A Survey of Reactive Metal Corrosion Data for Use in the SMOGG Gas Generation Model

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Preface

This report has been prepared by Serco under contract to Nirex and forms part of an ongoing programme of research commissioned by Nirex to underpin the long-term safety of a geological disposal facility for higher-activity radioactive wastes. Before it was published Nirex was subsumed into the NDA.

The report has been reviewed by NDA. However, references to Nirex in the text have been retained as they are appropriate for the period when this research was being performed. The views expressed and the conclusions drawn in this report are those of Serco and do not necessarily represent those of Nirex or the NDA.

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Abstract

The potential for gas generation from waste packages forms part of the assessment of the safety of geological disposal of intermediate-level and certain low-level radioactive wastes. Gas is expected to be produced by corrosion of metals, radiolysis of materials containing hydrogen (e.g. water), and microbial degradation of organic materials.

To address this issue, United Kingdom Nirex Limited commissioned Serco to develop a modelling tool for use in packaging proposal and safety assessment studies. The tool is called SMOGG (Simplified Model of Gas Generation), and considers gas generation from radioactive wastes in the UK National Inventory.

To carry out realistic calculations with SMOGG, it is necessary to parameterise the model with appropriate data for the corrosion rates of metals.

This report identifies the various corrosive environments that could be experienced by cement encapsulated metal wastes during their long-term management, and for each environment compiles relevant corrosion rate data for the reactive metals Magnox, aluminium and uranium from the literature. Where appropriate, these experimental data are used to calibrate the SMOGG corrosion model. Finally, parameters recommended for use in the SMOGG corrosion model for the reactive metals Magnox, aluminium and uranium are selected and tabulated.
Executive Summary

The potential for gas generation from waste packages forms part of the assessment of the safety of geological disposal of intermediate-level and certain low-level radioactive wastes. Gas is expected to be produced by corrosion of metals, radiolysis of materials containing hydrogen (e.g. water), and microbial degradation of organic materials.

To address this issue, Nirex commissioned Serco to develop a modelling tool for use in packaging proposal and safety assessment studies. The tool is called SMOGG (Simplified Model of Gas Generation), and considers gas generation from radioactive wastes in the UK National Inventory.

To carry out realistic calculations with SMOGG, it is necessary to parameterise the model with appropriate data for the corrosion rates of metals. A common feature exhibited by metal corrosion is a relatively high initial corrosion rate, which reduces over time to a long-term steady or slightly decreasing rate. The first phase may be considered as a period of "acute" corrosion and the long-term slower rate of corrosion as a period of "chronic" corrosion. SMOGG allows separate rates of corrosion to be specified for the acute and chronic phases. These corrosion rates are assumed to decrease exponentially with a time constant referred to as the characteristic time. The corrosion rates also may depend on temperature.

The reactive metals Magnox, aluminium and uranium may be present in some cement encapsulated wastes, and will corrode under aerobic and anaerobic alkaline conditions. Magnox and aluminium will corrode and generate hydrogen, and under anaerobic conditions uranium also will produce hydrogen.

This report identifies the various corrosive environments that could be experienced by these encapsulated metal wastes during their long-term management (i.e. during surface storage and transportation, and then in a deep geological repository, both before and after resaturation with a groundwater that could have a high chloride concentration). For each environment, relevant corrosion rate data for Magnox, aluminium and uranium were compiled from the literature. The effects on the corrosion rates of a number of variables (including oxygen concentration, temperature and chloride concentration) were considered.

These experimental data are reviewed critically, and, where appropriate, are used to calibrate the SMOGG corrosion model. From this information, parameters recommended for use in the SMOGG corrosion model for the reactive metals Magnox, aluminium and uranium are selected.

The parameters recommended for use in SMOGG for Magnox corrosion are:

- An initial acute corrosion rate of 2.52 µm a⁻¹ at 20°C.
- A characteristic time for the acute corrosion of 0.790a.
- An acute corrosion rate that increases with temperature according to an Arrhenius relationship:

\[
\exp \left[ - \frac{69000}{8.314472 \left( \frac{1}{T} - \frac{1}{293.15} \right)} \right]
\]

where \( T \) is the temperature [K].
- An initial chronic corrosion rate of 0.12 µm a⁻¹ at 20°C.
• A characteristic time for the chronic corrosion that essentially is infinite (making the rate constant).

• A chronic corrosion rate that increases with temperature according to an Arrhenius relationship:

\[
\exp \left[ -\frac{94000}{8.314472} \left( \frac{1}{T} - \frac{1}{293.15} \right) \right]
\]

• A corrosion rate that is independent of oxygen concentration.

• Initial acute and chronic corrosion rates that increase in the presence of significant chloride concentrations by a factor of 100. (The corrosion may be limited by local restrictions on the supply of water.)

The parameters recommended for use in SMOGG for aluminium corrosion are:

• An initial acute corrosion rate of 15,300 µm a\(^{-1}\).
• A characteristic time for the acute corrosion of 0.001a.
• An acute corrosion rate that is independent of temperature.
• An initial chronic corrosion rate of 24.5 µm a\(^{-1}\).
• A characteristic time for the chronic corrosion that is infinite, by assumption (making the rate constant).
• A chronic corrosion rate that is independent of temperature.
• A corrosion rate that is independent of oxygen and chloride concentrations.

The parameters recommended for use in SMOGG for uranium corrosion are:

(a) Aerobic conditions

• There is no identifiable phase of acute corrosion.
• An initial chronic corrosion rate (including an enhancement factor of 2 to accommodate the effect of irradiated metal fuel) of 1.58 µm a\(^{-1}\) at 20°C.
• A characteristic time for the chronic corrosion that essentially is infinite (making the rate constant).
• A chronic corrosion rate that increases with temperature according to an Arrhenius relationship:

\[
\exp \left[ -\frac{76900}{8.314472} \left( \frac{1}{T} - \frac{1}{293.15} \right) \right]
\]

(b) Anaerobic conditions

• There is no identifiable phase of acute corrosion.
• An initial chronic corrosion rate (including an enhancement factor of 2 to accommodate the effect of irradiated metal fuel) of 68.2 µm a\(^{-1}\) at 20°C.

• A characteristic time for the chronic corrosion that essentially is infinite (making the rate constant).

• A chronic corrosion rate that increases with temperature according to an Arrhenius relationship:

\[
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1 Introduction

The potential for gas generation from waste packages forms part of the assessment of the safety of geological disposal of intermediate-level (ILW) and certain low-level (LLW) radioactive wastes [1, 2]. Gas is expected to be produced by corrosion of metals, radiolysis of materials containing hydrogen e.g. water, and microbial degradation of organic materials.

To be able to address this issue, United Kingdom Nirex Limited commissioned Serco to develop a modelling tool for use in packaging proposal and safety assessment studies. The tool is called SMOGG (Simplified Model of Gas Generation) [3, 4], and considers gas generation from radioactive wastes in the UK National Inventory.

To carry out realistic calculations with SMOGG, it is necessary to parameterise the model with appropriate data for the corrosion rates of metals.

The reactive metals Magnox, aluminium and uranium may be present in some cement encapsulated wastes, and will corrode under aerobic and anaerobic alkaline conditions. Magnox and aluminium will corrode and generate hydrogen, and under anaerobic conditions uranium also will produce hydrogen.

This report identifies the various environments that could be experienced by these encapsulated metal wastes during their long-term management (i.e. during surface storage and transportation, and then in a geological repository, both before and after re-saturation with a groundwater that could have a high chloride concentration). For each environment, relevant corrosion rate data for Magnox, aluminium and uranium were compiled from the literature. The effects on the corrosion rates of a number of variables (including oxygen concentration, temperature and chloride concentration) were considered.

The experimental data are reviewed critically, and, where appropriate, are used to calibrate the SMOGG corrosion model. From this information, parameters recommended for use in the SMOGG corrosion model for the reactive metals Magnox, aluminium and uranium are selected.

Section 2 of this report describes the SMOGG corrosion model. The six sections that follow discuss the corrosion of Magnox, aluminium and uranium. Sections 3, 5 and 7 review the corrosion rate data for Magnox, aluminium and uranium respectively. Within each of these main sections there are sub-sections giving:

- a summary of information about the corrosion mechanisms for the metal; and
- corrosion rate data under a range of relevant conditions.

