigated, either by design or because of inherent reactions within the repository.

Two natural processes that will result in the consumption of gas are included. First, the conversion of H_2 and CO_2 to CH_4 is modelled as part of the microbial reaction scheme (Equation (4.19), Section 4.2.1.2). Methanogenesis is an important cause of gas consumption, since five moles of gas (four moles of H_2 and one mole of CO_2) are consumed for every mole of CH_4 produced.

Second, reaction between H_2S and dissolved metal ions, primarily Fe(II), will result in the formation (and rapid precipitation due to low solubility) of metal sulphides. Since Fe(II) will be the principal dissolved metal ion in the repository, the precipitation of metal sulphides is represented by

$$\mathrm{Fe(II)} + H_2S \rightarrow FeS + 2H^+ \tag{4.39}$$

where the stoichiometry of iron sulphide is uncertain, but is here represented by the species “FeS”. The kinetics of the precipitation of iron sulphide are taken to be first order with respect to the concentration of H_2S, on the basis that Fe(II) is likely to be present in excess in the system, and is given by

$$-\frac{dQ_{H2S}}{dt} = V_{FeS} C_{H2S} SV_v \tag{4.40}$$

where dQ_{H2S}/dt [mol s^{-1}] is the rate of change of the amount of H_2S in the repository, C_{H2S} [mol m^{-3}] is the concentration of H_2S, SV_V [m^3] is the saturated volume, and V_{FeS} [s^{-1}] is the first-order rate constant for the formation and precipitation of FeS, respectively.

“Gas scavengers” can also be deliberately added to the repository. For example, magnesium oxide is added to the WIPP facility to consume CO_2 via the precipitation of magnesium carbonate (Krumhansl et al. 2000). In GGM, this reaction is included to enable the effect of this gas mitigation strategy to be estimated:

$$5MgO + 5H_2O + 4CO_2 \rightarrow Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O \tag{4.41}$$

The rate of CO_2 removal by precipitation of magnesium carbonate is represented by

$$-\frac{dQ_{CO2}}{dt} = \frac{4}{5} Q_{MgO} V_{MgO} \tag{4.42}$$

where dQ_{CO2}/dt [mol s^{-1}] is the rate of change of the amount of CO_2 in the repository, respectively, Q_{MgO} [mol] is the quantity of MgO, and V_{MgO} [s^{-1}] is the first-order rate constant for the loss of MgO.

4.4.2 Carbonation of Concrete

Another potential sink for CO_2 in the repository is the carbonation of the cementitious material. The carbonation of concrete is represented by

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \tag{4.43}$$

This process could consume significant quantities of CO_2, especially if the repository is grouted.

The evolution of the concrete pore-water chemistry is a complex process. (Also, the OPG deep repository design for L&ILW does not use extensive amounts of concrete backfill.) The carbonation of concrete is not currently included in GGM.

Some effects of concrete can be readily included in the model, however. For example, the effect of extensive concrete backfill in reducing the void volume in the repository is simply accounted for through a change in input parameter values, as is the effect of the waste package grout on reducing the corrosion rate of metallic waste forms. However, effects on the degradation of organic materials, such as the alkaline hydrolysis of cellulose, are not currently included in GGM.

4.4.3 Water Availability

Once saturation in the repository reaches zero, the water consuming saturated phase reactions become limited by the rate of ingress of water from the geosphere. Rate constants for water-limited processes occurring in the vapour phase, including microbial processes, biomass generation and corrosion, are relative humidity dependent as described in Section 4.2.1.3 and Section 4.3.1. Other processes in the vapour phase are always active.

4.4.4 Gas Leakage and Influx

Gas can leak from the repository and be transported through the geosphere or, depending on the conditions, can move into the repository from the geosphere. The flow of gas through the geosphere is modelled by TOUGH2 independently of GGM using information about gas and water generation rates within the repository provided by GGM. The gas flow modelling enables the gas pressure at the repository to be calculated and fed back to GGM, which in turn uses this information to reassess the total number of moles of gas in the repository, to calculate the number of moles of gas which have leaked from or flowed into the repository and to repartition the gas in the repository between the vapour and saturated phases. When gas flows from the geosphere into the repository, its composition is assumed to match the composition of the existing gas within the repository. The validity of this assumption needs to be evaluated on a case by case basis depending on the assumed geosphere bulk gas and whether gas flowing into the repository is returning gas previously generated within the repository or ‘fresh’ bulk gas from the geosphere (see Section 7.3.4.8 for additional discussion of modelling of gas flux between the repository and the geosphere).

4.5 Implementation Of GGM

The definitions of all model parameters appearing in GGM model equations, including reactants, products and rate constants are given in Table 4.1. Full listings of model inputs and model outputs are given in Table 7.10 and Table 7.11.

4.5.1 Mass-Balance Equations

4.5.1.1 Organics

The three types of organic material considered are cellulose, IX resins, and plastics and rubbers. The mass-balance equations for each of these species are:

$$-\frac{dQ_C}{dt} = \varepsilon g\left(V_{C,a} + V_{C,b} + V_{C,c} + V_{C,d} + V_{C,e}\right)Q_C - \frac{5}{6}K_R(X_a + X_b + X_c + X_d + X_e)D \tag{4.44}$$

for cellulose,

$$-\frac{dQ_R}{dt} = \varepsilon g\left(V_{R,a} + V_{R,b} + V_{R,c} + V_{R,d} + V_{R,e}\right)Q_R \tag{4.45}$$

for IX resins, and

$$-\frac{dQ_P}{dt} = \varepsilon g\left(V_{P,a} + V_{P,b} + V_{P,c} + V_{P,d} + V_{P,e}\right)Q_P \tag{4.46}$$

for plastics and rubbers, where $V_{i,j}$ [s^{-1}] is the degradation rate constant for substrate i (i = C, R, P for cellulose, IX resins, and plastics and rubbers, respectively) under conditions j (j = a, b, c, d, e for aerobic respiration, denitrification, iron reduction, sulphate reduction, and methanogenesis, respectively). $V_{i,j} = V_i$ if j is the currently active TEA, and $V_{i,j} = 0$ otherwise, where V_i is the input degradation rate of organic substrate i. The constant ε in the above equations always has a value between 0 and 1. When the saturation is positive, it is equal to 1, but when the saturation is zero, it is reduced (if necessary) so as to balance the rate of consumption of water due to saturated phase reactions with the rate of ingress of water into the repository.

4.5.1.2 Metallic Materials

The rates of metal corrosion (in mol·s^{-1}) are given by

$$-\frac{dQ_1}{dt} = \frac{\rho_1}{M_1}\left(hA_{1,1}R_{1,1,1} + h\left(1 + \left(\frac{P_{CO2}}{P_{CO2}^{ref}}\right)^q\right)A_{1,1}R_{1,2,1} + \varepsilon A_{1,2}R_{1,1,2} + \varepsilon\left(1 + \left(\frac{P_{CO2}}{P_{CO2}^{ref}}\right)^q\right)A_{1,2}R_{1,2,2}\right) + \frac{1}{2}V_{FeOOH}Q_{FeOOH} \tag{4.47}$$

for carbon and galvanized steel,

$$-\frac{dQ_2}{dt} = \frac{\rho_2}{M_2}\left(hA_{2,1}R_{2,1,1} + hA_{2,1}R_{2,2,1} + \varepsilon A_{2,2}R_{2,1,2} + \varepsilon A_{2,2}R_{2,2,2}\right) \tag{4.48}$$

for passivated carbon steel,

$$-\frac{dQ_3}{dt} = \frac{\rho_3}{M_3}\left(hA_{3,1}R_{3,1,1} + h\left(1 + \left(\frac{P_{CO2}}{P_{CO2}^{ref}}\right)^q\right)A_{3,1}R_{3,2,1} + \varepsilon A_{3,2}R_{3,1,2} + \varepsilon\left(1 + \left(\frac{P_{CO2}}{P_{CO2}^{ref}}\right)^q\right)A_{3,2}R_{3,2,2}\right) \tag{4.49}$$

for stainless steel and Ni-based alloys, and

$$-\frac{dQ_4}{dt}=\frac{\rho_4}{M_4}\left(hA_{4,1}R_{4,1,1}+hA_{4,1}R_{4,2,1}+\varepsilon A_{4,2}R_{4,1,2}+\varepsilon A_{4,2}R_{4,2,2}\right) \tag{4.50}$$

for Zr alloys, where V_{FeOOH} is the first-order rate constant for the reduction of FeOOH via Equation (4.33) and the other terms are defined in Equation (4.37), Equation (4.38) and Table 4.1.

4.5.1.3 Gases

Six gaseous species are considered O_2, N_2, CO_2, H_2, H_2S, and CH_4. The total number of moles of gas is constantly being adjusted to take into account the flux of gas into or out of the repository (see Section 4.4.4). All gases partition between the gaseous and aqueous phases according to Equation (4.76), Equation (4.77) and Equation (4.78).

The contributions to the rate of change of the total number of moles of gas molecules within the repository due to reactions for the gaseous species are given below.

$$\begin{aligned}-\frac{dQ_{O2}}{dt}&=\varepsilon g(1-Y_a)[6V_{C,a}Q_C+10V_{R,a}Q_R+10V_{P,a}Q_P]\\&\quad+\left[\frac{3\rho_1}{4M_1}\left(hA_{1,1}R_{1,1,1}+\varepsilon A_{1,2}R_{1,1,2}\right)+\frac{3\rho_2}{4M_2}\left(hA_{2,1}R_{2,1,1}+\varepsilon A_{2,2}R_{2,1,2}\right)\right]\\&\quad+\left[\frac{3\rho_3}{4M_3}\left(hA_{3,1}R_{3,1,1}+\varepsilon A_{3,2}R_{3,1,2}\right)+\frac{\rho_4}{M_4}\left(hA_{4,1}R_{4,1,1}+\varepsilon A_{4,2}R_{4,1,2}\right)\right]\end{aligned} \tag{4.51}$$

for O_2,

$$\frac{dQ_{N2}}{dt}=\varepsilon g(1-Y_b)[2.4V_{C,b}Q_C+4V_{R,b}Q_R+4V_{P,b}Q_P] \tag{4.52}$$

for N_2,

$$\begin{aligned}\frac{dQ_{CO2}}{dt}&=\varepsilon g(1-Y_a)[6V_{C,a}Q_C+8V_{R,a}Q_R+8V_{P,a}Q_P]+\varepsilon g(1-Y_b)[6V_{C,b}Q_C+8V_{R,b}Q_R+8V_{P,b}Q_P]\\&\quad+\varepsilon g(1-Y_c)[6V_{C,c}Q_C+8V_{R,c}Q_R+8V_{P,c}Q_P]+\varepsilon g(1-Y_d)[6V_{C,d}Q_C+8V_{R,d}Q_R+8V_{P,d}Q_P]\\&\quad+\varepsilon g(1-Y_e)\left[3V_{C,e}Q_C+3V_{R,e}Q_R+3V_{P,e}Q_P\right]-\varepsilon g\frac{(1-Y_e)}{4}V_{H3}\left(C_{CO2}SV_v+hq_{CO2}\right)\\&\quad-2\varepsilon g(Y_aV_{R,a}+Y_bV_{R,b}+Y_cV_{R,c}+Y_dV_{R,d}+Y_eV_{R,e})Q_R\\&\quad-2\varepsilon g(Y_aV_{P,a}+Y_bV_{P,b}+Y_cV_{P,c}+Y_dV_{P,d}+Y_eV_{P,e})Q_P\\&\quad-\frac{1}{2}\varepsilon g\left(Y_cV_{H1}Q_{FeOOH}+Y_dV_{H2}C_{SO4}SV_v+Y_eV_{H3}\left(C_{CO2}SV_v+hq_{CO2}\right)\right)\\&\quad-\frac{\rho_1}{M_1}\left[\left(\frac{P_{CO2}}{P_{CO2}^{ref}}\right)^q\left(hA_{1,1}R_{1,2,1}+\varepsilon A_{1,2}R_{1,2,2}\right)\right]-\frac{\rho_3}{M_3}\left[\left(\frac{P_{CO2}}{P_{CO2}^{ref}}\right)^q\left(hA_{3,1}R_{3,2,1}+\varepsilon A_{3,2}R_{3,2,2}\right)\right]\\&\quad-\frac{4}{5}\varepsilon V_{MgO}Q_{MgO}\end{aligned} \tag{4.53}$$

for CO_2,

$$\begin{aligned}\frac{dQ_{H2}}{dt} = &-\varepsilon g(1-Y_c)V_{H1}Q_{FeOOH} - \varepsilon g(1-Y_d)V_{H2}C_{SO4}SV_v - \varepsilon g(1-Y_e)V_{H3}\left(C_{CO2}SV_v + hq_{CO2}\right)\\ &-\varepsilon gY_cV_{H1}C_{FeOOH}SV_v - \varepsilon gY_dV_{H2}C_{SO4}SV_v - \varepsilon gY_eV_{H3}\left(C_{CO2}SV_v + hq_{CO2}\right)\\ &+\frac{4}{3}\frac{\rho_1}{M_1}\left[\left(1+\frac{3}{4}\left(\frac{P_{CO2}}{P_{CO2}^{ref}}\right)^q\right)\left(hA_{1,1}R_{1,2,1} + \varepsilon A_{1,2}R_{1,2,2}\right)\right]\\ &+\frac{4}{3}\frac{\rho_2}{M_2}\left(hA_{2,1}R_{2,2,1} + \varepsilon A_{2,2}R_{2,2,2}\right) + \frac{4}{3}\frac{\rho_3}{M_3}\left[\left(1+\frac{3}{4}\left(\frac{P_{CO2}}{P_{CO2}^{ref}}\right)^q\right)\left(hA_{3,1}R_{3,2,1} + \varepsilon A_{3,2}R_{3,2,2}\right)\right]\\ &+\frac{2\rho_4}{M_4}\left(hA_{4,1}R_{4,2,1} + \varepsilon A_{4,2}R_{4,2,2}\right) + \frac{1}{2}V_{FeOOH}Q_{FeOOH}\end{aligned} \tag{4.54}$$

for H_2,

$$\begin{aligned}\frac{dQ_{H2S}}{dt} = &\,\varepsilon g(1-Y_d)\left[3V_{C,d}Q_C + 5V_{R,d}Q_R + 5V_{P,d}Q_P\right]\\ &+\varepsilon g\frac{(1-Y_d)}{4}V_{H2}C_{SO4}SV_v - V_{FeS}C_{H2S}SV_v\end{aligned} \tag{4.55}$$

for H_2S, and

$$\frac{dQ_{CH4}}{dt} = \varepsilon g(1-Y_e)\left[3V_{C,e}Q_C + 5V_{R,e}Q_R + 5V_{P,e}Q_P\right] + \varepsilon g\frac{(1-Y_e)}{4}V_{H3}\left(C_{CO2}SV_v + hq_{CO2}\right) \tag{4.56}$$

for CH_4.

4.5.1.4 Terminal Electron Acceptors

In addition to O_2, Fe(III), and CO_2, GGM also includes two other terminal electron acceptors, namely: nitrate and sulphate ions. The mass-balance equations for these latter two species are given by

$$-\frac{dC_{NO3}}{dt} = \varepsilon g\frac{(1-Y_b)}{SV_v}\left[4.8V_{C,b}Q_C + 8V_{R,b}Q_R + 8V_{P,b}Q_P\right] \tag{4.57}$$

for NO_3^-, and

$$-\frac{dC_{SO4}}{dt} = \varepsilon g\frac{(1-Y_d)}{SV_v}\left[3V_{C,d}Q_C + 5V_{R,d}Q_R + 5V_{P,d}Q_P\right] + \varepsilon g\frac{(1-Y_d)}{4}V_{H2}C_{SO4} \tag{4.58}$$

for SO_4^{2-}.

4.5.1.5 Biomass

Biomass is generated as a result of microbial metabolism, growth and decay of which consumes and produces water and needs to be tracked for an accurate water mass balance.

The biomass mass balances are given by

$$\frac{dX_a}{dt} = \varepsilon g Y_a \left(\frac{6}{5} V_{C,a} Q_C + 2V_{R,a} Q_R + 2V_{P,a} Q_P \right) - X_a D \tag{4.59}$$

for aerobes,

$$\frac{dX_b}{dt} = \varepsilon g Y_b \left(\frac{6}{5} V_{C,b} Q_C + 2V_{R,b} Q_R + 2V_{P,b} Q_P \right) - X_b D \tag{4.60}$$

for denitrifiers,

$$\frac{dX_c}{dt} = \varepsilon g Y_c \left(\frac{6}{5} V_{C,c} Q_C + 2V_{R,c} Q_R + 2V_{P,c} Q_P + \frac{1}{10} V_{H1} Q_{FeOOH} \right) - X_c D \tag{4.61}$$

for iron reducers,

$$\frac{dX_d}{dt} = \varepsilon g Y_d \left(\frac{6}{5} V_{C,d} Q_C + 2V_{R,d} Q_R + 2V_{P,d} Q_P + \frac{1}{10} S V_v V_{H2} C_{SO4} \right) - X_d D \tag{4.62}$$

for sulphate reducers, and

$$\frac{dX_e}{dt} = \varepsilon g Y_e \left(\frac{6}{5} V_{C,e} Q_C + 2V_{R,e} Q_R + 2V_{P,e} Q_P + \frac{1}{10} V_{H3} \left(C_{CO2} S V_v + h q_{CO2} \right) \right) - X_e D \tag{4.63}$$

for methanogens.

The total quantity of live (hydrated) biomass is given by $X_{tot} = X_a + X_b + X_c + X_d + X_e$. The total quantity of dead (dehydrated) biomass that cannot be recycled (X_{dead}) is also tracked in the code, and is given by

$$\frac{dX_{dead}}{dt} = (1 - K_R)(X_a + X_b + X_c + X_d + X_e) D . \tag{4.64}$$

4.5.1.6 Corrosion Products

A number of different corrosion products are tracked in the code, including FeOOH, $FeCO_3$, Fe_3O_4, and FeS. The mass-balance equations for these species are given by

$$\begin{aligned} \frac{dQ_{FeOOH}}{dt} = & -\varepsilon g(1 - Y_c)\left[24 V_{C,c} Q_C + 40 V_{R,c} Q_R + 40 V_{P,c} Q_P\right] - 2\varepsilon g(1 - Y_C) V_{H1} Q_{FeOOH} \\ & + \left[\frac{\rho_1}{M_1} \left(h A_{1,1} R_{1,1,1} + \varepsilon A_{1,2} R_{1,1,2} \right) + \frac{\rho_2}{M_2} \left(h A_{2,1} R_{2,1,1} + \varepsilon A_{2,2} R_{2,1,2} \right) + \frac{\rho_3}{M_3} \left(h A_{3,1} R_{3,1,1} + \varepsilon A_{3,2} R_{3,1,2} \right) \right] \\ & - Q_{FeOOH} V_{FeOOH} \end{aligned} \tag{4.65}$$

for FeOOH,

$$\frac{dQ_{FeCO3}}{dt} = \frac{\rho_1}{M_1} \left(\frac{P_{CO2}}{P_{CO2}^{ref}} \right)^q \left(h A_{1,1} R_{1,2,1} + \varepsilon A_{1,2} R_{1,2,2} \right) + \frac{\rho_3}{M_3} \left(\frac{P_{CO2}}{P_{CO2}^{ref}} \right)^q \left(h A_{3,1} R_{3,2,1} + \varepsilon A_{3,2} R_{3,2,2} \right) \tag{4.66}$$

for $FeCO_3$,

$$\begin{aligned}\frac{dQ_{Fe3O4}}{dt} &= \frac{\rho_1}{3M_1}\left(hA_{1,1}R_{1,2,1} + \varepsilon A_{1,2}R_{1,2,2}\right) + \frac{\rho_2}{3M_2}\left(hA_{2,1}R_{2,2,1} + \varepsilon A_{2,2}R_{2,2,2}\right) \\ &\quad + \frac{\rho_3}{3M_3}\left(hA_{3,1}R_{3,2,1} + \varepsilon A_{3,2}R_{3,2,2}\right) + \frac{1}{2}V_{FeOOH}Q_{FeOOH}\end{aligned} \tag{4.67}$$

for Fe_3O_4, and

$$\frac{dQ_{FeS}}{dt} = SV_vV_{FeS}C_{H2S} \tag{4.68}$$

for FeS.

4.5.1.7 Water

Water is consumed and produced by both microbial and corrosion reactions. The rate of generation of water is given by:

$$\frac{dQ_{H2O}}{dt} = -\varepsilon\frac{dC}{dt} + \frac{dD}{dt} \tag{4.69}$$

where

$$\begin{aligned}\frac{dC}{dt} = -S\left\{\begin{aligned}&(1-Y_a)[5V_{C,a}Q_C + 4V_{R,a}Q_R + 4V_{P,a}Q_P] + (1-Y_b)[7.4V_{C,b}Q_C + 8V_{R,b}Q_R + 8V_{P,b}Q_P] \\ &\quad -(1-Y_c)[7V_{C,c}Q_C + 16V_{R,c}Q_R + 16V_{P,c}Q_P] + (1-Y_d)[5V_{C,d}Q_C + 4V_{R,d}Q_R + 4V_{P,d}Q_P] \\ &\quad -(1-Y_e)[V_{C,e}Q_C + 6V_{R,e}Q_R + 6V_{P,e}Q_P] + (1-Y_d)SV_vV_{H2}C_{SO4} \\ &\quad +\frac{1}{2}(1-Y_e)V_{H3}\left(C_{CO2}SV_v + hq_{CO2}\right) \\ &\quad -27.4(Y_aV_{C,a} + Y_bV_{C,b} + Y_cV_{C,c} + Y_dV_{C,d} + Y_eV_{C,e})Q_C \\ &\quad -50(Y_aV_{R,a} + Y_bV_{R,b} + Y_cV_{R,c} + Y_dV_{R,d} + Y_eV_{R,e})Q_R \\ &\quad -50(Y_aV_{P,a} + Y_bV_{P,b} + Y_cV_{P,c} + Y_dV_{P,d} + Y_eV_{P,e})Q_P \\ &\quad -\frac{17}{10}\left(Y_cV_{H1}Q_{FeOOH} + Y_dV_{H2}C_{SO4}SV_v + Y_eV_{H3}\left(C_{CO2}SV_v + hq_{CO2}\right)\right) \\ &\quad -V_{MgO}Q_{MgO}\end{aligned}\right\} \\ &+\frac{\rho_1}{2M_1}(A_{1,2}R_{1,1,2}) + \frac{\rho_2}{2M_2}(A_{2,2}R_{2,1,2}) + \frac{\rho_3}{2M_3}(A_{3,2}R_{3,1,2}) \\ &+\frac{4}{3}\frac{\rho_1}{M_1}\left[\left(1 + \frac{3}{4}\left(\frac{P_{CO2}}{P_{CO2}^{ref}}\right)^q\right)\left(A_{1,2}R_{1,2,2}\right)\right] + \frac{4}{3}\frac{\rho_2}{M_2}\left[A_{2,2}R_{2,2,2}\right] \\ &+\frac{4}{3}\frac{\rho_3}{M_3}\left[\left(1 + \frac{3}{4}\left(\frac{P_{CO2}}{P_{CO2}^{ref}}\right)^q\right)\left(A_{3,2}R_{3,2,2}\right)\right] + \frac{2\rho_4}{M_4}\left[A_{4,2}R_{4,2,2}\right]\end{aligned} \tag{4.70}$$

is the rate of consumption of water due to processes that operate under saturated conditions only, and

$$
\begin{aligned}
\frac{dD}{dt} = (1-S)h \left\{ \begin{aligned}
&(1-Y_a)[5V_{C,a}Q_C + 4V_{R,a}Q_R + 4V_{P,a}Q_P] + (1-Y_b)[7.4V_{C,b}Q_C + 8V_{R,b}Q_R + 8V_{P,b}Q_P] \\
&\quad - (1-Y_c)[7V_{C,c}Q_C + 16V_{R,c}Q_R + 16V_{P,c}Q_P] + (1-Y_d)[5V_{C,d}Q_C + 4V_{R,d}Q_R + 4V_{P,d}Q_P] \\
&\quad - (1-Y_e)[V_{C,e}Q_C + 6V_{R,e}Q_R + 6V_{P,e}Q_P] + (1-Y_d)SV_vV_{H2}C_{SO4} \\
&\quad + \frac{1}{2}(1-Y_e)V_{H3}\left(C_{CO2}SV_v + hq_{CO2}\right) \\
&\quad - 27.4(Y_aV_{C,a} + Y_bV_{C,b} + Y_cV_{C,c} + Y_dV_{C,d} + Y_eV_{C,e})Q_C \\
&\quad - 50(Y_aV_{R,a} + Y_bV_{R,b} + Y_cV_{R,c} + Y_dV_{R,d} + Y_eV_{R,e})Q_R \\
&\quad - 50(Y_aV_{P,a} + Y_bV_{P,b} + Y_cV_{P,c} + Y_dV_{P,d} + Y_eV_{P,e})Q_P \\
&\quad - \frac{17}{10}\left(Y_cV_{H1}Q_{FeOOH} + Y_dV_{H2}C_{SO4}SV_v + Y_eV_{H3}\left(C_{CO2}SV_v + hq_{CO2}\right)\right) \\
&\quad - V_{MgO}Q_{MgO}
\end{aligned} \right\} \\
&+ 25(1-K_R)(X_a + X_b + X_c + X_d + X_e)D + \frac{137}{6}K_R(X_a + X_b + X_c + X_d + X_e)D \\
&- \frac{\rho_1}{2M_1}(A_{1,1}hR_{1,1,1}) - \frac{\rho_2}{2M_2}(A_{2,1}hR_{2,1,1}) - \frac{\rho_3}{2M_3}(A_{3,1}hR_{3,1,1}) \\
&- \frac{4}{3}\frac{\rho_1}{M_1}\left[\left(1 + \frac{3}{4}\left(\frac{P_{CO2}}{P_{CO2}^{ref}}\right)^q\right)\left(A_{1,1}hR_{1,2,1}\right)\right] - \frac{4}{3}\frac{\rho_2}{M_2}\left[A_{2,1}hR_{2,2,1}\right] \\
&- \frac{4}{3}\frac{\rho_3}{M_3}\left[\left(1 + \frac{3}{4}\left(\frac{P_{CO2}}{P_{CO2}^{ref}}\right)^q\right)\left(A_{3,1}hR_{3,2,1}\right)\right] - \frac{2\rho_4}{M_4}\left[A_{4,1}hR_{4,2,1}\right]
\end{aligned}
\tag{4.71}
$$

is the rate of generation of water due to the remaining terms, including the death of biomass and vapour phase processes.

4.5.1.8 Other Species

If MgO is added to the repository to mitigate the effect of CO_2, it is necessary to track the amount of remaining MgO. The amount of the product ($(Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O)$) is not specifically calculated in the code, but can be obtained from the loss of MgO and the stoichiometry of the reaction in Equation (4.41).

The mass-balance equation for MgO is given by:

$$
-\frac{dQ_{MgO}}{dt} = V_{MgO}Q_{MgO} \tag{4.72}
$$

4.5.2 Assumptions

A number of assumptions have been made in the development of GGM. Table 4.2, Table 4.3 and Table 4.4 list these assumptions and their basis for the conceptual microbial model, the conceptual corrosion model, and the overall gas generation model, respectively.

Table 4.2: Assumptions Included in Conceptual Microbial Model

Assumption	Basis
Conversion of organic polymer to its soluble intermediates is the rate-limiting step in the degradation of organics.	Mechanistically justifiable and simplifies modelling of microbial processes.
Degradation of IX resins is possible.	Degradation of IX resins is allowed, but they can be treated as recalcitrant by setting the appropriate rate constants to zero.
Degradation of plastics and rubbers is possible and can be treated in the same manner as the degradation of IX resins.	Degradation of plastics and rubbers is allowed, but they can be treated as recalcitrant by setting the appropriate rate constants to zero. The treatment of plastics and rubbers in the same manner as IX resins is a simplification, but preserves the basic conversion process from organic carbon to CH_4 and CO_2.
Kinetics of degradation of organic material are first order.	Reasonable assumption provided that value for rate constant is derived from experimental data on the same basis. Supported by the modelling of hydrolysis of polymers such as cellulose in other environments.
Microbial activity ceases at a water activity (A_w) below 0.6 and slows as the A_w falls below 0.8.	Consistent with data (Shreir 1976) and mechanistically justifiable.
Microbial kinetics are independent of the amount of biomass.	Simplifies the modelling of microbial kinetic processes. Essentially assumes that there is enough biomass that the rate has saturated (e.g., surfaces are fully covered by microbes).
Ammonia is present and does not limit biomass formation.	Simplifies the modelling of microbial processes by limiting the number of species in the model. It is also conservative with respect to gas generation, since it ensures microbial reactions proceed to completion. Microbial nitrogen fixation may also occur negating the requirement for ammonia as a nitrogen source.
There is sufficient pH-buffering capacity in the environment to permit consumption of acidic fermentation products.	Simplifies modelling of microbial processes. It is also conservative with respect to gas generation since it ensures microbial reactions proceed to completion.
Decay of one "mole" of biomass generates 25 moles of water.	Reasonable assumption based on mean water content of biomass of 80%.

Assumption	Basis
9 moles of bound water are freed per mole of styrene monomer as it degrades.	Calculation based on 40% bound water by weight for the resins and 8 moles of styrene monomer per 10 moles of dry resin.
Carbon from a fraction of the dead biomass is recycled.	Consistent with mechanistic understanding.
Availability of phosphorus and sulphur do not limit microbial growth.	Simplifying assumption for modelling purposes. It is also conservative with respect to gas generation since it ensures microbial reactions proceed to completion.
All microbes required to catalyze the reactions modelled are present within the repository.	This is also conservative with respect to gas generation since it ensures microbial reactions proceed to completion. Also mechanistically supportable since microbes will enter the repository via a range of routes.

Table 4.3: Assumptions Included in Conceptual Corrosion Model

Assumption	Basis
Vapour phase corrosion becomes active in the range 60-80% RH.	Mechanistically justifiable and commonly observed threshold from atmospheric corrosion studies.
Magnetite is the stable long-term anaerobic corrosion product of the corrosion of steel.	Reasonable assumption based on information available in the literature. Conservative in terms of the maximum amount of H_2 produced.
Corrosion of stainless steel and Ni-based alloys can be represented by the formation of FeOOH and Fe_3O_4 under aerobic and anaerobic conditions, respectively.	Simplifying assumption for modelling purposes. Reasonable assumption for stainless steels, which typically contain 60-80% Fe. Reasonable for Ni-based alloys as corrosion rate is low and amount of "Fe(III)" predicted to be formed from these materials is small compared with that formed from carbon and galvanized steels. Differences in amounts of H_2 formed because of difference in valences of corrosion products can be adjusted through value of initial inventory of these materials.
CO_2-enhanced corrosion occurs for carbon and galvanized steel and stainless steel and Ni-based alloys only.	Reasonable assumption based on evidence in the literature. Passive carbon steels are less likely to be affected due to pH-buffering capacity of cementitious materials (the assumed passivating agent). No evidence for enhanced effect of CO_2 on Zr alloys.

Table 4.4: Assumptions Included in the Overall Gas Generation Model

Assumption	Basis
Transport of species in the repository is rapid on the timescale of interest and no concentration gradients develop.	Simplifies modelling by removing the need to predict the spatial dependence of the concentrations of various species. Reasonable assumption for long time scale (years or more) of interest for a repository.
All Fe(III) formed is present as FeOOH and is available for microbial consumption and/or reductive dissolution.	Ferric corrosion products will likely be present as a mixture of Cl^-, SO_4^{2-}, and CO_3^{2-} - containing forms of Green Rust. However, provided the water mass balance is accurately predicted, the actual form of corrosion product is relatively unimportant since the concentrations of Cl^- and SO_4^{2-} are not tracked in the model. The solubility of Fe(III) is likely to be limited at the near-neutral to moderately alkaline pH values expected in the repository, so the assumption that the Fe(III) is available for microbial metabolism may result in an over-estimate of the extent of microbial iron reduction in the model.
Assumes first-order kinetics for the formation of magnesium carbonates from MgO.	Consistent with mechanistic understanding.
Kinetics of FeS precipitation are first order with respect to the concentration of H_2S.	Reasonable assumption based on known kinetics of reaction.
Excess Fe(II) available for precipitation of FeS.	Reasonable assumption based on large surface area and quantity of ferrous materials in repository and fact that sulphide will only be formed under anaerobic conditions.
Gas generation reactions and water transport are assumed to take place under isothermal conditions (based on a typical temperature of 22 °C at the repository horizon).	Temperatures in an L&ILW repository are expected to be around geosphere conditions due to the low heat sources. Long-term thermal changes in the geosphere will be driven by glacial cycling. At OPG's DGR, repository temperatures are expected to reach a minimum of 17 °C under glacial conditions compared with 22 °C at the present date.

4.5.3 Problem Solution Method

The GGM Version 2.1 model described here is implemented using FORTRAN 77 subroutines, thus enabling it to be driven by TOUGH2 which is also written in FORTRAN 77 (J3 2008).

GGM consists of first order coupled differential equations given by the mass balance equations and non-differential equations, such as Henry's law. The mass balance equations are evolved forward in time using a modified Euler time stepping scheme, and the non-differential equations are solved for the remaining variables at each time step.

In this model, gas is generated via degradation reactions in the saturated part of the repository and under unsaturated conditions if the relative humidity exceeds RH_{min} (typically set to 60%). The gas repartitions between the saturated and unsaturated parts of the repository according to Henry's Law effectively instantaneously. Gas partitioning has been treated mathematically to ensure that its numerical discretization can be implemented in a manner consistent with all the other processes and can be treated by evolving differential equations for the total number of moles in the repository. Details of this treatment of gas repartitioning are given in Section 4.6.

The GGM code has a large number of variables which are highly coupled. GGM uses an adaptive time stepping algorithm that chooses a time resolution sufficient to capture the changes that can occur on the disparate timescales of the various physical processes. There is also coupling with TOUGH2 via gas and water generation, pressure, saturation, relative humidity and void volume. For efficiency, GGM Version 2.1 does not require TOUGH2 and GGM to take the same time steps. GGM provides TOUGH2 with a suggested maximum time step based on the current rate of change of the GGM inputs and outputs.

4.6 Gas Repartitioning

4.6.1 Mathematical Encapsulation

Consider an enclosed volume V (m^3), with saturation S (-), at temperature T (K). Several ideal gas species exist in the volume. The total number of moles of gas i in the volume is known to be N_i. The gas partitions itself between the unsaturated and the saturated phases according to Henry's law. The equilibrium partial pressure, p_i (Pa), and number of moles of gas i, n_i (mol), in the unsaturated phase and the concentration of gas in solution in the saturated phase, c_i (mol m^{-3}), are the unknown variables.

Writing expressions for the total number of moles of gas in the system, the ideal gas law and Henry's law gives three equations for the three unknowns:

$$N_i = n_i + c_i SV \tag{4.73}$$

$$p_i(1-S)V = n_i RT \tag{4.74}$$

$$c_i = p_i K_i \tag{4.75}$$

where R (m^3 Pa K^{-1} mol^{-1}) is the molar gas constant and K_i (mol m^{-3} Pa^{-1}) is the solubility constant for gas i. These can be solved readily to give:

$$c_i = \frac{N_i}{V}\frac{RTK_i}{1+S(RTK_i - 1)} \tag{4.76}$$

$$p_i = \frac{1}{K_i}c_i \tag{4.77}$$

$$n_i = N_i - c_i SV \tag{4.78}$$

4.6.2 Implications for GGM

The total gas generation rate, Q_{air} (mol s^{-1}), can be calculated as

$$\begin{aligned} Q_{air} &= \sum_i \frac{\partial n_i}{\partial t} \\ &= \sum_i \left(\frac{\partial N_i}{\partial t} - \frac{\partial c_i}{\partial t} SV - c_i \frac{\partial S}{\partial t} V \right) \\ &= \sum_i \left[f_i V \frac{S(1-S)}{1+S(RTK_i - 1)} - RTK_i N_i \frac{\partial S}{\partial t} \left(\frac{1}{1+S(RTK_i - 1)} \right)^2 \right] \end{aligned} \quad . \tag{4.79}$$

using Equations (4.76) and (4.78).

The initial partial pressure of each gas in the repository is specified rather than the initial total number of moles. However, it is the initial total number of moles that is required as an initial condition for the mass balance equations. To determine the initial total number of moles of each gas in the repository, $N_i^{(0)}$, from the initial partial pressure, $p_i^{(0)}$, Equation (4.76) and Equation (4.77) are rearranged to give

$$N_i^{(0)} = p_i^{(0)} V \frac{1+S(RTK_i - 1)}{RT} \tag{4.80}$$

4.7 Relative Humidity Modulation

There are two options available for the relative humidity modulation function, h: a linear ramp and a smoothed linear ramp. These are described in the following sections.

The modulation is applied directly to all vapour phase corrosion rate constants: R_{111}, R_{121}, R_{211}, R_{221}, R_{311}, R_{321}, R_{411}, R_{421}. It is applied to vapour phase fraction of all microbial processes (apart from the death of biomass which is assumed to continue at its normal rate), g, via the expression:

$$g = S + (1-S)h\,. \tag{4.81}$$

The affected microbial rate constants are: V_{H1}, V_{H2}, V_{H3}, $V_{C,a}$, $V_{C,b}$, $V_{C,c}$, $V_{C,d}$, $V_{C,e}$, $V_{R,a}$, $V_{R,b}$, $V_{R,c}$, $V_{R,d}$, V_{Re}, $V_{P,a}$, $V_{P,b}$, $V_{P,c}$, $V_{P,d}$, $V_{P,e}$.