Sections 4, 6 and 8 select the parameters recommended for use in the SMOGG corrosion model for the reactive metals Magnox, aluminium and uranium respectively. Where appropriate, the experimental data are used to calibrate the SMOGG corrosion model. Finally, Section 9 summarises the parameters. (A companion report considers the corrosion rates of carbon steel, stainless steel and Zircaloy [5].)

This work was prepared by Serco Technical Consulting Services under contract to United Kingdom Nirex Limited (Nirex). The main technical work reported here was carried out initially in the period 1993 to 1997, but the literature review was updated and the data were reassessed in the period July 2006 to August 2006. The work forms part of the Nirex research programme. The information has been verified under arrangements established by Serco Technical Consulting Services. These arrangements have been approved by Nirex and are consistent with ISO 9001.
The views expressed and the conclusions reached are those of Serco Technical Consulting Services and do not necessarily represent those of Nirex or the NDA.
2 Corrosion of Reactive Metals

This section begins (see Subsections 2.1) by describing the SMOGG corrosion model for the reactive metals Magnox, aluminium and uranium. Next, Subsection 2.2 identifies the various environmental conditions that could influence the corrosion behaviour of these metal wastes during their long-term management. Finally, Subsection 2.3 provides a general overview of the literature review described in the subsequent sections.

2.1 SMOGG model

2.1.1 Corrosion reaction stoichiometries

The corrosion reactions for Magnox, aluminium and uranium included in SMOGG [3, 4] are listed below.

Magnox is an alloy, mainly of magnesium with small amounts of aluminium and other metals, used in cladding un-enriched uranium metal fuel. In SMOGG it is assumed that Magnox is pure magnesium, which reacts with water (under both aerobic and anaerobic conditions) to produce hydrogen according to the following overall stoichiometric equation:

\[ \text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{H}_2 \]  (2.1)

Aluminium is a reactive metal that corrodes under alkaline conditions \(^i\) (as expected for grouted wasteforms) to produce hydrogen:

\[ 2\text{Al} + 6\text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_3 + 3\text{H}_2 \]  (2.2)

Uranium corrodes under aerobic conditions to produce uranium oxides according to:

\[ \text{U} + 0.5 (2+x) \text{O}_2 \rightarrow \text{UO}_{2+x} \quad (0.2 < x < 0.4) \]  (2.3)

Although this reaction occurs without the production of gas, it is included in SMOGG because it may reduce the inventory of uranium available for the subsequent production of gas under the anaerobic conditions that will develop after repository closure.

Under anaerobic conditions, uranium corrodes to produce hydrogen according to:

\[ \text{U} + (2 + x) \text{H}_2\text{O} \rightarrow \text{UO}_{2+x} + (2+x) \text{H}_2 \quad (0.2 < x < 0.4) \]  (2.4)

For the purpose of the simplified model in SMOGG, the parameter \(x\) in the equation for uranium corrosion is set conservatively (as far as maximising hydrogen generation from a given mass of uranium corroding anaerobically is concerned) to the value \(x = 0.4\).

2.1.2 Corrosion model

A common feature exhibited by metal corrosion is a relatively high initial corrosion rate, which reduces over time to a long-term steady or slightly decreasing rate. The first phase may be considered as a period of "acute" corrosion and the long-term slower rate of corrosion as a

\(^i\) Aluminium also corrodes under acid conditions, but is strongly passivated at neutral pH.
period of “chronic” corrosion. The model implemented in SMOGG [3, 4] allows separate rates of corrosion to be specified for the acute and chronic phases.

The rate of movement of the position, \( s \) [m], of the surface of the metal is specified as:

\[
\frac{ds}{dt} = -k_a e^{-\frac{t}{t_a}} - k_c e^{-\frac{t}{t_c}}
\]

(2.5)

where

- \( t \) is the time during which corrosion is occurring [a];
- \( k_a \) is the initial acute corrosion rate [m a\(^{-1}\)];
- \( t_a \) is a characteristic time for the acute corrosion [a];
- \( k_c \) is the initial chronic corrosion rate [m a\(^{-1}\)];
- \( t_c \) is a characteristic time for the chronic corrosion [a].

This formulation provides a smooth transition between the two types of corrosion. Setting the characteristic time for either type of corrosion very large makes the rate for that type of corrosion effectively constant, and of course either rate can be set to zero if only a single rate is required. Note that, formally in the model, acute and chronic corrosion occur simultaneously at all times, but it is expected that the parameters will be chosen such that acute corrosion dominates at short times and chronic corrosion at long times.

Two characteristic metal shapes\(^\text{a}\) are allowed, spheres or plates, so that \( s \) corresponds to either a sphere radius, \( r \), or a plate surface position, \( h \), taken to be the distance from the mid-plane of the plate. For these two cases the rates of change of metal volume are

\[
\frac{dV}{dt} = V_s \frac{3dr}{r dt} = 4\pi r^2 \frac{dr}{dt}
\]

(2.6)

and, taking account of the fact that there are two corroding surfaces on a plate (i.e. neglecting corrosion of the thin edges),

\[
\frac{dV_p}{dt} = A_p \left( \frac{dh_1}{dt} + \frac{dh_2}{dt} \right)
\]

(2.7)

where

- \( V_s, V_p \) are the volumes of metal as spheres and plates; respectively [m\(^3\)];
- \( n_s \) is the number of metal spheres [-];
- \( A_p \) is the area of the plane of a metal plate [m\(^2\)];
- \( h_1, h_2 \) are the distances of the two surfaces of the plate from the mid-plane of the plate [m].

The rate of production of hydrogen gas, \( q_H \), is:

\[\text{Metals in the repository will be present in a variety of shapes, including irregular forms, wire and sheet metal. The corrosion behaviour of a metal depends on both its geometry and the ratio of surface area to volume. In SMOGG, a metal is assigned to a mixture of spheres and plates. These two geometries represent the two extremes of the ratio of surface area to volume, and therefore the two extremes of the rate of metal loss and gas generation.}\]
\[ q_H = -\eta_H \zeta \left( \frac{dV_s}{dt} + \frac{dV_p}{dt} \right) \tag{2.8} \]

where
\[ \eta_H \] is a stoichiometric coefficient giving the number of moles of hydrogen produced per mole of the metal corroded;
\[ \zeta \] is the molar density of the metal [mol m$^{-3}$].

There are equations analogous to Equation (2.8) for the consumption of:

- either water, in the case of Magnox and aluminium, or oxygen, in the case of uranium, during aerobic corrosion; and

- water during anaerobic corrosion.

During the transport and storage stages of the waste-package lifetime, it is assumed that the waste environment is aerobic (although it is recognised that some anaerobic regions could form). At closure there is a specified amount of oxygen in the vault atmosphere ensuring initially aerobic conditions. Conditions become anaerobic when this is exhausted.

Treatment of the effect of temperature on metal corrosion requires specification of (a) the variation of the temperature over the duration of the calculation, and (b) the dependence of the corrosion rates on temperature. The former is specified by the user in the form of a list of temperature values at a series of successive times. The latter, the temperature dependence of the corrosion rates, is also specified by the user in the form of input tables, this time of corrosion rate versus temperature. Corrosion rates at particular temperatures are obtained by linear interpolation from these tables. The characteristic times are assumed to be independent of temperature$^\text{iii}$.

2.1.3 Oxygen and water availability

The corrosion reactions for the reactive metals (i.e. Magnox, aluminium and uranium) consume oxygen or water.

The consumption of oxygen is important because its exhaustion controls the transition from aerobic to anaerobic conditions, and the onset of hydrogen production from uranium. The corrosion processes also consume or depend on the presence of water. For vented containers (considered to be all ILW and LLW containers), water will be freely available (both inside and outside the container) following full resaturation of the near field, but in earlier phases there is uncertainty about the availability of water.

During transport and storage SMOGG assumes that air flow through the vent ensures the environment in waste containers remains aerobic. This is probably an oversimplification, as it is possible that anaerobic niches may be present in these circumstances. However, as long as the niches are small in size relative to the waste volumes, the assumption of aerobic conditions during these phases is a reasonable assumption overall. Post-closure, when the wastes are isolated from the atmosphere, the oxygen remaining in the vaults at closure has to be consumed before the conditions become anaerobic.

During transport and storage, some water may be present in packages from the initial manufacture of the wasteform (e.g. grout porewater). Some water vapour may also diffuse into packages through the vent. Following repository closure, there will be a period of

$^\text{iii}$ In the case of Magnox, there is some experimental evidence to suggest that the characteristic time for the acute corrosion does depend on the past corrosive environment (see Subsection 4.5).
intermediate water saturation in the vaults (and in the waste packages), en route to full resaturation, which may take anything from a few years to a thousand or more years, depending on the properties of the host rock. During the period of partial saturation, the vault humidity may be at 100%. It is not clear to what extent the gas generating processes in packages into which liquid water has not yet percolated will be inhibited by water availability. SMOGG assumes water flows at a constant rate into a package and its associated backfill until they are fully saturated\(^\text{iv}\). Water availability is monitored during this period of resaturation, and the corrosion reactions are scaled back if consumption exceeds availability.

### 2.2 Environmental conditions

In order to identify the environments for which corrosion data are required, a summary of the conditions expected to arise in the interior of a waste package [6] is given below. The various environments affecting the waste package can be divided into:

- those pre-backfilling (including filling, storage, transport and emplacement in the repository); and
- those post-backfilling (including repository closure).

A further distinction is drawn between atmospheric and aqueous (i.e. fully saturated) exposure, since corrosion is different for these two environments.

#### 2.2.1 Conditions pre-backfilling

**(a) Atmospheric exposure**

The ambient temperature of the atmosphere in contact with the waste container during fabrication, filling, above-ground storage, transport and underground storage will probably be in the range 5°C to 35°C\(^\text{v}\). The internal temperature of the package will be determined by the external temperature and the small amount of heat generated by the wasteform. Temperature cycling during storage may cause condensation / evaporation cycles, but radiation-induced heating will tend to counteract this effect. The relative humidity inside the package will be a function of the water content of the wasteform and, if the container is vented, the external relative humidity.

**(b) Aqueous exposure**

If a concrete liner or internal grout is used, the interior surface of the container, and the waste if it is encapsulated, will be subjected to an aerobic, alkaline, cementitious environment. If a concrete liner and internal grout are not used, and if water is present in the waste, the interior of the package may be exposed to an aerobic, near-neutral environment (or to an aerobic, acidic environment if acidic residues are present in the waste). The pH and chloride concentration will depend on the composition of the waste. During this stage, corrosion will depend on the availability of water. It is possible that localised regions of anoxic conditions could develop within the wasteform as a result of corrosion or microbial activity, although it

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\(^\text{iv}\) This model, with its assumption of a constant rate of groundwater inflow, is simplistic. Even if the pressure in a vault were kept close to atmospheric pressure, the rate of groundwater inflow to the vault would reduce over some timescale before tending to a nearly steady-state. The timescale will depend on the geological environment. Actually, the pressure in the vault will rise, firstly because as water fills up the void space the gas will be gradually compressed, and secondly because additional gas will be generated. As the pressure rises, the rate of groundwater inflow will decrease.

\(^\text{v}\) The IAEA Regulations for a Type B transport package assume a temperature range from -10°C to 53°C.
seems likely that most of the wasteform will remain oxic assuming air can enter through a container vent.

2.2.2 Conditions post-backfilling

After placement, the containers may be surrounded with Nirex Reference Vault Backfill (NRVB) [7], which is an Ordinary Portland Cement (OPC)-based material. When the repository is full the remaining tunnels will be backfilled and the repository closed. In the early years after closure the temperature within some parts of the repository may rise to 80°C\textsuperscript{vi}, mainly due to chemical reactions such as curing of the backfill. After closure, groundwater will flow back into the repository, resaturating all the excavated and backfilled spaces. The rate of resaturation will depend on the way the repository has been operated, the backfill and the host rock permeabilities, and the regional head gradient. The groundwater is expected to contain very low concentrations of oxygen and therefore will impose anaerobic conditions within the repository. Corrosion and microbial activity also will reduce the oxygen concentration in the repository. The inflowing groundwater may contain significant concentrations of chloride ions (up to tens of thousands ppm).

\textbf{(a) Atmospheric exposure}

Initially regions of the package could be exposed to an aerobic atmosphere, from air trapped in voids. These voids will become anaerobic as a result of corrosion or microbial activity.

\textbf{(b) Aqueous exposure}

If a concrete liner or internal grout is used, the interior surface of the container, and the waste if it is encapsulated, will be exposed initially (i.e. after backfilling, but before resaturation) to an aerobic, alkaline (pH 12.5–13) aqueous phase, which may contain chloride. The initial chloride concentration of any aqueous phase will depend on the chloride content of the waste. If a concrete liner and internal grout are not used, and the waste is not dry, neutral or even acidic solutions could be present initially.

After resaturation, the interior of the package will be exposed to aerobic, alkaline (pH 12.5–13) porewater which has mixed with groundwater. The chloride concentration is expected to increase as the repository resaturates and groundwater enters the container via a gas vent or a corrosion-induced penetration. Eventually the solution will become anaerobic. Once the repository is completely resaturated and anaerobic, the interior of the package will be exposed to an anaerobic, high pH, aqueous phase that may contain high concentrations of chloride ions and a mixture of other inorganic salts.

2.3 Introduction to the review of corrosion data

For the purposes of the literature survey only general corrosion has been considered. Localised forms of corrosion, such as pitting and stress corrosion cracking, have largely been ignored, since, although they may result in areas of corrosion that may lead to a loss of integrity, they are unlikely to contribute significantly to total metal loss or gas generation.

Apart from the material properties (e.g. composition, metallurgical state, etc.) and the presence of moisture, the primary factors determining the corrosion rates of metals are the oxygen concentration and pH at the metal surface. The oxygen concentration at the metal surface depends on the rate of diffusion of oxygen through the surrounding media and whether there are any other restrictions or factors controlling the supply of oxygen (e.g. convection currents).

\textsuperscript{vi} This estimate of the maximum temperature is regarded as conservative now; a more realistic estimate of the maximum temperature is 50°C.
Many other variables affect the corrosion rate of metals under water saturated conditions. These include: the time of exposure, temperature, the concentrations of anions and cations (particularly chloride), the previous history of the surface (e.g. whether it is freshly prepared, pre-corroded, or still covered with the mill scale produced during metal production), the formation of surface scale, the physical and chemical properties of the cementitious materials used to encapsulate the waste, hydrodynamic conditions, the concentrations of dissolved gases (e.g. \( \text{CO}_2 \), \( \text{H}_2\text{S} \)), differential aeration and radiation levels. For atmospheric corrosion, the important parameters include: relative humidity, frequency of wetting (or “time of wetness”) and the presence of chloride particulates and sulphur dioxide in the atmosphere.

Some of these variables are interconnected. For example, the solubility of oxygen in a chloride solution depends on the temperature, the chloride concentration, the atmospheric pressure and the concentration of oxygen in the gaseous phase. Furthermore, the corrosion process itself may change the environment at the metal surface, leading to a subsequent change in corrosion rate (e.g. corrosion consumes oxygen and changes the pH due to the reduction of oxygen to form hydroxide, and as a result the corrosion rate decreases).

A range of corrosion rates is provided for the conditions expected in a repository, as well as a best-estimate value from within that range.

Extensive literature searches were carried out in several bibliographic databases. The Dechema corrosion handbooks \[8\] also contained useful bibliographies, and overviews of the corrosion behaviour of both magnesium and aluminium are contained in a text book by Godard \[9\]. Additional (commercial) references, in particular reports from the Product Evaluation Task Force (PETF), were identified through discussion with co-workers in the research field. A comprehensive set of references was collected and a critical review carried out.
3 Corrosion Data for Magnox

3.1 Introduction

A search has been made of the literature since 1970 for papers relating to the corrosion of magnesium and Magnox, which is >99 wt% magnesium. Forty one papers and reports were selected as being relevant. They can be divided into:

- General reviews and papers investigating the mechanism of corrosion at all pHs.
- Determinations of the corrosion under reactor storage pond conditions.
- Investigations of the corrosion of fuel cladding in water at the higher temperatures that might be realised inside a fuel transport flask in the event of an external fire.
- Measurement of the gas evolved from Magnox cladding encapsulated in various cement pastes in 500L drums.
- A paper describing the corrosion of Magnox encapsulated in cement in water held at 80°C.