4.7.1 Type 1: Linear Ramp

The relative humidity modulation function is taken as varying linearly between RH_{min}=0.6 and RH_{max}=0.8:

$$h(RH) = \begin{cases} 1 & 1 < X \\ X & 0 < X < 1, \\ 0 & X < 0 \end{cases} \quad \text{where} \quad X = \left(\frac{RH - RH_{min}}{RH_{max} - RH_{min}} \right) \tag{4.82}$$

4.7.2 Type 2: Smoothed Linear Ramp

This is a variation on the linear ramp that has a continuous first derivative due to the introduction of curvature at end of the ramp. The following values are hard-wired: β=0.1, ε=0.05.

$$h(RH) = \begin{cases} 1 - \dfrac{(1-X)^2}{B + A(1-X)} & 1 - \beta < X \\ \varepsilon + C(X - \beta) & \beta < X < 1 - \beta \\ \dfrac{X^2}{B + AX} & X < \beta \end{cases} \tag{4.83}$$

where

$$X = \left(\frac{RH - RH_{min}}{RH_{max} - RH_{min}} \right), \ A = \frac{\beta(2 - \alpha\gamma)}{\varepsilon}, \ B = \frac{\beta^2}{\varepsilon}\left(\frac{\alpha\beta}{\varepsilon} - 1 \right), \ C = \frac{1 - 2\varepsilon}{1 - 2\beta}$$

4.8 Water-Limiting Conditions

Considering the water balance for the repository

$$\frac{dA_{H2O}}{dt} = \frac{dQ_{H2O}}{dt} + J_{H2O} = -\varepsilon \frac{dC}{dt} + \frac{dD}{dt} + J_{H2O} \tag{4.84}$$

where dA_{H2O}/dt (mol s^{-1}) is the rate of change of the amount of water in the repository, dQ_{H2O}/dt (mol s^{-1}) is the rate of production of water via the gas generation reactions, which splits into components dC/dt and dD/dt given by Equations (4.70) and (4.71) and J_{H2O} (mol s^{-1}) is the rate of ingress of water into the repository.

Under normal circumstances, the water consuming saturated phase reactions will proceed at their normal rate and $\varepsilon = 1$ will be set. Once zero saturation has been reached, if water consuming reactions continue to proceed at a sufficient rate, the saturation will remain zero and $dA_{H2O}/dt = 0$. Under such circumstances, the saturated phase water consuming reactions to consume water that naturally wil be allowed to enter the repository, but not to draw water into the repository. This is achieved by choosing ε so that the rate of saturated phase water consumption is balanced by the natural rate of water ingress. Then,

$$\varepsilon = \frac{\frac{dD}{dt} + J_{H2O}}{\frac{dC}{dt}} \qquad (4.85)$$

holds, provided that the rate of water consumption due to saturated phase processes, dC/dt, is positive and the rate of increase of water due to other gas generation reactions and water ingress is less than the rate of water consumption. This ensures that $0 \leq \varepsilon \leq 1$.

5. THEORY – TOUGH2

TOUGH2 is a general-purpose numerical simulation program for multi-phase fluid and heat flow in porous and fractured media developed by the Lawrence Berkeley National Laboratory (Pruess et al. 1999). TOUGH2 is modular, setting up equations and solving them in a general form, with specific definitions for the fluid mixture, such as phase components and primary variables, provided in a single fluid property or Equation-of-State (EOS) module. Only one EOS module can be linked to TOUGH2 at a time, and T2GGM uses the EOS3 module, which simulates the transport of air and water.

TOUGH2 describes advective fluid flow using a multi-phase extension of Darcy's law and diffusive flow using a multi-phase extension of Fick's law. For numerical simulation, equations are solved at each node within a discretized space. Space discretization uses the Integral Finite Difference (IFD) method. In contrast to most field modeling approaches, the IFD method does not assume any spatial configuration or connectivity of nodes. Elements (or blocks) define the volumetric properties of nodes. Connections define the flows between nodes. There is no *a priori* assumption about how nodes are connected.

The EOS3 module defines two-phase flow of water and air, or single-phase flow of water or air. Thermophysical properties of water are represented by steam-table equations, while the air is treated as ideal gas. Dissolution of air in water is modeled with Henry's law. For T2GGM Version 2.1, an option is provide to represent the gas phase by an alternative gas, either CH_4, CO_2 or H_2.

The phase relationship between gas and liquid is based on a capillary pressure function and a relative permeability function. T2GGM includes the standard functions available within TOUGH2/EOS3. Additionally, a modified Van Genuchten formulation was ported from iTOUGH2 (Finsterle 1999). This modified formulation addresses a shortcoming with the standard van Genuchten model where capillary pressure goes to infinity as liquid saturation approaches the residual liquid saturation value. In the modified formulation, the capillary pressure function is extended as a linear function at low saturations.

Several additional subroutine calls were added to TOUGH2 which are responsible for managing the interface with GGM in order to perform tasks such as initialization, time stepping and updating of sources and sinks based on GGM output data. The interface is described in more detail in Chapter 7.

T2GGM Version 2.1 includes a parallel version, based on TOUGH2-MP. The TOUGH2-MP version uses the same GGM code as T2GGM, but requires a slightly different interface on the TOUGH2 side of the code. The different interface is required to address the parallelization of the code: TOUGH2-MP partitions the grid and assigns each processor a portion of the grid. Consequently, the TOUGH2–GGM interface must collect the appropriate parameters required by GGM from the appropriate processors (namely the processors conducting calculation on the repository nodes), and similarly, must distribute GGM outputs to these same processors.

6. REQUIREMENTS SPECIFICATION

6.1 Introduction

This section specifies the technical and user requirements for the numerical implementation of the GGM and its integration with the TOUGH2 gas transport code. Requirements for the TOUGH2 software are not included here.

This specification applies to T2GGM and T2GGM-MP Version 2.1, which consists of GGM Version 2.1, and TOUGH2 Version 2.1 or TOUGH2-MP Version 2.1 with the EOS3 equation of state module.

6.2 General Requirements

6.2.1 Regulatory Policies

There are no regulatory policies that T2GGM is required to meet.

6.2.2 QA Requirements

TOUGH2 is owned and maintained by Lawrence Berkeley Laboratories (LBNL). Any software QA requirements for TOUGH2 are internal to LBNL.

The modifications to TOUGH2 as used to support the T2GGM integration were developed for NWMO by Geofirma Engineering Ltd. The GGM software package was developed for NWMO by Quintessa Limited.

Requirement Number	Requirement
2.2.1	T2GGM software must be maintained consistent with the QA requirements of NWMO for Technical Computing Software (NWMO 2010).
2.2.2	GGM software development must be consistent with Quintessa Limited's QA requirements (International Standard ISO 9001:2008, including the requirements of the TickIT 5.5 standard for software development).
2.2.3	TOUGH2 modifications undertaken for GGM integration must be consistent with Geofirma Engineering's ISO 9001:2008 work instructions (WI) for software development.

6.2.3 Reliability

The code should be demonstrated to be accurately solving the equations which form the model presented in the Theory Manual (Chapter 4). This requirement is assessed as part of the verification process.

Requirement Number	Requirement
2.3.1	During the verification stage, the code should be demonstrated to accurately implement the model over a broad range of different input parameters, both with the driver program and when integrated with the gas transport code.
2.3.2	During the verification stage, it should be demonstrated that there is convergence towards a single stable solution as the numerical controls on accuracy are tightened.

6.2.4 Maintainability

Requirement Number	Requirement
2.4.1	The GGM code should be accompanied by a detailed design description/architectural design.
2.4.3	The GGM code should be written in such a way as to be easily maintainable following standard coding practice (use of code comments, subroutines to encapsulate logic etc.).

GGM only requires a FORTRAN-77 compiler in order for it to be compiled. Since this is also a requirement of the TOUGH2 gas transport code into which it is integrated, there are no additional maintainability issues concerning software.

6.2.5 Security

There are no security requirements for this software.

6.2.6 Intended Operating Environment

Requirement Number	Requirement
2.6.1	T2GGM is intended to be operated in a single- or multi-processor Windows environment.

6.2.7 Reference Design

There is no reference design for this software.

6.2.8 Intended User

Requirement Number	Requirement
2.8.1	GGM is designed such that a scientific consultant who is familiar with TOUGH2 and FORTRAN 77 can integrate GGM with TOUGH2.
2.8.2	T2GGM is designed such that consultants who are familiar with gas modelling using TOUGH2, and with the relevant GGM theory described in this report, can use T2GGM.

6.3 Specific Requirements

6.3.1 Design Aspects

Requirement Number	Requirement
3.1.1	GGM should contain a calculation subroutine that will take the time, average repository pressure, repository saturation, relative humidity and void volume as inputs from TOUGH2, from which it will step GGM forward in time from a previous time step and calculate gas and water generation rates and a suggested maximum time step for subsequent iterations.
3.1.2	GGM should contain initialization subroutines that read in the parameters and initial conditions from a file, and which initialize the communication between GGM and TOUGH2.
3.1.3	GGM should contain an independent driver program to allow standalone operation. The driver program will mimic the TOUGH2 subroutine calls, and will include a simple model for water saturation and gas pressure evolution suitable for testing the GGM.
3.1.4	GGM will read in the initial conditions and parameters from an input file during the initialization phase.
3.1.5	GGM should be connected to input/output units to which the input parameters will be read and echoed, to which GGM data will be sent at every calculation step or at specified intervals and to which diagnostic and other standard output will be sent.
3.1.6	GGM should provide a maximum suggested subsequent time step to TOUGH2.

6.3.2 Hardware Interfaces

There are no hardware interface requirements.

6.3.3 Software Interfaces

T2GGM does not interface with any other software. GGM interfaces with the TOUGH2 gas transport code through subroutines and common blocks. New common blocks were designed to facilitate the interface. Existing TOUGH2 common blocks were not modified.

Requirement Number	Requirement
3.3.1	GGM may access information from TOUGH2 during initialization, such as unit numbers, via common blocks rather than subroutine arguments.

6.3.4 User Interface

Requirement Number	Requirement
3.4.1	GGM will read from a unit number provided by TOUGH2 during the initialization phase.
3.4.2	When operating in standalone mode GGM will present the user with a description of each input and provide its units before requesting that its value be entered. This output will be sent to a unit number that can be set by the calling code.
3.4.3	It should be possible to automate the input of GGM data using a file based method and a sample input file should be provided with the code. T2GGM should be able to use this method to call GGM.
3.4.4	During the calculation phase, no user interaction with T2GGM is required.

6.3.5 Input and Output Requirements

Requirement Number	Requirement
3.5.1	The units used internally for all GGM quantities during the calculation phase should be those defined in the Theory Manual (Chapter 4) (SI base units).
3.5.2	The units used when inputting data should be those given for the relevant quantities in the relevant Data Report (QUINTESSA and GEOFIRMA 2011).
3.5.3	The code may need to convert units internally.
3.5.4	When outputting data, numerical values should be presented using the maximum precision supported by the corresponding data type.
3.5.5	Fixed width, tab or comma separated format should be used when outputting column based data so that it can be readily imported into a spreadsheet or graphing program.

Requirement Number	Requirement
3.5.6	When echoing the input data, a three column format should be used. The first column should indicate the parameter name,the second should indicate the internal units used, and the third should indicate the value of the parameter in the internal units.
3.5.7	Initial header rows of the calculation output file should be preceded by a hash (#) comment character. The first uncommented line should be a header row containing the (internal) names of all of GGM variables, input and output quantities. Subsequently, the values of those parameters should be appended to the file as additional rows.

6.3.6 Performance Requirements

It is expected that when GGM is run independently of TOUGH2, the solver should take, at most, a couple of minutes to complete. GGM suggests the size of the subsequent time step that TOUGH2 should take. Since TOUGH2 requires a larger real\physical time period per computational time step than GGM does, a large number of small time steps can affect TOUGH2 run times significantly.

Requirement Number	Requirement
3.6.1	See requirement 3.1.6.

6.3.7 Portability Requirements

Requirement Number	Requirement
3.7.1	The code should be written adhering to the FORTRAN 77 standard (J3 2008) and should refrain from using vendor specific features so that it can be compiled by all standards-conforming compilers.

6.3.8 File Size and Type Requirements

Requirement Number	Requirement
3.8.1	It should be possible to limit the frequency with which GGM results are output to file during the calculation phase using an initialization parameter set by TOUGH2. This should enable the output file size to be controlled.
3.8.2	TOUGH2 node and connection output is written by default in text form to the main output file. The volume of T2GGM output makes this approach intractable. Node output will be written to file NOUT. Connection output will be written to file COUT.

Requirement Number	Requirement
3.8.3	NOUT and COUT output is text format by default. A binary format shall be supported to reduce output file size and speed post-processing.
3.8.4	TOUGH_MP writes COFT and FOFT text output associated with nodes or connections being assembled on a processor in the default directory of each processor. This leads to errors in assembling the complete results. An option shall be supported to write FOFT and COFT output in a specified directory.
3.8.5	The default FOFT and COFT output formats are extremely inefficient and are prone to errors on parsing. A new file format shall be developed that is optimized for machine post-processing.

6.3.9 Data Structure and Data Flow Requirements

Requirement Number	Requirement
3.9.1	GGM initialization data should be stored in a common block so that they can be used by the initialization and calculation subroutines.
3.9.2	GGM should not modify any TOUGH2 parameters to which access is provided via common blocks, specifically during the calculation phase. Code for constants and common blocks should be stored in ‘include files’ to ensure that they are used consistently between subroutines.

6.3.10 Programming Language

Requirement Number	Requirement
3.10.1	See requirement 3.7.1.

6.3.11 Programming Practices and Requirements

Requirement Number	Requirement
3.11.1	All GGM variables should be explicitly typed.
3.11.2	GGM input parameters, constants, variables, indexes into arrays and subroutine names should all have prefixes that identify them as such. Where possible, names of variables should be given names that identify them with their corresponding symbols in the Theory Manual (Chapter 4).

6.3.12 Imposed Physical or Mathematical Models or Numerical Algorithms

GGM predicts the evolution of the partial pressures and mole fractions of the individual gas components in the repository. However , the gas transport code TOUGH2 requires a single gas generation rate as an output of GGM. Requirement 12.3 concerns the calculation of the gas generation rate from GGM output.

Requirement Number	Requirement
3.12.1	The GGM mathematical model is to be implemented as described in the Theory Manual (Chapter 4).
3.12.2	The GGM time discretization method should be one which is stable even for relatively coarse time steps.
3.12.3	GGM will convert its total gas generation rate to an equivalent gas generation rate in kg s^{-1} for use by TOUGH2 by using the effective molar mass of the gas.
3.12.5	GGM will track sources and sinks of C, Fe and H_2O within the repository, and fluxes into and out of the repository, and thus demonstrate mass balance of those quantities for the repository system.

6.3.13 Error Detection and Handling Requirements

Requirement Number	Requirement
3.13.1	The GGM numerical implementation should identify and provide a method for dealing with negative values of quantities which are only physical when positive, should they occur, but the time discretization should be set-up to avoid this situation where possible.

6.3.14 Accuracy Targets

Requirement Number	Requirement
3.14.1	A time resolution test should be undertaken to check that the GGM parameters controlling solution accuracy are sufficiently accurate to result in a stable converged solution.

7. DESIGN DESCRIPTION

7.1 Introduction

This section, which also serves as a programmer manual, describes the approaches that are used for:

- Implementing the GGM Version 2.1 as described in the Theory Manual (Chapter 4) using FORTRAN 77; and
- Integrating GGM Version 2.1 with the TOUGH2 gas transport codes (TOUGH2 Version 2.1 and TOUGH2-MP Version 2.1).

GGM is implemented as a set of subroutines called by TOUGH2. The general flow of information between TOUGH2 and GGM is shown in Figure 1.1. The basic assumptions, coding conventions and implementation approach are described in the following sections.

The current versions of TOUGH2 and TOUGH2-MP combined with GGM are called T2GGM and T2GGM-MP Version 2.1.

7.2 Description

This section describes the software architecture. The design is intended to meet the requirements set out in Chapter 6.

All coding aims to minimize changes to the existing TOUGH2 code base. GGM support routines are coded as new subroutines and not as new sections within existing TOUGH2 subroutines. GGM common blocks are not be exposed to existing TOUGH2 codes. T2GGM Version 2.1 uses the EOS3 equations of state for air and water, with an option to use CH_4, CO_2 or H_2 (instead of air) as an alternative gas.

GGM software consists of:

- A calculation subroutine, GGMCALC, that takes the time, average repository pressure, average repository saturation, average relative humidity, void volume and flow of water into the repository as inputs and calculates gas and water generation rates;
- Initialization subroutines, GGMCINIT and GGMCREAD that read in the parameters and initial conditions from file, and which initialize the communication between GGM and TOUGH2;
- Other subroutines and functions acting as a service to the those described above; and
- A driver program, DRIVER, that mimics the subroutine calls that TOUGH2 would make using a model for the interaction between GGM and TOUGH2 and which adapts to the time steps suggested by GGM.

The integration subroutines added to the TOUGH2 software to interface with GGM consists of:

- Initialization subroutines, GGMIINIT, GGMIREAD and GGMISET that call the corresponding GGM subroutines responsible for reading in data and initializing communication;
- GGMTSTEP and GGMQU subroutines that are responsible for updating source and sink terms; and

- TRANSGGM - subroutine to transform source/sink node numbering to local node numbers for the MP version.

Other minor TOUGH2 modifications consist of the following.

- The ability to model different gases - overrides hard coded internal values for air with values appropriate for selected gas. Default values can be overridden.
- The selection of alternative output formats. Binary file formats for node and connection data are much more efficient and are faster to post-process.
- The selection of single output directory for COFT/FOFT files.
- The runtime allocation of output times - allows more than 100 output times to be specified.
- Modified van Genuchten relative permeability and capillary pressure functions from iTOUGH.

The connection between these subroutines is summarized in Figure 7.1. These GGM and TOUGH2 interface modules are identical in function for T2GGM and T2GGM-MP. The MP versions of the subroutines contain additional code to broadcast/receive calculation results to/from different computation nodes.

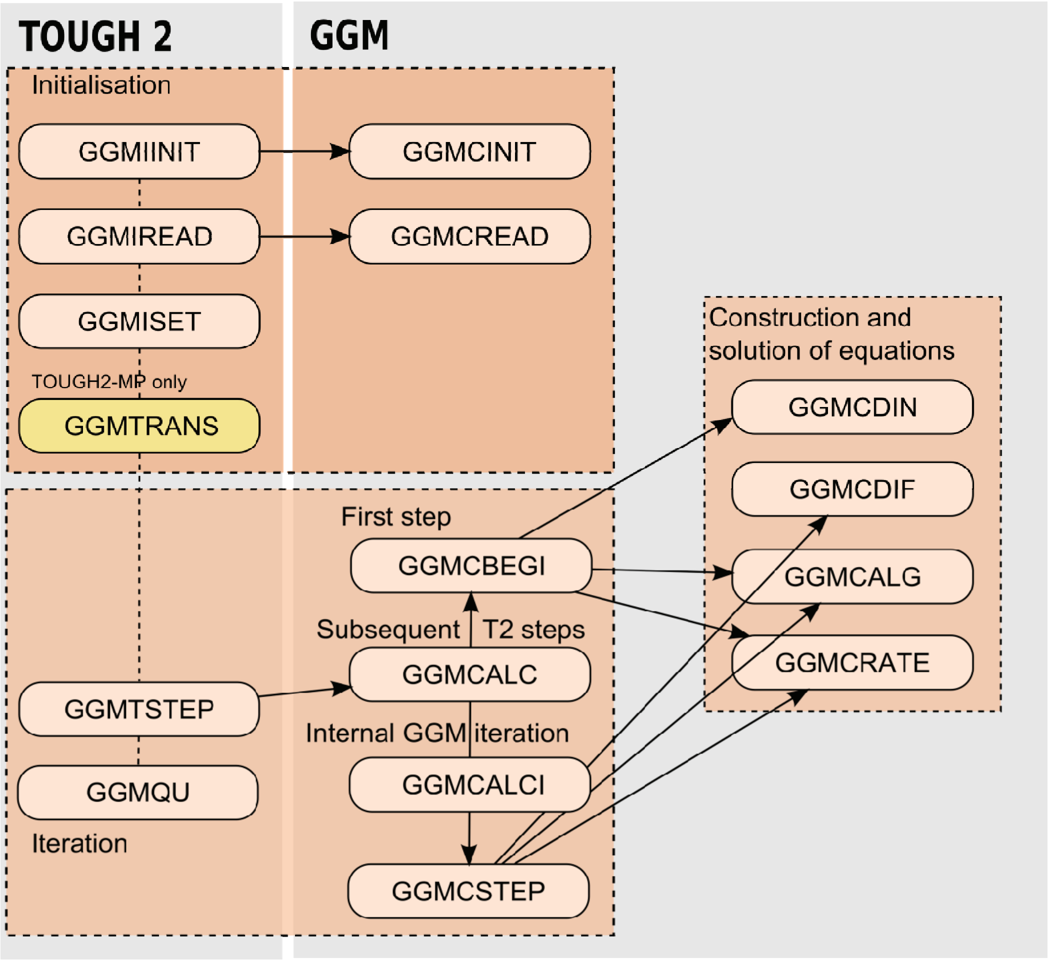

Figure 7.1: The GGM Subroutine Calling Hierarchy for T2GGM

7.2.1 Program Flow

The basic T2GGM program flow is as follows. The names of TOUGH2 subroutines are **underlined bold** in the text below.

1. Execute TOUGH2 as the primary code.
2. Read all input using TOUGH2 subroutine **INPUT**. TOUGH2 has a unique approach to reading input that allows different input groups to be read in any particular order. The input file is parsed by keyword, and then data associated with each keyword is read and pre-processed. Subsequently the input data is written out in a specific format to a separate file. For example, source and sink data is specified by keyword GENER and then written to a text file called GENER.
3. Subroutine **RFILE** reads all post-processed files in the correct order (material properties, mesh, source sink, etc.)
4. Subroutine **CYCIT** controls time step execution making sure that time step sizes and output target times are honoured.
5. For each time step, subroutine **MULTI** assembles the flow equations. Sources and sinks are added within **MULTI** with a call to subroutine **QU**. **LINEQ** is called to solve the system of equations. If the residual is too large, or there are errors in phase assembly, the time step is reduced, and the equations reassembled by **MULTI**, and solved again. The process continues until either: convergence is achieved, or a fatal error occurs, or termination criteria are met. GGM interface routines are called in this stage,
6. After successful completion of a time step, subroutine **CONVER** is called to update all the state variables.
7. Execution continues under control of **CYCIT** until the final output time is attained, or until the solution reaches steady state.

The basic GGM program flow is as follows.

1. The initial conditions and parameters are read from standard input during the initialization phase. A file containing the input parameters can then be redirected to the program in order to supply the necessary inputs in an automated manner. GGM is connected to input/output units supplied by TOUGH2 to which the input parameters are echoed, to which GGM solution data is sent at every calculation or at specified intervals and to which GGM messages are sent.
2. GGMCALC calls GGMCALCI as many times as necessary to step up to the time specified by TOUGH2. GGMCALCI interpolates TOUGH2 provided inputs over the specified time range and provides a suggested next time step to be taken by TOUGH2. TOUGH2 puts in controls to ensure that the maximum time step taken is not restrictive. If the maximum time step requested is not achievable, TOUGH2 will write a message to a log file or the console warning of this.
3. GGMCALC calls a subroutine GGMCSTEP, responsible for stepping GGM forward in time from a previous time step.
4. GGMCSTEP routine in turn calls subroutines GGMCDIF, responsible for evolving the differential equations forward in time, GGMCALG, responsible for solving the algebraic equations given the values of the variables solved using the differential equations, and GGMCRATE, responsible for calculating the rates of the differential variables needed at the subsequent time step. Details of the interfaces for each of these subroutines are given in Section 7.3.3.2.

5. After GGMCSTEP has brought GGM model up to the current TOUGH2 time, it calculates gas and water generation rates. An equivalent gas generation rate is calculated using an effective molar mass of air or gas.
6. A suggested maximum time step for subsequent iterations is calculated by GGMCALCI using the approach outlined in Section 7.3.4. This is passed back to GGMCALC.

7.2.2 Component Descriptions

One FORTRAN source file, GGMCALC.f, containing GGM initialization and calculation subroutines, and several include files is required to implement GGM. Routines in GGMCALC subroutine do not access any TOUGH2 variables or common blocks.

A FORTRAN source file, DRIVER.f, contains the standalone GGM driver program.

A FORTRAN source file, GGMT2.f, contains the TOUGH2 integration code. This code accesses (but does not modify) the TOUGH2 control variables (number of elements, number of phases, etc.), element and connection property data (names, volumes, porosity, etc.), and the EOS variables (pressure, liquid saturation, etc.). Only the matrix assembly right hand side variable is modified, where GGM calculated gas/water sink and source terms are included (Subroutine GGMQU).

The specific inputs and outputs for the individual calculation routines within each file are described in detail in Section 7.3.

7.2.3 Requirements Verification

Table 7.1 links the requirements set out in the Requirements Specification (Chapter 6) with the implementation.

7.3 Detailed Design

The sub-sections that follow provide a detailed description for how GGM is implemented and integrated with TOUGH2 and TOUGH2-MP.

7.3.1 Conventions

7.3.1.1 General Conventions

The follow general conventions are adhered to:

- Data storage for GGM parameters and for TOUGH2 integration variables are in labelled COMMON blocks starting with letters GGM.
- A single shared common block GGMIOU is used by both code sections to specify output file IO unit numbers. Other common blocks specific to GGM integration code within TOUGH2 (for example, containing indexes and allocations for gas source nodes) start with letters GGMI.
- GGMI and GGMIOU groups of COMMON blocks are in separate include files (e.g., GGMI.INC and GGMIOU.INC).

Table 7.1: Comparison of the Requirements Specification and Code Implementation

Requirement Number	Requirement	Implementation
QA REQUIREMENTS		
2.2.1	T2GGM software must be maintained consistent with the QA requirements of NWMO for Technical Computing Software (NWMO 2010).	Implemented.
2.2.2	GGM software development must be consistent with Quintessa Limited's QA requirements (International Standard ISO 9001:2008, including the requirements of the TickIT 5.5 standard for software development).	Implemented.
RELIABILITY		
2.3.1	During the verification stage, the code should be demonstrated to accurately implement the model over a broad range of different input parameters, both with the driver program and when integrated with the gas transport code.	Not applicable to the design stage.
2.3.2	During the verification stage, it should be demonstrated that there is convergence towards a single stable solution as the numerical controls on accuracy are tightened.	Not applicable to the design stage.
MAINTAINABILITY		
2.4.1	The GGM code should be accompanied by a detailed design description/architectural design.	Satisfied by this document.
2.4.3	The GGM code should be written in such a way as to be easily maintainable following standard coding practice (use of code comments, subroutines to encapsulate logic etc.).	Implemented.
SECURITY		
No requirements		

Requirement Number	Requirement	Implementation
INTENDED OPERATING ENVIRONMENT		
2.6.1	T2GGM is intended to be operated in a single- or multi-processor Windows environment	Implemented. The T2GGM interface has been designed to function with both the single processor and multi-processor versions of TOUGH2.
REFERENCE DESIGN		
No requirements		
INTENDED USER		
2.8.1	GGM is designed such that a scientific consultant who is familiar with TOUGH2 and FORTRAN 77 can integrate GGM with TOUGH2.	Implemented
2.8.2	T2GGM is designed such that consultants who are familiar with gas modelling using TOUGH2, and with the relevant GGM theory described in this report, can use T2GGM.	Implemented
DESIGN ASPECTS		
3.1.1	GGM should contain a calculation subroutine that will take the time, average repository pressure, repository saturation, relative humidity and void volume as inputs from TOUGH2, from which it will step GGM forward in time from a previous time step and calculate gas and water generation rates and a suggested maximum time step for subsequent iterations.	Implemented in subroutine GGMCALC.
3.1.2	GGM should contain initialization subroutines that read in the parameters and initial conditions from file, and which initialize the communication between GGM and TOUGH2	Implemented in subroutines GGMCINIT and GGMCREAD.
3.1.3	GGM should contain an independent driver program. The driver program will mimic the TOUGH2 subroutine calls, and will include a simple model for water saturation and gas pressure evolution suitable for testing the GGM.	Implemented in the program DRIVER, which includes a model of the interaction between GGM and TOUGH2, providing it with saturation, pressure and relative humidity profiles.

Requirement Number	Requirement	Implementation
3.1.4	GGM will read in the initial conditions and parameters from an input file during the initialization phase.	Initial conditions and parameters are read from standard input. These inputs can be placed in a file with each input on a separate line and redirected to the program.
3.1.5	GGM should be connected to input/output units to which the input parameters will be read and echoed, to which GGM data will be sent at every calculation step or at specified intervals and to which diagnostic and other standard output will be sent.	GGM is connected to the IGGMREAD, IGGMCALC, IGGMMSG, IGGMINPT and IGGMOUPT units shared with TOUGH2 using the COMMON block GGMIOU. Input parameters are echoed to IGGMREAD, calculation data are written to IGGMCALC, diagnostic messages are sent to IGGMMSG. Other user input and output is read and sent to the IGGMINPT and IGGMOUPT units. An input parameter LOGTR controls the minimum amount of time to wait between writes to the output file.
3.1.6	GGM should provide a maximum suggested subsequent time step to TOUGH2.	Implemented. See Section 7.3.4.2.
HARDWARE INTERFACES		
No requirements		
SOFTWARE INTERFACES		
3.3.1	GGM may access information from TOUGH2 during initialization, such as unit numbers, via common blocks rather than subroutine arguments.	IO unit numbers are shared using common blocks.
USER INTERFACE		
3.4.1	GGM will read from a unit number provided by TOUGH2 during the initialization phase.	Implemented.

Requirement Number	Requirement	Implementation
3.4.2	When operating in standalone mode GGM will present the user with a description of each input and provide its units before requesting that its value be entered. This output will be sent to a unit number that can be set by the calling code.	Implemented.
3.4.3	It should be possible to automate the input of GGM data using a file based method and a sample input file should be provided with the code. T2GGM should be able to use this method to call GGM.	File redirection can be used to automate the input of data.
3.4.4	During the calculation phase, no user interaction with T2GGM is required.	No user interaction is required.
INPUT AND OUTPUT REQUIREMENTS		
3.5.1	The units used internally for all GGM quantities during the calculation phase should be those defined in the Theory Manual (Chapter 4) (SI base units).	Implemented.
3.5.2	The units used when inputting data should be those given for the relevant quantities in the relevant Data Report (QUINTESSA and GEOFIRMA 2011).	Implemented.
3.5.3	The code may need to convert units internally.	Conversion takes place immediately after the variables have been read in. The converted input parameters are echoed to the IGGMREAD output unit along with their names and units.
3.5.4	When outputting data, numerical values should be presented using the maximum precision supported by the corresponding data type.	Implemented.
3.5.5	Fixed width, tab or comma separated format should be used when outputting column based data so that it can be readily imported into a spreadsheet or graphing program.	The output is fixed width and space separated. Text fields are enclosed in quotes.

Requirement Number	Requirement	Implementation
3.5.6	When echoing the input data, a three column format should be used. The first column should indicate the parameter name and the second should indicate the internal units used and the third should indicate the value of the parameter in the internal units.	Implemented.
3.5.7	Initial header rows of the calculation output file should be preceded by a hash (#) comment character. The first uncommented line should be a header row containing the (internal) names of all of GGM variables, input and output quantities. Subsequently, the values of those parameters should be appended to the file as additional rows.	The final format use includes header lines that provide the following information: The first line is commented and contains indexes into the algebraic or differential variable arrays for the variables, or 0 if the quantity being output is not a variable. These numbers are used to identify variables within error and warning messages output to the relevant output unit. The second line is commented and defines the units. The third line is uncommented and contains the names of the quantities in those columns.
PERFORMANCE REQUIREMENTS		
3.6.1	See requirement 3.1.6.	Implemented. See Section 7.3.4.2 for details. TOUGH2-MP was implemented and TOUGH2 and GGM timesteps were decoupled for Version 2.0 in order to improve performance.

Requirement Number	Requirement	Implementation
PORTABILITY REQUIREMENTS		
3.7.1	The code should be written adhering to the FORTRAN 77 standard (J3 2008) and should refrain from using vendor specific features so that it can be compiled by all standards-conforming compilers.	The standalone GGM code was compiled and tested with two FORTRAN 77 compilers, g95 (FSF 2008) and f77 (FSF 2004), both using all the available standards compliance compiler options. The final T2GGM build is compiled and linked with the Intel Fortran compiler Version 9.1, Visual Studio 2005 integration.
FILE SIZE AND TYPE REQUIREMENTS		
3.8.1	It should be possible to limit the frequency with which GGM results are output to file during the calculation phase using an initialization parameter set by TOUGH2. This should enable the output file size to be controlled.	A parameter, LOGTR, is supplied as an input parameter. This controls the minimum amount of time to wait between writes to the output file.
DATA STRUCTURE AND DATA FLOW REQUIREMENTS		
3.9.1	GGM initialization data should be stored in a common block so that it can be they can be used by the initialization and calculation subroutines.	Initialization parameters are stored in GGMCIP common block.
3.9.2	GGM should not modify any TOUGH2 parameters to which access is provided via common blocks, specifically during the calculation phase. Code for constants and common blocks should be stored in 'include files' to ensure that they are used consistently between subroutines.	Implemented.
PROGRAMMING LANGAGE		
3.10.1	See requirement 3.7.1.	Implemented.

Requirement Number	Requirement	Implementation
PROGRAMMING PRACTICES AND REQUIREMENTES		
3.11.1	All GGM variables should be explicitly typed.	IMPLICIT NONE is used throughout to ensure that this is the case.
3.11.2	GGM input parameters, constants, variables, indexes into arrays and subroutine names should all have prefixes that identify them as such. Where possible, names of variables should be given names that identify them with their corresponding symbols in the Theory Manual (Chapter 4).	Implemented. See Table 7.2 for the naming conventions.
IMPOSED PHYSICAL OR MATHEMATICAL MODELS OR NUMERICAL ALGORITHMS		
3.12.1	The GGM mathematical model is to be implemented as described in the Theory Manual (Chapter 4).	Implemented.
3.12.2	The GGM time discretization method should be one which is stable even for relatively coarse time steps.	A Modified-Euler Scheme is implemented. See Section 7.3.4.1.
3.12.3	GGM will convert its total gas generation rate to an equivalent gas generation rate in kg s^{-1} for use by TOUGH2 by using the effective molar mass of the gas.	Implemented.
3.12.5	GGM will track sources and sinks of C, Fe and H_2O within the repository, and fluxes into and out of the repository, and thus demonstrate mass balance of those quantities for the repository system.	Implemented.
ERROR DETECTION AND HANDLING REQUIREMENTS		
3.13.1	The GGM numerical implementation should identify and provide a method for dealing with negative values of quantities which are only physical when positive, should they occur, but the time discretization should be set-up to avoid this situation where possible.	Implemented. See Section 7.3.3.2.
ACCURACY TARGETS		
3.14.1	A time resolution test should be undertaken to check that the GGM parameters controlling solution accuracy are sufficiently accurate to result in a stable converged solution.	Implemented. See Chapter 8.

7.3.1.2 GGM Conventions

A summary of the naming conventions to be used for variables within GGM calculation routines are summarized in Table 7.2. All arrays are dimensioned using FORTRAN parameter values. GGM integration variables within TOUGH2 follow TOUGH2 naming conventions.

7.3.1.3 TOUGH2 Conventions

The following conventions are specific to TOUGH2.

All TOUGH2 modifications are to be bracketed with comment lines containing the keyword GGM, GGM Version #, (starting with V1) and the date of the modification. For example:

```
C***********************************************

C********************* GGM V1  FEB08

C***********************************************
```

A summary of the naming conventions to be used within GGM integration code are summarized in Table 7.3.

Table 7.2: Naming Conventions for GGM Variables

Prefix	Is followed by	Fortran Type	Meaning
GGMC	Characters. See below.	Common block	Holds variables specific to GGM calculations.
GGMCP	Nothing	Common block	Holds parameters used by multiple subroutines.
GGMCIP	Nothing	Common block	Holds variables that are input parameters.
GGMCO	Nothing	Common block	Holds variables passed to GGM directly from TOUGH2 via subroutine arguments during the initialization phase.
GGMCSTP	Nothing	Common block	Holds variables that need to be shared between GGMCALC subroutine and the subroutines that it calls.
P	Up to 7 characters corresponding to the name given in the Theory Manual (Chapter 4).	Variable	A parameter. Initialized in GGMCREAD, stored in GGMCIP common block. Should not be modified during the calculation.

Prefix	Is followed by	Fortran Type	Meaning
PI	Up to 6 characters corresponding to the name given in the Theory Manual (Chapter 4).	Variable	A parameter that holds the initial value of a differential variable.
LP	The name of a parameter. See above.	Variable	A local version of a parameter that is defined in GGMCRATE subroutine. Used to facilitate the switching of rate constants to zero when certain conditions apply. See Section 7.3.3.2.
AEV	A number indicating the time step. 0 = current, 1 = previous, etc.	Array	Contains variables solved by algebraic equations.
DEV	A number indicating the time step. 0 = current, 1 = previous, etc.	Array	Contains variables solved by differential equations.
DER	A number indicating the time step. 0 = current, 1 = previous, etc.	Array	Contains the rates of the differential variables.
FMT	Up to 6 characters identifying the type and precision of the output.	Parameter	Holds part of a format specifier for formatting output.
CN	Up to 6 characters naming the parameter.	Parameter	A parameter that holds a double precision constant.
I	Up to 7 characters. See below.	Parameter	An integer parameter.
IC	A letter. ‘A’ to ‘E’	Parameter	An index for the current terminal electron acceptor reaction stage.

Prefix	Is followed by	Fortran Type	Meaning
IA	Up to 6 characters corresponding to the name in the Theory Manual (Chapter 4).	Parameter	An index into the algebraic variable arrays (AEV).
ID	Up to 6 characters corresponding to the name in the Theory Manual (Chapter 4).	Parameter	An index into the differential variable arrays (DEV, DER).
NI	A character indicating the type of list: ‘C’, ‘A’ or ‘D’.	Parameter	The number of indices of a given type.

Table 7.3: Naming Conventions within the TOUGH2 Integration Code

Prefix	Is followed by	Fortran Type	Meaning
GGMICTRL	Nothing	Common block	Holds variable defining GGM usage (IGGM: 0 = no, 1 = yes).
GGMIDT	Nothing	Common block	Holds current GGM time step maximum (GGMDTMX).
GGMIEL	Nothing	Common block	Holds variables containing number of repository, source and sink elements, element names, indexes, and scaling factors.
GGMINORM	Nothing	Common block	Holds flags to determine (1) whether to renormalize element scale factors in order to redistribute injection flow to all repository elements with the injected phase already present in the element (extraction flow is always redistributed only to repository elements with the appropriate phase available), and (2) to recalculate scale factors based on the volume of water/gas available in the injection elements.

Prefix	Is followed by	Fortran Type	Meaning
GGMIRSAT	Nothing	Common block	Holds residual saturations for gas below which gas (respectively) cannot be removed from the repository. Hold control variables for liquid saturation control which governs minimum residual liquid saturation and normalization of liquid extraction.
GGMIRHLIM	Nothing	Common block	Holds RH control variables which scale RH as minimum liquid saturation limits are reached. Also holds RHLIMMIN parameter, which determines the RH threshold below which extraction of water from an element stops.
GGMIQ	Nothing	Common block	Stores flows for each repository element, as calculated by GGM and distributed based on the scale factors.

7.3.2 Program Structure

The hierarchical structure of the subroutines that provide the interface between TOUGH2 and GGM and that perform GGM calculations are presented in Figure 7.1. The arrows indicate a subroutine call, and point from the caller to the subroutine being called. A dashed line indicates the order in which the calls are expected to be executed.

The subroutines on the left are implemented in TOUGH2 to enable it to communicate with GGM. A single GGM driver program has been written that imitates these subroutine calls using a given saturation curve or model for the interaction between GGM and TOUGH2.

There are three categories of subroutine:

- Initialization;
- Iteration; and
- Equation construction and solution.

7.3.3 Detailed Design Description

This section provides detailed descriptions of the subroutines in the subroutine calling hierarchy given in Figure 7.1. The TOUGH2 subroutines are described in Section 7.3.3.1 and GGM subroutines are described in Section 7.3.3.2.

7.3.3.1 TOUGH2

The primary required changes to the structure of the existing TOUGH2 source code are the addition of calls in order to drive GGM. The additional subroutines that are implemented are placed in a file GGMT2.f. These are described in Table 7.4.

The following are high-level descriptions of modifications made to existing TOUGH2 source code. The names of existing TOUGH2 subroutines that are modified are **underlined bold** in the text below.

1. Called GGMIINIT at start of the **INPUT** subroutine.
2. Added processing of GGMIN input keyword and, if found, called GGMIREAD, after TOUGH2 keyword processing loop in the **INPUT** subroutine. *Note that if the keyword GGMIN is not present in the input file, then GGM is not be used and TOUGH2 runs normally.*
3. Added processing of ALTGAS input keyword to the **INPUT** subroutine. If found, read alternative gas to be used (specified as either AIR, CH4, CO2 or H2) and any parameter overrides (Henry's constant, molar mass, or isothermal viscosity may be specified as an input). Note that if the keyword ALTGAS is not present in the input file, air with the associated default EOS3 parameters is be used as the gas. The values for Henry's constant, molar mass and viscosity are set within the **EOS** subroutine, using the inputs specified within the ALTGAS input record or default values. Details on the ALTGAS input record are provided in Section 7.3.4.10.
4. Added processing of INTER keyword to the **INPUT** subroutine. If found, read flag for binary NOUT/COUT output, and flag for single FOFT/COFT directory. If found read path to specified FOFT/COFT directory. Binary output files are opened in the TOUGH2 main program. Binary output is written in the **FINALOUT** subroutine.
5. Added call to GGMISET immediately after the **RFILE** subroutine call in main program. Element names, element volumes, porosities and connection names will have been read, allowing GGM input elements to be post-processed.
6. For TOUGH2-MP implementation, added call to GGMtrans in the **CYCIT** subroutine after grid has been partitioned between processors. This routine post-processes GGM specific element and connection related arrays for the newly partitioned grid (local processor element and connection numbering is different from the global numbering).
7. Added call to GGMTSTEP to set source and sink terms before start of first time step in the **CYCIT** subroutine. GGMSTEP calls the GGMCALC subroutine.
8. Added call to GGMQU before call to the **QU** subroutine in the **MULTI** subroutine. This adds GGM calculated source and sink terms to the right hand side vector during the matrix assembly step.
9. Added call to GGMTSTEP immediately after the **CONVER** subroutine has been called after a time step is successfully completed. This updates GGM source and sink terms for use in the next time step.
10. Added line after call the GGMTSTEP that compares DELT (time step size) to GGMDTMX and adjusts DELT for subsequent time steps if necessary.

Note that the TOUGH2-MP implementation also requires additional modifications to the parallelization subroutine **ALLREPLICOM** that ensures GGM variables are passed to each processor.

The modified van Genuchten formulations from iTOUGH2 were implemented directly in the **PCAP** and **RELP** subroutines.

Interfaces for each of the subroutines to be written in file GGMT2.f are provided in Table 7.4.

Table 7.4: Subroutines to be Implemented in GGMT2.f

Subroutine	Description
GGMIINIT	1) Sets GGM common block variables to initial values if required. IGGM in COMMON block GGMICTRL is set to 0. GGMDTMAX is set to 0.0. COMMON block GGMIOU input and output unit numbers (e.g., IGGMREAD etc.) is initialized to available logical unit numbers. 2) Attaches logical units IGGMMSG to output file GGMMSG (used by GGMCINIT). 3) Calls GGMCINIT. Does not access any TOUGH2 variables.
GGMIREAD	1) Reads all GGM integration input variables from standard input. COMMON block GGMINORM variables required are: NORMG – If not equal to zero, gas injection flow is distributed to all gas source elements with a gas saturation greater than zero. NORML – If not equal to zero, liquid injection flow is distributed to all liquid sink elements with a liquid saturation greater than zero. SCALEFACTORG – If not equal to zero, scale factors distribute GGM flows to the gas source elements are calculated at each time step based on the amount of gas available in each source element. These scale factors replace values read into the XGASSRC array described below. May increase run times, but increase model stability. SCALEFACTORL – If not equal to zero, scale factors distribute GGM flows to the liquid sink elements are calculated at each time step based on the amount of water available in each sink element. These scale factors replace values read into the XLIQSNK array described below. May increase run times, but increase model stability. COMMON block GGMIRSAT variables required are: GASRSAT – Residual gas saturation, below which no gas can be removed from the repository (if QAIR is less than zero). USELIQCTRL - flag (0, 1) to control whether liquid saturation limits are enforced. NORML is only applied if USELIQCRTL is set to 1. LSATOFFVAL - used only if USELIQCTRL = 1. The liquid saturation below which no water is extracted from a liquid sink element. Water extraction is also eliminated for an element if the element RH is below RHMINLIM (see below). If one or more elements have saturations greater than LSATOFFVAL and NORML is true, then liquid injection flow is distributed. If all liquid sink elements are below LSATOFFVAL, then no liquid is

Subroutine	Description
	extracted. If this condition is true, then RH is set to RHLIMMIN (see below) on subsequent time steps, until at least saturation in at least one liquid extraction element exceeds LSATONVAL. LSATONVAL - the minimum saturation threshold required for one or more liquid extraction elements for liquid extraction to resume, after it has been previously terminated due to saturation at all liquid extraction nodes being less than LSATOFFVAL. COMMON block GGMIRHLIM variables required are: USERHCTRL - flag (0, 1) which determines whether RH input to GGM is scaled based on residual liquid saturations. This is the most effective way to balance GGM water consumption with geosphere inflow as it slows down vapour phase reactions gradually as a saturation limit is reached. RHLSATMIN - minimum liquid saturation for RH control RHLSATMAX - maximum liquid saturation for RH control RHLIMMIN - RH value for minimum saturation and lower limit of element RH for liquid extraction from an element. This value should be equivalent to PRHMIN in order to maintain correspondence to GGM, however, it is included as a separate parameter for stability reasons: it may be practical to have a value greater than PRHMIN to minimize stability issues at single liquid sink elements if the repository does not become fully de-saturated with liquid (i.e., repository liquid saturation remains above LSATONVAL) over the course of the simulation. The code fragment below describes the scaling approach

```
IF ((RH.GT.RHLIMMIN).AND.(USERHCTRL.EQ.1))THEN
  RHMULT = TANH((STOT-RHLSATMIN)/(0.5*(RHLSATMAX-
  RHLSATMIN)))
  IF (RHMULT.GT.1.0) RHMULT = 1.0;
  IF (RHMULT.LT.0.0) RHMULT = 0.0;
                    RH = RHLIMMIN + (RH - RHLIMMIN) * RHMULT;
END IF
```

Subroutine	Description
	COMMON block GGMIEL variables required are: VOLFAC – repository volume factor

Subroutine	Description
	NREPO – number of repository elements EREP(NREP) – names of repository elements NGASSRC – number of gas source elements EGASSRC(NREP) – names of gas source elements XGASSRC(NGASSRC) – scaling factor for each source element NLIQSNK – number of liquid sink elements ELIQSNK(NREP) – names of liquid sink elements XLIQSNK (NLIQSNK) – scaling factor for each sink element NREPCONN – number of connections contributing water to the repository EREPCONN(NREPCONN) – names of connections contributing water to the repository EREPSIDE (NREPCONN) – names of element on repository side of the connection Note that gas source and liquid sink elements may be the same. Also note that although gas source and liquid sink elements are expected to be in the repository this is not checked. Nodes should be specified using standard TOUGH2 node naming conventions. 2) Attaches logical units IGGMREAD and IGGMCALC to output files GGMREAD and GGMCALC. 3) Echoes all input to IGGMREAD unit. 4) Calls GGMCREAD. 5) Sets IGGM in COMMON block GGMICTRL to 1. Does not access any TOUGH2 variables.
GGMISET	Performs pre-run processing. Returns immediately with no action if IGGM is 0. 1) Checks element and connection names from input and determines associated numbers (global numbers in the case of TOUGH2-MP): IELREP(NREPO) – element numbers of repository IEGASSRC (NGASSRC) – numbers of gas source elements

Subroutine	Description
	IELIQSNK (NLIQSNK) – numbers of liquid sink elements IREPCONN(NREPCONN) – numbers of connections contributing water to the repository. CONNSIGN – sign (positive/negative) to transform flow parameter into a flow into the repository. Note that implementation for connections is slightly different in TOUGH2-MP, due to the way global and local numbering is handled. For the TOUGH2-MP implementation: • The element numbers associated with the connection are determined within IREPCONN1(NREPCONN) and IREPCONN2(NREPCONN). • The element number on the repository side of the connection (should be same as IREPCONN1 or IREPCONN2) is determined and stored in IREPCONNSIDE(NREPCONN). • CONNSIGN is determined later in GGMtrans, using IREPCONNSIDE. 2) Also creates arrays mapping gas source indexes to repository indexes (IMAPGASREP(NREPO)) and mapping liquid sink indexes to repository indexes (IMAPLIQREP(NREPO), required for calculating scale factors. For TOUGH2-MP implementation, this mapping is done in GGMtrans. Accesses TOUGH2 variables NEL (number of elements), ELEM (element names), ELEMINDEX(global element index numbers, TOUGH2-MP only), NCON (number of connections), and ELEM1 and ELEM2 (element names for connections). Does not modify any TOUGH2 variables.
GGMtrans	Performs pre-run processing for TOUGH2-MP implementation: 1) Transforms global index numbering to local processor index numbering for IELREP, IEGASSRC, IELIQSNK. 2) Transforms arrays XGASSRC and XLIQSNK to local index numbering. 3) Determines local connection number from IREPCONN1 and IREPCONN2 and stores in IREPCONN(NREPCONN) and determines CONNSIGN(NREPCONN).
GGMTSTEP	Called at start of simulation and end of each successful time step. Returns immediately with no action if IGGM is 0.

Subroutine	Description
	Otherwise, fills in common block GGMQU values: 1) Calculates the following repository values to pass to GGMCALC: • repository volume (this volume may change slightly at each time step due to compressibility of materials defined as repository elements), • average air pressure at all defined repository elements, • total liquid saturation of repository., • relative humidity (RH) of the repository. RH is scaled if USERHCTRL is set to 1 • flow of water into the repository, and • if specified by the SCALEFACTORG and SCALEFACTORL flags, calculates scale factors for distributing GGM flows to sink/source elements according to the amount of water available in each element. 2) Calls GGMCALC to get total gas mass generation rate, water consumption rate, and maximum time step size for next time step. 3) Allocates total gas generation to gas source elements according to scaling factors. If gas extraction (negative gas generation rate) or NORMG flag set to a value other than zero, normalizes the scaling factors to all gas source elements with a gas saturation greater than GASRSAT (preventing gas extraction from elements with no gas available). If scale factors are normalized, message written in GGMMSG file. Values stored in array GGMQGAS. 4) Allocates total liquid consumption rate to liquid sink nodes according to scaling factors. If liquid extraction (negative liquid generation rate) or NORML flag set to a value other than zero, normalizes the scaling factors to all liquid sink elements with a liquid saturation greater than LSTATOFFVAL or an RH greater than RHLIMMIN (preventing water extraction from elements with no water available). If scale factors are normalized, message written in GGMMSG file. Values stored in array GGMQLIQ. Accesses TOUGH2 variables NK1, NSEC, NEQ1, NBK, X (equation of state solution variables specifically for pressure), PAR (secondary parameters, specifically for mass fraction of gas that is air, liquid saturation and gas saturation), AMA and AMS (molar mass of air and water respectively), EVOL, PHI and FLO. Does not modify any TOUGH2 variables.

Subroutine	Description
GGMQU	Called during each iteration of the matrix solution. Returns immediately with no action if IGGM is 0. Otherwise, adds source and sink rates in GGMQGAS and GGMQLIQ to appropriate positions in RHS vector for matrix solution. TOUGH2 routine QU provides prototype for element/phase/RHS vector numbering. Accesses TOUGH2 variables FORD, NEQ and EVOL. Modifies TOUGH2 variable R (right hand side vector for matrix solution).

7.3.3.2 GGM

Interfaces for each of the subroutines in the file GGMCALC.f are provided in Table 7.5. The following list describes the actions to be performed during the main GGM subroutine calls.

- GGMCVER: Writes the current GGM version to the given output unit.
- GGMCINIT is called. This calls GGMCVER, echoing GGM version to the standard output and to the diagnostic output file.
- GGMCREAD: For each item of input data its description, required units (as specified in the relevant Data Report) and variable name are output to screen; it is read in to a variable that is stored in GGMCIP common block in file GGMCI.INC; it is converted to GGM's internal units; and the name, internal units, and internal value are written to the IGGMREAD output unit.
- GGMCALC calls GGMCALCI as many times as necessary to step from the previous TOUGH2 time step to the current one. TOUGH2 input values are interpolated using GGMCIABC, GGMCIABC0 and GGMCINTE.
- GGMCALCI uses a logical variable IS1RUN with default value .TRUE. as an indicator of the fact that this is the first time the routine is called. This is set to .FALSE. at the end of the first call. The first time this is called, it calls GGMCBEGI to calculate the initial conditions (which itself calls GGMCDIN, GGMCALG and GGMCRATE in turn.) From this data the output quantities, QAIR and QLIQ are calculated. The routine outputs the column headers to the IGGMCALC output unit, as well as the first line of calculated data. Diagnostic messages are sent to the IGGMMSG unit. The newly calculated data are saved in arrays marking them as the previous time's data.
- On subsequent calls to GGMCALCI, it calls GGMCSTEP (which itself calls GGMCDIF, GGMCALG and GGMCRATE in turn) to evolve the solution forward in time. From this data the output quantities, QAIR and QLIQ are calculated. The routine outputs the calculated data to the IGGMCALC output unit if required. The newly calculated data are saved in arrays marking them as the previous time's data.

- GGMCBEGI calculates the initial condition, first solving the algebraic equations and then calculating the initial rates.
- GGMCDIN initializes the values of the differential variables, by accessing the parameters stored in the GGMCIP common block.
- GGMCDIF evolves the differential variables forward in time from the old to the new time step using the algorithm given in Section 7.3.4.1.
- GGMCALG determines the algebraic variables at the current time step.
- GGMCRATE determines the rate of change of the differential variables at the current time step. This uses the function GGMCHFUN to calculate the relative humidity scaling factor and itself calls GGMCHLIN or GGMCHSRP.
- GGMCHFUN calculates the relative humidity scaling factor by calling the appropriate function. If the PHTYPE input parameter is 1 then a linear ramp is calculated using GGMCHLIN. If it is 2 then a smoothed linear ramp is calculated using GGMCHSRP.
- GGMCHLIN is a linear relative humidity ramp function.
- GGMCHSRP is a smoothed linear relative humidity ramp function.
- GGMCDCHK checks the validity of the values of the differential variables. If any are negative when they should not be, they are set to zero and a message is sent to the diagnostic output unit.
- GGMCACHK checks the validity of the values of the algebraic variables. If any are negative when they should not be, they are set to zero and a message is sent to the diagnostic output unit.
- GGMCUTEA updates the terminal electron acceptor stage algebraic variables based on the old vector of algebraic variables, the new time and the new vector of differential variables.

Table 7.5: Subroutines and Functions to be Implemented in GGMCALC.f

Subroutine/Function	Parameters	Description
GGMCVER	Writes the GGM Version number to the specified unit number.	
	UNITNO	Input - The unit number to output the version to.
GGMCINIT	Initializes all variables required by GGM calculation routines.	
GGMCREAD	Reads all GGM calculation input variables from standard input. Echoes all input to IGGMREAD unit.	
GGMCALC	Main calculation routine – called at simulation start and at the end of each successful primary time step to provide gas generation and water consumption rates for next time step. Calls GGMCALCI to calculate intermediate timesteps. Echoes subroutine input and output and calculated values to an output file attached to logical unit IGGMCALC (defined in COMMON block GGMIOU), with a frequency set by the DMINTY input parameter. Diagnostic messages are sent to the IGGMMSG unit.	
	TIME	Input – simulation time (seconds).
	PAVG	Input - The total gas pressure in the repository as calculated by TOUGH2 (Pa).

Subroutine/Function	Parameters	Description
	STOT	Input – Total repository saturation (dimensionless). (STOT * REPVOL = volume of water in repository) Output – The total repository saturation actually assumed. The saturation is kept at a minimum value set by the PMINSAT threshold input parameter. (volume of liquid in repository = STOT0 * REPVOL).
	RH	Input – The fractional relative humidity (dimensionless).
	VV	Input – The repository void volume.
	INRATE	Input – Total rate of ingress of repository water (kg s^{-1}).
	PEMMA	Input – The equivalent molar mass of bulk gas (kg mol^{-1}).
	QAIR	Output - the equivalent gas generation rate (kg s^{-1}), with the convention that positive is generation, is negative consumption. This is calculated from the gas generation rate.
	QLIQ	Output – calculated generation rate of geosphere water (kg s^{-1}). This is expected to be primarily negative, indicating consumption of water by microbial processes.
	DTMAX	Output – maximum time step size for next step (s).
GGMCALCI	Intermediate calculation routine – called multiple times by GGMCALC to calculate intermediate time steps. Diagnostic messages are sent to the IGGMMSG unit.	
	TIME	Input – simulation time (seconds).
	PAVG	Input - The total gas pressure in the repository as calculated by TOUGH2 (Pa).
	STOT	Input – Total repository saturation (dimensionless). (STOT * REPVOL = volume of liquid in repository) Output – The total repository saturation actually assumed. The saturation is kept at a minimum value set by the PMINSAT threshold input parameter. (volume of liquid in repository = STOT0 * REPVOL).
	RH	Input – The fractional relative humidity (dimensionless).

Subroutine/Function	Parameters	Description
	VV	Input – The repository void volume.
	INRATE	Input – The total rate of ingress of geosphere water into the repository (kg s^{-1}).
	QAIR	Output - the equivalent gas generation rate (kg s^{-1}), with the convention that positive is generation, is negative consumption. This is calculated from the gas generation rate.
	QLIQ	Output – calculated generation rate of geosphere water (kg s^{-1}). This is expected to be primarily negative, indicating consumption of water by microbial processes.
	DTMAX	Output – maximum time step size for next step (s).
	AAIR	Output – the total amount of geosphere bulk gas in the repository (kg).
	AH2O	Output – the total amount of geosphere water in the repository (kg).
GGMCBEGI	Executed on the first call to GGMCALC by GGMCALC. Sets up the initial conditions.	
	TNEW	Input – The time (s) at which to calculate the initial conditions.
	DNEW(NID)	Output – An array containing the values of the differential variables at the time of the initial condition. NID is the number of differential variables, defined as a parameter in GGMCP.INC.
	ANEW(NIA)	Output – An array containing the values of the algebraic variables at the time of the initial conditions. NIA is the number of algebraic variables, defined as a parameter in GGMCP.INC.
	RNEW(NID)	Output – An array containing the rates of the differential variables at the initial condition, calculated using the rate equations.
GGMCSTEP	Executed on the second and subsequent calls to subroutine GGMCALC by GGMCALC. Evolves GGM solution from the old time to the new time.	
	TOLD	Input – The previous time (s).
	DOLD(NID)	Input – An array containing the values of the differential variables at the previous time.

Subroutine/Function	Parameters	Description
	AOLD(NIA)	Input – An array containing the values of the algebraic variables at the previous time.
	ROLD(NID)	Input – An array containing the rates of the differential variables at the previous time.
	TNEW	Input – The time (s) to which GGM must be evolved.
	DNEW(NID)	Output – An array containing the values of the differential variables at the new time.
	ANEW(NIA)	Output – An array containing the values of the algebraic variables at the new time.
	RNEW(NID)	Output – An array containing the rates of the differential variables at the new time.
GGMCDIN	Specifies the initial conditions for the differential variables. Called once by GGMCBEGI.	
	TNEW	Input – The time (s) at which the initial conditions are being specified.
	DNEW(NID)	Output – An array containing the values of the differential variables at the time of the initial conditions.
GGMCDIF	Evolves the differential variables forward in time from the old to the new time using the rate equations. Called by GGMCSTEP.	
	TOLD	Input – The previous time (s).
	DOLD(NID)	Input – An array containing the values of the differential variables at the previous time.
	AOLD(NIA)	Input – An array containing the values of the algebraic variables at the previous time.
	ROLD(NID)	Input – An array containing the rates of the differential variables at the previous time.
	TNEW	Input – The time (s) to which the differential variables must be evolved.
	DNEW(NID)	Output – An array containing the values of the differential variables at the new time.
GGMCALG	Calculates the values of the algebraic variables at the new time using the values of the differential variables already calculated. Called by GGMCSTEP and GGMCBEGI.	
	TNEW	Input – The time (s) to which the differential variables must be evolved.
	DNEW(NID)	Input – An array containing the values of the differential variables at the new time.

Subroutine/Function	Parameters	Description
	ANEW(NIA)	Output – An array containing the values of the algebraic variables at the new time.
GGMCRATE	Calculates the rates of the differential variables at the new time. Called by GGMCSTEP and GGMCBEGI.	
	TNEW	Input – The time (s) to which GGM must be evolved.
	DNEW(NID)	Input – An array containing the values of the differential variables at the new time.
	ANEW(NIA)	Input – An array containing the values of the algebraic variables at the new time.
	RNEW(NID)	Output – An array containing the rates of the differential variables at the new time.
GGMCDCHK	Checks the validity of the values of the differential variables.	
	WARN	Input – Whether or not to send warnings to the diagnostic error file.
	TNEW	Input – The time (s).
	DNEW(NID)	Input and output – The array of differential variables. Variables that have become negative but which should remain positive are set to zero.
GGMCACHK	Checks the validity of the values of the algebraic variables.	
	WARN	Input – Whether or not to send warnings to the diagnostic error file.
	TNEW	Input – The time (s).
	ANEW(NIA)	Input and output – The array of algebraic variables. Variables that have become negative but which should remain positive are set to zero.
GGMCUTEA	Updates the electron acceptor stage algebraic variable.	
	WARN	Input – Whether or not to send warnings to the diagnostic error file.
	AOLD(NIA)	Input – The array of algebraic variables at the previous time step.
	ROLD(NID)	Input – The array of the rates of change of the differential variables at the previous time step.
	TNEW	Input – The current time.
	DNEW(NID)	Input – The current array of differential variables.

<table>
<tr><th>Subroutine/Function</th><th>Parameters</th><th>Description</th></tr>
<tr><td></td><td>ANEW(NIA)</td><td>Input and output – The currently array of algebraic variables, but with the terminal electron acceptor stage variable updated.</td></tr>
<tr><td rowspan="3">GGMCHLIN</td><td colspan="2">A function which calculates the linear relative humidity modulation factor (-).</td></tr>
<tr><td>RH</td><td>Input – The fractional relative humidity (-).</td></tr>
<tr><td>Function output</td><td>The relative linear relative humidity modulation factor (-).</td></tr>
<tr><td rowspan="3">GGMCHSRP</td><td colspan="2">A function which calculates the smoothed linear relative humidity modulation factor (-).</td></tr>
<tr><td>RH</td><td>Input – The fractional relative humidity (-).</td></tr>
<tr><td>Function output</td><td>The relative linear relative humidity modulation factor (-).</td></tr>
<tr><td rowspan="3">GGMCHFUN</td><td colspan="2">A function which calculates the relative humidity modulation factor (-).</td></tr>
<tr><td>RH</td><td>Input – The fractional relative humidity (-).</td></tr>
<tr><td>Function output</td><td>The linear relative humidity modulation factor (-).</td></tr>
</table>

7.3.4 Implementation Details

7.3.4.1 Time Discretization

The equations and variables of GGM presented in the Theory Manual (Chapter 4) can be split into two categories for the purposes of time discretization, classed here as “differential” and “algebraic”. Denoting the vector of all differential variables by C and the vector of all algebraic variables by A, gives the system of equations:

$$\frac{\partial C}{\partial t} = F(A, C) \tag{7.1}$$

$$A = H(C) \tag{7.2}$$

where F and H are functions of the variables corresponding to equations in the Theory Manual (Chapter 4). The differential equations correspond to the rate equations. This differential-algebraic system is evolved using a Modified-Euler forward step scheme. Letting t_n and t_{n+1} be the current and subsequent time steps and defining the time step $\Delta t = t_{n+1} - t_n$, the discretized version can be written:

$$C_{n+1} = C_n + \frac{\Delta t}{2}\left[F(A_n, C_n) + F\left(A^*_{n+1}, C^*_{n+1}\right)\right] \tag{7.3}$$

$$A_{n+1} = H(C_{n+1}) \tag{7.4}$$

where the starred variables are calculated at an intermediate step:

$$C^*_{n+1} = C_n + \Delta t F(A_n, C_n) \tag{7.3a}$$

$$A^*_{n+1} = H(C^*_{n+1}) \tag{7.4a}$$

Initially, either elements of C_0 or A_0 must be specified and all must be consistent with the algebraic equations $A_0 = H(C_0)$. Denoting the vector of all the rates of the differential equations by R and the vector of initial differential variables given by C^*_0, the final time discretization that is solved at each time step, $n = 1,2,...$ is:

$$C_{n+1} = C_n + \frac{\Delta t}{2}\left[R_n + R^*_{n+1}\right] \tag{7.5}$$

$$A_{n+1} = H(C_{n+1}) \tag{7.6}$$

$$R_{n+1} = F(A_{n+1}, C_{n+1}) \tag{7.7}$$

where the intermediate step is given by

$$C^*_{n+1} = C_n + \Delta t R_n \tag{7.5a}$$

$$A^*_{n+1} = H(C^*_{n+1}) \tag{7.6a}$$

$$R^*_{n+1} = F(A^*_{n+1}, C^*_{n+1}) \tag{7.7a}$$

and with the initial evaluation given by:

$$C_0 = C^*_0 \tag{7.8}$$

$$A_0 = H(C_0) \tag{7.9}$$

$$R_0 = F(A_0, C_0) \tag{7.10}$$

In the practical implementation of this scheme, the vector C is synonymous with the array prefixed by DEV, the vector A is synonymous with the array AEV and the vector R is synonymous with the array DER. Equations (7.5) and (7.5a) are implemented in the subroutine GGMCDIF, Equations (7.6), (7.6a) and (7.9) in the subroutine GGMCALG, Equations (7.7), (7.7a) and (7.10) in the subroutine GGMCRATE and Equation (7.8) in the subroutine GGMCDIN.

7.3.4.2 Time Step Control

The time step is controlled in such a way as to achieve two goals. Firstly, the size of the time steps taken should be small enough so that physical quantities that must remain positive or zero cannot become negative at the next time step. The second goal is to provide control over the accuracy with which the equations are being solved. Each differential variable is assessed to determine whether it should be used to control the time step. There are two situations in which a differential variable is not used to control the time step:

1) The value of the variable and its rate are both less than or equal to zero (which is unphysical and so should not occur under normal circumstances).
2) The rate of change of the variable is smaller than the value of the error control parameter PEPSR (ε_R).

If neither of these two conditions is met, then the variable is used to control the time step. If the value of the variable is between 0 and PEPSC (ε_C), a small value, and if the rate of change of the variable is negative and would make the value of the variable negative at the next time step, then a time step that would make this variable approximate to zero at the next step is calculated using the Modified-Euler approximation to the rate. That calculated time step is used if it would reduce the next time step from that planned.

Otherwise, a time step is calculated based on an error control approach. The suggested restriction on the time step is calculated by insisting that the maximum relative change in a differential variable cannot exceed some value PEPS (ε), where $0 < \varepsilon << 1$, specified as an input parameter:

$$\max\left\{\left|\frac{\mathrm{C}_{n+1} - \mathrm{C}_\mathrm{n}}{\mathrm{C}_\mathrm{n}}\right|\right\} \le \varepsilon \tag{7.11}$$

Using Equation (7.5), this provides the following restriction on the time steps:

$$\Delta \mathrm{t} \le \varepsilon \min\left|\frac{\mathrm{C}_\mathrm{n}}{\mathrm{R}_\mathrm{n}}\right| \tag{7.12}$$

In practice, the following expression is used which ensures that reasonable size time steps are taken, once the value of a variable becomes very small.

$$\Delta \mathrm{t} \le \varepsilon \min\left|\frac{\mathrm{C}_\mathrm{n} + \varepsilon}{\mathrm{R}_\mathrm{n}}\right| \tag{7.13}$$

This process is repeated for all variables, and the smallest calculated time step is selected. In summary, the time step returned by the GGMCALCI subroutine is:

$$\mathrm{T}_\mathrm{out} = \varepsilon \min\left\{\left|\frac{\mathrm{C}_\mathrm{n} + \varepsilon}{\mathrm{R}_\mathrm{n}}\right| \text{where} \left|\mathrm{C}_\mathrm{n}\right| > \varepsilon_\mathrm{C} \text{ and} \left|\mathrm{R}_\mathrm{n}\right| > \varepsilon_\mathrm{R}\right\} \tag{7.14}$$

The same approach is used by the GGMCALC subroutine in deciding the size of the intermediate GGM time steps between subsequent TOUGH2 time steps.

7.3.4.3 Interpolation

Results from use of an earlier version of T2GGM for the preliminary postclosure safety assessment of OPG's proposed DGR for L&ILW (Calder et al. 2009) show that the GGM inputs supplied by TOUGH2 (pressure, saturation, relative humidity, void volume and rate of ingress of water) are effectively continuous and smooth. While they may occasionally undergo more rapid changes, they are generally on a longer time scale than the gas generation processes. A linear approach to interpolating the GGM inputs between TOUGH2 time steps has been implemented. A quadratic interpolation approach was initially tested, but this proved to be unstable at times. The linear interpolation approach has the added benefit that quantities such as saturation remain within physical bounds at all times.

7.3.4.4 Unphysical Values

Variables corresponding to quantities that are only physical when not negative, but which attain negative values due to the coarseness of the time stepping, are set to zero. At the same time, a message is sent to a diagnostic file so providing an alert that the time step control parameters need to be refined.

7.3.4.5 Reaction Switching

The reactions governing the degradation of organics occur in a well-defined sequence. A (algebraic) variable is used to track the reaction stage, having the value of one during aerobic respiration, two once aerobic respiration is complete (denitrification), three once denitrification is complete (iron reduction), four once iron reduction is complete (sulphate reduction) and five once sulphate reduction is complete (methanogenesis). The variable is initialized to one, and is reassessed after the differential and algebraic variables have been calculated, but before the rates have been calculated between the calls to the subroutines GGMCALG and GGMCRATE. If the concentration of the previous terminal electron acceptor falls below a cut-off value, C_c (mol m^{-3}) and is still being consumed (indicated by a decrease in concentration between the previous and current times or negative rate at the previous time step), then the next stage is assumed to have started.

Then, at start of the GGMCRATE subroutine where the rate equations are calculated, local values of the rate constants are defined. All rate constants are set to zero except for those corresponding to the current terminal electron acceptor stage, which are set to the value defined in the input parameters. Certain additional constraints are applied to the rate constants as defined in the Theory Manual (Chapter 4).

7.3.4.6 Enhanced Carbon Dioxide Corrosion

Enhanced CO_2 corrosion only occurs under anaerobic conditions and when the CO_2 partial pressure is sufficiently high. Therefore, the enhancement factor,

$$\left(\frac{P_{CO2}}{P_{CO2}^{ref}}\right)^q \tag{7.14}$$

is stored as a separate local variable that is set to zero when the concentration of O_2 is above the cut-off concentration C_C, that is also used for reaction switching.

7.3.4.7 Water Generation

Changes in the amount of water in the repository can be decomposed into two components: 1) Changes due to the microbial degradation and corrosion reactions occurring inside the repository as modelled by GGM and 2) Changes in the amount of water due to influx and outflux from the geosphere. This section clarifies how the changes in the amount of water and hence saturation are tracked by TOUGH2 and GGM.

TOUGH2

At the end of every time step GGM reports the current liquid generation rate, Q_{liq} (kg s^{-1}) to TOUGH2. TOUGH2 divides this liquid generation rate between all TOUGH2 model elements representing the repository, portioning the generation rate based on element size and applying the liquid generation rate to each repository element as a sink (or source if the liquid generation rate is positive). TOUGH2 assumes that this rate is constant for the duration of the proceeding time step. At the next time step TOUGH2 calculates and reports to GGM the total saturation in the repository, calculated as the volume-weighted average saturation of all elements representing the repository and the calculated rate of ingress of water into the repository. As the liquid generation rate calculated by GGM is applied to each element representing the repository as a sink or source, changes in the amounts of water in the repository calculated by GGM are inherently taken into account in TOUGH2’s calculation of the saturation at each element.

Note that in dividing the liquid generation rate between repository elements, the GGM/TOUGH2 interface considers the saturation within each element if the liquid generation rate is a negative (sink) or if requested by the user (with the NORML flag). If the liquid saturation in any of the repository elements is equal to zero, the scale factors used to portion the liquid generation rate are normalized to portion the liquid generation rate between all repository elements with a liquid saturation greater than zero. If the liquid generation rate is positive then the saturation of the elements will always be increased so no such action needs to be taken.

GGM

At the beginning of every time step GGM calculates the total amount of water present from the saturation, S_{tot} (-) and void volume V_V (m^3), specified by TOUGH2 and the density of water, ρ_{H2O} (kg m^{-3}). Since TOUGH2 is responsible for tracking the total amount of water and providing this information via the saturation, it is not necessary for GGM to calculate this by evolving the rate equation for the amount of water given in the Theory Manual (Chapter 4). Rather, the total amount of water present is calculated as (neglecting water vapour)

$$S_{tot} V_V \rho_{H2O} \tag{7.16}$$

GGM is responsible for calculating the total liquid generation rate due to processes occurring within the repository, Q_{liq}. The total number of moles of water generated per second, R_{H2O} (mol s^{-1}) due to processes occurring within the repository is

$$R_{H2O} = \frac{dQ_{H2O}}{dt} \tag{7.17}$$

where Q_{H2O} is defined in the Theory Manual (Chapter 4). The liquid generation rate can then calculated as

$$Q_{liq} = R_{H2O} m_{liq} \tag{7.18}$$

where m_{liq} is the molar mass of the liquid (water) in the repository.

7.3.4.8 Gas Transport and Gas Pressure Rescaling

TOUGH2 models the transport of gas into or out of the repository. This results in an increase or drop in gas pressure within the repository. TOUGH2 is able to supply the GGM with its calculated average repository gas pressure. The GGM must use this pressure information to calculate the flux of gas into or out of the repository so that it can be taken into consideration when performing the gas generation calculations. While TOUGH2 models the unsaturated phase as a single bulk gas (air, CO_2, CH_4 or H_2), GGM tracks the amounts and pressures of individual gas components (O_2, CO_2, N_2, H_2, H_2S and CH_4). In order to take into account the loss of gas from the repository, the partial pressures (and therefore the amounts and concentrations) of the individual gas components are rescaled at each time step such that the total pressure of gas in the repository as modelled by GGM matches the average pressure of bulk gas in the repository as calculated by TOUGH2. The total flux of gas into or out of the repository is calculated from the change in pressure due to the rescaling. It is assumed that the composition of gas leaving or entering the repository has the same composition as the gas already in the repository. While this is clearly a sensible model for gas leaving the repository, it may or may not be a sensible model for gas entering the repository and the effect of this assumption will have to be evaluated on a case by case basis.