This section begins by describing earlier reviews and by setting out the basic electrochemical knowledge that is needed to understand the corrosion mechanisms. There are then sections on the nature of the corrosion product films formed on magnesium, the effects on corrosion of anions other than hydroxide, the effects of elevated temperatures and the consequences of encapsulation in cement. The concluding section discusses the corrosion of encapsulated Magnox swarf at 80°C.

3.2 Reviews

Up until the mid-1990s, five reviews of Magnox corrosion had been published, four quite recently (1987–93) [10–13] and one in 1967 [14]. Comparing the former reviews with the latter review shows that many theories are long standing ones. Magnesium alloys would be very desirable lightweight structural materials for automotive and aerospace applications if the corrosion rates were not so high in the outdoor atmosphere and upon splashing by, or immersion in, salt water. Attempts have been made to put this susceptibility to positive advantage by using magnesium in batteries and as sacrificial anodes for cathodic protection. The corrosion of a few chosen alloys in hot carbon dioxide and in water at high pH are areas of specific interest to the nuclear industry.

There are two main aspects to corrosion, namely the electrochemical and the metallurgical. The most recent review of corrosion mechanisms is by Makar and Kruger [13]. The review in the Metals Handbook [10] gives good coverage to environmental factors and includes a section on designing to avoid galvanic corrosion.

All the reviews discuss the effects of impurities and alloying, but that by Steen Hansen [12] gives more details about the composition of the second phases formed. Atmospheric corrosion is considered by both Bothwell [14] and Ferrando [11] and the latter also addresses aerospace applications and magnesium-graphite composites.
3.3 The electrochemical mechanism for aqueous corrosion of magnesium

3.3.1 Thermodynamics

The basic process in corrosion is the oxidation of magnesium from the zero valence state (metal) to the +2 valence state. In water this is an electrochemical reaction which uses either dissolved oxygen or water as the oxidant. The half reaction involving the oxidation of magnesium is:

\[ \text{Mg} \rightarrow \text{Mg}^{2+} + 2e^- \]  \hspace{1cm} (3.1)

and the other half reaction is the reduction of either oxygen,

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \]  \hspace{1cm} (3.2)

which occurs only in well aerated solutions at positive potentials, or the reduction of water or protons:

\[ 2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \]  \hspace{1cm} (3.3)

\[ 2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- + \text{H}_2 \]  \hspace{1cm} (3.4)

which take place at more negative potentials in acid and alkaline solutions respectively. All the reduction reactions remove \( \text{H}^+ \) or generate \( \text{OH}^- \) and drive the solution more alkaline unless it is well buffered or very large in volume in relation to the surface area of the corroding magnesium. In experiments where this is not so the pH will rise and eventually the solubility product of \( \text{Mg(OH)}_2 \), brucite, will be exceeded and the solid hydroxide will be precipitated according to the reaction

\[ \text{Mg}^{2+} + 2\text{OH}^- \rightarrow \text{Mg(OH)}_2 \]  \hspace{1cm} (3.5)

The formation of such a surface film is observed only at a pH of 10.4 or higher.

The ranges of potentials over which the various components (Mg metal, \( \text{Mg}^{2+} \) and \( \text{Mg(OH)}_2 \)) are thermodynamically stable can be read from a Pourbaix diagram (Figure 1). Figure 1 indicates [13] that at pH values below about 9 magnesium metal will corrode to \( \text{Mg}^{2+} \) at all potentials more positive than -2.4 V versus the normal hydrogen electrode (NHE). At higher pH values it will form \( \text{Mg(OH)}_2 \) at all potentials more positive than -2.7V. MgO was not considered as it is unstable in water, forming \( \text{Mg(OH)}_2 \). In practice the steady potentials observed for magnesium at all pH values greater than 7 are more positive than predicted on thermodynamic grounds by at least one volt and therefore it is likely that multilayer surface films exist. If thermodynamic data for \( \text{Mg}^- \) and \( \text{MgH}_2 \) are included (Perrault [15]) it appears that the latter would replace metallic Mg as the solid phase if there were an overpressure of hydrogen, and that \( \text{Mg}^- \) might have a narrow range of stability at potentials between those at which the hydride and \( \text{Mg}^{2+} \) were stable [15]. Kirby [16] states that the magnesium hydroxide / magnesium interface is thermodynamically unstable, favouring instead a triplex layer of metal, oxide and hydroxide. Such a layer, with or without the addition of magnesium hydride, is a possibility. The calculations by Perrault [15] did not include the possibility of oxide layers.
3.3.2 Rate of electrochemical reactions

Corrosion in aqueous solution is an electrochemical reaction and its rate can be understood in terms of the current / applied voltage curves. Isolated pieces of metal in an aqueous solution corrode and take up a defined potential, known as the corrosion (or open circuit) potential at which the anodic and cathodic currents are equal. The factors determining this potential for magnesium, as described by Fabjan [17], are shown diagrammatically in Figure 2.

In the case of oxygen and hydrogen the cathodic current densities should increase exponentially with the deviations of the voltages below their respective $E_0$ values in alkaline solutions (about +0.4 and -0.83V (NHE) respectively). The increase in the cathodic current for oxygen is limited by the rate of diffusion of oxygen to the metal surface, since oxygen is only sparingly soluble in water (Curve A, Figure 2). This is not the case for the reduction of water and here the slope of the linear voltage / log(current) plot is a measure of the irreversibility of the reduction of water at the cathode. The slope (the Tafel slope) is least for the reversible reductions at noble metal cathodes (Curve B, Figure 2) and greatest for the markedly more irreversible reductions at the oxide or hydroxide covered surfaces of alkaline earth metals (Curve C, Figure 2). The low current part of Curve C was thought to be affected by the reduction of traces of oxygen or hydrogen peroxide.

The rate of dissolution of the magnesium anode and hence the anodic current would be expected to rise rapidly with increasing voltage, but the effect of the passive film on the metal has to be taken into account. Extensive measurements of the current / voltage curves for magnesium anodes in the passive region in solutions saturated in Mg(OH)$_2$ (pH 10.5) and in 0.01M Na$_2$CO$_3$ (pH 10.5), 0.01M NaOH (pH 12) and 0.1M NaOH (pH 13) have been made by Blanchet and Corion [18] and by Thomas and Weber [19].

Curve D in Figure 2 is typical of the behaviour in the absence of chloride (<1 ppm) or other ions which damage the film. The resistance of the passive film is very high and the intersection of the anodic and cathodic curves occurs at positive voltages at which only oxygen and not water is reduced cathodically (Curve A). More usually the film resistance would be lower (Curve E) due to the presence of chloride and SO$_4^{2-}$ ions, which induce localised corrosion by pitting in the passive region. The system would then settle to a potential a few hundred mV more positive than -1.6V. In this case the principal cathodic reaction would be the reduction of water to hydrogen, which is relatively irreversible on a Mg surface (Curve C). If the magnesium were connected electrically to a metal (e.g. iron) on which water is reduced to hydrogen with a small overvoltage (Curve B), or if the magnesium itself contained inclusions of iron, the voltage would shift more positive and the corrosion current would be much larger.

In 0.1M KOH + 3M KCl solution the resistance of the film is so low (Curve F) that it is difficult to polarise the Mg electrode without applying large currents (advantageous in battery applications) and the cathodic current curve for hydrogen cannot be plotted at all above -1500 mV (Curve G).

In this way the electrochemical behaviour of magnesium can be explained semi-quantitatively with the aid of a resistive passive film, but the prediction of the initial potential depends on an unlikely hydrogen overpotential. This suggests that there might be still other phases interposed between the magnesium and the solution.

Corrosion rates can be expressed in a number of different ways. The results in the papers have been reduced to a common unit of µm a$^{-1}$ by means of the following equivalences$^{vii}$:

\[ 1 \mu A \ cm^{-2} = 1.09 \ mg \ dm^{-2} \ d^{-1} \ (i.e. \ mdd) = 0.1 \ litres \ (at \ NTP) \ H_2 \ m^{-2} \ d^{-1} = 22.8 \ \mu m \ a^{-1} \]

$^{vii}$ The physical parameters required for the conversion are: the density, 1740 kg m$^{-3}$; the molar mass, 24.305 g mol$^{-1}$; and the number of electrons in the reaction, 2.
3.4 Corrosion and metallurgy

Studies have been made of the effect of alloying elements on the corrosion rate; most of the data in reviews [11–13] are derived from the original work by Hanawalt. Al, Zn, Pb, Sn, and Mn have little or no effect on the corrosion rate of magnesium and so Al and Zn are used as alloying elements. A typical Magnox alloy has the following composition [20] (wt%): Al 0.80; Zn 0.005; Si 0.008; Cu 0.005; Mn 0.005; Fe 0.003; Sn 0.005; Ni 0.002; Ca 0.005; Pb 0.005; Be 0.005; Mg balance. Aluminium at concentrations of >10% dramatically improves the corrosion resistance in 3% NaCl solution saturated with Mg(OH)$_2$, through the formation of hydroxide films in which some Mg$^{2+}$ ions are replaced by Al$^{3+}$ to form pyroaurite-sjogrenite type compounds [21]. More recently rare earth elements have been introduced into alloys, leading to reductions in the corrosion rates in chloride solutions of one to two orders of magnitude [22]. Metals more noble than Mg, such as Fe, Ni, Co and Cu, produce inclusions which accelerate the corrosion by acting as cathodes at which hydrogen can be released with little overvoltage.

The concentrations at which these metals precipitate from cooled magnesium alloys are quite low, the tolerance levels [10] being 1,000 ppm Cu, 150 ppm Fe and 5 ppm Ni. These second phases are noble (i.e. unreactive) metal rich alloys [12] like Al$_3$Fe. The purity requirements were alleviated by the discovery 70 years ago that the addition of small amounts of Mn (2,000 ppm) improved the corrosion resistance [13]. The Mn forms Al-Fe-Mn particles which separate out and it also produces second phases in the cooled alloys which are less noble (i.e. more likely to corrode) [12]. There is a better correlation of corrosion rates with the Fe / Mn ratio than with the Fe / Mg ratio. Alloying Mg with Si has no effect on corrosion behaviour as Mg$_2$Si has a corrosion potential similar to that of Mg.

3.5 The nature of the passive film

3.5.1 The film at pH >11

(a) Measurements of composition

The film composition should be simplest when the metal is in contact with very pure water. In such circumstances the film is very thin and since there is no buffering capacity the pH tends to rise. Consequently most studies of the unmodified film have been made at high pH values where the film is thicker and the pH well buffered.

A number of determinations of the composition have been made in solutions of NaOH with very low levels of aggressive anions such as chloride or SO$_4^{2-}$. The technique used most frequently is X-ray diffraction (XRD), but measurements have also been made by electron diffraction (ED), Auger Electron Spectroscopy (AES) with depth profiling, electron energy loss spectroscopy (EELS), non-dispersive X-ray analysers attached to electron microscopes (SEM-EDAX), transmission electron microscopy (TEM), Rutherford Backscattering Spectroscopy (RBS) using 2.9 MeV $^4$He ions and Infra-Red Spectrometry (IR). Most measurements of the lattice parameters by XRD have shown that the film consisted of a Mg(OH)$_2$-like material with slight deviations from the pattern for bulk Mg(OH)$_2$. This, and the low line intensities, has led to the suggestion that the film is partially amorphous and TEM measurements have shown the presence of randomly oriented platelets about 30 nm by 300 nm.

The O/Mg ratio as measured by RBS [28] (1.85–1.95) corresponded to Mg(OH)$_2$, and the OH absorption band was found in IR spectrometry [23, 24]. The thin layers of oxide present initially on the samples were observed to hydrate rapidly in water [13], though the thicker films (5–50 µm) found on specimens pre-oxidised in reactor conditions reacted slowly enough [29] (2 µm in 100 days) to allow the coexistence of MgO and Mg(OH)$_2$ during corrosion measurements. If the voltage imposed on a magnesium electrode is so negative that water is reduced rapidly, the current density and the concentration of hydrogen atoms at the metal surface become high and MgH$_2$ is formed [13, 26]. Nazarov et al. [26] removed the black
films produced in their experiments and measured the hydrogen evolved upon heating during differential thermal analyses, so confirming the presence of a hydride.

(b) In-situ measurements – the barrier layer

Measurements of composition have all involved removing the films from the solutions, but this does not seem to have invalidated the results since the most labile species, MgH$_2$ and Mg(OH)$_2$, were detected nevertheless. In-situ measurements using ellipsometry [30, 31], current-voltage plots in conjunction with an AC bridge [23], and $^{18}$O isotopic measurements [28] have yielded information about the physical nature of the film.

Ellipsometry [30, 31] measures the ratio of the reflection coefficients for light parallel and perpendicular to the plane of incidence. The ratio is a function of the thickness and refractive index of the film. The best fitting curve indicated that the film had a refractive index of 1.48, compared with 1.56 for Mg(OH)$_2$ and 1.75 for MgO. This suggested strongly that the film contained water as well as magnesium hydroxide, and that it was porous. The initial measurements, supported by depth profiling by secondary ion mass spectrometry (SIMS) with argon ion etching, indicated that there was an oxide layer 20–40 nm thick left after the initial etching and polishing. This film thickened from 40 to 85 nm on standing in air saturated 0.01M NaOH for 90 min, but thereafter grew more slowly in a linear manner reaching only 100–120 nm after 7 hours. During this period the composition of the outer part of this film changed to that of water and Mg(OH)$_2$. This indicated that whilst the film laid down early on might have been protective this might not have been so for the outer part of the film, as otherwise the thickness would have increased in proportion to the square root of its age. Kirby [16] found that the corrosion of Magnox in 0.005M NaOH (pH 11.5) was rapid to begin with, but that within 50 days the rate had fallen to a constant low value of about 0.2 µm a$^{-1}$. The thickness of the corrosion film at this point would have been about 300 nm if it were Mg(OH)$_2$ or 100 nm if it were MgO.

Murakami and Sato [23] made measurements on magnesium electrodes anodised in NaOH solutions with concentrations ranging from 0.1 to 10 M at potentials from -1.6 to +2.0V against a Hg/HgO reference electrode. The anodically deposited film was judged to be porous and AC bridge readings at 1000 Hz gave a film resistance in the range 5–10 $\Omega$ cm$^2$ and a capacitance of 5–10 µF cm$^{-2}$. The film resistance was low and the capacitance was rather lower than the authors expected for an electrical double layer. The polarisation curve showed a substantial voltage range (-1.6 to +2.0V) over which the current density was less than 10 µA cm$^{-2}$, which is equivalent to a corrosion rate of 225 µm a$^{-1}$. This is a much greater rate than those recorded for open-circuit corrosion in such solutions (1–10 µm a$^{-1}$), but the potentials involved are more positive than the corrosion potential. Thick porous films have also been observed in ex-situ examination by scanning electron microscopy of anodically generated films [27]. These observations have led to the view that the porous film that is stable in alkaline solutions does not have a resistance high enough to represent a barrier film, and that the protection is provided by a thin oxide film beneath the hydroxide. Although the existence of such a film may be inferred, particularly from the common observation of a steady corrosion rate, it has never been detected directly, apart from in oxide films formed in air. RBS [26] measurements would have detected a second layer thicker than 100 nm and ellipsometry one thicker than 5–10 nm [30].