GGM rescales the partial pressure of each gas component so that the total pressure of gas in the repository is consistent with that calculated and supplied by TOUGH2. This is done as follows. The total pressure of gas in the repository is first calculated as

$$\mathrm{P_{GGM}} = \sum_{g} \mathrm{p_g} \tag{7.20}$$

where g represents indexing over gas components and $\mathrm{p_g}$ is the partial pressure of each gas component in the repository. A gas pressure scaling factor,

$$\mathrm{GPSF} = \frac{\mathrm{P_{T2}}}{\mathrm{P_{GGM}}} \tag{7.21}$$

is then calculated where $\mathrm{P_{T2}}$ is the pressure of bulk gas calculated by TOUGH2. The partial pressure of each gas component is rescaled such that the total pressure of gas in the repository is equal to the total pressure of gas as calculated by TOUGH2:

$$p_g \rightarrow \frac{p_g}{GPSF} \tag{7.22}$$

The concentrations of the dissolved gases in solution are then recalculated using Henry's law as given in Equation (4.75), and the total number of moles of each gas is updated using the ideal gas equations of state using Equation (4.76).

7.3.4.9 Rate of Change of Saturation

The gas generation rate is calculated within GGM using Equation (4.79) of Chapter 4. This equation requires knowledge of the rate of change of saturation. TOUGH2 does not have simple access to this quantity and so GGM must calculate it based on knowledge of the saturation at the current and previous time steps. In order to improve the accuracy with which this is calculated compared to a simple first order scheme, a higher order discretization scheme based upon knowledge of the previous two time steps is employed:

$$\left.\frac{\mathrm{dS}}{\mathrm{dt}}\right|_{t_0} \sim \frac{(\delta_1+\delta_2)^2 \mathrm{S}(t_1) - \delta_1{}^2 \mathrm{S}(t_2) - \delta_2{}^2(2\delta_1+\delta_2)\mathrm{S}(t_0)}{\delta_1(\delta_1+\delta_2)(2\delta_1+\delta_2)} \tag{7.23}$$

Here, S is the saturation, t_0, t_1 and t_2 are the current, first and second previous time steps, $\delta_1 = t_0 - t_1$ and $\delta_2 = t_1 - t_2$.

7.3.4.10 Alternative Gases

The EOS3 module used by T2GGM assumes that air is the gas, however, an alternative gas may be specified by changing the Henry's constant, molar mass, specific heat capacity (not used in isothermal T2GGM calculations), and viscosity. Viscosity is calculated as a temperature dependent variable within TOUGH2.

A new input record, ALTGAS is read, providing the alternative gas to be used, as well as alternative parameter values. Alternative gases considered include CH_4, CO_2, H_2 and He. Default values for each gas are hard-coded into TOUGH2 subroutine EOS in a manner similar to the existing air parameters; however, the input record for ALTGAS provides the ability to override any of the default parameter values. Details of the inputs are specified in Table 7.6.

Table 7.6: ALTGAS Input Record

Parameter	Format	Description
ALTGA	A5	First line of record. Once these characters have been read, the following line is read, containing the parameters detailed below.
ALTGAS	A5	Characters specifying the gas to use: AIR, CO2, CH4, H2 or HE.
VISC_METHOD	I5	Integer flag specifying the viscosity calculation to use. A value less than or equal to zero uses the EOS3 default viscosity calculation for air. Greater than zero uses the TMVOC based viscosity calculation specific to the gas specified by ALTGAS.
ALT_H	E10.4	Alternative value of Henry's constant to be used. Units are: (mole fraction) Pa^{-1}.
ALT_AMA	E10.4	Alternative value of molar mass to be used. Units are: g mol^{-1}.
ALT_CVGAS	E10.4	Alternative value of specific heat capacity to be used. Units are: J kg^{-1} K^{-1}.
ALT_VISCG	E10.4	Alternative value of isothermal viscosity to be used. Units are: Pa s.

As previously mentioned, viscosity is calculated as a temperature dependent parameter specifically for air. New temperature dependent viscosity routines were included, based on routines found in TMVOC which consider the multiple gases, including CH_4, CO_2, H_2 and He.

The parameters defined for the gas are echoed in the standard output. Hard-coded values specified in the EOS subroutine are given in Table 7.7.

Table 7.7: ALTGAS Constant Values

ALTGAS ID	Henry's Law Constant (H) (mole fraction Pa^{-1})	Molecular Weight (AMA) (g mol^{-1})	Specific Heat Capacity (CVGAS) (J kg^{-1} K^{-1})
AIR	1.0E-10	28.96	733
H2	2.82E-11	2.016	0.0143
CO2	1.23E-09	44.00	839
CH4	4.93E-11	16.043	2191
HE	6.72E-11	4.003	5193.1

7.3.4.11 Scale Factors

The generation and consumption of gas and water calculated by GGM is distributed to a series of elements representing the repository. The source or sink of gas and water for each repository element is calculated by multiplying the repository generation or consumption rate calculated by GGM by a scale factor, with a scale factor defined for each repository element. The sum of scale factors for the gas or water source/sink elements must equal to one. Note that a subset of elements at the top of the repository is typically specified as gas source elements, and a subset of elements at the bottom of the repository is typically used for water sink elements.

For T2GGM version up to and including Version 1.3, these scale factors are specified by the user in the input file. Generally, these specified values were calculated as the volumetric contribution of each element (i.e., element volume/total volume of all source/sink elements). During the implementation of the TOUGH2-MP version of T2GGM for Version 2.0, stability issues were encountered as water was extracted from elements at the edge of the repository with little to no water, whereas the repository as a whole had sufficient water for water extraction.

Consequently, an option was provided to allow the T2GGM code to calculate the scale factors at each time step, based on the amount of gas/water available in each element. This type of scale factor minimizes the problem described above, allotting the greater portion of water extraction at elements with the greatest amount of water. For gas, the scale factor calculation is simply the amount of gas in a gas-source element divided by the total amount of gas in all gas-source elements. The amount of gas is calculated from the volume of gas in the element and the density of gas in the element. For water, this calculation entails a similar calculation as for gas, with the additional consideration of the amount of vapour in each element.

The calculation of scale factors at each time step results in a small increase in the number of calculations required at each time step, however, the potential improvement in stability offsets this small increase in run time.

7.3.4.12 Built-in Parameters

Both the GGM and T2GGM use a number of parameters which are not configurable via standard input files. These parameters cannot be changed without modification and recompilation of the affected codes. The GGM parameters are summarized in Table 7.8.

Hard coded T2GGM parameters consist primarily of ALTGAS properties previously described in Table 7.7. Additional parameters are defined in GGMI.INC (Table 7.9).

Table 7.8: Built-in GGM Parameters

Name	Description	Value	Units
MINSTEPS	The minimum allowed time step	3600.0	s
CNSMALL	A small magnitude below which warning messages are not logged for negative numbers.	1.0E-18	(various)
CNSTK	The temperature at 0 degrees Celsius	273.15	K
CNR	The molar gas constant	8.314472	m^3 Pa K^{-1} mol^{-1}
CNYRS	The number of seconds in a year	31556926	s
CNMMH	The molar mass of H	0.00100794	kg mol^{-1}
CNMMS	The molar mass of S	0.032065	kg mol^{-1}
CNMMN	The molar mass of N	0.014007	kg mol^{-1}
CNMMO	The molar mass of O	0.0159994	kg mol^{-1}
CNMMC	The molar mass of C	0.012	kg mol^{-1}
PIRESBW	The number of moles of bound water per mole of styrene monomer. A value of 9 corresponds to resin bound water content of 40% by weight.	9	-

Table 7.9: Built-in T2GGM Parameters

Name	Description	Value	Units
RCONST	Universal gas constant	8314.56	
AMS	Molar mass of water	18.016	g mol^{-1}
CTOK	Conversion from ºC to K	273.15	
MAXVAP	Maximum vapour pressure at 20 ºC for RH calculation	2340.05	Pa

7.3.4.13 Temperature

GGM accepts rate constants, physical parameters, such as the density of water and temperature as inputs. T2GGM also has its own temperature input parameter.

GGM has no inbuilt knowledge of the change in reaction rates and physical parameters with temperature. The GGM temperature input parameter is used in calculations involving the equation state for the gas components only.

It is the user’s responsibility to ensure that the reaction rates, physical parameters, GGM and T2GGM temperature input parameters are all specified at a consistent temperature.

T2GGM should be used in isothermal mode only with a constant temperature of 20 to 25ºC. Use outside this range will require that MAXVAP be changed to ensure that RH calculations are appropriate.

7.3.5 Internal Interfaces

Data is transferred through the common blocks as described in Section 7.3.1 and via the arguments for subroutines GGMCINIT, GGMCREAD and GGMCALC described in Table 7.5.

Note that subroutines in GGMCALC.f do not access any TOUGH2 variables directly. TOUGH2 variable access and modification is limited to subroutines in GGMT2.f as described in Section 7.3.3.1.

7.3.5.1 Repository and Geosphere Water

Internally GGM models water as saline and ascribes it:

- A single constant density in kg m^{-3} representative of the average water density within the repository via the PRLIQ input parameter; and
- A molar mass in kg mol^{-1} for saline water via the PMLIQ input parameter.

(See Table 7.10 for a complete list of input parameters.) TOUGH2 models the water in the geosphere as fresh water whose density can vary in space and time via an equation of state (temperature and pressure, not salinity). To be consistent it is necessary to convert water related inputs and outputs at the interface between TOUGH2 and GGM to account for the different water models (fresh versus saline). To do this, geosphere water molar mass and typical geosphere water density are also supplied as inputs to GGM via the parameters PMLIQT2 and PRLIQT2 respectively (see Table 7.10), and the conversion between fresh and saline water is carried out within GGM.

In the following, the conversion factors implemented within the GGM are derived. For a given volume of water, V in m^3, TOUGH2 and the GGM have different notions of the number of moles of water. TOUGH2 models

$$V * PRLIQT2 / PMLIQT2$$

moles of geosphere (fresh) water, while the GGM models

$$V * PRLIQ / PMLIQ$$

moles of repository (saline) water. Therefore, one mole of repository water is equivalent to k moles of geosphere water, where

$$k = (PRLIQT2 / PMLIQT2) / (PRLIQ / PMLIQ)$$

On input to GGM, TOUGH2 supplies the average water saturation, STOT (-), and the rate of ingress, INRATE (kg s^{-1}) of geosphere water. From this, the number of moles of repository water is calculated as

$$VV * STOT * PRLIQ / PMLIQ$$

where VV is the void volume of the repository (m^3) supplied by TOUGH2. The rate of ingress of repository water in mol s^{-1} is calculated as

$$INRATE / (k * PMLIQT2) = (INRATE / PMLIQ) * (PRLIQ / PRLIQT2)$$

On output, GGM calculates the rate of generation of repository water, QLIQ (kg s^{-1}), from which it supplies TOUGH2 with the rate of generation of geosphere water calculated as

$$QLIQ * k * (PMLIQT2 / PMLIQ) = QLIQ * (PRLIQT2 / PRLIQ)$$

7.3.6 External Interfaces

GGM integration input variables are read from standard input by the subroutine GGMCREAD. A summary of all the input variables in the order in which they are read is given in Table 7.10. The values used for these parameters in the postclosure safety assessment for OPG's proposed DGR for L&ILW are given in QUINTESSA and GEOFIRMA (2011). The name, description and units of each parameter are output to the console before it is read in. All input is echoed to file as described previously. Note that GGM accepts as input the initial masses of the organic substrates (PIMORG1, PIMORG2 and PIMORG3) and effective molar masses (PMORG1, PMORG2, PMORG3) which define the mass per mole of the relevant functional group. This allows the total number of moles of each of the relevant functional groups to be calculated by GGM. GGM output file variables are listed in Table 7.11.

No error handling is performed for file input or output. It is assumed that the file units are correctly opened and closed by TOUGH2.

Table 7.10: GGM Input Variables

Input Variable Name	Description	Input Units	Internal Units	Reference to Data Report (QUINTESSA and GEOFIRMA 2011)
Surface areas of metals				
PA1	Carbon and galvanized steel	m^2	m^2	Table 4.13
PA2	Passivated carbon steel	m^2	m^2	
PA3	Stainless steel and Ni-based alloys	m^2	m^2	
PA4	Zr alloys	m^2	m^2	
Biomass Decay				
PD	Biomass decay rate	a^{-1}	s^{-1}	Section 3.6.6.4
Solubility constants				
PKCO2	CO_2	mol L^{-1} MPa^{-1}	mol m^{-3} Pa^{-1}	Table 3.19
PKH2	H_2	mol L^{-1} MPa^{-1}	mol m^{-3} Pa^{-1}	
PKH2S	H_2S	mol L^{-1} MPa^{-1}	mol m^{-3} Pa^{-1}	
PKCH4	CH_4	mol L^{-1} MPa^{-1}	mol m^{-3} Pa^{-1}	
PKO2	O_2	mol L^{-1} MPa^{-1}	mol m^{-3} Pa^{-1}	
PKN2	N_2	mol L^{-1} MPa^{-1}	mol m^{-3} Pa^{-1}	
Effective molar mass of metals				
PM1	Mass of carbon and galvanized steel per mole of equivalent iron. (See Section 4.3.1.1)	kg mol^{-1}	kg mol^{-1}	Section 3.6.5.3
PM2	Mass of passivated carbon steel per mole of equivalent iron. (See Section 4.3.1.2)	kg mol^{-1}	kg mol^{-1}	

Input Variable Name	Description	Input Units	Internal Units	Reference to Data Report (QUINTESSA and GEOFIRMA 2011)
PM3	Mass of stainless steel and Ni-based alloys per mole of equivalent iron. (See Section 4.3.1.3)	kg mol^{-1}	kg mol^{-1}	Section 3.6.5.3
PM4	Mass of zirconium alloys per mole of equivalent zirconium. (See Section 4.3.1.4)	kg mol^{-1}	kg mol^{-1}	
CO_2 Enhanced corrosion				
PPRCO2	Reference partial pressure of CO_2 for enhancement of corrosion	MPa	Pa	Section 3.6.5.2
Corrosion rate				
PR111	Carbon and galvanized steel corrosion rate Aerobic conditions Unsaturated conditions	µm a^{-1}	m s^{-1}	Table 3.20
PR112	Carbon and galvanized steel corrosion rate Aerobic conditions Saturated conditions	µm a^{-1}	m s^{-1}	Table E.1
PR121	Carbon and galvanized steel corrosion rate Anaerobic conditions Unsaturated conditions	µm a^{-1}	m s^{-1}	Table 3.20
PR122	Carbon and galvanized steel corrosion rate Anaerobic conditions Saturated conditions	µm a^{-1}	m s^{-1}	
PR211	Passivated carbon steel corrosion rate Aerobic conditions Unsaturated conditions	µm a^{-1}	m s^{-1}	Table 3.20

Input Variable Name	Description	Input Units	Internal Units	Reference to Data Report (QUINTESSA and GEOFIRMA 2011)
PR212	Passivated carbon steel corrosion rate Aerobic conditions Saturated conditions	$\mu m\ a^{-1}$	$m\ s^{-1}$	Table E.2
PR221	Passivated carbon steel corrosion rate Anaerobic conditions Unsaturated conditions	$\mu m\ a^{-1}$	$m\ s^{-1}$	Table 3.20
PR222	Passivated carbon steel corrosion rate Anaerobic conditions Saturated conditions	$\mu m\ a^{-1}$	$m\ s^{-1}$	
PR311	Stainless steel and Ni-based alloys corrosion rate Aerobic conditions Unsaturated conditions	$\mu m\ a^{-1}$	$m\ s^{-1}$	Table 3.20
PR312	Stainless steel and Ni-based alloys corrosion rate Aerobic conditions Saturated conditions	$\mu m\ a^{-1}$	$m\ s^{-1}$	Table E.3
PR321	Stainless steel and Ni-based alloys corrosion rate Anaerobic conditions Unsaturated conditions	$\mu m\ a^{-1}$	$m\ s^{-1}$	Table 3.20
PR322	Stainless steel and Ni-based alloys corrosion rate Anaerobic conditions Saturated conditions	$\mu m\ a^{-1}$	$m\ s^{-1}$	

Input Variable Name	Description	Input Units	Internal Units	Reference to Data Report (QUINTESSA and GEOFIRMA 2011)
PR411	Zr alloys corrosion rate Aerobic conditions Unsaturated conditions	µm a^{-1}	m s^{-1}	Table 3.20
PR412	Zr alloys corrosion rate Aerobic conditions Saturated conditions	µm a^{-1}	m s^{-1}	Table E.4
PR421	Zr alloys corrosion rate Anaerobic conditions Unsaturated conditions	µm a^{-1}	m s^{-1}	Table 3.20
PR422	Zr alloys corrosion rate Anaerobic conditions Saturated conditions	µm a^{-1}	m s^{-1}	
Rate constants for organic degradation				
PVCA	Cellulose under aerobic degradation	a^{-1}	s^{-1}	Table 3.21
PVCB	Cellulose under denitrification	a^{-1}	s^{-1}	
PVCC	Cellulose under ferric-ion reduction	a^{-1}	s^{-1}	
PVCD	Cellulose under sulphate reduction	a^{-1}	s^{-1}	
PVCE	Cellulose under methanogenesis	a^{-1}	s^{-1}	
PVRA	IX resins under aerobic degradation	a^{-1}	s^{-1}	
PVRB	IX resins under denitrification	a^{-1}	s^{-1}	
PVRC	IX resins under ferric-ion reduction	a^{-1}	s^{-1}	

Input Variable Name	Description	Input Units	Internal Units	Reference to Data Report (QUINTESSA and GEOFIRMA 2011)
PVRD	IX resins under sulphate reduction	a^{-1}	s^{-1}	
PVRE	IX resins under methanogenesis	a^{-1}	s^{-1}	
PVPA	Plastics and rubbers under aerobic degradation	a^{-1}	s^{-1}	Assumed the same as for IX resins
PVPB	Plastics and rubbers under denitrification	a^{-1}	s^{-1}	
PVPC	Plastics and rubbers under ferric-ion reduction	a^{-1}	s^{-1}	
PVPD	Plastics and rubbers under sulphate reduction	a^{-1}	s^{-1}	
PVPE	Plastics and rubbers under methanogenesis	a^{-1}	s^{-1}	
PVFES	Rate constant for the precipitation of FeS	s^{-1}	s^{-1}	Section 3.6.7.2
PVFEOO	Rate constant for the reductive dissolution of FeOOH	s^{-1}	s^{-1}	Section 3.6.7.3
PVMGO	Rate constant for the conversion of Magnesium Oxide to Magnesium Carbonate	s^{-1}	s^{-1}	-
Rate constants for hydrogen kinetic reactions				
PVH1	Microbial oxidation of H_2 via iron reduction	a^{-1}	s^{-1}	Section 3.6.6.2
PVH2	Microbial oxidation of H_2 via sulphate reduction	a^{-1}	s^{-1}	
PVH3	Microbial generation of methane	a^{-1}	s^{-1}	
Biomass yield coefficients				
PYA	Aerobic degradation	-	-	Table 3.22
PYB	Denitrification	-	-	
PYC	Ferric-ion reduction	-	-	

Input Variable Name	Description	Input Units	Internal Units	Reference to Data Report (QUINTESSA and GEOFIRMA 2011)
PYD	Sulphate reduction	-	-	
PYE	Methanogenesis	-	-	
Biomass recycling				
PKR	Fraction of dead biomass recycled as cellulose	-	-	Section 3.6.6.5
CO_2 Enhanced corrosion				
PE	Exponent for the enhancement of corrosion by CO_2	-	-	Section 3.6.5.2
Densities of metals				
PRO1	Carbon and galvanized steel	kg m^{-3}	kg m^{-3}	Section 3.4.1 (Last paragraph)
PRO2	Passivated carbon steel	kg m^{-3}	kg m^{-3}	
PRO3	Stainless steel and Ni-based alloys	kg m^{-3}	kg m^{-3}	
PRO4	Zr alloys	kg m^{-3}	kg m^{-3}	
Miscellaneous				
PEMMA	Effective molar mass of gas in the geosphere	g mol^{-1}	kg mol-1	Section 3.6.7.1
PT	Repository temperature	ºC	K	Section 5.1
PRLIQ	Density of the water (saline) in the repository as modelled by GGM	kg m^{-3}	kg m^{-3}	Table 5.3
PMLIQ	Molar mass of the water (saline) in the repository as modelled by GGM	kg mol^{-1}	kg mol^{-1}	Table 5.3

Input Variable Name	Description	Input Units	Internal Units	Reference to Data Report (QUINTESSA and GEOFIRMA 2011)
PRLIQT2	Density of the geosphere water (fresh)	kg m^{-3}	kg m^{-3}	1000 kg m^{-3}, representative of average geosphere water densities[7]
PMLIQT2	Molar mass of the geosphere water (fresh)	kg mol^{-1}	kg mol^{-1}	Table 5.3
Effective molar mass of the organic substrates				
PMORG1	Mass of actual cellulose substrate per mole equivalent cellulose. (See Section 4.2.1.1)	kg mol^{-1}	kg mol^{-1}	Section 3.6.6.1 (Last two paragraphs)
PMORG2	Mass of actual IX resins substrate per mole equivalent styrene monomer. (See Section 4.2.1.1)	kg mol^{-1}	kg mol^{-1}	
PMORG3	Mass of actual plastics and rubbers substrate per mole equivalent styrene monomer. (See Section 4.2.1.1)	kg mol^{-1}	kg mol^{-1}	
Initial concentrations				
PIQNO3	Initial quantity of nitrates in repository	kg	mol	Section 3.6.2
PICSO4	Initial concentration of sulphates in reposit ory water	kg m^{-3}	mol m^{-3}	
PICFEO	Initial concentration of Fe(III) in repository water	mol m^{-3}	mol m^{-3}	

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[7] A density of freshwater of 998 kg m^{-3} at 0.1 MPa is given in Table 5.3 of the data report. This is at the lower end of the spectrum of water densities expected at the repository where pressures may increase approximately 100-fold over the course of the simulation. TOUGH2 calculates water densities varying in the approximate range 997.9 to 1002.3 kg m^{-3}. The intermediate value 1000 kg m^{-3} is chosen as being representative of average geosphere water density.

Input Variable Name	Description	Input Units	Internal Units	Reference to Data Report (QUINTESSA and GEOFIRMA 2011)
Initial gas partial pressures				
PIPO2	O_2	MPa	Pa	Table 3.23
PIPCO2	CO_2	MPa	Pa	
PIPN2	N_2	MPa	Pa	
PIPH2	H_2	MPa	Pa	
PIPH2S	H_2S	MPa	Pa	
PIPCH4	CH_4	MPa	Pa	
Initial masses of organic substrates				
PIMORG1	Cellulose	kg	kg	Table 4.10
PIMORG2	IX resins (dry)	kg	kg	
PIMORG3	Plastics and rubbers	kg	kg	
Initial quantities of metallic materials				
PIQ1	Carbon and galvanized steel	kg	mol	Table 4.12
PIQ2	Passivated carbon steel	kg	mol	
PIQ3	Stainless steel and Ni-based alloys	kg	mol	
PIQ4	Zr alloys	kg	mol	
Initial amounts of biomass species				
PIXA	Aerobes	mol	mol	Section 3.6.2
PIXB	Denitrifiers	mol	mol	
PIXC	Iron reducers	mol	mol	

Input Variable Name	Description	Input Units	Internal Units	Reference to Data Report (QUINTESSA and GEOFIRMA 2011)
PIXD	Sulphate reducers	mol	mol	
PIXE	Methanogens	mol	mol	
Initial amounts of other materials				
PIQFEC	$FeCO_3$	mol	mol	Section 3.6.2
PIQFE3	Fe_3O_4	mol	mol	
PIQFES	FeS	mol	mol	
PIQMGO	MgO	mol	mol	The data report does not specify an initial inventory. Zero assumed.
Time step and output control				
PEPS	Specifies the maximum fractional change allowed in a differential variable per time step. Controls the maximum time step reported to TOUGH2.	-	-	-
PEPSC	Cut-off value below which differential variables are not used to control the suggested timestep.	mixed	mixed	-
PEPSR	Cut-off value below which the rate of a differential variable is not used to control the suggested time step.	mixed	mixed	-

Input Variable Name	Description	Input Units	Internal Units	Reference to Data Report (QUINTESSA and GEOFIRMA 2011)
LOGTR	Log base 10 of the ratio of times of subsequent writes to the output file. The next output time occurs at approximately (last output time)*10^(LOGTR), and allows output to be generated with a resolution suitable for plotting on a logarithmic scale, consistent with the way it is usually displayed.	-	-	-
PMINSAT	Saturation below which the water consuming reactions are controlled to prevent them from drawing water into the repository.	-	-	-
PHUM	T or F. (True or false) Specifies whether relative humidity dependent behaviour is enabled. When set to F it is assumed that the relative humidity is sufficiently high to allow all vapour phase processes to proceed.	-	-	-
PRHMIN	Relative Humidity value (fractional) below which all vapour phase corrosion and microbial reactions are modelled as having ceased	-	-	Section 3.6.5.4
PRHMAX	Relative Humidity value (fractional) above which all vapour phase corrosion and microbial reactions are modelled as fully active.	-	-	Section 3.6.5.4
PHTYPE	Type of relative humidity modulation function to use. An integer. Can currently be 1 = linear ramp, or 2 = smoothed linear ramp.	-	-	-

Table 7.11: GGM Output File Variables

Output Column Name	Description	Units
TIME	Time	s
DELTAT	Difference between the current and previous calculation times	s
QAIR	Gas generation rate	$kg\ s^{-1}$
QLIQ	The geosphere water generation rate	$kg\ s^{-1}$
IAS	Saturation	-
IAGWV	Saturated volume	m^3
IAVAV	Unsaturated volume	m^3
IATEAS	Terminal electron acceptor stage	-
IACFEO	The effective concentration of FeOOH were it to be dissolved in the saturated phase	$mol\ m^{-3}$
IAPCO2	Partial pressure of CO_2	Pa
IAPH2	Partial pressure of H_2	Pa
IAPH2S	Partial pressure of H_2S	Pa
IAPCH4	Partial pressure of CH_4	Pa
IAPO2	Partial pressure of O_2	Pa
IAPN2	Partial pressure of N_2	Pa
IAPGAS	Total gas pressure	Pa
IANGAS	Quantity of gas in the unsaturated phase (Sum of the number of moles of all the individual gases.)	mol
IAMAIR	Equivalent mass of gas (IANGAS * the equivalent molar mass of gas constant)	kg
IACCO2	Concentration of CO_2 in repository water	$mol\ m^{-3}$
IACH2	Concentration of H_2 in repository water	$mol\ m^{-3}$
IACH2S	Concentration of H_2S in repository water	$mol\ m^{-3}$
IACCH4	Concentration of CH_4 in repository water	$mol\ m^{-3}$
IACO2	Concentration of O_2 in repository water	$mol\ m^{-3}$
IACN2	Concentration of N_2 in repository water	$mol\ m^{-3}$
IANCO2	Total number of moles of CO_2 in the unsaturated phase	mol
IANH2	Total number of moles of H_2 in the unsaturated phase	mol
IANH2S	Total number of moles of H_2S in the unsaturated phase	mol

Output Column Name	Description	Units
IANCH4	Total number of moles of CH_4 in the unsaturated phase	mol
IANO2	Total number of moles of O_2 in the unsaturated phase	mol
IANN2	Total number of moles of N_2 in the unsaturated phase	mol
IAQGAS	Gas generation rate	mol s^{-1}
IAQAIR	Equivalent gas generation rate	kg s^{-1}
IAA11	Surface area of carbon and galvanized steel under unsaturated conditions	m^2
IAA21	Surface area of passivated carbon steel under unsaturated conditions	m^2
IAA31	Surface area of stainless steel and Ni-based alloys under unsaturated conditions	m^2
IAA41	Surface area of Amount of Zr alloys under unsaturated conditions	m^2
IAA12	Surface area of carbon and galvanized steel under saturated conditions	m^2
IAA22	Surface area of passivated carbon steel under saturated conditions	m^2
IAA32	Surface area of stainless steel and Ni-based alloys under saturated conditions	m^2
IAA42	Surface area of Zr alloys under saturated conditions	m^2
IARH2O	Rate of change of the amount of H_2O	mol s^{-1}
IAQH2O	Amount of H_2O	mol
IAQLIQ	The repository water generation rate	kg s^{-1}
IAGPSF	Gas pressure scaling factor. (See Section 7.3.4.8)	kg kg^{-1}
IARCDV	Rate controlling differential variable number	-
IARH	Relative humidity (fractional)	-
IAH	Relative humidity modulation factor h(RH) at the current relative humidity	-
IAXTOT	Amount of live (hydrated) biomass	mol
IAWATEPS	Water consuming reaction rate scaling factor	-
IADWDT	Rate of increase of amount of repository water	mol s^{-1}
IADCDT	Rate of consumption of repository water due to saturated phase reactions	mol s^{-1}

Output Column Name	Description	Units
IADDDT	Rate of generation of repository water due to other reactions	mol s^{-1}
IADIDT	Rate at which repository water is entering	mol s^{-1}
IDCNO3	Concentration of NO_3	mol m^{-3}
IDQFEO	Amount of FeOOH	mol
IDCSO4	Concentration of SO_4	mol m^{-3}
IDQC	Amount of cellulose monomer	mol
IDQR	Amount of styrene monomer	mol
IDQP	Amount of styrene monomer from plastics and rubber	mol
IDQ1	Amount of carbon and galvanized steel	mol
IDQ2	Amount of passivated carbon steel	mol
IDQ3	Amount of stainless steel and Ni-based alloys	mol
IDQ4	Amount of Zr alloys	mol
IDXA	Amount of aerobes	mol
IDXB	Amount of denitrifiers	mol
IDXC	Amount of iron reducers	mol
IDXD	Amount of sulphate reducers	mol
IDXE	Amount of methanogens	mol
IDQFEC	Amount of $FeCO_3$	mol
IDQFE3	Amount of Fe_3O_4	mol
IDQFES	Amount of FeS	mol
IDQMGO	Amount of MgO	mol
IDNCO2	Total number of moles of CO_2	mol
IDNH2	Total number of moles of H_2	mol
IDNH2S	Total number of moles of H_2S	mol
IDNCH4	Total number of moles of CH_4	mol
IDNO2	Total number of moles of O_2	mol
IDNN2	Total number of moles of N_2	mol
IDXDIED	Total amount of biomass that has died	mol
IDXDEAD	Total amount of dead (dehydrated) and non-recyclable biomass	mol
IDICO2	Amount of CO_2 that has left the repository	mol

Output Column Name	Description	Units
IDIH2	Amount of H_2 that has left the repository	mol
IDIH2S	Amount of H_2S that has left the repository	mol
IDICH4	Amount of CH_4 that has left the repository	mol
IDIO2	Amount of O_2 that has left the repository	mol
IDIN2	Amount of N_2 that has left the repository	mol
IDNGH2O	Cumulative amount of water that has been generated by the gas generation reactions	mol
IDQZRO2	Total amount of ZrO_2	mol

8. VERIFICATION

8.1 Introduction

Verification for T2GGM Version 2.1 is presented here and is built upon the verification undertaken for previous Versions 2.0, 1.3, 1.2, 1.1 and 1.0.

Verification, as defined in the NWMO Software Procedures (NWMO 2010) involves the checking of the software against its specifications. The specific types of verification documented in this Verification section are:

1. Verification that the code is functioning correctly, in particular by performing unit tests, some of which were identified in the Requirements Specification (Chapter 6);
2. Verification that the results of GGM are consistent with Theory Manual (Chapter 4); and
3. Verification that the results are plausible.

Validation of the results, defined in NWMO (2010) as the determination of the accuracy and applicability of the software results with respect to their intended application, is discussed separately in Chapter 9.

GGM was first tested independently. Verifications results for GGM Versions 1.0 to 2.0 and GGM Version 2.1 are provided in Sections 8.2 to 8.7. The coupled codes T2GGM and T2GGM-MP were then tested. Results of verification for T2GGM and T2GGM-MP are provided in Sections 8.8 to 8.13.

8.2 GGM Version 1.0 Verification Results

GGM can be used as a standalone code, driven by a driver program. In the absence of coupling with TOUGH2, synthetic saturation and pressure profiles must be used to drive GGM. The main profile that was used to test GGM as a standalone code was the following:

The saturation increases at a constant rate such that, in the absence of the corrosion and microbial degradation reactions, the repository would be completely saturated over a period of 1000 years. The pressure is held fixed at atmospheric pressure.

8.2.1 Consistency of Code with the Theory Manual and Design Documentation

Requirement 2.3.1 of the Requirements Specification (Chapter 6) states that the code should be demonstrated to be implemented in a manner that is consistent with the model. GGM was independently reviewed at Quintessa in order to check for consistency of the code with the Theory Manual (Chapter 4) and Design Description (Chapter 7).

The scope of the review was to check that the equations summarized in the Theory Manual (Chapter 4) are accurately implemented in the code (subroutine GGMCALC and subroutines called from within it), according to the plan for doing so set out in the Design Description (Chapter 7). (Section 7.3.3.2 of the Design Description sets out the implementation details.)

The review found no significant errors. Minor issues were identified with the code which did not impact on results (incorrect comments in code and a variable whose name did not correspond with the documentation) and these were resolved.

8.2.2 Code Maintainability

GGM Version 1.0 code underwent a Quintessa Code Maintainability Walkthrough. The scope of this walkthrough was to verify that the code adheres to Quintessa's QA requirements (including TickIT) that ensure good coding practices and future maintainability of the code. Issues identified during the coding walkthrough were resolved.

8.2.3 Standards Conformance

The code was compiled using both the g95 and g77 compilers under Cygwin on Windows as described in Requirement 3.7.1 in the Design Documentation. The compile settings were chosen to enable strict tests for ANSI FORTRAN 77 standards conformance, all available compile time warnings (unused and uninitialized variables, etc.), as well as run-time array bounds checking. The results produced using the executables compiled by the two codes were indistinguishable when plotted on the same graph over one million years.

8.2.4 Convergence Tests

Tests for numerical convergence and stability were undertaken for Version 1.0 in order to select appropriate solver parameters. Subsequent changes to the GGM model and time stepping algorithm in newer versions required that these tests should be retaken. Please see Section 8.6.7 for the most recent results.

8.3 GGM Version 1.1 Verification Results

Changes were made to GGM Version 1.0 based on internal review comments (see the Change History Record in Appendix A). These changes were independently reviewed for consistency with the updated Theory Manual (Chapter 4).

8.4 GGM Version 1.2 Verification Results

Changes were made to GGM Version 1.1 to allow optimization, allow the enforcement of a minimum saturation and to fix some minor bugs (see the Change History Record in Appendix A). No additional independent verification was undertaken at this stage.

An optimization study was carried out which showed that the rapid consumption of the relatively small initial quantities of terminal electron acceptors in the iron and sulphate reduction stages could lead to very small GGM time steps. These could have a noticeable impact on T2GGM run times while having minimal impact on the subsequent gas generation behaviour, dominated by the evolution of CO_2, H_2 and CH_4. In the event that insufficient nitrates and iron oxides are initially present to produce large quantities of nitrogen gas and hydrogen sulphide, it may be more efficient to use zero as the initial condition.

8.5 GGM Version 1.3 Verification Results

Version 1.3 involved changes resulting from extensive verification of GGM Version 1.2, but did not include any new capabilities. Several types of verification were fed into the changes that were made for Version 1.3. These included:

- A thorough review of the theory and rate equations and corresponding code;
- Comparison with the results of similar models by independent review; and
- Verification of GGM Version 1.3 against a test suite.

At Version 1.3, mass balance stack plots for the following quantities: C, Fe, H, N, O and H_2O, were introduced as a means of demonstrating conservation of mass. They proved to be useful and so continue to be used to ensure that conservation of mass is being respected. The latest results and the theory behind mass balance stack plots can be found in Section 8.6.6. These Version 2.0 results supersede those at Version 1.3.

8.5.1 GGM Test Suite

The GGM test suite was run for GGM Version 1.3 and it passed all tests. For the latest test suite results, please see Section 8.6.1.

8.6 GGM Version 2.0 Verification Results

8.6.1 GGM Test Suite

This section presents the results of four sets of GGM test cases:

- Set 1 examines the behaviour of GGM when excess water is present in the repository by isolating and testing particular groups of processes;
- Set 2 looks at the effect that switching off various reactions within the GGM has on the gas pressure in the repository and on mass balance;
- Set 3 tests the relative humidity behaviour; and
- Set 4 tests the low water saturation behaviour.

A description of the tests and the test results are presented in Table 8.1 to Table 8.4.

The cases were run using GGM Version 2.0 in standalone mode with a simple driver program. The driver program includes a basic model that approximates the repository response (pressure, saturation and relative humidity) that has been very roughly fitted to results of a full T2GGM simulation. (A rough fitting is appropriate since the aim here is not to reproduce T2GGM results exactly, but to ensure that GGM behaves correctly over a sensible range of parameters.) The flux of gas into and out of the repository is dependent on a fine balance between the evolution of the saturation and pressure. The coarseness of the approximations employed in the driver program means that gas can flow back into the repository during times of rapid change. However, this does not limit the ability of the tests to check that the relevant chemical processes are being correctly modelled and that mass balance is being maintained.

Table 8.3 provides the results of the relative humidity test cases. Each of these cases achieved zero saturation at some point during the run, allowing water-limited behaviour and the effect of humidity on gas generation to be observed.