(c) Site of film growth

When samples of Magnox were exposed at 90–140°C, first to NaOH solutions with concentrations in the range 0.005 to 0.19M (pH 11 to 13.2) and then to similar solutions made from water enriched to 10% in H$^{2}$H$^{18}$O, it was found that the layer of $^{18}$O-enriched magnesium hydroxide was beneath the normal hydroxide and next to the metal surface [28]. If the order of exposure were reversed the enriched layer was on the surface. This indicated that new magnesium hydroxide was created at the base of the film and that OH$^{-}$ diffused from the solution through the film, or diffused laterally if local cathodes were present to reduce water, to react with Mg$^{2+}$ ions which remained close to metal surface. Since the film appeared to be both amorphous and porous it seemed likely that this diffusion was through the aqueous phase and not through the solid. If this were so, water could also permeate to cathodic areas
and hydrogen diffuse outwards during open circuit corrosion. Since the corrosion rate was increased by only an order of magnitude in going from open circuit to galvanic corrosion, using a separate cathode of low polarisability, Kirby [16] argued that the rate-determining step was the anodic process, in which case the diffusion of Mg$^{2+}$ ions occurred through a MgO layer next to the metal.

In summary, the surface film on magnesium in alkaline solutions containing negligible amounts of aggressive ions appears to consist of an outer layer of permeable or porous magnesium hydroxide which thickens from beneath with time, and a thin barrier layer next to the metal which could be magnesium oxide, or in circumstances of high cathodic current density, magnesium hydride.

3.5.2 The film at pH 7–10.4

The pH of a saturated Mg(OH)$_2$ solution is 10.4 and the equilibrium Mg$^{2+}$ ion concentration is $1.2 \times 10^{-4}$ M. Consequently, the composition of surface films formed at, say, pH 8–9 should give information on the barrier layer in the absence of any porous hydroxide layer, which will not form because the ionic concentrations will be below the solubility product. In fact measurements in borate or sodium carbonate buffer solution are rare. Several experiments have been done with pure water at 100°C and a larger number with NaCl solutions of various strengths. In these experiments the pH would rise as corrosion proceeded, so it is unclear whether Mg(OH)$_2$ would have been precipitated.

Long et al. [32] measured the reflectivity of films formed in borate buffer using X-rays of a wavelength near the oxygen K-absorption edge and found that the first shell O-Mg distance was closer to that for MgO for the films on pure Mg or AZ61 alloy (composition, wt%: Al 5.8-7.2; Zn 0.4-1.5; Mn 0.15 min; Si 0.10 max; Mg balance), but was closer to Mg(OH)$_2$ for Mg-15%Al and Mg-30%Al alloys. Case and Hilton [29] reported tests in 2.5 $10^{-3}$ M Na$_2$CO$_3$. The corrosion rates (up to 420 µm a$^{-1}$) were an order of magnitude greater than at pH 11 and the film formed was a mixture of Mg(OH)$_2$ and magnesium hydroxycarbonate, Mg$_2$(OH)$_2$CO$_3$.3H$_2$O. The buffering was limited because carbon dioxide was absorbed from the air. Tests in pure water are unbuffered, and Case and Hilton reported very high initial corrosion rates (2100 µm a$^{-1}$) declining by an order of magnitude in 48 hours and subsiding to 42 µm a$^{-1}$ after 600 days. The pH rose to 10.4 early in the test and subsequently fell to 9.5 as CO$_2$ was absorbed. By then the greater part of the corrosion film had formed and was primarily Mg(OH)$_2$. Experiments with boiling water [13] produced a film which was Mg(OH)$_2$ and Long’s experiments with humid air at 100°C gave the same results as the borate buffer.

To summarise, in the pH range 7–10.4, Mg(OH)$_2$ and sometimes MgO films have been found, but the prevalence of the hydroxide may be due solely to the lack of pH control in most experiments.

3.6 The effect of anions other than hydroxide

The effect of fluoride ion on the corrosion of magnesium has been widely studied because it is an effective corrosion inhibitor for magnesium. Chloride ion, on the other hand, is an aggressive ion which accelerates the corrosion by damaging the passive barrier. At pH 11.5, sulphate, carbonate and silicate are less aggressive than chloride and nitrate is more or less benign.

3.6.1 The fluoride ion

The behaviour of magnesium in alkaline fluoride solutions has been reported by Gulbrandsen et al. [27] who reviewed earlier publications and concluded that there is a substantial difference between the effect of fluoride at ambient temperature and at 90-140°C. Case and Hilton [29] recorded that Blanchet had found that in 0.024M NaF solution the corrosion rates at 80°C and 95°C were reduced to 8 and 25 µm a$^{-1}$ respectively. Flasks containing spent nuclear fuel are required to withstand an 800°C fire for 30 minutes and in the
case of Magnox fuel the water in the flasks is made 0.05M in fluoride ion to restrict the corrosion rate and limit the pressure build up due to the evolution of hydrogen [24] by achieving a concentration of 0.35 mg F cm$^{-2}$ of Magnox surface. The nature of the protective film formed at 75–140°C in 0.05M fluoride was investigated by Bradford et al. [28] who showed that the fluorine was uniformly distributed through the film to give an average composition of Mg(OH)$_{2-x}$F$_x$. It was not possible to determine whether this was a substitution compound (fluoride is a smaller ion than OH$^-$ and could readily substitute in the layer lattice) or a mechanical mixture of Mg(OH)$_2$ and MgF$_2$. If a film is grown first in NaOH and then in NaF, the F is concentrated at the base of the film, confirming the observations made with $^{18}$O that the film grows from below (see Section 3.5.1 (c)). The exchange of fluoride ions with a hydroxide film is relatively slow, but corrosion rates are reduced when even a small amount of fluoride has been taken up. This suggests that the corrosion rate is related not to the properties of the bulk film but to those of an underlying barrier film.

Some fluoride contamination of reactor ponds is inevitable as a consequence of fuel transfers, but Robins [24] was unable to find any effect on corrosion rates at 2.5 $10^{-3}$ M fluoride, nor to find any F in the corrosion film. Harvey [31] found that 0.05M fluoride also did not reduce the currents in voltage sweep experiments nor become incorporated in the film. These results are understandable from the work of Gulbrandsen et al. [27] and it is clear that there is a substantial difference between the effect of fluoride at ambient temperature and at 90–140°C. Gulbrandsen measured the partial anodic current density at open circuit over the pH range 6.9 to 13.9 and for fluoride ion concentrations of $10^{-3}$ to 3M. This current was unaffected by fluoride ion concentrations up to 0.1M but was strongly dependent on the pH. It fell from 10 µA cm$^{-2}$ (225 µm a$^{-1}$) at pH 8 to 1 µA cm$^{-2}$ (23 µm a$^{-1}$) at pH 11.5 to 0.1 µA cm$^{-2}$ (2 µm a$^{-1}$) at pH 12.9. Between 0.1 and 1M fluoride the lower currents passed through peaks about a decade larger than their steady values before all three declined to very small values (0.01 µA cm$^{-2}$) at higher fluoride concentrations. Before this transition the film consisted mainly of porous MgO / Mg(OH)$_2$. After the transition, at medium fluoride concentrations and lower pH, MgF$_3$ was also found, whilst at higher fluoride concentrations and pH, KMF$_2$ was present.

Once the transition to a fluoride-containing film had taken place the film was protective and resistant to passivity breakdown up to electrode potentials of +10V. Both the inverse electrode capacitance and the initial Tafel slope increased essentially linearly with the applied potential which was indicative of a compact, insulating barrier-type film on passive metals. Using a film capacitor model it was possible to calculate that the rate of increase of film thickness with applied voltage (anodisation ratio) was 1.0 nm V$^{-1}$ in 2.0 M KF at pH 12.9 and 2.0 nm V$^{-1}$ in 0.08M NaF. Calculations from the initial Tafel slope gave 3.5 nm V$^{-1}$ and 1.3 nm V$^{-1}$ in the two cases. These calculations confirm that the barrier films need not be very thick to be protective and that the experimental evidence is that at ambient temperature it requires fluoride ion concentrations greater than 1M to replace the oxide / hydroxide barrier layer with a more protective fluoride-containing one. This is not entirely surprising as the solubility product of MgF$_2$ is more than three orders of magnitude greater than that of Mg(OH)$_2$.

To summarise, the fluoride ion concentration must be greater than 1M if a protective film is to form in alkaline solutions at ambient temperatures. This is in contrast to the situation at 90–140°C where a concentration of 0.05M will suffice (because of the change in the solubility of MgF$_2$ with temperature).

### 3.6.2 The chloride ion

In contrast with fluoride the chloride ion has a damaging effect on the protective film although the details of the interaction with the film are not well known. MgCl$_2$.6H$_2$O and Mg$_3$(OH)$_2$Cl.4H$_2$O have been identified in 3% NaCl [13] and the latter [33] in borate buffer (pH 9.8) containing high concentrations of chloride. The electrochemical effects are well documented.
Cyclic voltammetry is a particularly useful technique for rapidly surveying the changes. The basis of this technique is as follows. If a Mg electrode is biased from $E_{\text{corr}}$ to increasingly positive (anodic or passive) potentials, the current which flows due to the dissolution of Mg (the leakage current) is limited by the resistance of the film. The film thickens in proportion to the additional voltage so that the current is roughly constant until the film breaks down at voltage $E_b$ and the current rises sharply. If the voltage is reduced there is a hysteresis effect and the current falls in a different way until it is negligible at $E_p$, the repassivation potential. Thereafter the current changes sign and increases again as the metal becomes a cathode for the generation of hydrogen. A typical plot obtained by cyclic voltammetry is shown in Figure 3. The breakdown of the film leads to pitting, or localised corrosion, which if the current density becomes large enough may develop into general corrosion. The breakdown potential $E_b$ is always higher than $E_p$ (which may be near to $E_{\text{corr}}$) and as long as $E_p < E_{\text{corr}}$ the metal may be considered to be immune to local corrosion.

The first effect of chloride ion may be seen in the change in the breakdown potential. Harvey [31] found that in 0.005M NaOH (pH 11.5) the breakdown potential for Magnox remained at least two volts above the corrosion potential until the chloride concentration exceeded 100 ppm (0.0028M) and that at 1,000 ppm $E_b$ was below $E_{\text{corr}}$, so that the film had already broken down at the corrosion potential. The addition of 1,000 ppm (0.05M) fluoride had no effect on etched specimens, but raised the breakdown potential of samples soaked for 1000 hr in the NaOH to three volts above the corrosion potential. In all cases $E_p$ was just below $E_{\text{corr}}$ so that corrosion, once initiated, would continue. A large range of Mg alloys were examined in a series of go / no-go experiments performed by Mitrovic-Scepanovic and Brigham [34] who showed that the critical concentration of chloride for localised corrosion to occur, was in the range 70–700 ppm in 0.01M NaOH (pH 12). They found that adding hydrogen peroxide to shift the potential more positive was useful in defining the critical chloride concentration.

A second aspect of the effect of chloride is the increased leakage current from the pitting of the film in the anodic voltage range. This is signalled by the modest shift to more negative corrosion potentials as the chloride ion concentration increases. This is necessary to generate the increasing cathodic current. Tunold et al. [35] found that in saturated Mg(OH)$_2$ solution (pH 10.4) the corrosion potentials in 6, 60, 600, and 6,000 ppm chloride were -1060, -1140, -1270 and -1410 mV (NHE) respectively for pure Mg and -990, -1090, -1180 and -1310 mV respectively for alloy AZ 63 (5.6% Al and 2.9% Zn).

(a) Effect of chloride ion on galvanic and crevice corrosion

Kirby [16] investigated the effect that galvanic coupling to a steel basket and the presence of crevices might have on the tolerance of Magnox clad fuel to chloride ion. Connection to a steel cathode through a zero resistance ammeter showed that the effect of coupling was to pull the magnesium electrode several hundred millivolts more positive as the overvoltage required to pass the cathodic corrosion current was less on a large steel cathode. This reduced the critical level for film breakdown to about 10 ppm chloride and if a crevice was also present the lower pH in the crevice reduced the level still further to about 1 ppm. If the Magnox had been pre-soaked in NaOH solution free from chloride for 5 days prior to exposure, then the critical level might rise to 5 ppm. The actual galvanic coupling in a cooling pond was found to be very variable depending on the resistance of the electrical contact between the corroded metals.

The variation of the passivity / pitting boundary with chloride ion concentration was investigated by Carney and Marsh [20] who found that for plain specimens of Magnox electrically coupled to steel and immersed in solutions at 40°C the critical pH for breakdown was given by:

$$\text{pH} = 12.0 + 0.46 \log [\text{Cl}^-]$$

where the chloride concentration is in ppm. This expression holds over the pH range 11.5 to 13.0 and the error in pH is ± 0.6 for 95% confidence limits. The critical pH is 11.5 at 0.1 ppm.
chloride and it is 13.0 at 150 ppm chloride. If a crevice is also present the expression becomes:

\[
pH = 12.7 + 0.22 \log [\text{Cl}^-] \tag{3.7}\n\]

which holds over the rather narrow range between pH 12.5 and pH 13.0. The critical pH is 12.5 at 0.1 ppm chloride and it is 13.1 at 100 ppm chloride. 1,000 ppm fluoride was observed to be beneficial in extending the passive range.

(b) Spalling of the film

With galvanic coupling the corrosion rates were high enough for the films to grow within the duration of the experiments (16–185 days) to such thicknesses that they broke and spalled under their internal stresses [16]. The thickness varied from 0.4 to 5 µm in different experiments, with an average of 2 µm. Similar breakaway corrosion has been observed in experiments in NaOH at elevated temperatures [25], where the thickness at breakaway varied from 9 µm at 80°C to 0.3 µm at 120°C. The corrosion rate during breakaway rose as the square of the time before peaking and then settling to a lower plateau. The peak corrosion rates were proportional to the square root of the initial chloride ion concentrations, but the plateau rates were essentially independent of these and in the range 250–440 µm a⁻¹. This behaviour suggests that not only the hydroxide film, but also any barrier layer is disrupted in spalling.

In summary, the presence of chloride ion increases the chance of breakdown of the passive film, leading to localised corrosion. Even when this does not happen, the leakage current through the passive film is increased. At pH 11.5, as in a cooling pond, the tolerance for chloride is about 1,000 ppm in the presence of 1,000 ppm of fluoride, 100 ppm in the absence of fluoride, 10 ppm for a sample coupled to steel and 1 ppm for a specimen containing a crevice as well. These tolerances rise with pH. When films become more than a few microns thick they may spall with big increases in the corrosion rate.

3.6.3 The sulphate ion

The sulphate ion produces a smaller acceleration of the corrosion rate than chloride at the same weight concentration [18]. The corrosion potential and cyclic voltammetry curves have been recorded by Tyfield and Martin for magnesium in the presence of sulphate [36]. They showed that unlike chloride solution \( E_p \) was always less than \( E_{corr} \) and \( E_p \) falling rapidly towards \( E_{corr} \) at 100 ppm chloride), \( E_p \) was well above \( E_{corr} \) in SO₄²⁻ solution until a level of 100 ppm was reached. Consequently below 100 ppm, sulphate may have a lesser effect than chloride, but at higher concentrations they may have more similarity. The AC impedance technique has also been used to compare the nature of the electrode surface in both chloride and sulphate solutions [37]. An AC impedance diagram (Nyquist plot) shows the resistive and capacitive components of the impedance of the film at frequencies between a few mHz and about 1 kHz. The high frequency loop on the diagram (1–1000 Hz) gives a resistance related to a combination of (charge transfer resistance and film resistance) and a parallel capacitance. The low frequency loop is attributed to the relaxation of mass transport through the solid due to the accumulation of corrosion products.

Both loops were observed for magnesium in 0.5M Na₂SO₄, the high frequency loop giving a film resistance \( R \) of 65 Ω cm⁻² and a film capacitance, \( C \), of 19.4 µF cm⁻², but only the high frequency loop was found in 0.5M NaCl. These differences suggest that the film in sulphate solutions is significantly different to that formed in chloride solutions.