Table 8.1: GGM Test Suite: Set 1 (General, Excess Water)

Case	Main Reaction*	Water Conditions	Aerobic/ Anaerobic	Status
1	Fe corrosion	Excess water	Anaerobic	Run OK. • Good mass balance on all species. • No oscillatory or unstable behaviour. • Partial resaturation of repository between 100 and 20,000 years (IAQH2O increases from 2E+08 to 1.5E+09 moles of water).
2	Cellulose degradation (no biomass production)	Excess water	Anaerobic	Run OK. • Good mass balance on all species. • No oscillatory or unstable behaviour.
3A	Biomass (no decay or recycling)	N/A	N/A	• Mass balance on Biomass OK.
3B	Biomass with decay (no recycling)	N/A	N/A	• Mass balance on Biomass OK.
3C	Biomass with decay and recycling	N/A	N/A	• Mass balance on Biomass OK.
4	Fe corrosion and cellulose degradation (no biomass) with methanogenic reaction ($4H_2 + CO_2 = CH_4 + 2H_20$)	Excess water	Anaerobic	• Mass balance on Carbon, Iron and Nitrogen OK. • No instability was observed (which had been observed in the previous round of testing).
5	Cellulose degradation with biomass decay and recycling (initial biomass set to 1.5E5 units)	Excess water	Anaerobic	• Mass balance on Carbon and Nitrogen OK.

Case	Main Reaction*	Water Conditions	Aerobic/ Anaerobic	Status
6	Fe Corrosion and Cellulose degradation with biomass production, decay and recycling	Excess water	Anaerobic	• Mass balance on Carbon, Iron and Nitrogen OK.
7A	Cellulose degradation with biomass production (Yield Factor set to 0.23)	N/A	Anaerobic	• Mass balance on Carbon OK. • No oscillatory or unstable behaviour.
7B	Cellulose degradation with biomass production (Yield Factor set to 1.0)	N/A	Anaerobic	• Good mass balance on Carbon.
7C	Cellulose degradation with biomass production and biomass decay	N/A	Anaerobic	• Mass balance on Carbon OK. • No oscillatory or unstable behaviour.
8	Cellulose degradation with biomass decay and recycling, biomass produced from cellulose	Excess water	Anaerobic	• Mass balance on Carbon OK. • No oscillatory or unstable behaviour.
9	Corrosion (all species), Organic degradation, No biomass	Low water saturation (Reactions continue when minimum saturation level reached)	Anaerobic	• Mass balance on Carbon, Iron and Nitrogen OK.

Note: *No sulphate and nitrate reactions.

Table 8.2: GGM Test Suite: Set 2 (Mass Balance)

Case	Reactions removed from GGM Test Run	Status
1	• As Received – All processes defined in the theory (See Chapter 4) activated.	Run OK. • Good mass balance on Carbon and Iron.
2	• No biomass production – biomass yield factors (PYA, PYB, PYC, PYD, PYE) set to 0	Run OK. • Good mass balance on Carbon and Iron.
3	• No nitrate reactions – Initial amount of nitrate set to 0	Run OK. • Good mass balance on Carbon and Iron.
4	• No sulphate reactions – Initial amount of sulphate set to 0	Run OK. • Good mass balance on Carbon and Iron.
5	• Anaerobic – Initial concentration of oxygen in the gas set to 0	Run OK. • Good mass balance on Carbon and Iron.
6	• No Methanogenic Reaction – Rate constant for the methane generation from hydrogen oxidation (PVH3) set to 0	Run OK. • Good mass balance on Carbon and Iron.
7	• No biomass production– biomass yield factors (PYA, PYB, PYC, PYD, PYE) set to 0 • No nitrate reactions– Initial amount of nitrate set to 0 • No sulphate reactions– Initial amount of sulphate set to 0 • Anaerobic– initial concentration of oxygen in the gas set to 0 • All other processes left in	Run OK. • Good mass balance on Carbon and Iron.
8	• No biomass production– biomass yield factors (PYA, PYB, PYC, PYD, PYE) set to 0 • No nitrate reactions– Initial amount of nitrate set to 0 • No sulphate reactions– Initial amount of sulphate set to 0 • All other processes left in	Run OK. • Good mass balance on Carbon and Iron.

Case	Reactions removed from GGM Test Run	Status
9	• No nitrate reactions– Initial amount of nitrate set to 0 • No sulphate reactions– Initial amount of sulphate set to 0 • Anaerobic– initial concentration of oxygen in the gas set to 0 • All other processes left in	Run OK. • Good mass balance on Carbon and Iron
10	• No nitrate reactions– Initial amount of nitrate set to 0 • No sulphate reactions– Initial amount of sulphate set to 0 • Anaerobic– initial concentration of oxygen in the gas set to 0 • No methanogenic • All other processes left in	Run OK. • Good mass balance on Carbon and Iron.

Table 8.3: GGM Test Suite: Set 3 (Relative Humidity)

Case	Test	Test Case	Findings
1-B-1 No RH dependent behaviour	A selection of tests from GGM test suite should be re-run and compared with results using GGM Version 1.3. Both should have relative humidity dependent behaviour switched off, PHUM false. This implements the assumption that the relative humidity is always sufficiently high to allow all processes to proceed, regardless of the RH supplied by T2.	Set 1 – Test Case 2	The relative humidity scaling factor IAH is fixed at 1 as required, even though the RH is changing. The amounts of cellulosic organics in the repository continue to drop even once the saturation has reached zero and the relative humidity has dropped below the lower threshold for microbial activity.
		Set 1 – Test Case 1	The relative humidity scaling factor IAH is fixed at 1 as required, even though the RH is changing. The amounts of metallics in the repository continue to drop even once the saturation has reached zero.
		Set 1 – Test Case 6	The relative humidity scaling factor IAH is fixed at 1 as required, even though the RH is changing. The amounts of organics and metallics in the repository continue to drop even once the saturation has reached zero and the relative humidity has dropped below the lower threshold for microbial activity.

Case	Test	Test Case	Findings
1-B-2 Slow RH changes	The driver program should be configured to change the relative humidity linearly from 1 to 0 over a long time period (10 years to 100,000 years)	Set 1 – Test Case 7a	1. No oscillatory or unstable behaviour was observed. 2. The results showed that reaction rates slowed, reaching zero at RHmin. 3. Good mass balance of all species.
		Set 1 – Test Case 8	1. No oscillatory or unstable behaviour was observed. 2. The results showed that reaction rates slowed, reaching zero at RHmin. 3. Good mass balance of all species.
		Set 1 – Test Case 9	1. No oscillatory or unstable behaviour was observed. 2. The results showed that reaction rates slowed, reaching zero at RHmin. 3. Good mass balance of all species.
1-B-3 Sharp RH changes	The driver program should be configured to change the relative humidity linearly from 1 to 0 over a short time period (10 years to 100,000 years)	Set 1 – Test Case 7b	1. No oscillatory or unstable behaviour was observed. 2. The results showed that reaction rates slowed, reaching zero at RHmin. 3. Good mass balance of all species.
		Set 1 – Test Case 8	1. No oscillatory or unstable behaviour was observed. 2. The results showed that reaction rates slowed, reaching zero at RHmin. 3. Good mass balance of all species.
		Set 1 – Test Case 9	1. No oscillatory or unstable behaviour was observed. 2. The results showed that reaction rates slowed, reaching zero at RHmin. 3. Good mass balance of all species.

Table 8.4: GGM Test Suite: Set 4 (Low Water Saturation)

Case	Test	Test Case	Findings
1-C-1 Positive Water Saturation	A standard GGM Full test case which does not result in zero saturation should be re-run with the updated code	Set 1 - Test Cases 1, 2, 3, 4, 5, 6, 7, 8 and 9	All cases can be run successfully, none resulting in zero saturation behaviour.
1-C-2 Low Water Saturation	Tests 01C, 02C and 03C, 1B, 1C, 2B, 2C, 4B 4C, 5B, 5C, 6B, 6C, 8B, 8C, 9A, and 9B of the GGM Version 1.3 test suite all reached the minimum saturation level. These should all be re-run	Set 1 – Test Cases 1, 2, 4, 5, 6, 8 and 9	Zero saturation was reached for all cases. This was achieved by changing the PAMB variable in the DRIVER.TXT file to 1E5 Pa. For all cases, the reactions continued when zero saturation was reached (due to the humidity behaviour). As zero saturation was reached, and the reactions continued using the water from humid air, the transition was smooth.

8.6.2 Relative Humidity

For Version 2.0, the code was updated to allow a linear ramp in the rates for vapour phase microbial and corrosion processes, going from zero to their full values over a specified relative humidity range as discussed in Section 4.7.

Table 8.3 details the tests that were applied to ensure that this new functionality is correctly implemented.

8.6.3 Zero-Saturation Behaviour

The behaviour of GGM at zero saturation has been altered to limit the water consuming saturated phase reactions based on the rate of ingress of water from the geosphere as described in Section 4.8. The tests for this new behaviour are described in Table 8.4.

8.6.4 Subroutine Reorganization

For GGM Version 2.0, some reorganization of GGM subroutines was undertaken as an intermediate step on the way to implementing the improved runtimes functionality. This reorganization was tested to ensure that no errors were introduced. The results are given in Table 8.5.

8.6.5 Time Step Control

For GGM Version 2.0, updates were made to the time stepping algorithm to decouple the time steps from those of TOUGH2. The associated tests are given in Table 8.6.

8.6.6 Demonstration of Conservation of Mass

Stack plots are used to investigate that conservation of mass is being respected for C, Fe and water.

The current implementation of biomass and biomass recycling does not include a model of the full nitrogen cycle. Rather, sufficient NH_3 is always assumed to be present (see Section 4.2.1.3). Furthermore, H^+ is not fully tracked in the iron reduction and sulphate reduction stages for the microbial hydrogen metabolism (see Section 4.2.1.2). As a result, the mass for N and H atoms is not conserved when biomass and the iron and sulphate reduction stages are active in the model.

8.6.6.1 Stack Plot Theory

The theory behind the stack plots will now be introduced. Let IA be the initial amount of the quantity in question, CE be the cumulative amount which has entered the repository, CG be the cumulative amount which has been generated within the repository and TA be the total amount currently in the repository. Then, conservation of mass states that

$$IA + CE + CG - TA = 0$$

Table 8.5: Subroutine Reorganization Test Results

Reference	Name	Test	Success Criterion	Test Results
2-A-1	Correct argument passing	To ensure that input and output values are passed correctly between GGMCALC and GGMCALCI after the reorganization an intermediate step is to require GGMCALC to call GGMCALCI directly. A full GGM standalone test case is then be re-run.	The test results should be identical.	The results were identical.

Table 8.6: Timestep Control Test Results

Reference	Name	Test	Success Criterion	Test Results
2-D-1	GGM Time Step Selection	The full base case is re-run using GGM standalone and set-up to output every GGM time step.	This is considered to have succeeded if GGM can be seen to be taking intermediate time steps that step up to the TOUGH2 timesteps. It is considered to have failed the changes in time as GGM steps up to the TOUGH2 timesteps have a noticeable impact on the results, in which case the 0.05% step-up threshold may need to be re-evaluated.	Intermediate timesteps step up to TOUGH2 timesteps as required. The solution is smooth, with no noticeable discontinuities at the TOUGH2 timesteps.
2-D-2	GGM Accuracy	The GGM Version 1.3 time step accuracy tests should be re-run.	The output should show the same convergence as the time steps are refined.	Passed. See Section 8.6.7.

Reference	Name	Test	Success Criterion	Test Results
2-D-3	GGM Accuracy (2)	Selected tests from the GGM Test Suite are re-run.	There should be no qualitative changes in the results.	Passed. Tests 1-B-1 and 1-C-1 were run before and after the code updates and no qualitative changes in results were observed. Results plotted over one million years where practically identical.
2-D-4	TOUGH2 integration	The full and simplified base cases are re-run with TOUGH.	There should be no qualitative changes in results. Run times should be reduced compared to Version 1.	See Section 8.12.3.

For C, H, O, N and Fe the total amount in the system can be expressed as the sum of the total amounts in each of the forms in which it may exist in the model. The aim of the stack plot is to show whether this balance is respected, that is to show that the sum of the individual components is constant. On a stack plot only positive contributions can be shown. Therefore, the conservation equation is rearranged so that the left hand side is constant and the references for the source and flux terms are shifted so that they are zero based. This gives:

$$IA + MAX(CE) + MAX(CG) = TA + (MAX(CE) - CE) + (MAX(CG) - CG)$$

The stack plot is formed by including a single stack for each contribution to each term on the right hand side of this expression. If conservation of mass is respected, then the height of the stack is constant.

C, H, O and N can leave and enter the repository in gaseous form (CO_2, H_2, N_2, CH_4 and H_2S) and H and O can leave and enter in the form of water. Thus, it is necessary to calculate those fluxes in order to complete the calculation. While the gas fluxes are calculated independently by GGM, the cumulative amount of water entering the repository is calculated within GGM by assuming that conservation of mass for water holds. Therefore, to check conservation of mass for water, an independent calculation of the amount of water entering the repository is required. This calculation was undertaken by TOUGH2. The results are given in Section 8.7.1.

8.6.6.2 Results

Figure 8.1 and Figure 8.2 show stack plots for the number of moles of C and Fe atoms. The test case is from an OPG DGR for L&ILW modelling case. The results were generated using T2GGM for a preliminary run of the Normal Evolution Reference Case (NE-RC). It can be seen that conservation of mass is respected for these quantities.

8.6.7 Numerical Convergence and Stability

Requirement 2.3.2 of the Requirements Specification (Chapter 6) states that the code should be demonstrated to converge towards a single stable solution as the time resolution is increased and Requirement 3.14.1 states that the effects of changing the time resolution should be checked as part of the verification process.

The following are the results of an investigation into the effect of the various time control parameters on GGM Version 2.0. These were initially checked for GGM Version 1.0 (Section 8.2.4), but changes to GGM model and time stepping algorithm have required that these tests are retaken at subsequent versions.

There are three input parameters that affect the time step proposed by GGM (as described in Table 7.10). The most important of these, PEPS, is the maximum fractional change in a controlled differential variable that is allowed over any time step. The other two are PEPSC and PEPSR, which are cut-offs for the values of the differential variables and the rates of change of the differential variables, below which they are no longer controlled and have no influence on the suggested time step.

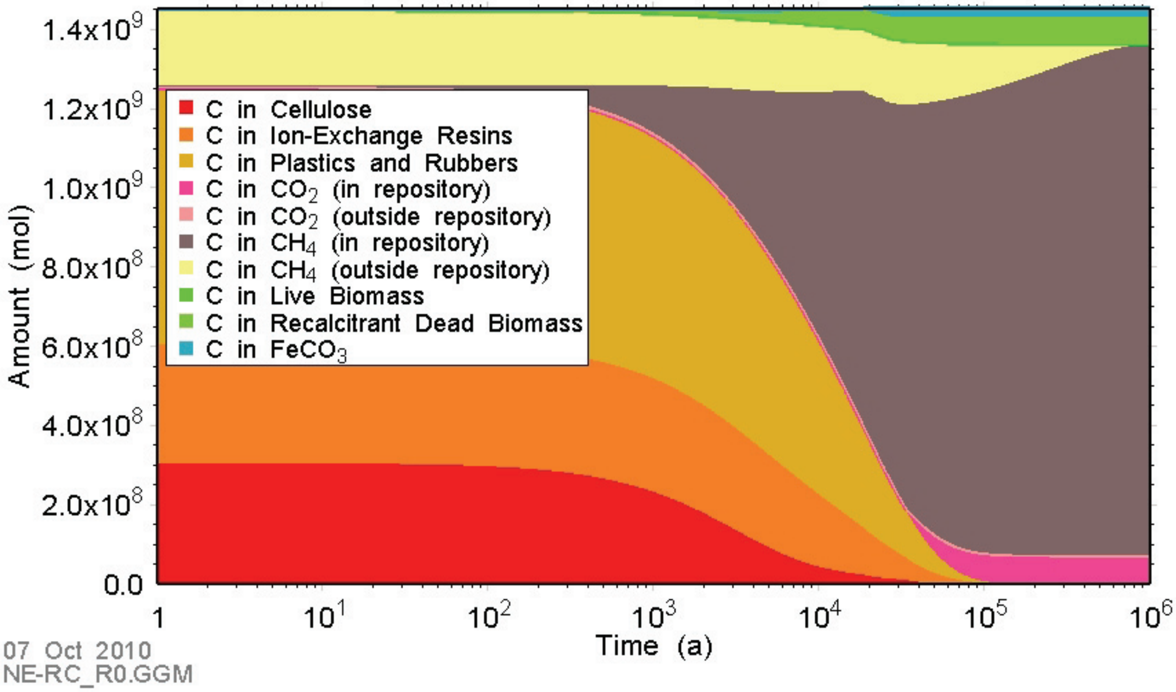


Figure 8.1: Stack Plot for C Atoms

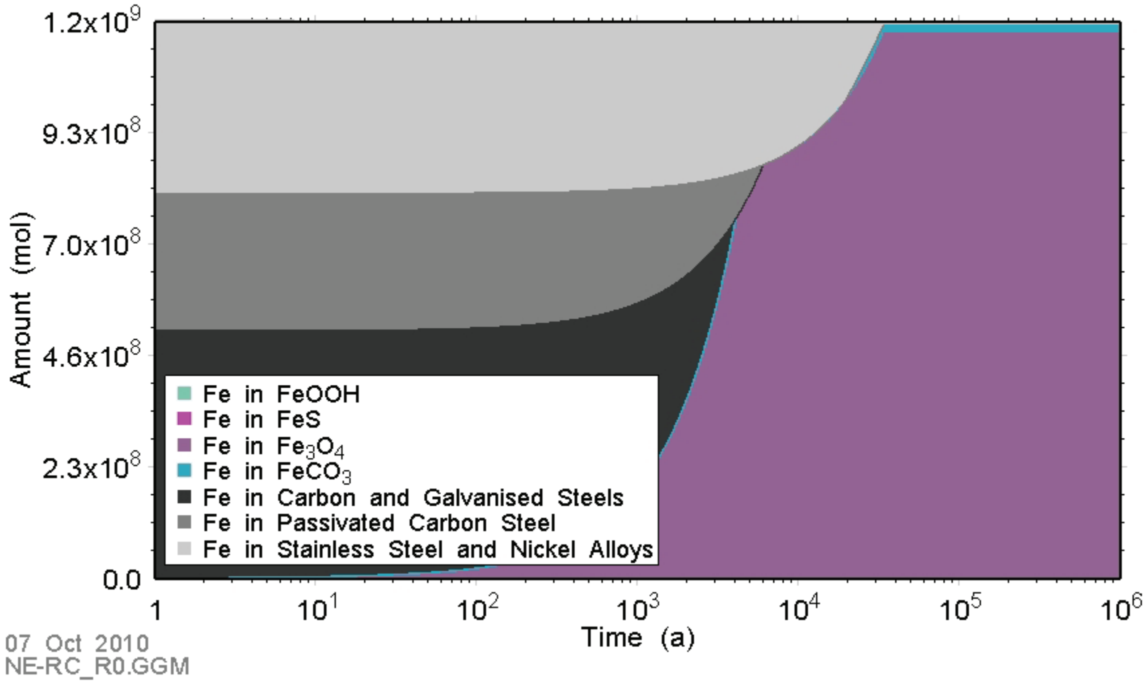


Figure 8.2: Stack Plot for Fe Atoms

For these tests, the full T2GGM Version 2.0 NE-RC reference case dataset was used. The driver program was set up to allow pressure to increase in response to gas generation and to undergo exponential type decay towards the ambient gas pressure as gas enters the geosphere. Similarly, the model for water was set up to take into account water consumption within the repository and to undergo exponential type decay driven by the difference from hydrostatic pressure at the repository horizon. The model was then roughly fitted to T2GGM results. This was done to ensure that the time step control tests are performed under realistic conditions, with sensible pressure and saturation profiles.

Four sets of time step control parameters were used in the test (see Table 8.7). The low and medium tests have resolutions similar to those used for Version 1, so the solution is expected to have practically converged by this point. The higher resolution cases have been introduced to verify this convergence and tighten up on some minor instabilities resulting from the stiffness of the equations being solved.

Table 8.7: Time Step Control Test Case Parameters

Test Case	PEPS	PEPSC	PEPSR
Low resolution	1.0×10^{-1}	1.0×10^{-8}	1.0×10^{-8}
Medium resolution	1.0×10^{-2}	1.0×10^{-10}	1.0×10^{-10}
High resolution 1	1.0×10^{-2}	1.0×10^{-18}	1.0×10^{-30}
High resolution 2	1.0×10^{-2}	1.0×10^{-25}	1.0×10^{-40}

A basic requirement is that the time step control parameters are sufficiently accurate to ensure conservation of moles of the most important quantities, C and Fe. Conservation of moles of the key quantities was well respected, except for the lowest resolution parameters which result in a gain in the amount of Carbon in the system towards 1 Ma (see Figure 8.3).

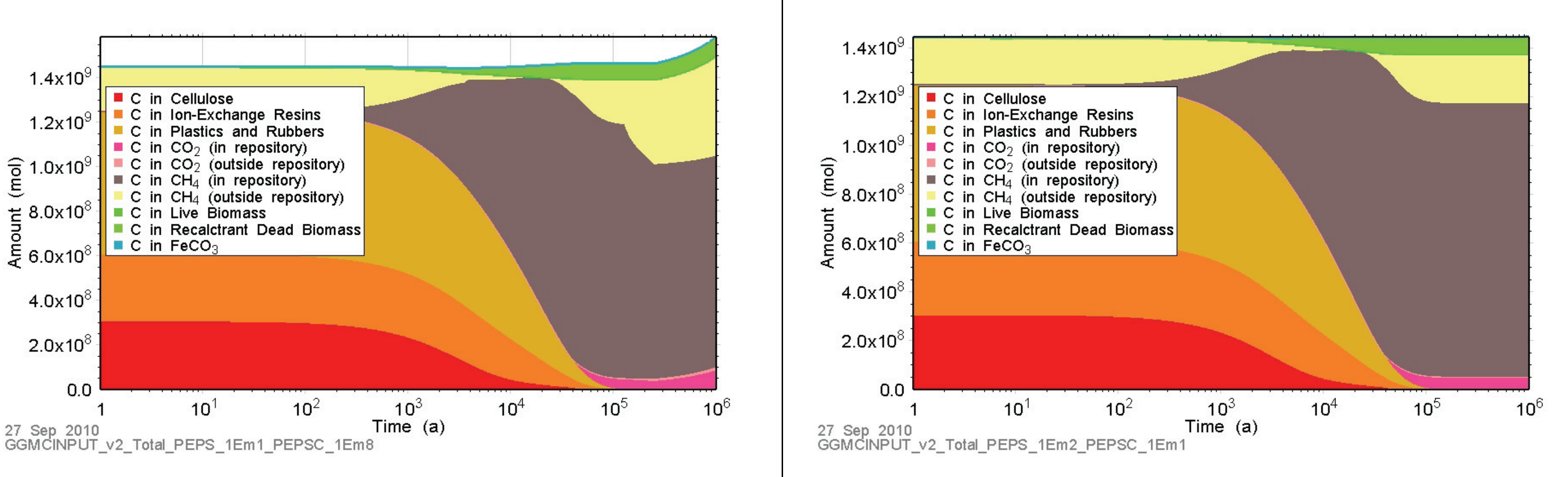
In terms of coupling with T2GGM, the most important parameters are the gas and liquid generation rates output by GGM. These are shown in Figure 8.4 for each of the test cases. The results are almost identical and no new features appear as the time step resolution is increased.

Some instability was in the amount of methane biomass (IDXE) was observed for the low case as the amount remaining decayed (see Figure 8.5). Note the logarithmic scale being used on both axes. This instability was resolved by tightening up the time step control parameters. For the high resolution cases the instability has been removed.

The full results of both high resolution parameter sets were practically identical and no other instabilities were observed. It is therefore recommended to use the High Resolution 1 parameter set, which is the slightly quicker of the two.

Low Resolution

Medium Resolution



High Resolution 1

High Resolution 2

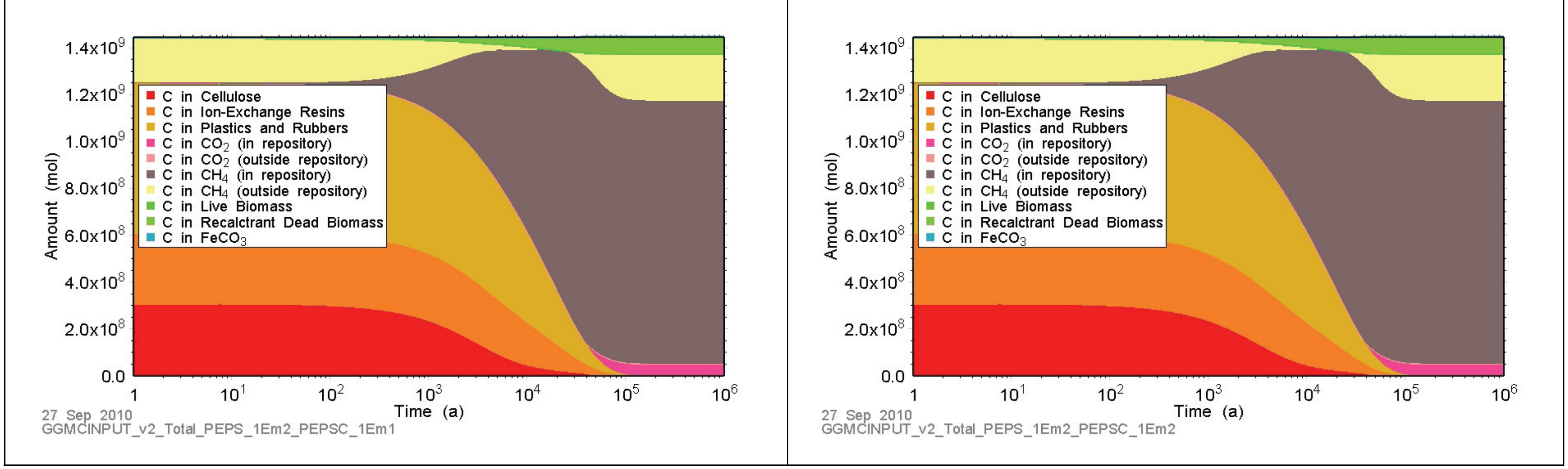
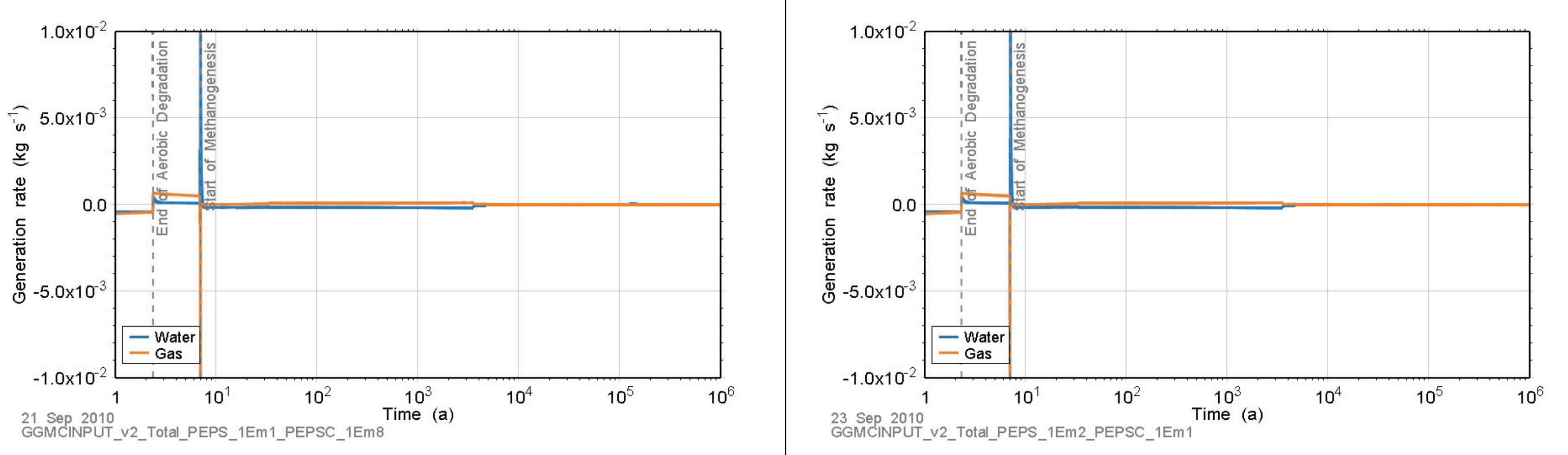


Figure 8.3: Mole Balance for Carbon Atoms

Low Resolution **Medium Resolution**



High Resolution 1 **High Resolution 2**

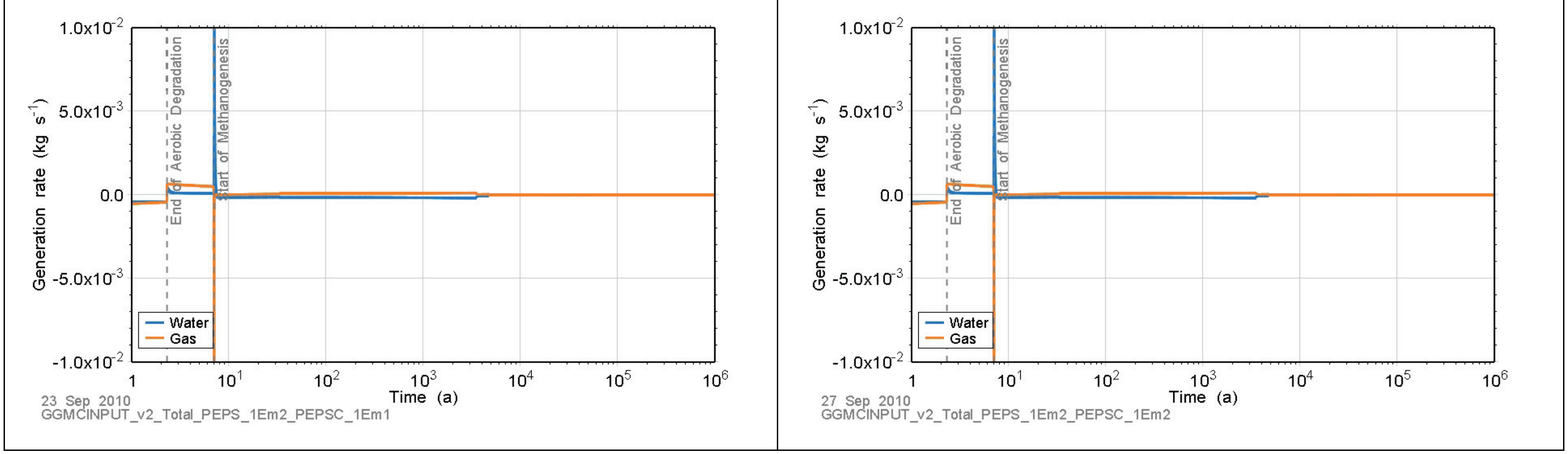
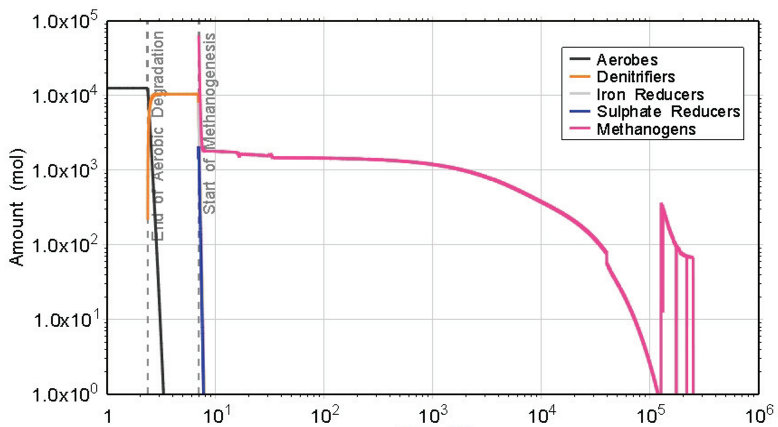


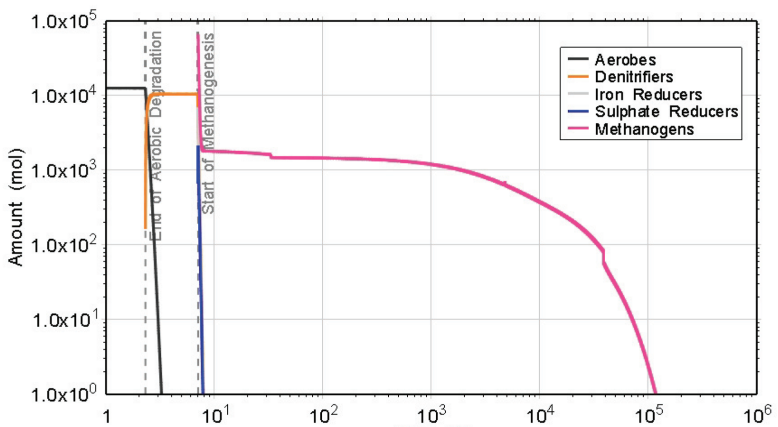
Figure 8.4: Gas (QAIR) and Water (QLIQ) Generation Rates

Low Resolution



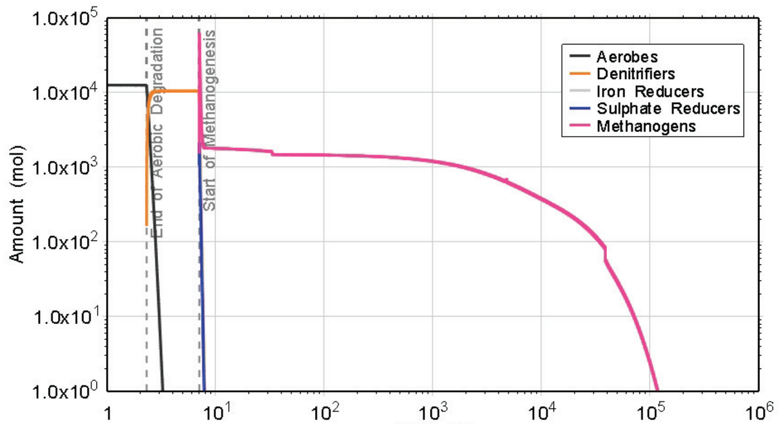
27 Sep 2010
GGMCINPUT_v2_Total_PEPS_1Em1_PEPSC_1Em8

Medium Resolution



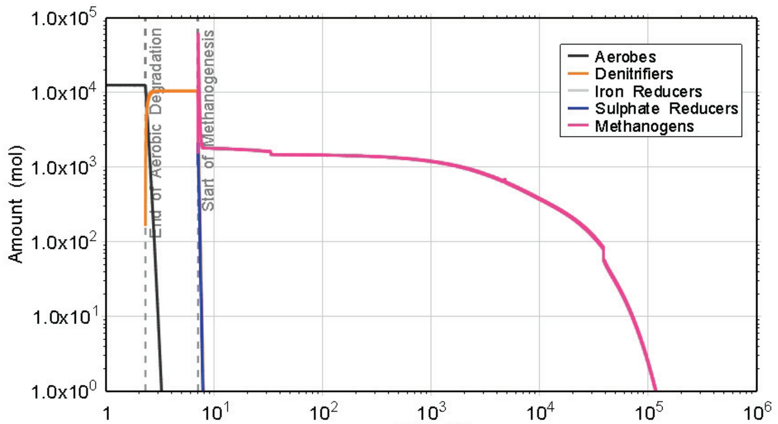
27 Sep 2010
GGMCINPUT_v2_Total_PEPS_1Em2_PEPSC_1Em1

High Resolution 1



27 Sep 2010
GGMCINPUT_v2_Total_PEPS_1Em2_PEPSC_1Em1

High Resolution 2



27 Sep 2010
GGMCINPUT_v2_Total_PEPS_1Em2_PEPSC_1Em2

Figure 8.5: Live Biomass (IDXA to IDXE), Dead and Recalcitrant Biomass (IDXDEAD) and the Terminal Electron Acceptor Stage (IATEAS)

8.7 GGM Version 2.1 Verification Results

The changes from Version 2.0 to Version 2.1 affect the integration of TOUGH2 and GGM.

TOUGH2 models the water as fresh, while GGM models it as saline, and so GGM was modelled to handle the conversion between the different models for water. To accomplish this two additional input parameters, PRLIQT2 and PMLIQT2, were added to the GGM input file specifying the density and molar mass of TOUGH2's water respectively. These were then used to scale the GGM input and output so as to convert the relevant parameters (saturation, water ingress rate and water generation rate) between TOUGH2, which calculates flow rates in kg/s, and GGM, which uses molar rates.

The GGM theory was not modified and so a full re-run of the GGM test suite was not required. The updated input files and code modifications were checked against the updated documentation (Table 7.10 and Section 7.3.5.1). The modifications were verified by running the integrated T2GGM code and checking for consistency in the flux of water into and out of the repository as calculated independently by GGM and TOUGH2, as presented in the following section.

A smoothed relative humidity function was implemented for Version 2.1. This is a slight variation on the existing linear relative humidity function, designed to avoid oscillations caused by the discontinuities at either end of the ramp.

8.7.1 Water Mass Balance

There are several components to the water mass balance:

- The total amount of water in the repository, which is provided as an input to GGM by TOUGH2;
- The cumulative amount of water generated (or consumed) within the repository, which is calculated by GGM; and
- The cumulative amount of water that has entered the repository.

The cumulative amount of water that has entered the repository is not used or calculated by GGM. It can either be calculated assuming water mass balance, or it can be calculated from the time integral of the rate of influx of water into the repository, which is provided by TOUGH2. Comparing these two calculations of the amount of water that has entered the repository allows us to determine how accurately mass balance for water is being respected.

For the OPG DGR safety assessment, calculation cases were run in two modes: conservative Non-Water-Limited (NWL) and more realistic Water-Limited (WL) gas generation modes. NWL cases do not remove water consumed in gas generation reactions from the repository. This allows gas-generation reactions to continue even if they would require water in excess of that provided by the geosphere. WL cases remove consumed water from the repository. Both modes limit reactions if there is insufficient water in the repository to support the reactions. (See GEOFIRMA and QUINTESSA (2011) for further information about these modes.)

Figure 8.6 plots the components of the water mass balance for the repository as a function of time for a preliminary run of the OPG DGR safetyassessment *water-limited simplified* base case (NE-SBC WL): The total amount of water in the repository, the cumulative amount of water generated within the repository and the cumulative amount of water that has entered calculated

a) from the TOUGH2 rate of water influx (dotted) and b) assuming mass balance (solid grey). The y-axis shows moles of geosphere water, which is modelled as saline water (TOUGH2 models water as fresh water). The negative sign of the water generated curve indicates that water is being consumed. The two curves showing the water that has entered from the geosphere are coincident, demonstrating water mass balance.

Figure 8.7 plots the components of the water mass balance for the repository as a function of time for a preliminary run of the same safety assessment but *non-water-limited* simplified base case (NE-SBC NWL). For a *non-water-limited* case, the contribution from any water consumed by the GGM (shown in cyan) is ignored within TOUGH2. Thus, the geosphere calculation proceeds as if no water is being consumed by the GGM and the amount of water in the repository at any time has the same profile as the amount of water that has entered the repository (shifted by a constant equal to the initial amount of water in the repository).

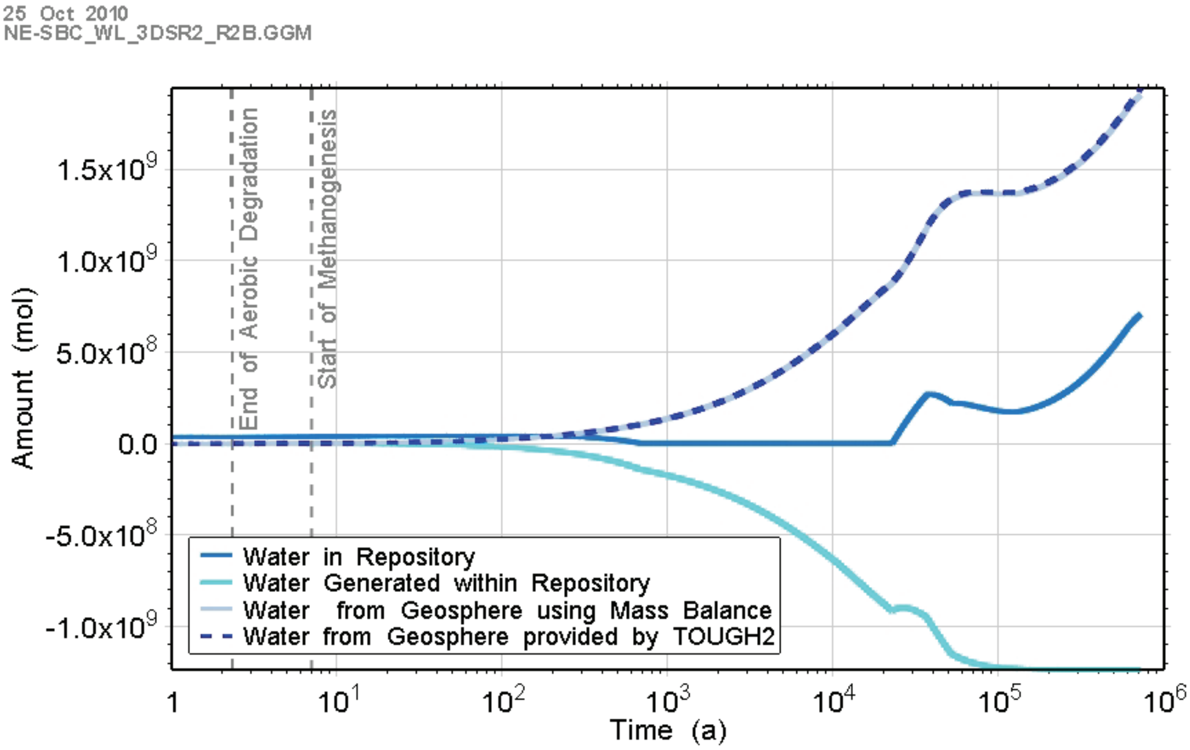


Figure 8.6: Water-balance (Water-limited)

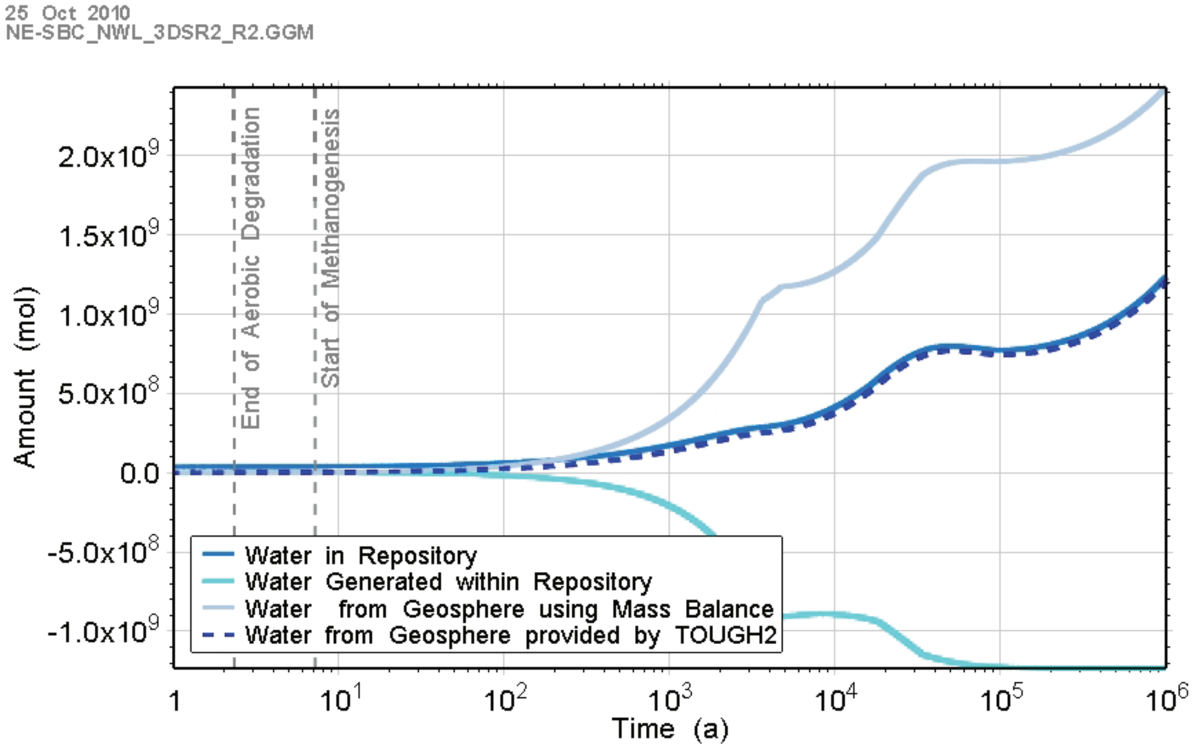


Figure 8.7: Water-balance (Non-water-limited)

8.7.2 Relative Humidity

The rate constants for vapour phase processes are scaled as a function of relative humidity using a relative humidity modulation function. Prior to Version 2.1, a linear ramp function was used, that increases the rates between zero and their values are complete saturation linearly from RH=0.6 to 0.8 (see Section 4.7.1). It was observed that when running the coupled T2GGM code under water-limited conditions the sharp discontinuity at the lower end of the relative humidity ramp could magnify the effects of small fluctuations leading to instability. To mitigate this artefact of the discontinuity in the relative humidity curve, a smoothed linear ramp was implemented as a minor variation to the linear ramp (see Section 4.7.2). To check that the function was correctly implemented and that it has minimal impact on the results a GGM standalone test case was re-run. The relative humidity scaling factor was plotted as a function of relative humidity to ensure that the function has the correct form (see Figure 8.8.). The GGM results with the smoothed linear ramp were practically indistinguishable from the results with the plain linear ramp.

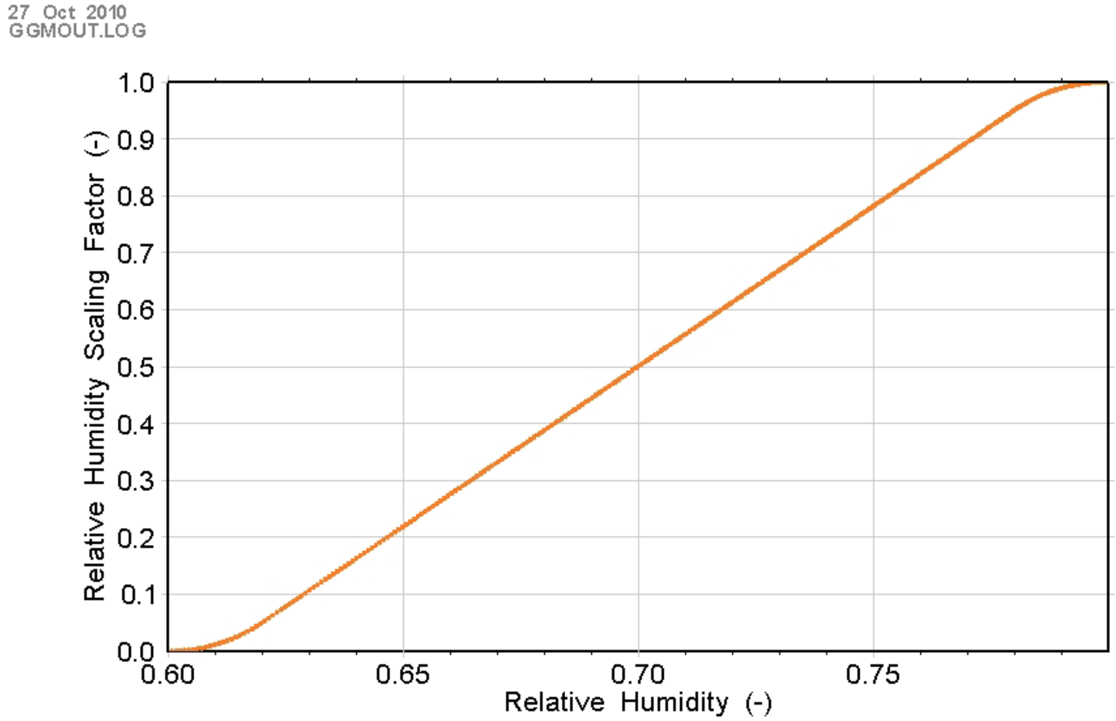


Figure 8.8: Calculated Smoothed-ramp Relative Humidity Scaling Factor

8.8 T2GGM Version 1.0 Verification Results

Version 1.0 of the integrated T2GGM code was tested with a 2D radial detailed slice with representation of the repository and shaft.

8.8.1 Code Maintainability

The T2GGM Version 1.0 code underwent a code walkthrough by an independent reviewer at Geofirma. The scope of this walkthrough is to verify that the code adheres to Geofirma's QA requirements and the T2GGM code requirements (Chapter 6).

8.8.2 Accuracy Tests

Requirement 2.3.2 of the Requirements Specification (Chapter 6) states that the code should be demonstrated to converge towards a single stable solution as the time resolution is increased and Requirement 3.14.1 states that the effects of changing the time resolution should be checked as part of the verification process.

As with the GGM code, the accuracy testing for T2GGM examined the three input parameters that affect the time step: PEPS, PEPSC and PEPSR. For this version of T2GGM, a value of PEPS=0.01 and values of PEPSC and PESPR of $1.0\text{x}10^{-8}$ were found to be sufficient for convergence.

8.8.3 Relative Humidity

Tests on the response of the system to relative humidity showed that having a sharp change in behaviour at a given relative humidity could lead to instabilities caused by oscillations around the threshold. In a subsequent version of the code, the step change in behaviour with relative humidity was removed and replaced with a linear change

8.8.4 The Limit of Zero Saturation

Modifications were made to the GGM code during verification and testing of this version to help work around problems arising at zero saturation. Note that those modifications were removed at Version 2.0 during implementation of an improved model for zero saturation behaviour (Section 4.8).

8.9 T2GGM Version 1.1 Verification Results

Changes were made to GGM Version 1.1, and not the TOUGH2 portion of the code (see the Version Tracking Record in Appendix A). No T2GGM verification was undertaken at this stage.

8.10 T2GGM Version 1.2 Verification Results

Changes were made to GGM Version 1.2, and not the TOUGH2 portion of the code (see the Version Tracking Record in Appendix A). No T2GGM verification was undertaken at this stage. As part of the validation exercise (Chapter 9), the results generated at this version also underwent external peer review.

8.11 T2GGM Version 1.3 Verification Results

Changes in this version related to the GGM component of T2GGM are verified in Section 8.5. Changes made to improve consistency in the representation of the repository void volume between TOUGH2 and GGM are verified in Section 8.11.1. The results using this version were also subject to independent validation for one reference case (Chapter 9).

8.11.1 Verification of Repository Void Volume Changes

The primary change to the integrated T2GGM Version 1.3 was to calculate the repository void volume dynamically based on rock compressibility, porosity and element volumes, and pass the repository void volume to GGM at each time step. This new repository void volume calculation was verified in two ways: (1) ensuring the initial void volume is as expected; and (2) ensuring the water mass balance is correct. The second verification step was selected as discrepancies in the water mass balance highlighted the issue of inconsistent void volumes between GGM and TOUGH2 components of the T2GGM model. Simulations showed that at Version 1.2 there was a relatively large difference between the amount of water entering/leaving the repository from/to the geosphere as demonstrated by TOUGH2 results and the mass balance of GGM results. With the Version 1.3 model with updated parameters, only a small difference between the amount of water entering/leaving the repository from/to the geosphere was observed. The small difference that does exist is attributed to the coarse time discretization of the TOUGH2 results.

8.12 T2GGM Version 2.0 Verification Results

Changes in this version related to the GGM Version 2.0 component of T2GGM Version 2.0 are verified in Section 8.6. This section verifies T2GGM code changes related to relative humidity, zero saturation, timestep control, TOUGH2-MP and the use of alternative gases.

8.12.1 Relative Humidity

Relative humidity code modifications were tested by running the NE-UG-GT case (normal evolution with updated geosphere parameters) from the 2009 Gas Report (Calder et al. 2009) with the updated T2GGM code. The case previously resulted in a sharp drop in relative humidity around the time the saturation dropped to zero. This test was judged to have been successful if: (1) there was no oscillatory or unstable behaviour, and (2) the results show that vapour phase reaction rates slowed, reaching zero at RH_{min}, and conservation of mass continues to be respected.

The NE-UG-GT was successfully completed to approximately 50 000 years. At this point, the simulation was impeded by very small time steps resulting from a TOUGH2 related issue. As the relative humidity and zero saturation components of the case had been successfully modelled by 50 000 years, this was considered a sufficient test for the relative humidity related changes.

As the relative humidity of the NE-UG-GT case dropped below the thresholds of 0.8 and 0.6, and rose above the threshold of 0.6 again, no oscillatory or unstable behaviour was observed. Figure 8.9 shows the relative humidity and relative humidity modulation factor for the NE-UG-GT case. Note that there are oscillations in the relative humidity calculated by TOUGH2 and passed to GGM, due to very small oscillations in the mass fraction of gas that is air that are magnified by the relative humidity calculation. These oscillations also occur in simulations where the relative humidity function is turned off, and do not appear to impact other model parameters.

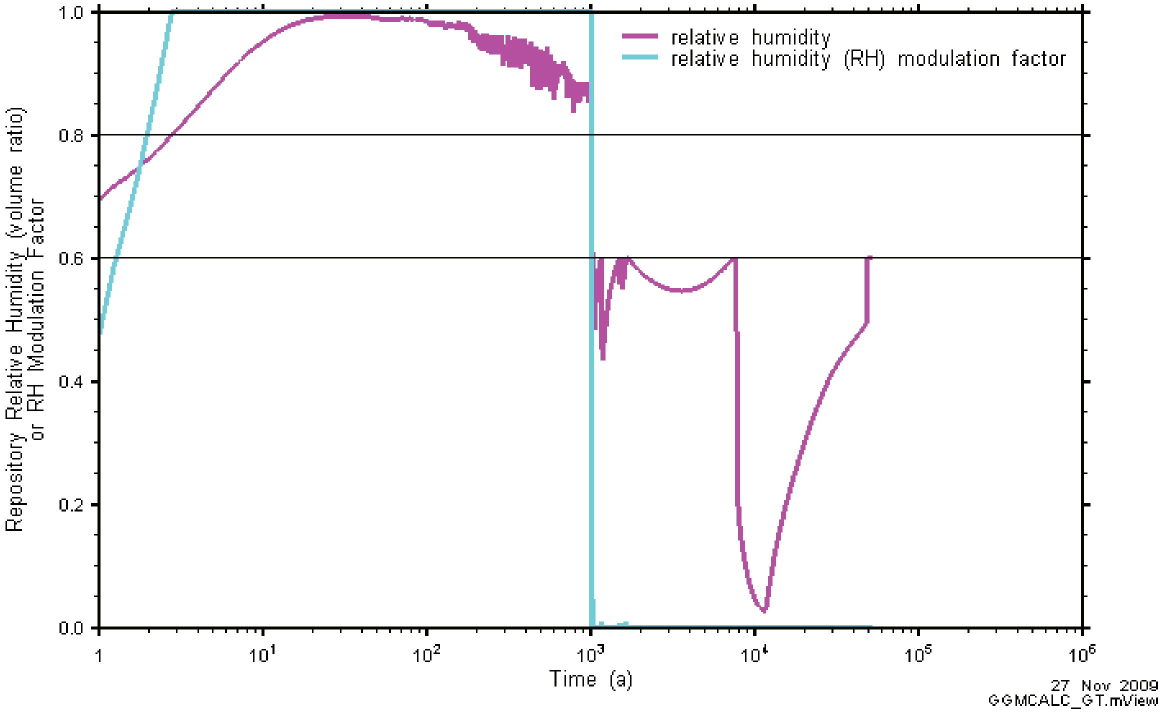


Figure 8.9: Relative Humidity and Relative Humidity Modulation Factor for the NE-UG-GT Test Case

Vapour phase reaction rates slowed to zero as the relative humidity decreased to 0.6, as shown by the amount of metallic and organic wastes, shown in Figure 8.10 and Figure 8.11. The consumption of these wastes stops completely as the RH modulation goes to zero. Also, mass balance for C and Fe is preserved as shown in Figure 8.12 through Figure 8.13, respectively. (Note that some quantities on the stack plots can take negative values, such as the amount of water that has entered the repository if more has left than has entered. In that case the bands corresponding to those quantities are shifted by a constant value to ensure a positive band thickness. Those quantities are marked on the stackplots.)

As the test criteria were achieved and the relative humidity code modifications were successfully verified.

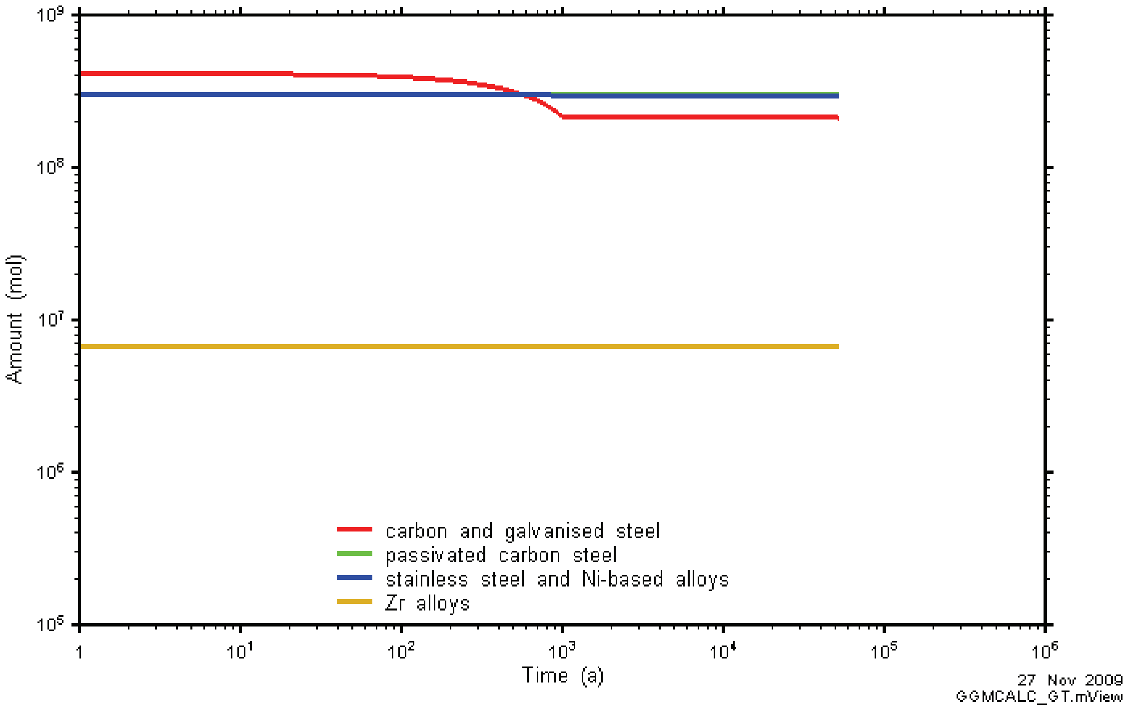


Figure 8.10: Amount of Metallic Wastes for the NE-UG-GT Case

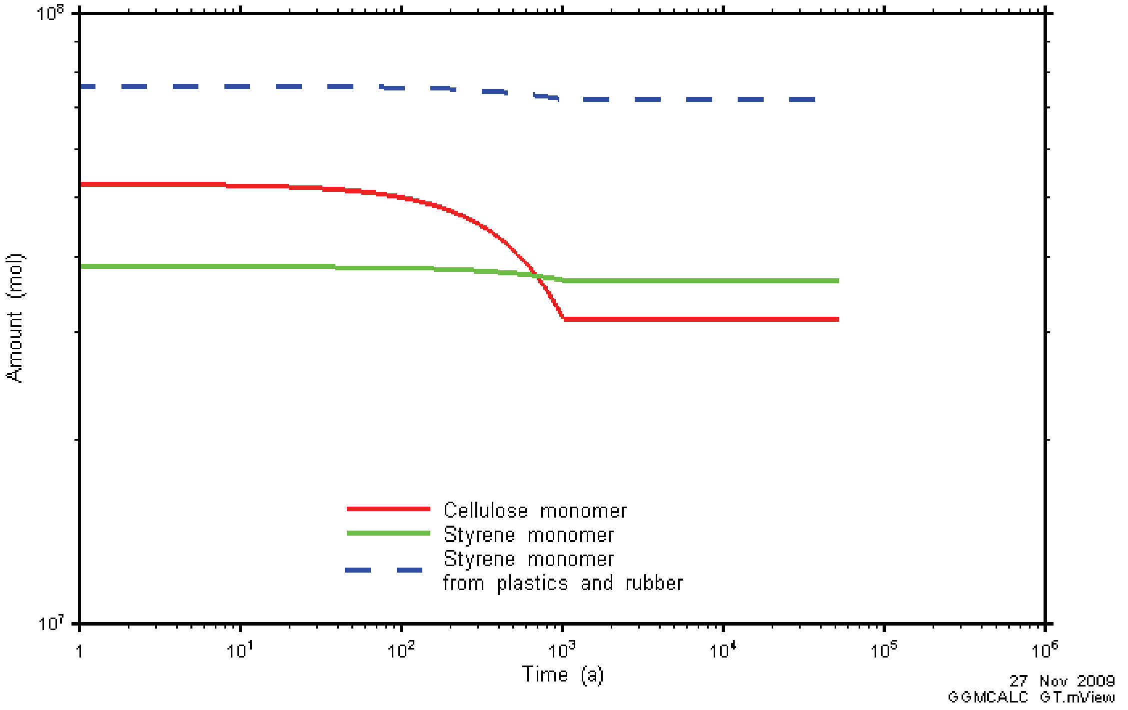
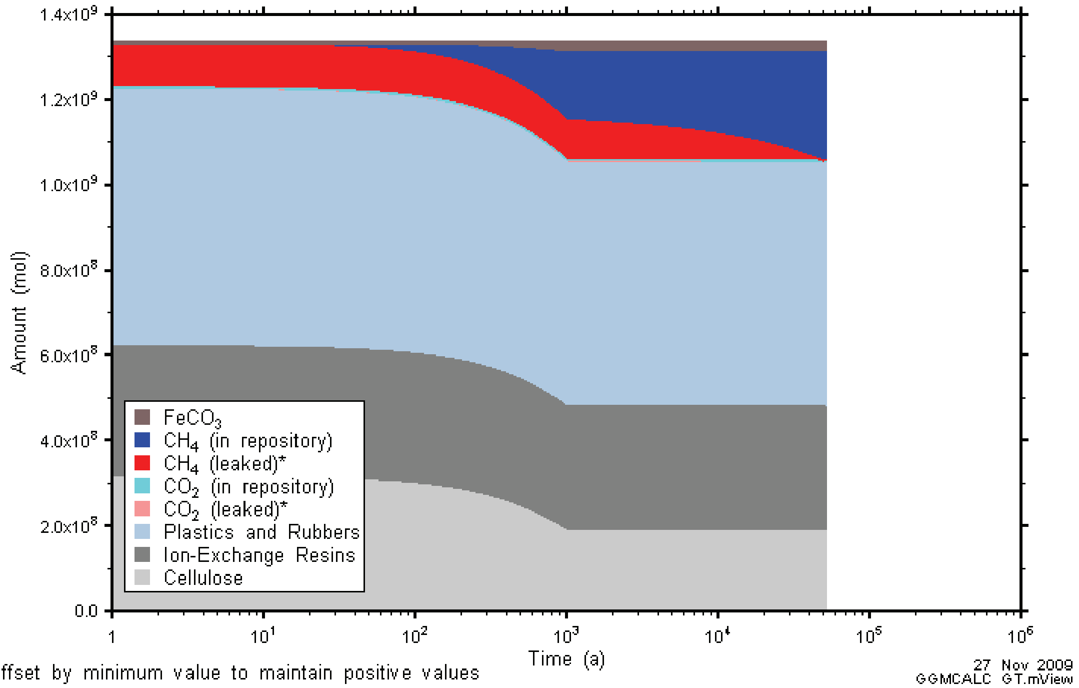


Figure 8.11: Amount of Organic Wastes for the NE-UG-GT Case



* Offset by minimum value to maintain positive values

Figure 8.12: Carbon Mass Balance for the NE-UG-GT Case

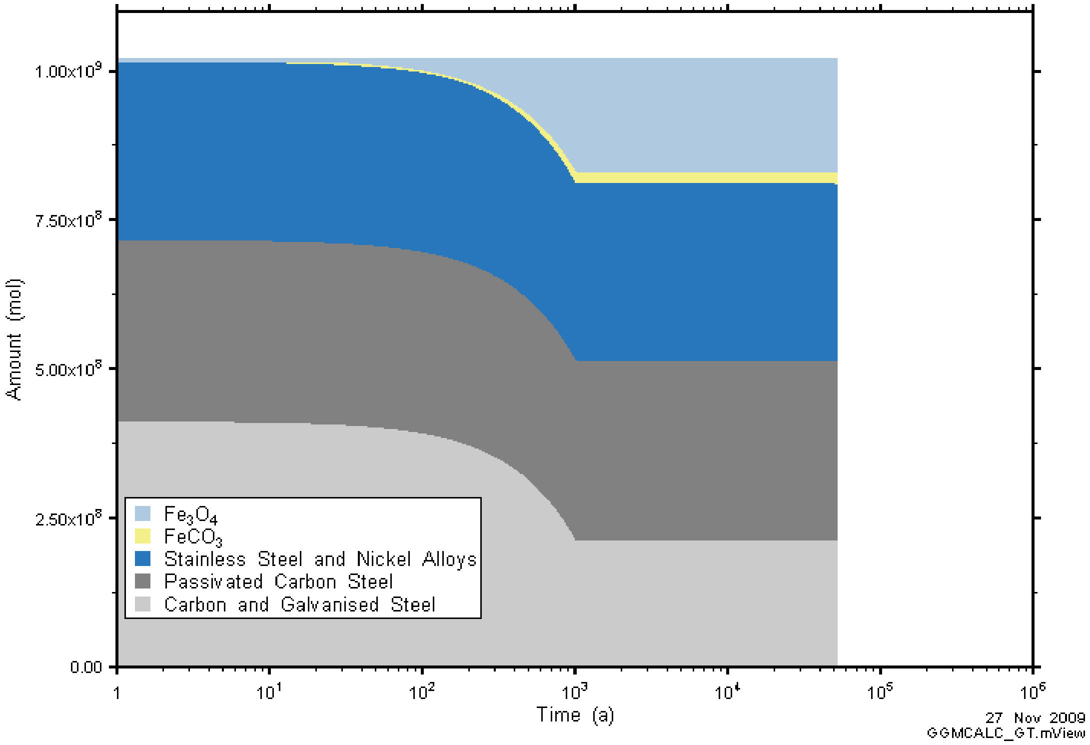


Figure 8.13: Fe Mass Balance for the NE-UG-GT Case

8.12.2 Zero Saturation

Similarly to the relative humidity verification and as described in Section 8.12.1, model behaviour at zero saturation was modified by running the NE-UG-GT (normal evolution, updated geosphere) case from the 2009 Gas Report (Calder et al. 2009) with the Version 2.0 T2GGM code. This test was judged to have been successful if:

1. There is no oscillatory or unstable behaviour;
2. The results show that the water consuming reactions ramp down once zero saturation has been achieved;
3. Conservation of mass continues to be respected; and
4. Internal review of the results judge them to be plausible.

As previously discussed and shown above for the NE-UG-GT case in Section 8.12.1, the simulation was both stable (no oscillatory behaviour) and conservation of mass was preserved.

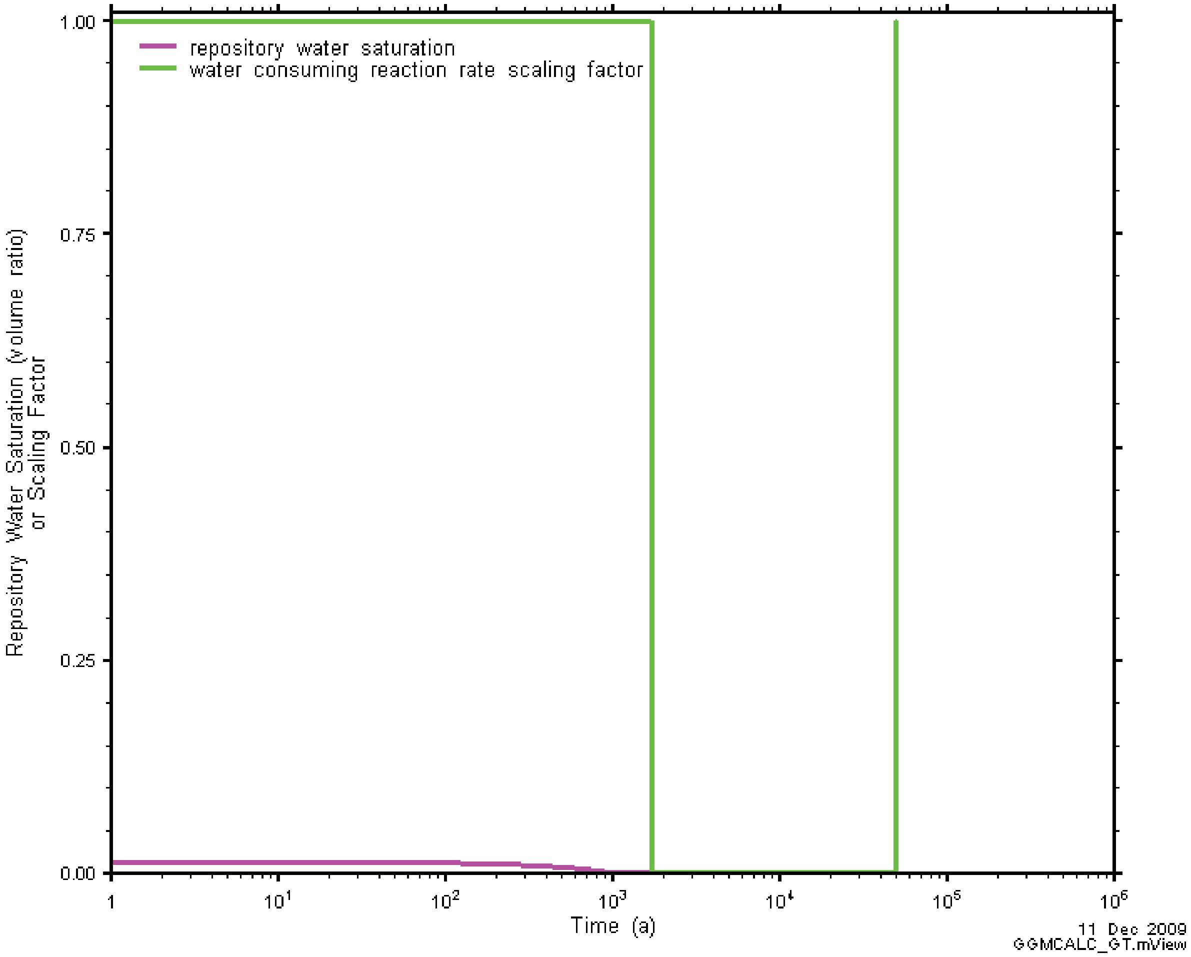


Figure 8.14: Repository Water Saturation for the NE-UG-GT Case

Water saturation, as shown in Figure 8.14, goes to zero at approximately the same time as relative humidity goes to below the 0.6 threshold as shown in Figure 8.9. The water consuming reaction rate scaling factor is also shown in Figure 8.14 (note that the water consuming reaction rate scaling factor is plotted to be zero if the rate of water consumed by saturated reactions, dC/dt, was zero), and the rates of water consumption/generation and flow into the repository are shown in Figure 8.15. As expected, the water consumption reaction rate scaling factor goes to zero at the same time as the water saturation goes to zero, and increases to one as the repository saturation increases above zero towards the end of the simulation.

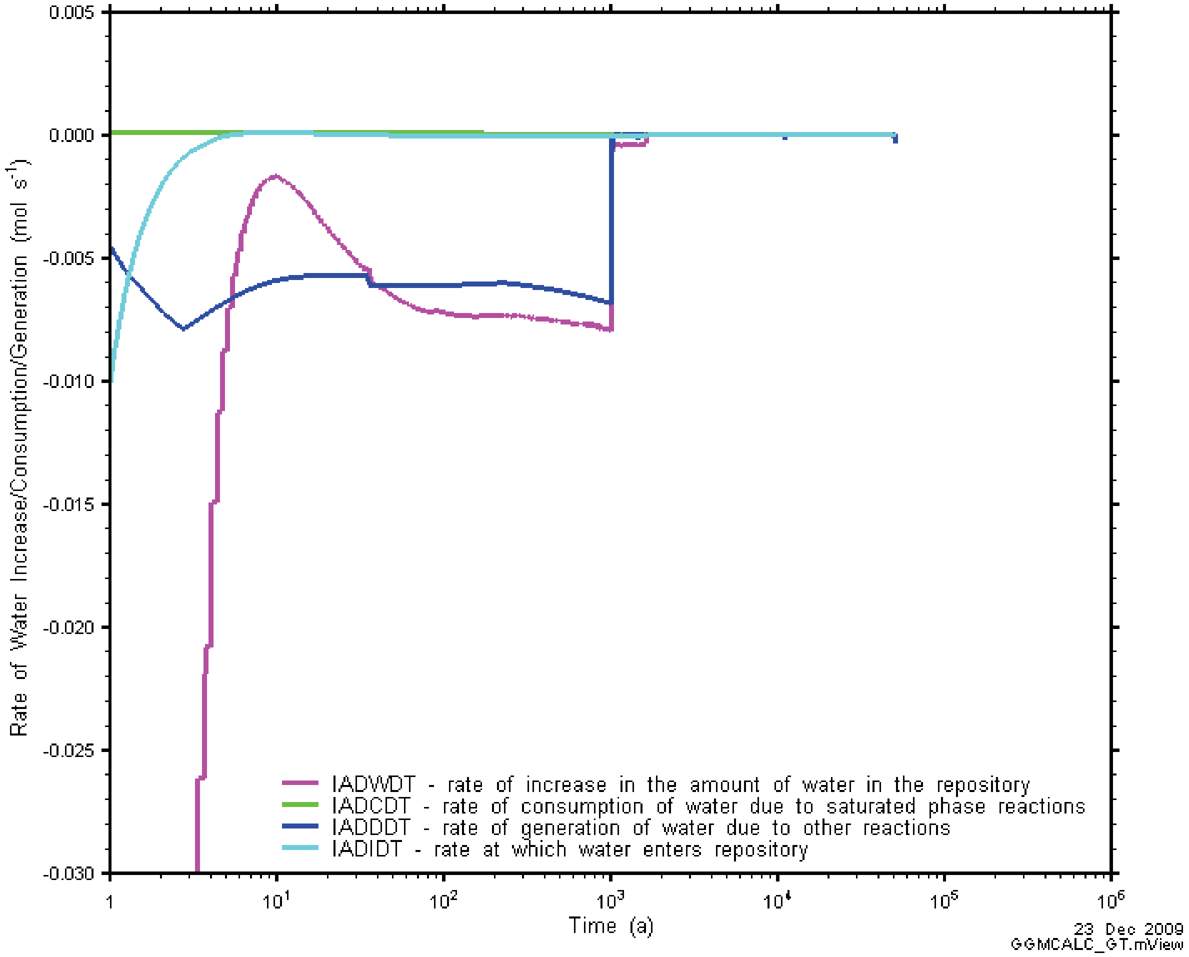


Figure 8.15: Rate of Water Increase, Consumption, Generation and Flow into the Repository for the NE-UG-GT Case

8.12.3 Time Step Control

As described in Table 8.6, Test Case 2-D-4 verifies the time step control changes to T2GGM by running the NE-UG-BC (normal evolution, updated geosphere) full and simplified cases. (The simplified case excludes the initial TEA stages and biomass from the GGM.) There should be no qualitative changes in results and run times should be reduced compared to those produced by GGM Version 1.3.

The NE-UG-BC simplified was successfully completed, with negligible changes to the results. Run times for the Version 1.3 code was approximately 1 day and 4 hours. Run times for the Version 2.0 code were approximately 2 hours, with the relative humidity flag turned off (although note that relative humidity remains above 0.6 for the duration of the simulation, except for two very brief dips below 0.6). An additional simulation was conducted with the relative humidity flag turned on; however, this simulation also increased the permeability of water in the repository at low water saturations and set the residual water saturation in the repository to zero as is expected for this model using Version 2.0 of the code. The relative permeability of water in the repository was decreased at low saturations and a small residual saturation in the repository was specified for models using Version 1.3 of the code to avoid stability problems encountered as relative humidity decreased below 0.6 and the repository reached zero saturation, which are two issues addressed in the newer version. Run times for this model were approximately 2 days and 15 hours. The increased run time is likely due to the changes in repository permeability.

The NE-UG-BC full case was also successfully completed, with negligible changes to the results. Run times for the Version 1.3 code were approximately 2 days and 8 hours and for the Version 2.0 code, 2.5 hours (RH flag turned off). Turning on the RH flag, and making the same parameter changes as to the simplified case with the RH flag turned on as described above, run times for the Version 2.0 code were approximately 5 days.

8.12.4 T2GGM-MP (A TOUGH2-MP implementation of T2GGM)

The TOUGH2-MP implementation of the T2GGM code was verified by simulating the NE-UG-BC with the new parallel code. This new code is referred to as T2GGM-MP.

It should be noted that the two-phase flow problem posed by the NE-UG-BC is difficult to solve.

The new TOUGH2-MP code uses a different solver and time stepping scheme than T2GGM, and this initially resulted in the simulation stalling due to very small timesteps resulting from oscillations in phase evolution and disappearance at one or two grid elements. In particular, the T2GGM-MP code had difficulties solving for elements within the repository; both at elements with low water or gas saturations and at elements where water was being extracted by GGM when water saturations were low.

The T2GGM-MP simulation was completed successfully by doing the following.

- Using the new Version 2.0 option to calculate the scaling factors for distribution of air generation and liquid consumption calculated by GGM among those elements specified as source and sink nodes in the (case specific) TOUGH2 grid. In particular, this minimized the amount of liquid that was removed from elements at the edge of the repository which were almost fully saturated with gas, and allowed the simulation to complete successfully.
- GGM relative humidity flag PHUM was switched off. As relative humidity stays close to one for the duration of the simulation, this flag would not have any impact on the results.
- Extraction of liquid from an element was stopped if no saturated water is left in the element, but the relative humidity in the element is still high. This prevents early instabilities resulting from water extraction at elements on the edge of the repository that are nearly dry; however, once the repository begins to desaturate with water it creates a minor discrepancy between

GGM and TOUGH2 (as GGM continues to consume very small amounts of liquid, but TOUGH2 no longer extracts liquid.) The extent of such a discrepancy can be checked using water balance plots such as Figure 8.6 and is generally negligible.

Results are near identical between the two simulations. Run times for the T2GGM-MP solution were slower than for the original T2GGM solution (7.5 hours vs. 2 hours for T2GGM). While it was expected that the T2GGM-MP solution would be faster, these slower run times are attributed to the differences in solver and time stepping scheme resulting in smaller timesteps and increased difficulty solving at elements within the repository, as well as the fact that only two processors were used for the TOUGH2-MP simulation. Experience running 3D simulations with the T2GGM-MP has shown appreciable improvements in run time when large grids (>100 000 nodes) are simulated on multiple processors.

The stability issues associated with this test case are not ideal, however they are not considered pertinent for the purposes of this test case. This test case was conducted to verify the implementation of the T2GGM-MP code, which it completed successfully.

8.12.5 Alternative gases

Several test cases were completed to ensure the alternative reference geosphere gases were correctly implemented. First, the NE-UG-BC was re-run, with air specified as the alternative gas, to ensure results are identical. As well, this case was re-run with the alternative viscosity method (TMVOC based viscosity calculation rather than the default EOS3 method), to ensure results are identical. Secondly, the NE-UG-BC was re-run using CH_4, CO_2 and H_2 as the alternative gas, to ensure the correct parameters are used. T2GGM output echoes the parameters used by the model and these echoed outputs were compared to the specified values. Repository pressure results were also checked. All simulations completed as expected; the air simulations were identical to previous versions, and the alternative gas simulations parameter output had the correct values. The simulation results for alternate gases were different, as would be expected given different viscosities and Henry's law constants (see Figure 8.16 for example).

8.13 T2GGM Version 2.1 Verification Results

Only a minor change was made to TOUGH2 between Version 2.0 and 2.1 to ensure stability of calculations to small fluctuations in relative humidity.

Verification of consistency between TOUGH2 and GGM in the modelling of water influx is given in Section 8.7.

8.13.1 Relative Humidity

Relative humidity related code modifications for V2.1 were two-fold:

1. The RH was modified within T2 before being passed to GGM. As repository saturations approach a defined lower limit, RH is scaled to limit vapour phase reactions; and
2. The relative humidity curve was smoothed within GGM to reduce oscillatory behaviour (see Section 4.7.)

The V2 Postclosure safety assessment NE-SBC WL results verify correct implementation of the modifications. RH is reduced as repository saturation approaches the specified lower limit (0.0001). RH increases as saturation subsequently increases. Minimal oscillation is detected.

8.14 Analysis Summary

GGM Version 2.1 has been demonstrated to be able to accurately solve the equations described in the Theory Manual (Chapter 4) and to be implemented as described in the Design Documentation (Chapter 7). It has been shown that GGM is suitable for use as a module that can be interfaced with the TOUGH2 gas transport code, the combined code being T2GGM Version 2.1. The following time step control parameters were identified as being suitable for accurate resolution of GGM equations: PEPS: 1.0 x 10^{-2}, PEPSC: 1.0 x 10^{-18}, and PEPSR: 1.0 x 10^{-30}. With these time resolution parameters, the standalone GGM takes several minutes to run and the integrated T2GGM code takes between several hours and several days to run depending on the case.

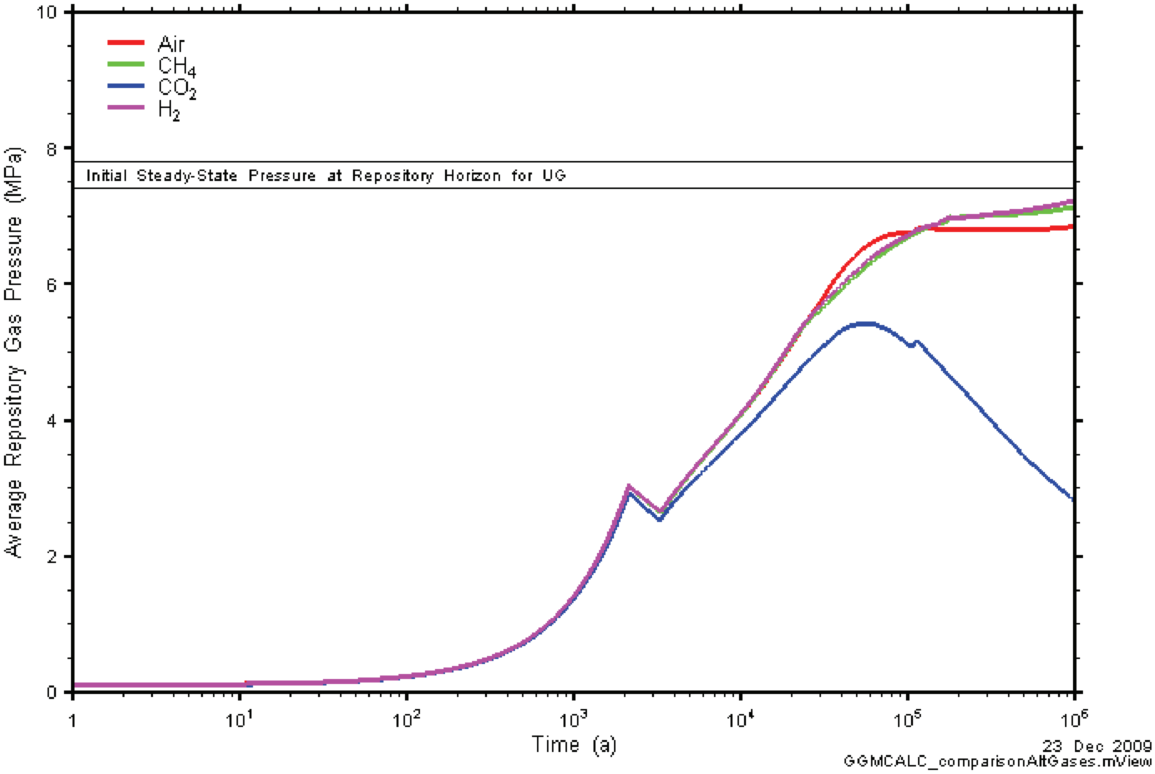


Figure 8.16: Repository Gas Pressure for NE-UG-BC with Alternative Bulk Geosphere Gas Properties

9. VALIDATION

Validation, as defined in the NWMO Software Procedures (NWMO 2010) involves determining the accuracy of the software results with respect to its intended application. The results of T2GGM are intended to calculate:

- The magnitude and timing of the peak gas pressure;
- The evolution of the repository saturation;
- The rates of gas and water generation within the repository; and
- The flux of gas and water through the geosphere.

Validation of T2GGM has been undertaken as a process of continuously testing the code and increasing confidence in the results. The approach taken to validation combines expert review, comparisons with independent calculations, and comparisons against experiment.

The main validations to date are below.

- The TOUGH2 gas transport model is a widely used model for two-phase flow and gas transport in geological media, including for deep geologic repositories (e.g., Talandier et al 2006).
- The GGM gas generation model is consistent with general literature and with approaches adopted in other waste management organizations for similar models. All results have undergone internal review by the experts responsible for developing GGM Theory. Results for T2GGM Version 1.2 also underwent external peer review.
- T2GGM Version 1.3 transport results were compared with an oil & gas industry-standard gas modelling code GEM for one reference case (ARC 2010). Due to inherent differences in the code purposes, only a limited comparison was possible, but the results were consistent.
- T2GGM Version 2.1 demonstrates mass balance for the key modelled species.
- At Version 2.0, GGM was compared against data from the Finnish large scale Gas Generation Experiment (GGE) (see Appendix B).
- Only minor changes were made at Version 2.1.

10. USER MANUAL

10.1 TOUGH2

For general usage of TOUGH2, please see the TOUGH2 User's Guide (Pruess et al. 1999). For specific details relating to the implementation of GGM, please see the Detailed Design Description (Chapter 7).

GGM processing is invoked using the GGMIN keyword in the TOUGH2 input data file. See Table 7.4 for a description of variable functions. Input records are as given below in Table 10.1.

Table 10.1: GGMIN Input Records

Record	Variables	Format
1	NORMG, NORML, SCALEFACTORG,SCALEFACTORL	4I2
2	VOLFAC	E
3	GASRSAT	*
4	USELIQCTRL	*
5	LSATOFFVAL	*
6	LSATONVAL	*
7	USERHCTRL	*
8	RHLSATMIN	*
9	RHLSATMAX	*
10	RHLIMMIN	*
11	NREPO	I5
12	EREP(I) - NREPO lines	A5
13	NGASSRC	I5
14	EGASSRC(I), XGASSRC(I) - NGASSRC lines	A5,E
15	NLIQSINK	I5
16	ELIQSNK(I), XLIQSNK(I) - NLIQSNK lines	A5,E
17	NREPCONN	I5
18	EREPCONN(I), EREPSIDE(I) - NREPCONN lines	A10,1X,A5
19	Blank line	
20	GGM input data	

Alternative gas processing is invoked by the ALTGAS keyword. Table 7.6 provides the function of the alternative gas variables. Table 10.2 describes ALTGAS input.

Table 10.2: ALTGAS Input Records

Record	Variables	Format
1	ALTGAS, VISC_METHOD, ALT_H, ALT_AMA, ALT_CVGAS, ALT_VISCG	A5, I5, 4E10.4

The modified van Genuchten capillary pressure and relative permeability functions are invoked using ICP and IRP = 14 in the ROCKS section.

Binary output file and COFT/FOFT path for MP are invoked with the INTER keyword.

Table 10.3: INTER Input Records

Record	Variables	Format
1	BINOUT - if set to non-zero, binary output files are produced	I5
2	IFPATH - if set to non-zero, MP FOFT and COFT output is written to a separate file by each processor.	I5
3	FPATH - output path if IFPATH is non-zero	A80

10.2 GGM

GGM consists of a set of FORTRAN 77 subroutines that are compiled with TOUGH2. Details of the interface between GGM and TOUGH2, including descriptions of the various subroutines, their arguments and calling sequences are all given in the Design Description, Chapter 7. Table 7.10 and Table 7.11 describe the GGM Input and Output variables.

In order to drive the GGM module, in addition to configuring TOUGH2 to provide the necessary run-time information via subroutine arguments, a file containing all input and solution control parameters must be prepared. Example input files are provided with the source code containing input data that is consistent with the relevant Data report (QUINTESSA and GEOFIRMA 2011). A description of each of the input parameters is given in Table 7.10. GGM sends its output to a FORTRAN unit with the format described in the Design Description. This output can be directed to file and analyzed as appropriate. Note that for extremely long runs very large output files (several gigabytes in size) may be produced if output is requested at every internal time step. The LOGTR input parameter can be used to control how often GGM sends output to the output file unit.

GGM can also be compiled and run in standalone mode for testing purposes. Compilation scripts that can be run in a Linux environment or on Windows using Cygwin are provided with the source code for this purpose. Further details can be found with the README file provided with the software.

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12. ABBREVIATIONS AND ACRONYMS

DGR	Deep Geologic Repository
EOS	Equation-of-State
GGE	Gas Generation Experiment
GGM	Gas Generation Model
IFD	Integral Finite Difference
IX	Ion-Exchange
LBNL	Lawrence Berkeley National Laboratory
L&ILW	Low and Intermediate Level Waste
NE	Normal Evolution Scenario
NE-RC	Reference Case
NE-SBC	Simplified Base Case
NWL	Non-Water Limited
NWMO	Nuclear Waste Management Organizaton
OPG	Ontario Power Generation
RH	Relative Humidity
TEA	Terminal Electron Acceptor
WI	Work Instruction
WIPP	Waste Isolation Pilot Plant
WL	Water Limited

APPENDICES

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APPENDIX A: CHANGE HISTORY

A.1 T2GGM Version 1.0

The initial development version of the coupled Gas Generation and Transport Model was called T2GGM Version 1.0. The initial development version went through several incremental updates to improve its stability, such as the implementation of more advanced time stepping methods and to allow improved coupling of TOUGH2 and GGM by ensuring a consistent view of the total gas pressure is held by both.

A.2 T2GGM Version 1.1

T2GGM results created using the final Version 1.0 development version were submitted for review by the developers of GGM theory; Fraser King and Paul Humphreys in May 2008.

This review identified several bugs and some inconsistencies that were resolved by updating the gas generation model. The most significant changes were as follows:

- The introduction of recycling of dead biomass;
- The treatment of organic wastes as amounts rather than concentrations;
- Ensuring that corrosion reactions were switched off once the relevant supplies of metallic wastes had been depleted; and
- Ensuring that reaction pathways for organic waste degradation and the conversion of hydrogen and carbon dioxide to methane were active under the right conditions.

The updated version was called T2GGM Version 1.1.

A.3 T2GGM Version 1.2

Subsequent to Version 1.1 an optimization study (Section 8.4) was undertaken which involved the development of an additional input flag that can be set to allow simplifications to the way that the shortest terminal electron acceptor stages are modelled in order to improve T2GGM run times. In addition, to improve model stability, an effective residual gas and water saturation was implemented in the repository, preventing further gas or water extraction from the repository. A bug with the labelling of the output units for biomass was also fixed. This version of the code was labelled T2GGM Version 1.2.

A.4 T2GGM Version 1.3

Version 1.3 of T2GGM corrects issues identified with Version 1.2 identified during:

- A review of T2GGM Version 1.2 by Serco Assurance (UK);
- A thorough internal review of the mass balance equations; and
- Additional testing of the standalone GGM.

The following updates were made to GGM.

- Reformulation of the model for biomass and biomass recycling. The modifications correct some errors, ensure conservation of mass of water and carbon, alter the way in which dead biomass is defined, and allow the amount of live (hydrated) biomass to be output.
- The theory was updated to ensure that degradation and corrosion reactions can continue in the vapour phase provided that there is sufficient humidity. This involved introducing a new model parameter into the theory which acts as a switch depending on the humidity and modifying expressions involving the concentration of CO_2.

- Correction of a typographic error in an equation.
- GGM was modified to calculate the total number of moles of each gas component that are transported from the repository into the geosphere at each time step and the cumulative number of moles of each gas component that have left the repository. This was to enable full mass balances to be calculated and checked.
- The theory and GGM model modified to calculate and output the amount of ZrO_2 corrosion product to enable the full mass balance for O to be calculated.
- The model for the FeOOH corrosion product was modified to make it amount based rather than concentration based.
- Modifications to give better control over the frequency with which GGM produces output.
- An error was fixed in calculating the microbial rate constants when the reactions were hydrogen limited.
- The TOUGH2 interface was updated to allow the repository void volume to be set dynamically by TOUGH2 using its calculations based on rock compressibility and porosity.
- Fixed an error whereby the initial mass and molar mass of styrene monomers were being used in place of those for plastics and rubbers.
- Fixed error identified by the test suite which was preventing corrosion reactions from proceeding when there was no hydrogen and the rate of production due to corrosion was greater than the rate of consumption of hydrogen due to microbial processes.
- Updated the time step control algorithm for improved performance and stability.

The following updates were made to TOUGH2.

- Calculated repository void volume dynamically based on rock compressibility, porosity and element volumes, and passed the repository volume to GGM at each time step.
- Fixed an error that was setting water extraction to zero for the remainder of the simulation once it was set to zero once (water is not extracted if not available).

A.4 T2GGM Version 2.0

The changes made to GGM are as follows.

- Replacement of the relative humidity threshold with a linear relative humidity ramp.
- Implementation of an improved model for zero-saturation behaviour that limits saturated phase water consuming reactions at zero saturation.
- Run-time improvements through the decoupling of TOUGH2 and GGM time steps.

The changes made to TOUGH2 are as follows.

- Implementation of a multi-processor version of TOUGH2 called TOUGH2-MP and its interface with GGM.
- Implementation of an option to use an alternative geosphere gas such as CH_4, CO_2 or H_2 instead of air.

A.5 T2GGM Version 2.1

The changes from Version 2.0 to Version 2.1 affect the integration of TOUGH2 and GGM.

GGM was modelled to handle the conversion between the freshwater assumed by TOUGH2 and the saline water assumed by GGM by correcting for density and molar mass differences when passing water amounts between the two models. Modifications were made to improve the stability of T2GGM to small fluctuations in relative humidity.

APPENDIX B: GGE EXPERIMENTAL COMPARISON

B.1 Introduction

Data from the Finnish large scale Gas Generation Experiment (GGE) (Small et al. 2008) was chosen as a test case for GGM Version 2.0. This experiment has a number of features that make it suitable as a test case:

- Well characterized waste inventory;
- Highly instrumented resulting in a well-defined data set;
- Model input parameters outlined by Small et al. (2008); and
- Modelling carried out by Small et al. (2008) allows a model inter-comparison exercise and an experimental test case to be carried out simultaneously.

The modelling carried out by Small et al. (2008) uses a biogeochemical reaction-transport code called GRM. This models the transport of species under an imposed flow-field in saturated groundwater. The solute transport calculation is sequentially coupled to an equilibrium chemical speciation calculation using the PHREEQE source code.

Investigations have been carried out for the entire GGE and for individual waste drums. This note outlines the results of the initial comparisons between the GGM and the GGE experimental data.

B.2 GGM Input Parameters

Table B-1 provides the GGM input parameter values used for comparisons against results obtained from the entire GGE. The GGM driver program was set-up to use: a constant total gas pressure of 10^5 Pa, a constant saturation of 100%, a repository volume of 16.7 m^3 and an initial mass of water of 1.67×10^4 kg.

Table B-2 to Table B-5 provide the GGM parameters that were changed when modelling individual drums 1596021 (94% biodegradable), 1596023 (6% biodegradable), 1596025 (36% biodegradable) and 1596027 (37% biodegradable) of the GGE experiment. In addition, the repository volume and mass of water provided to the driver program when modelling individual drums was set to 0.2 m^3 and 200 kg respectively, corresponding to the volume and mass of water that fills a single drum.

The parameters used for the GGM simulations were generally the rate constants and other standard input parameters from T2GGM runs as documented in Walke et al. (2009), with the exception of the case-specific volumes and material characteristics.

Table B.1: GGM Input Parameters for Comparison Against the Full GGE

Input Variable Name	Description	Input Units	Input Values	Justification or Reference
Surface areas of metals				
PA1	Carbon and galvanized steel	m^2	96.5	Based on the total mass of metal of 379.4 kg, the density for C-steel below, and the assumption that the mean thickness of metal for both drums and waste is 1 mm (Small et al. 2008), multiplied by a factor of two to account for both sides of the waste forms and internal and external surfaces of the drum, all of which are assumed to be wetted. The calculated surface area of the drums alone (74.9 m^2, inner and outer surfaces) is consistent with the standard size of a 200-L drum.
PA2	Passivated carbon steel	m^2	0	Based on assumption that neither the drum materials nor the metallic wastes (assumed to also be represented by C-steel) were passivated at any time, despite the pH>9 for the first 4-5 years of the GGE. The assumption of active C-steel corrosion may be reasonable since the internal surfaces of the drum and the metallic wastes are unlikely to have been exposed to alkaline tank water due to the production of organic acids inside the drums.
PA3	Stainless steel and Ni-based alloys	m^2	0	Based on assumption that “acid-proof steel” tank does not contribute to gas generation and that metallic wastes can be categorized as C-steel, as per Small et al. (2008).
PA4	Zr alloys	m^2	0	Based on assumption of no fuel cladding waste in ILW.

Input Variable Name	Description	Input Units	Input Values	Justification or Reference
Biomass Decay				
PD	Biomass decay rate	a^{-1}	0.7	Section 3.6.6.4 (Walke et al. 2009).
Solubility constants				
PKCO2	CO_2	$mol\ L^{-1}\ MPa^{-1}$	6.9E-2	Table 3-22 (Walke et al. 2009).
PKH2	H_2	$mol\ L^{-1}\ MPa^{-1}$	1.6E-3	
PKH2S	H_2S	$mol\ L^{-1}\ MPa^{-1}$	1.1	
PKCH4	CH_4	$mol\ L^{-1}\ MPa^{-1}$	2.8E-3	
PKO2	O_2	$mol\ L^{-1}\ MPa^{-1}$	8.9E-3	
PKN2	N_2	$mol\ L^{-1}\ MPa^{-1}$	6.7E-3	
Effective molar mass of metals				
PM1	Mass of carbon and galvanized steel per mole of GGM iron	$kg\ mol^{-1}$	0.05585	Section 3.6.5.3 (Walke et al. 2009).
PM2	Mass of passivated carbon steel per mole of GGM iron	$kg\ mol^{-1}$	0.05585	
PM3	Mass of stainless steel and Ni-based alloys per mole of GGM iron	$kg\ mol^{-1}$	0.0562	
PM4	Mass of zirconium alloys per mole of GGM zirconium	$kg\ mol^{-1}$	0.09126	
CO_2 Enhanced corrosion				
PPRCO2	Reference partial pressure of CO_2 for enhancement of corrosion	MPa	0.05	Section 3.6.5.2 (Walke et al. 2009).

Input Variable Name	Description	Input Units	Input Values	Justification or Reference
Corrosion rate				
PR111	Carbon and galvanized steel Aerobic conditions Unsaturated conditions	µm a^{-1}	10.0	Table 3-24 (Walke et al. 2009).
PR112	Carbon and galvanized steel Aerobic conditions Saturated conditions	µm a^{-1}	30.0	Table C-1 (Walke et al. 2009).
PR121	Carbon and galvanized steel Anaerobic conditions Unsaturated conditions	µm a^{-1}	2.0	Table 3-24 (Walke et al. 2009).
PR122	Carbon and galvanized steel Anaerobic conditions Saturated conditions	µm a^{-1}	2.0	
PR211	Passivated carbon steel Aerobic conditions Unsaturated conditions	µm a^{-1}	0.1	Table 3-24 (Walke et al. 2009).
PR212	Passivated carbon steel Aerobic conditions Saturated conditions	µm a^{-1}	0.1	Table C-2 (Walke et al. 2009).
PR221	Passivated carbon steel Anaerobic conditions Unsaturated conditions	µm a^{-1}	0.1	Table 3-24 (Walke et al. 2009).

Input Variable Name	Description	Input Units	Input Values	Justification or Reference
PR222	Passivated carbon steel Anaerobic conditions Saturated conditions	$\mu m\ a^{-1}$	0.1	
PR311	Stainless steel and Ni-based alloys Aerobic conditions Unsaturated conditions	$\mu m\ a^{-1}$	0.1	Table 3-24 (Walke et al. 2009).
PR312	Stainless steel and Ni-based alloys Aerobic conditions Saturated conditions	$\mu m\ a^{-1}$	0.1	Table C-3 (Walke et al. 2009).
PR321	Stainless steel and Ni-based alloys Anaerobic conditions Unsaturated conditions	$\mu m\ a^{-1}$	0.1	Table 3-24 (Walke et al. 2009).
PR322	Stainless steel and Ni-based alloys Anaerobic conditions Saturated conditions	$\mu m\ a^{-1}$	0.1	
PR411	Zr alloys Aerobic conditions Unsaturated conditions	$\mu m\ a^{-1}$	0.01	Table 3-24 (Walke et al. 2009).
PR412	Zr alloys Aerobic conditions Saturated conditions	$\mu m\ a^{-1}$	0.01	Table C-4 (Walke et al. 2009).

Input Variable Name	Description	Input Units	Input Values	Justification or Reference
PR421	Zr alloys Anaerobic conditions Unsaturated conditions	µm a^{-1}	0.01	Table 3-24 (Walke et al. 2009).
PR422	Zr alloys Anaerobic conditions Saturated conditions	µm a^{-1}	0.01	
Rate constants for organic degradation				
PVCA	Cellulose under aerobic degradation	a^{-1}	1.5E-3	Table 3-25 (Walke et al. 2009).
PVCB	Cellulose under denitrification	a^{-1}	1.5E-3	
PVCC	Cellulose under ferric-ion reduction	a^{-1}	5.0E-4	
PVCD	Cellulose under sulphate reduction	a^{-1}	5.0E-4	
PVCE	Cellulose under methanogenesis	a^{-1}	5.0E-4	
PVRA	IX resins under aerobic degradation	a^{-1}	5.0E-4	
PVRB	IX resins under denitrification	a^{-1}	5.0E-4	
PVRC	IX resins under ferric-ion reduction	a^{-1}	5.0E-5	
PVRD	IX resins under sulphate reduction	a^{-1}	5.0E-5	

Input Variable Name	Description	Input Units	Input Values	Justification or Reference
PVRE	IX resins under methanogenesis	a^{-1}	5.0E-5	
PVPA	Plastics and rubbers under aerobic degradation	a^{-1}	5.0E-4	Assumed the same as for IX resins
PVPB	Plastics and rubbers under denitrification	a^{-1}	5.0E-4	
PVPC	Plastics and rubbers under ferric-ion reduction	a^{-1}	5.0E-5	
PVPD	Plastics and rubbers under sulphate reduction	a^{-1}	5.0E-5	
PVPE	Plastics and rubbers under methanogenesis	a^{-1}	5.0E-5	
PVFES	Rate constant for the precipitation of FeS	$s^{-`}$	15.0	Section 3.6.7.2 (Walke et al. 2009).
PVFEOO	Rate constant for the reductive dissolution of FeOOH	$s^{-`}$	1.0E-8	Section 3.6.7.3 (Walke et al. 2009).
PVMGO	Rate constant for the conversion of Magnesium Oxide to Magnesium Carbonate	s^{-1}	0.0	-
Rate constants for hydrogen kinetic reactions				
PVH1	Microbial oxidation of H_2 via iron reduction	a^{-1}	250	H_2 consumption is expected to be very fast. The values used here are consistent with Section 3.6.6.2 (QUINTESSA and GEOFIRMA 2011).
PVH2	Microbial oxidation of H_2 via sulphate reduction	a^{-1}	250	
PVH3	Microbial generation of methane	a^{-1}	250	

Input Variable Name	Description	Input Units	Input Values	Justification or Reference
Biomass yield coefficients				
PYA	Aerobic degradation	-	0.6	Table 3-26 (Walke et al. 2009).
PYB	Denitrification	-	0.5	
PYC	Ferric-ion reduction	-	0.23	
PYD	Sulphate reduction	-	0.23	
PYE	Methanogenesis	-	0.23	
Biomass recycling				
PKR	The fraction of dead biomass recycled as cellulose	-	0.9	Section 3.6.6.5 (Walke et al. 2009)
CO_2 Enhanced corrosion				
PE	Exponent for the enhancement of corrosion by CO_2	-	0.67	Section 3.6.5.2 (Walke et al. 2009).
Densities of metals				
PRO1	Carbon and galvanized steel	kg m^{-3}	7860	Section 3.4.1 (Walke et al. 2009) (Last paragraph).
PRO2	Passivated carbon steel	kg m^{-3}	7860	
PRO3	Stainless steel and Ni-based alloys	kg m^{-3}	8100	
PRO4	Zr alloys	kg m^{-3}	6500	
Miscellaneous				
PEMMA	The effective molar mass of air	g mol^{-1}	28.97	Section 3.6.7.1 (Walke et al. 2009).
PT	The repository temperature	°C	9.5	Small et al. (2008) state that 8 ^{o}C is maintained in water at bottom and 11 ^{o}C at top. This is an average.

Input Variable Name	Description	Input Units	Input Values	Justification or Reference
PRLIQ	The density of the liquid in the repository	kg m^{-3}	1000	Table 5-3 (Walke et al. 2009).
PMLIQ	The molar mass of the liquid in the repository	kg mol^{-1}	0.018	This is the molar mass of pure water at 20 ^{o}C.
Effective molar mass of the organic substrates				
PMORG1	Mass of actual cellulose per mole GGM cellulose	kg mol^{-1}	0.162	Section 3.6.6.1 (Walke et al. 2009) (Last two paragraphs).
PMORG2	Mass of actual IX resins per mole GGM styrene monomer	kg mol^{-1}	0.1508	
PMORG3	Mass of actual plastics and rubbers per mole GGM styrene monomer	kg mol^{-1}	0.104	
Initial concentrations				
PIQNO3	The initial quantity of nitrates	kg	1.0E-3	From Table 4, Small et al. (2008). Concentration 0.001 mol m^{-3}, multiplied by water volume 0.2 m^3 to get total number of moles, then by molar mass of NO^{3-} (62.0050 g mol^{-1}) to get total mass of nitrates.
PICSO4	The initial concentration of sulphates	kg m^{-3}	5.0E-2	Table 4 (Small et al. 2008).
PICFEO	The initial concentration of Fe(III)	mol m^{-3}	0	Table 4 (Small et al. 2008).
Initial gas partial pressures				
PIPO2	O_2	MPa	2.12E-2	Table 3-27 (Walke et al. 2009). Initial pressure H_2S assumed zero.
PIPCO2	CO_2	MPa	3.18E-5	

Input Variable Name	Description	Input Units	Input Values	Justification or Reference
PIPN2	N_2	MPa	7.91E-2	
PIPH2	H_2	MPa	5.07E-6	
PIPH2S	H_2S	MPa	0	
PIPCH4	CH_4	MPa	2.03E-7	
Initial masses of organic substrates				
PIMORG1	Cellulose	kg	620	Total mass of 'more reactive' cellulose from Table 3 of Small et al. (2008).
PIMORG2	IX resins	kg	0	-
PIMORG3	Plastics and rubbers	kg	596	Total mass of less reactive cellulose data from Small et al. (2008).
Initial quantities of metallic materials				
PIQ1	Carbon and galvanized steel	kg	379.4	Based on the total mass of drums + waste of 379.4 kg and effective molar mass for C-steel, PM1
PIQ2	Passivated carbon steel	kg	0	See comment for PA2.
PIQ3	Stainless steel and Ni-based alloys	kg	0	See comment for PA3.
PIQ4	Zr alloys	kg	0	See comment for PA4.
Initial amounts of biomass species				
PIXA	Aerobes	mol	0	Since degradation rates are decoupled from biomass concentrations, these initial values can be set to zero.

Input Variable Name	Description	Input Units	Input Values	Justification or Reference
PIXB	Denitrifiers	mol	0	Since degradation rates are decoupled from biomass concentrations, these initial values can be set to zero.
PIXC	Iron reducers	mol	0	Since degradation rates are decoupled from biomass concentrations, these initial values can be set to zero.
PIXD	Sulphate reducers	mol	0	Since degradation rates are decoupled from biomass concentrations, these initial values can be set to zero.
PIXE	Methanogens	mol	0	Since degradation rates are decoupled from biomass concentrations, these initial values can be set to zero.
Initial amounts of other materials				
PIQFEC	$FeCO_3$	mol	0	
PIQFE3	Fe_3O_4	mol	0	
PIQFES	FeS	mol	0	
PIQMGO	MgO	mol	0	
Timestep and output control				
PEPS	Specifies the maximum fractional change allowed in a differential variable per time step. Controls the maximum timestep reported to TOUGH2.	-	0.01	See Section 8.6.7.

Input Variable Name	Description	Input Units	Input Values	Justification or Reference
PEPSC	The cut-off value below which differential variables are not used to control the suggested timestep.	mixed	1.0E-18	See Section 8.6.7.
PEPSR	The cut-off value below which the rate of a differential variable is not used to control the suggested timestep.	mixed	1.0E-30	See Section 8.6.7.
LOGTR	Log base 10 of the ratio of times of subsequent writes to the output file. The next output time occurs at approximately (last output time)*10^(LOGTR), and allows output to be generated with a resolution suitable for plotting on a logarithmic scale, consistent with the way it is usually displayed.	-	1.0E-3	-
PMINSAT	The saturation below which the water consuming reactions are controlled to prevent them from drawing water into the repository.	-	1.0E-10	-
PHUM	T or F. (True or false) Specifies whether relative humidity dependent behaviour is enabled.	-	F	-

Input Variable Name	Description	Input Units	Input Values	Justification or Reference
PRHMIN	A Relative Humidity value (fractional) below which all vapour phase corrosion and microbial reactions are modelled as having ceased	-	0.6	Section 3.6.5.4 (QUINTESSA and GEOFIRMA 2011).
PRHMAX	A Relative Humidity value (fractional) above which all vapour phase corrosion and microbial reactions are modelled as fully active.	-	0.8	Section 3.6.5.4 (QUINTESSA and GEOFIRMA 2011).
PHTYPE	The type of relative humidity modulation function to use. An integer. Can currently only be 1 = linear.	-	1	-

Table B.2: Drum 1596021 Specific GGM Input Parameters

Input Variable Name	Description	Input Units	Input Values	Justification or Reference
Surface areas of metals				
PA1	Carbon and galvanized steel	m^2	4.7	Based on the same assumptions as for the Entire GGE simulation, but pro-rated for a single drum containing no metallic waste.
Initial concentrations				
PIQNO3	The initial quantity of nitrates	kg	1.2E-5	See Table 4, Small et al. (2008). Concentration 0.001 mol m^{-3}, multiplied by water volume 0.2 m^3 to get total number of moles, then by molar mass of NO^{3-} (62.0050 g mol^{-1}) to get total mass of nitrates.
Initial masses of organic substrates				
PIMORG1	Cellulose	kg	77	Table 3 (Small et al. 2008).
PIMORG3	Plastics and rubbers	kg	5	Table 3 (Small et al. 2008).
Initial quantities of metallic materials				
PIQ1	Carbon and galvanized steel	kg	18.4	Based on a mass of 18.4 kg for Drum 1596021 (Table 3 from Small et al. (2008)) and the effective molecular mass given above.

Table B.3: Drum 1596023 Specific GGM Input Parameters

Input Variable Name	Description	Input Units	Input Values	Justification or Reference
Surface areas of metals				
PA1	Carbon and galvanized steel	m^2	6.2	Based on the same assumptions as for the Entire GGE simulation, but pro-rated for a single drum containing 4 kg metallic waste.
Initial concentrations				
PIQNO3	The initial quantity of nitrates	kg	1.2E-5	See Table 4, Small et al. (2008). Concentration 0.001 mol m^{-3}, multiplied by water volume 0.2 m^3 to get total number of moles, then by molar mass of NO^{3-} (62.0050 g mol^{-1}) to get total mass of nitrates.
Initial masses of organic substrates				
PIMORG1	Cellulose	kg	6	See Table 3 of Small et al. (2008).
PIMORG3	Plastics and rubbers	kg	37	See Table 3 of Small et al. (2008).
Initial quantities of metallic materials				
PIQ1	Carbon and galvanized steel	kg	24.4	Based on a mass of 22.4 kg for Drum 1596023 (Table 3, Small et al. 2008) and the effective molecular mass given above.

Table B.4: Drum 1596025 Specific GGM Input Parameters

Input Variable Name	Description	Input Units	Input Values	Justification or Reference
Surface areas of metals				
PA1	Carbon and galvanized steel	m^2	4.9	Based on the same assumptions as for the Entire GGE simulation, but pro-rated for a single drum containing 1 kg metallic waste.
Initial concentrations				
PIQNO3	The initial quantity of nitrates	kg	1.2E-5	See Table 4, Small et al. (2008). Concentration 0.001 mol m^{-3}, multiplied by water volume 0.2 m^3 to get total number of moles, then by molar mass of NO^{3-} (62.0050 g mol^{-1}) to get total mass of nitrates.
Initial masses of organic substrates				
PIMORG1	Cellulose	kg	44	See Table 3, Small et al. (2008).
PIMORG3	Plastics and rubbers	kg	45	See Table 3, Small et al. (2008).
Initial quantities of metallic materials				
PIQ1	Carbon and galvanized steel	kg	19.4	Based on a mass of 19.4 kg for Drum 1596025 (Table 3, Small et al. 2008) and the effective molecular mass given above.

Table B.5: Drum 1596027 Specific GGM Input Parameters

Input Variable Name	Description	Input Units	Input Values	Justification or Reference
Surface areas of metals				
PA1	Carbon and galvanized steel	m^2	5.2	Based on the same assumptions as for the Entire GGE simulation, but pro-rated for a single drum containing 2 kg metallic waste.
Initial concentrations				
PIQNO3	The initial quantity of nitrates	kg	1.2E-5	See Table 4, Small et al. (2008). Concentration 0.001 mol m^{-3}, multiplied by water volume 0.2 m^3 to get total number of moles, then by molar mass of NO^{3-} (62.0050 g mol^{-1}) to get total mass of nitrates.
Initial masses of organic substrates				
PIMORG1	Cellulose	kg	38	See Table 3, Small et al. (2008).
PIMORG3	Plastics and rubbers	kg	38	See Table 3, Small et al. (2008).
Initial quantities of metallic materials				
PIQ1	Carbon and galvanized steel	kg	20.4	Based on a mass of 20.4 kg for Drum 1596027 (Table 3, Small et al. 2008) and the effective molecular mass given above.

B.2 Model Results for the Entire GGE

The total volume of gas generated by GGM is in good agreement with the total volume recorded from the GGE (Figure B.1). The apparent agreement in the GGE and GGM gas generation curves being in part due to the fact that there is a greater lag in the experimental data (Figure B.1). The lag in the experimental data is likely to be due the consumption of oxygen trapped within the system which results in a net loss of gas due to the greater solubility of carbon dioxide when compared to oxygen. Such lags in initial gas generation are common in gas generation experiments (Beadle 2001, Beadle 2002).

Differences between modelled and experimental data are clearer, when gas composition data is compared (Figure B.2 and Figure B.3). In the modelled profiles (Figure B.2) hydrogen dominates, where as in the experimental data methane is the dominant gas (Figure B.3) with hydrogen only detected in the initial two years of the experiment. GGM models the conversion of hydrogen to methane using sulphate and carbon dioxide as an electron acceptor:

$$4H_2 + SO_4^{2-} + 2H^+ \rightarrow H_2S + 4H_2O \quad \text{hydrogen oxidation via sulphate reduction} \quad (B.1)$$

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \quad \text{methane generation from hydrogen oxidation} \quad (B.2)$$

The low level of hydrogen metabolism within GGM runs appears to be due to the low availability of sulphate and carbon dioxide. Given low initial sulphate concentrations, the most obvious route for increased hydrogen metabolism is via greater carbon dioxide availability. GGM generates low levels of carbon dioxide which agrees with the experimental data. Hydrogen and carbon dioxide are converted to methane in a 4:1 ratio, Equation (B.2), resulting in lower levels of carbon dioxide being required to metabolize the excess hydrogen in the system. Investigation of the other carbon containing species within the model indicates that carbon is being held up in three forms, i.e., live biomass, dead biomass and $FeCO_3$ (Figure B.4). Only live biomass contains sufficient carbon to meet the carbon dioxide deficit needed to oxidize the excess hydrogen in the system. Consequently, an increase in microbial death rate might result in more carbon dioxide available within the system.

However, since the conversion of hydrogen to methane results in a net reduction of the overall number of moles of gas generated (Equation (B.2)), providing sufficient carbon dioxide to remove the hydrogen modelled by GGM would result in an overall reduction in the volume of gas generated and an associated loss of fit between experimental and modelled total gas volumes. In Figure B-1 the “Original Degradation Rate” shows the theoretical total volume of gas if sufficient additional carbon dioxide was available to convert the remaining hydrogen to methane.

In order to reduce the levels of hydrogen while maintaining the overall levels of gas, additional carbon dioxide and methane is required. The only source of additional carbon dioxide and methane within the model is via an increase in the degradation of polymeric waste components, i.e., cellulose and/or plastics. This implies that the actual degradation rate of these waste components within the GGE is greater than that employed in these initial model runs.

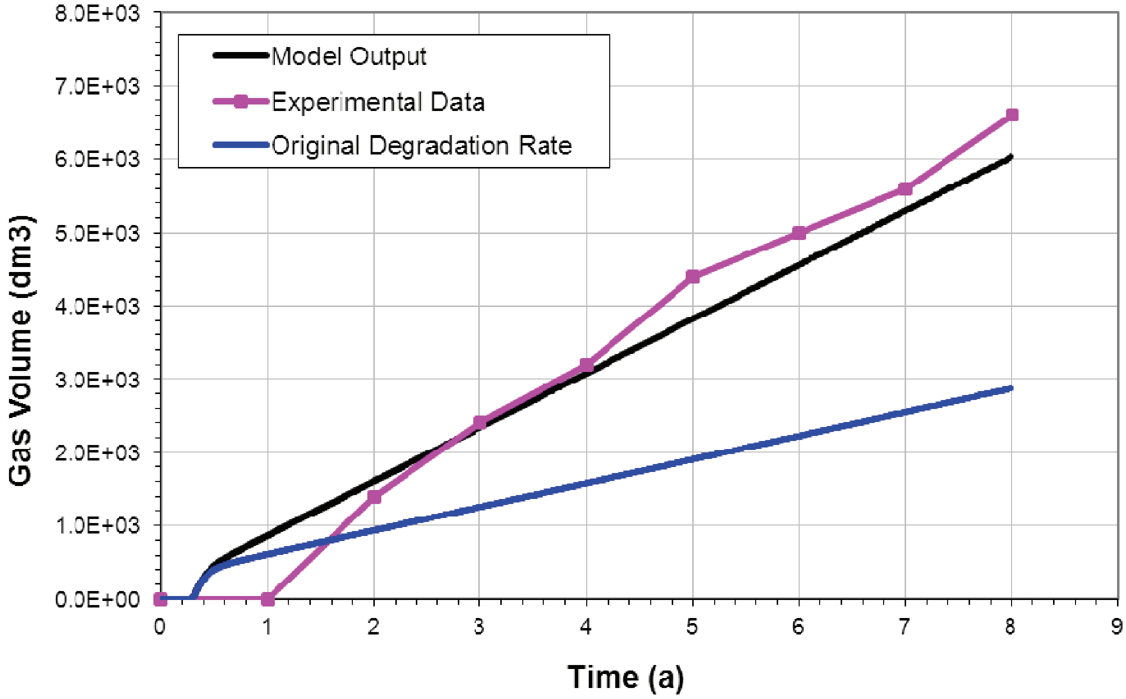

Figure B.1: Modelled and Experimental Total Gas Volumes

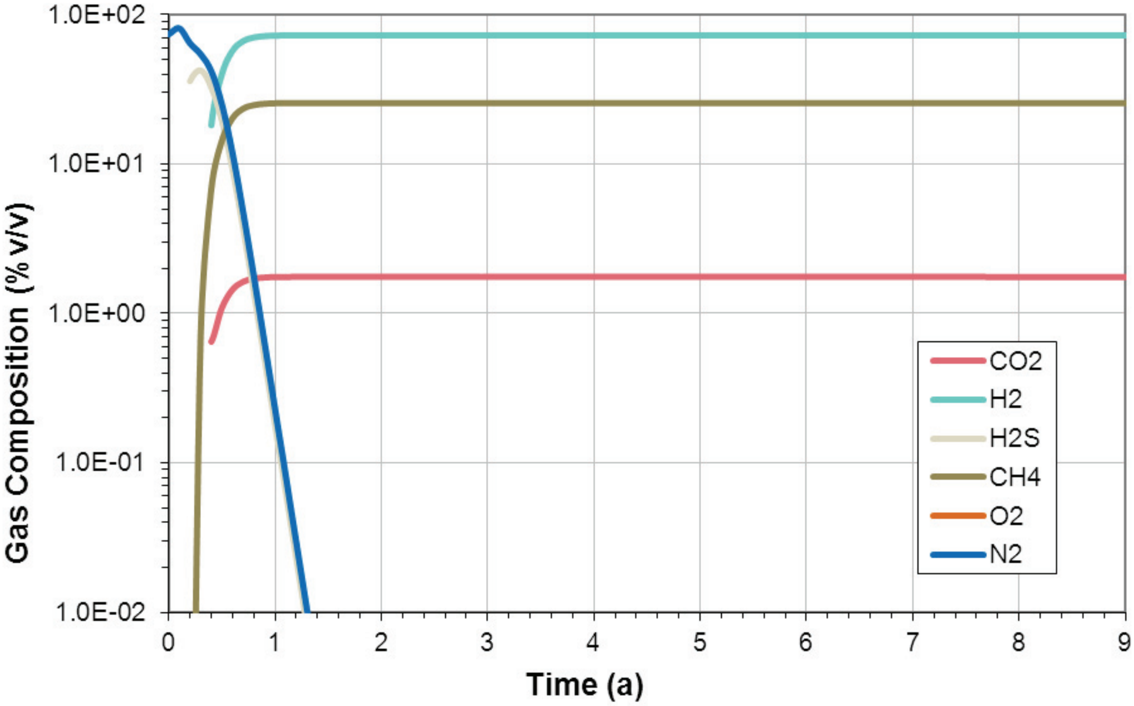

Figure B.2: Modelled Gas Composition Evolution

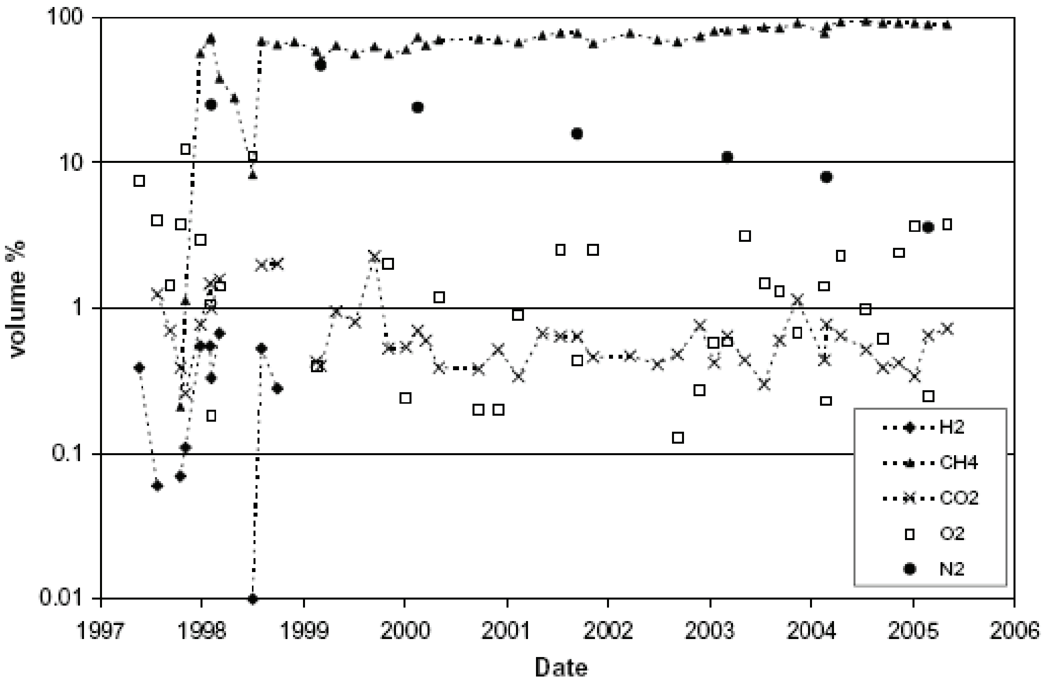

Figure B.3: GGE Gas Composition Evolution (Small et al. 2008)

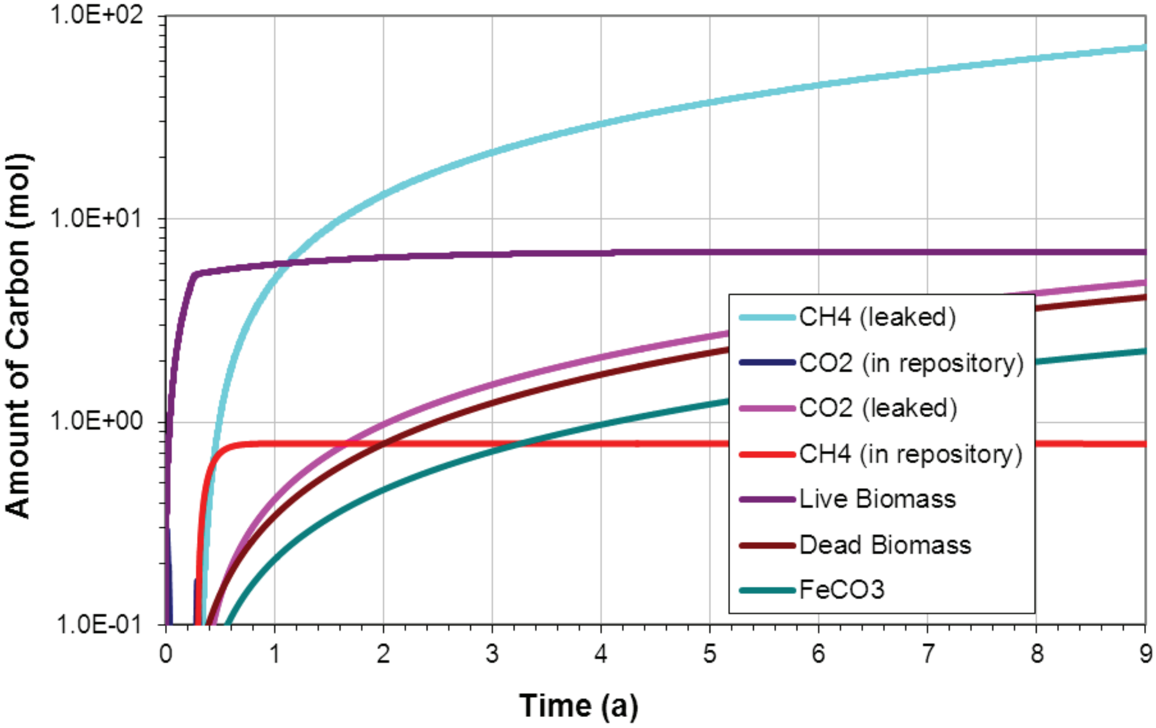

Figure B.4: Carbon Partitioning within the GGM Run

B.2.1 Model Runs with an Increased Cellulose Degradation Rate

In order to increase the availability of carbon dioxide and methane within the system, the cellulose degradation rate was increased fivefold. This increase in cellulose degradation rate resulted in a similar overall fit between modelled and experimental gas generation data to that seen with the original cellulose degradation rate (Figure B.5). The major difference between modelled and experimental data is the lack of a lag in bulk gas generation. The experimental data has a lag period of approximately a year before significant gas generation takes place.

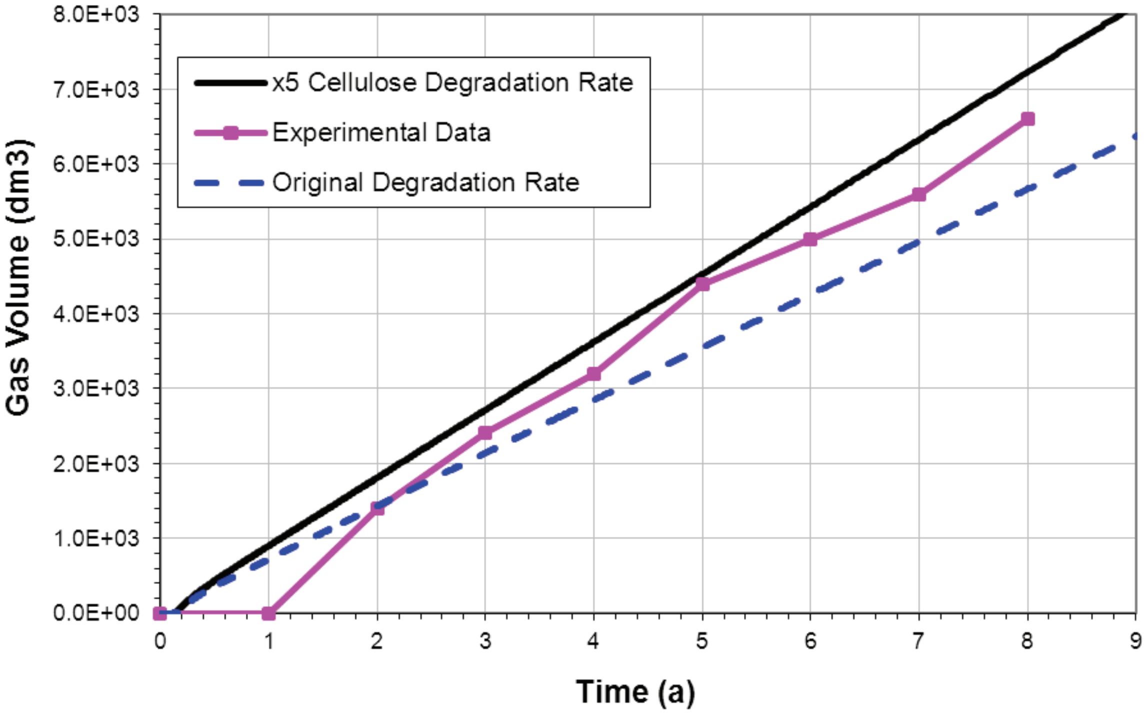

Figure B.5: Revised Modelled and Experimental Total Gas Volumes

This increase in cellulose degradation rate has also improved the agreement between modelled and experimental gas composition data (c.f. Figure B.3 and Figure B.6). The gas generated within the model is dominated by methane which is in agreement with the GGE data. There is also an absence of hydrogen within the GGM simulation which agrees with GGE in that significant hydrogen concentrations were only detected for approximately the first 2 years of operation, after which no further hydrogen was detected.

This is likely to be due to a combination of events including the time taken by the hydrogen consuming microbial populations within the experiment to become established. This is a process which is not modelled by GGM and consequently the model is not able to simulate these early stages of the experiment.

The GGM output overestimates the amount of carbon dioxide within the experiment (compare Figure B.3 and Figure B.6) with GGM predicting a carbon dioxide level of approximately 20% (Figure B.6) whereas the experimental data indicates a lower level between 0.1 and 1% (Figure B.3). This lack of agreement between GGM and the experimental data may be due to GGM not modelling the generation of a full range of carbonate species within the GGE. This is reflected by the more comprehensive geochemical simulations performed by the GRM code generating a better agreement with experimental carbon dioxide levels.

Experimental data from the GGE also shows significant levels of both oxygen and nitrogen (Figure B.3) persisting throughout the experiment, whereas these gases are either consumed (oxygen) or diluted out of the GGM simulations within the first 2 years of the simulation (Figure B.6). However, as Small et al. (2008) points out: “It is suspected that the O_2 and N_2 present in the headspace mainly represent trapped air, such as within plastic bags, which is isolated from the predominant anaerobic regions of the waste until it is released”. The trapping of oxygen and nitrogen within the waste packages cannot be simulated by GGM, which explains the observed discrepancy between modelled and experimental data.

The only other gas considered by GGM is hydrogen sulphide. This was not observed in the simulation (Figure B.6) nor detected in the GGE head space analysis (Figure B.3) (Small et al. 2008). The lack of hydrogen sulphide in the GGE headspace is likely to reflect the reactivity of the gas in an anaerobic environment with significant amounts of metals.

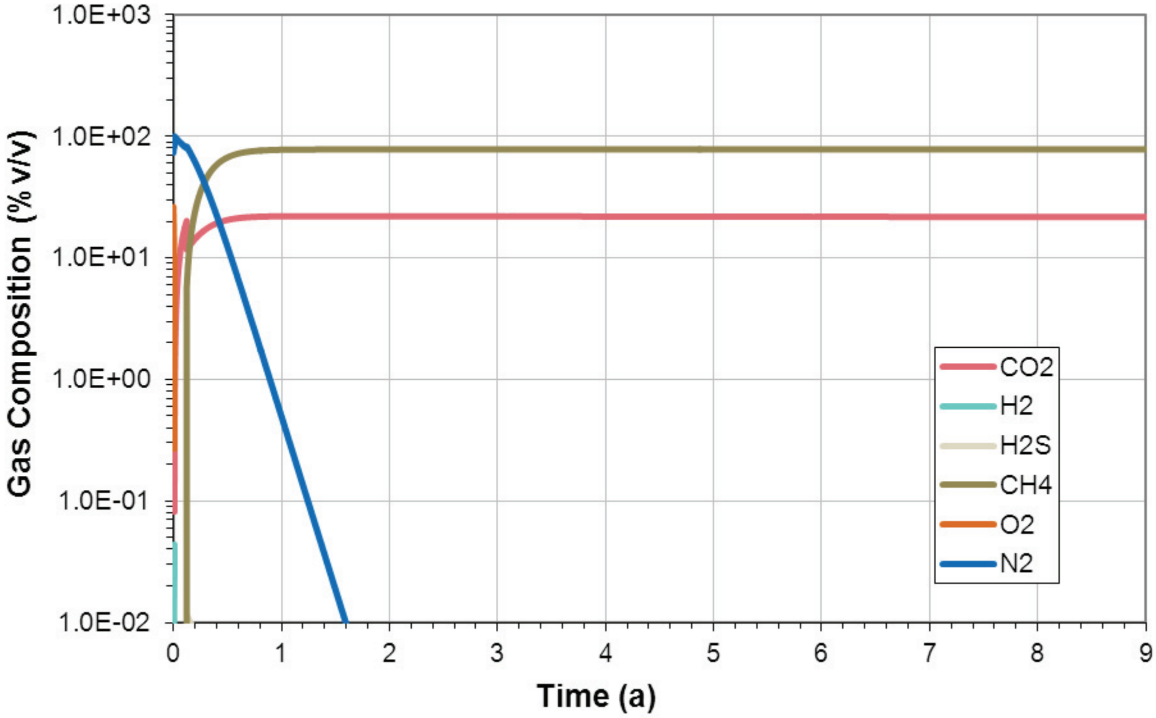

Figure B.6: Revised Modelled Gas Composition Profiles

B.3 Model Results for the Individual Drums

A number of individual waste drums within the GGE are instrumented allowing individual data sets to be collated. Four of these drums were modelled by GGM (Table B.6), providing a high cellulose, a low cellulose and two intermediate cellulose cases. Time dependent data (such as volume of gas generated, percentage volume of gas components, pH and aqueous concentration) for nitrate, sulphate and microbial load are available for these drums.

Table B.6: Individual Drum Inventories

Drum Id	Metal (kg)	Cellulose (kg)	Plastics & Rubber (kg)	Total (kg)
1596021	18.4	77	5	100.4
1596023	24.4	6	37	67.4
1596025	19.4	44	45	108.4
1596027	20.4	37	38	96.4

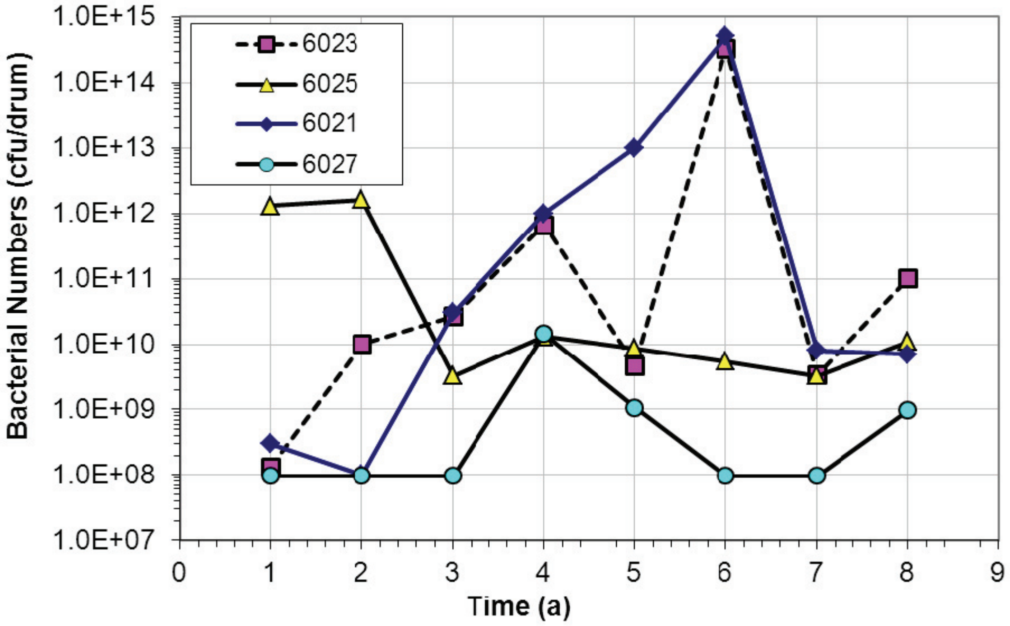

Figure B.7: Microbial Biomass Levels in Specified Waste Drums

B.3.1 Microbial Load

GGE data is available on the microbial load in each of the individual drums is expressed in terms of colony forming units (cfu) per mg. In order to make a comparison with GGM output, GGE data was converted to cfu per drum (Figure B.7) using the total waste inventories of each drum (Table B.6). For comparison purposes GGM output was converted to the same units using a mass value per microbial cell of $9.5x10^{-13}$ g (Neidherdt et al. 1990), the same value as that used by Small et al. (2008). The experimental data exhibits considerable variability. This may reflect the fact that as the GGE environment matures, the microbial population becomes dominated by obligate anaerobes which are more difficult to culture.

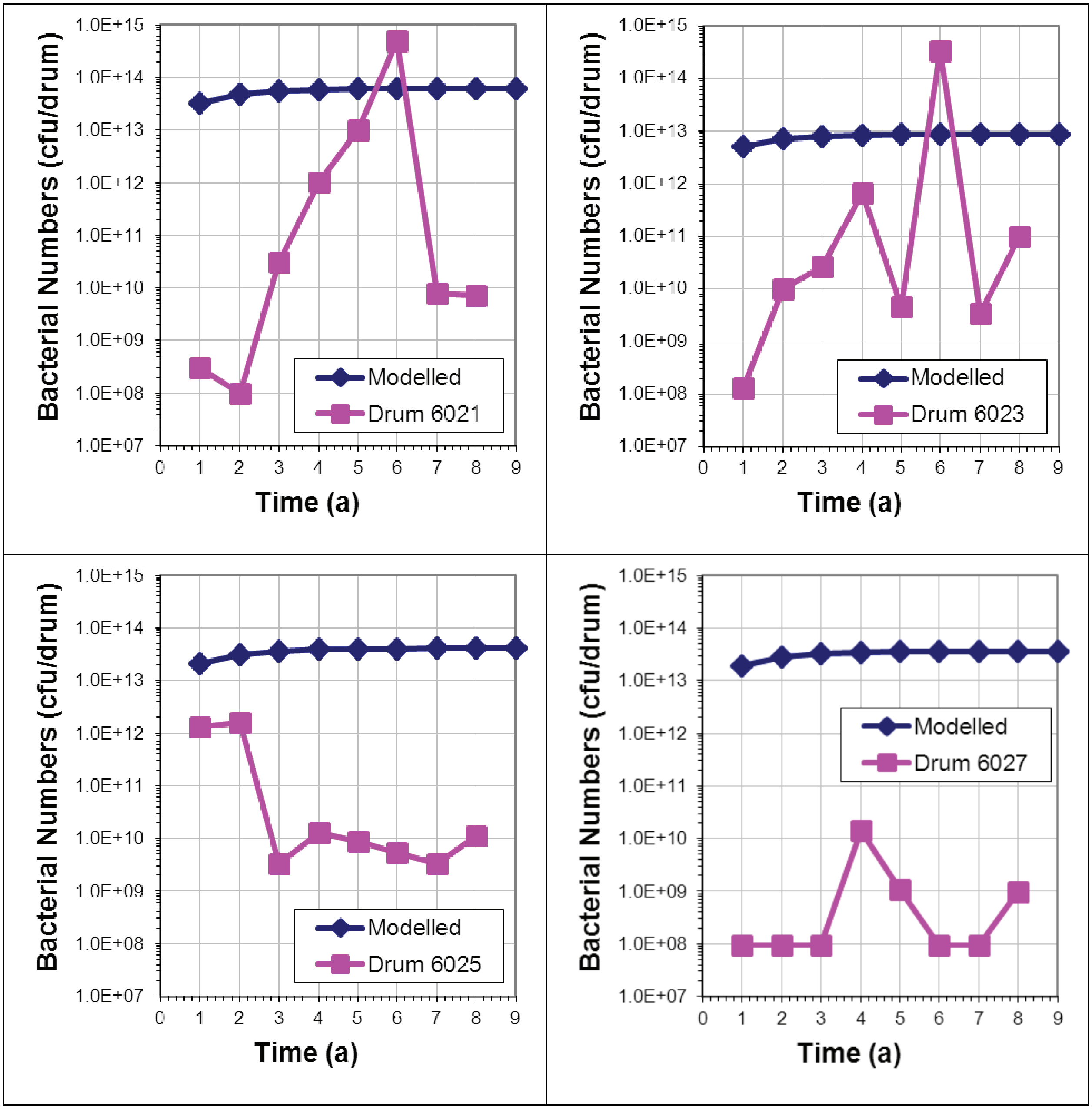

Figure B.8: Modelled and Experimental Bacterial Numbers

GGM predicted higher microbial populations than measured in the drums (Figure B.8, a-d), with a more constant level across the period modelled. However, it is recognized that only a fraction of environmental microorganisms are culturable (<1% to <0.1%, Tanner 2007, and Hallbeck and Pedersen 2008). The lack of fit between modelled and experimental levels of microbial biomass, may also be due to the dominance of anaerobes (methanogens in GGM, Figure B.9), a group that is difficult to culture.

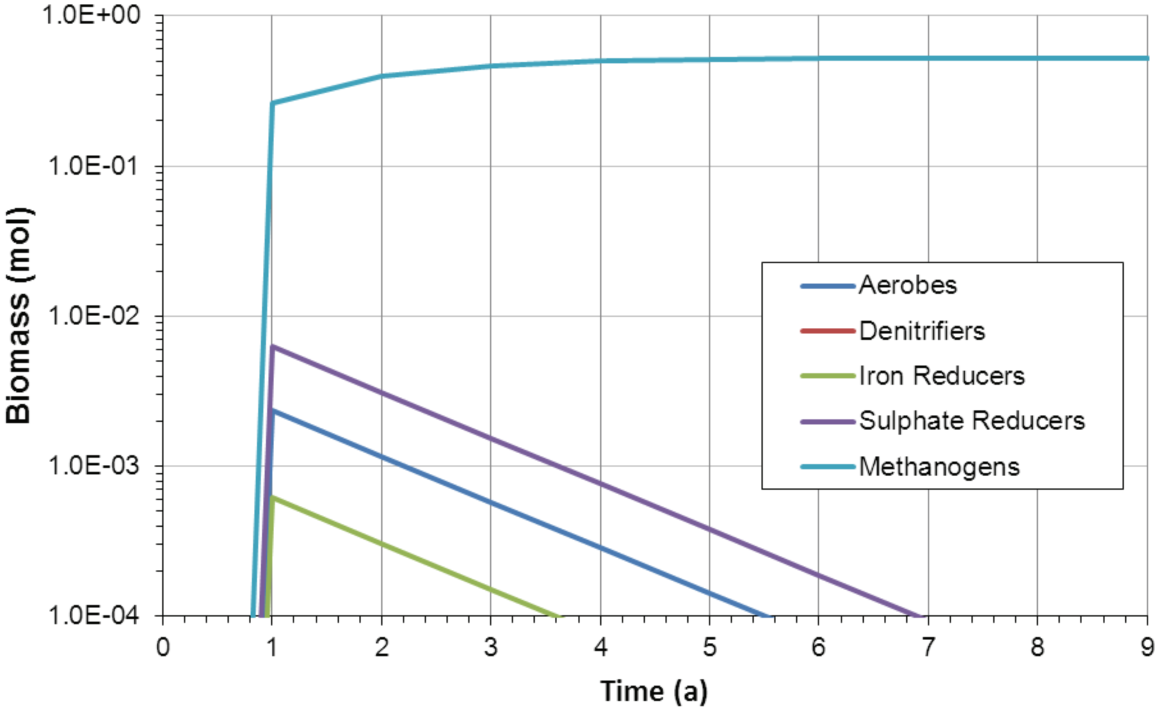

Figure B.9: Evolution of Microbial Groups During GGM Simulations of Waste Drums

B.3.2 Nitrate and Sulphate Levels

The evolution of nitrate and sulphate levels in GGE drums containing low and high cellulose levels are published by Small et al. (2008). However, as pointed out by Small et al., the levels of nitrate and sulphate found in the waste drums is greater than that present in the water initially used to saturate the GGE, suggesting that they are present in the waste used in the experiment. Since the GGM simulations utilize the levels of nitrate and sulphate in the water as input parameters, GGM models a much more rapid loss of both nitrate and sulphate than is seen in the data for the individual waste drums. The absence of detailed nitrate and sulphate inventories for individual waste drums means that more accurate modelling is not possible.

B.3.3 Gas Generation from Individual Waste Drums

Although experimental gas generation data from individual waste drums is not available, the relationship between gas generation and cellulose levels in individual drums was investigated by Small et al. (2008). They demonstrated a linear relationship between carbon dioxide generation and mass of cellulose present in the individual waste drums (Figure B.10) based on GRM simulations. A similar linear relationship was found in the GGM simulations of individual waste drums (Figure B.11); however, in this case the slope of the line is steeper. The difference between the two model outputs is due to the fact that the GRM model produces higher levels of hydrogen than the GGM model.

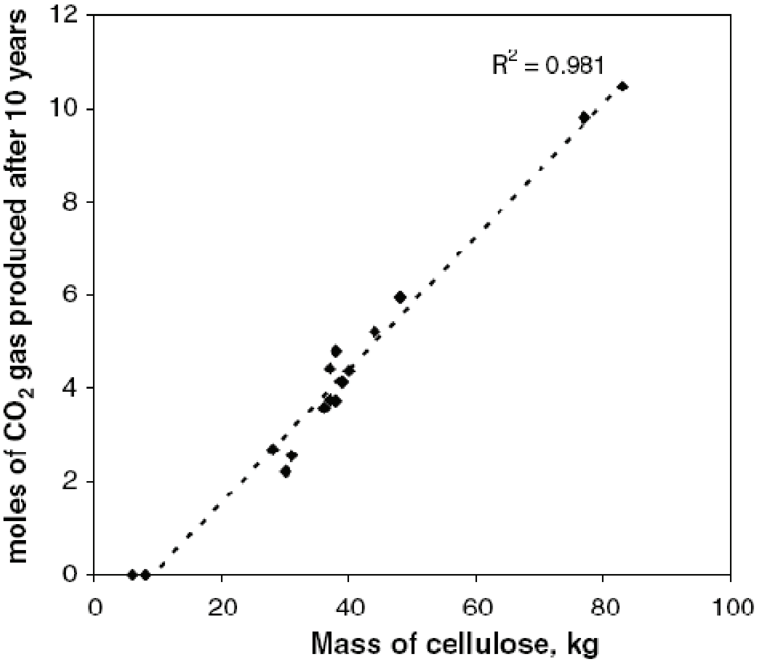

Figure B.10: Relationship Between Carbon Dioxide Generation and Waste Drum Cellulose Inventory in GRM Runs

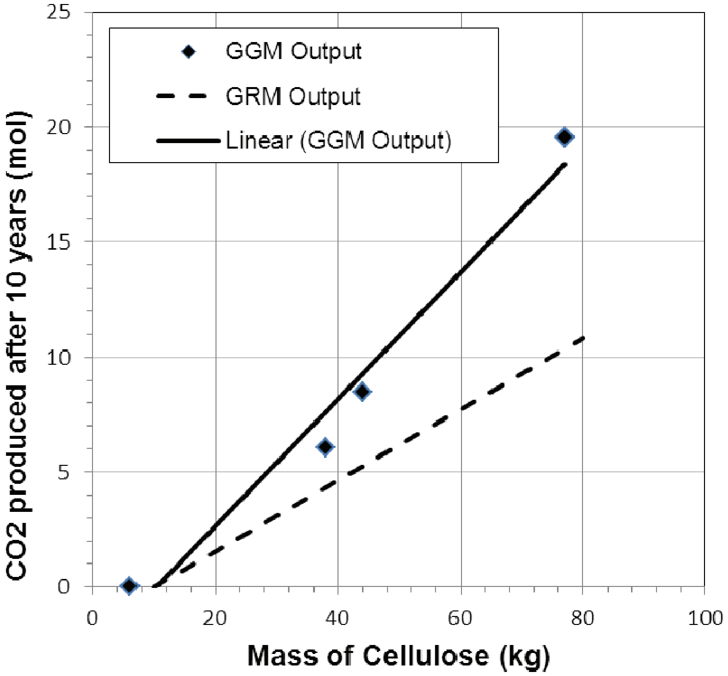

Figure B.11: Relationship Between Carbon Dioxide Generation and Waste Drum Cellulose Inventory in GGM Runs

B.4 Conclusions

The results of this comparison indicate a general agreement between the predictions of GGM and a relevant large-scale experiment over a several year period. GGM is a relatively simple model that is intended to represent the long-term response. In this comparison, the results of GGM, using the default reaction rate parameters, reasonably estimate (or bound) the total gas amounts produced.

B.5 References

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