3.6.4 Silicate, carbonate and nitrate ions

Although measurements on specimens with crevices did show some corrosion in 10 ppm SiO₃²⁻ solutions, Kirby [16] rated silicate as less aggressive than sulphate and very little effect has been observed in cooling ponds [29]. Bradford et al. [25] investigated the corrosion of
Magnox in NaOH at elevated temperatures specifically to see if discrepancies in earlier measurements were due to the leaching of silicates from glass autoclave liners. They found that corrosion rates were higher in the presence of silicates, but that the difference fell with temperature and became undetectable below 40°C. X-ray powder diffraction patterns of material spalled in these experiments showed that it consisted mainly of brucite, Mg(OH)$_2$, together with smaller amounts of a chlorite, with a general formula of $(\text{Mg,FeAl})_6(\text{Al,Si})_4\text{O}_{10}(\text{OH})_2$. Thinner films examined by IR contained brucite, material resembling hornblende, Ca$_2$Na(Mg,Fe$^{II}$)$_4(\text{Al,Fe}^{III},\text{Ti})_3\text{Si}_6\text{O}_{22}(\text{O,OH})_2$, and talc, Mg$_3$Si$_4\text{O}_{10}(\text{OH})_2$. Three hundred parts per million of carbonate ion appeared to have no effect on corrosion rates [38] when the system was buffered at a pH of more than 10.5.

The only effect of nitrate appears to be to shift the corrosion potential to slightly more positive potentials [36] possibly because the overvoltage for the cathodic reduction reactions is reduced by the introduction of an alternative process:

$$\text{NO}_3^- + \text{H}_2\text{O} + 2\text{e}^- \Rightarrow \text{NO}_2^- + 2\text{OH}^- \quad (3.8)$$

### 3.7 The negative difference effect

In the open circuit corrosion of magnesium there is usually agreement between the weight changes observed and those expected from the hydrogen evolved. Discrepancies can arise from uncertainties as to what the weight changes mean, especially with pre-oxidised specimens where some of the change may be due to the hydration of the pre-existing oxide. Treating with a solution of CrO$_3$ and AgNO$_3$ to remove all the film gives weight changes that also need interpretation [24].

When magnesium is connected electrically to a separate platinum or steel cathode, as in electrochemical experiments or in field applications where magnesium is used as a sacrificial anode, a third measurement is possible, namely that of the current flowing to the separate cathode. Generally the weight of metal lost is greater than that expected from the current measurement [13]. This is referred to as the "negative difference effect" and increases the cost of using sacrificial anodes. Two kinds of theories have been proposed to explain this [35]. One is that some monovalent magnesium is formed; the other is that localised corrosion is enhanced, in the sense that the anode and cathode are both on the same piece of metal. This does not register as current at the remote cathode. These theories will be discussed in greater detail below.

#### 3.7.1 Monovalent magnesium ions

If the oxidation process were:

$$\text{Mg} \Rightarrow \text{Mg}^+ + \text{e}^- \quad (3.9)$$

the current efficiency of a sacrificial anode would be halved compared to the normal two-electron oxidation reaction. However, monovalent magnesium can be no more than a metastable intermediate and it could not accumulate indefinitely. At some point it would convert to stable divalent magnesium via the reactions:

$$\text{Mg}^+ \Rightarrow \text{Mg}^{2+} + \text{e}^- \quad (3.10)$$

or

$$\text{Mg}^+ + 2\text{OH}^- \Rightarrow \text{Mg(OH)}_2 + \text{e}^- \quad (3.11)$$
Both reactions require an anode at which to discharge electrons, which would then be recorded as part of the anodic current. Thus the building up of a steady state concentration of Mg$^+$ might temporarily reduce the coulombic efficiency of the anode, but it is unlikely that this could be sustained for any length of time.

### 3.7.2 Enhanced local corrosion

In laboratory experiments the negative difference effect has been quantified in the equation \[ I_{\text{obs}} = I_{\text{corr}} + (1 + k) I_{\text{Mg}} \] (3.12)

where
- $I_{\text{obs}}$ is the observed rate of corrosion converted to a current density,
- $I_{\text{corr}}$ is the open circuit corrosion rate converted to a current density,
- $I_{\text{Mg}}$ is the actual current density at the Mg electrode, and
- $K$ is a constant.

1. One interpretation of the enhanced local corrosion mechanism was put forward by Robinson and King [39]. To generate anodic current densities of the order of mA cm$^{-2}$ requires either that the anode be biased to a positive potential at which the film breaks down or that there be sufficient chloride present to lead to film breakdown at more negative potentials. Robinson and King argued that the increased breakdown of the protective film would lead to a parallel increase in the local corrosion. This would probably be proportional to the applied current, so that $k$ would appear to be greater than zero. The $I_{\text{corr}}$ term in the equation implies that the currents flowing at the corrosion potential continue unaltered as the anode is biased to other potentials. This is unlikely to be true for any significant shift in potential, but by the same token $I_{\text{corr}}$ will be small compared to the imposed currents.

2. Another possibility is that unreacted magnesium may be detached from the electrode and subsequently corrode out of electrical contact with the anode. The detachment from the anode would damage the protective film, as in the first theory. This detached open circuit corrosion would have the effect of increasing $I_{\text{corr}}$. Metal has been seen to fall from anodes, but it has been discounted as being too little. However, Brossard and Piron [33] have examined the porous film in-situ and have found fine metallic particles trapped within it.

3. Finally, the formation of MgH$_2$ has been proposed. Although magnesium hydride is usually produced by the cathodic polarisation of magnesium, Nazarov et al. [26] pointed out that the reaction:

$$\text{Mg} + 2\text{H}_2\text{O} + 2e^- \rightarrow \text{MgH}_2 + 2\text{OH}^- \quad E_0 = -0.64V$$

(3.13)

could take place at the corrosion potential in cathodic areas in preference to:

$$2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad E_0 = -0.83V$$

(3.14)

and the subsequent hydrolysis of the hydride would remove more magnesium from the anode without generating any more current:

$$\text{MgH}_2 + 2\text{H}_2\text{O} = \text{Mg(OH)}_2 + \text{H}_2$$

(3.15)

The overall reaction would be:
Mg + 4H₂O +2e⁻ = Mg(OH)₂ + H₂ + 2OH⁻  \hspace{1cm} (3.16)

Nazarov et al. [26] showed that at high current densities in 0.1M NaCl a steady state quantity of hydride could be formed and that this quantity increased with the current density. Hydride formation would, like monovalent ion formation, depress the coulombic efficiency for a time only. It could be distinguished from the first and second explanations as they lead to an expected increase in the evolution of hydrogen from the magnesium, and hydride formation reduces it.

Although the third theory may be applicable to the timescale of laboratory experiments the second seems more appropriate to the longer duration of cathodic protection.

3.8 The effect of temperature

The corrosion of Magnox in sodium hydroxide solution at temperatures in the range 40–120°C was investigated by the CEGB in connection with the effect of fires on fuel transport flasks. The results obtained in autoclaves with glass liners gave higher corrosion rates than those in other experiments and Bradford et al. [25] made measurements to see if this was due to the presence of dissolved silicate. The corrosion rates above 80°C were also large enough to lead to breakaway of the film within the duration of the experiment in silicate-free solutions, so the post-breakaway corrosion rate was also investigated.

Sodium hydroxide solutions were made up to cover the pH range 11.4 to 13, and silicate was added to give a concentration of 130 ppm in some solutions. Within the scatter of the results the corrosion rates at elevated temperatures showed no correlation with pH. The rates of corrosion were monitored by the hydrogen evolved and confirmed by a weight measurement at the end of the experiment. The kinetics were linear, in that after an initial surge the rate of increase of film thickness was constant. The corrosion rates in silicate-free solutions showed transitions to a higher breakaway rate whilst those in silicate solutions quickly adjusted to a higher constant rate. Pre-oxidised specimens showed a gradual transition to higher rates (i.e. did not show linear corrosion), probably because the oxide was hydrating at the same time, and a sudden transition to breakaway corrosion was not observed.

The results are shown in Figures 4 and 5. In Figure 4 the logarithms of the pre-breakaway corrosion rates are plotted against the reciprocal of the absolute temperature, $T$. In silicate free solutions at 40–120°C the rate is given by,

$$\text{Rate} = 1.2 \times 10^{15} \exp \left( -\frac{10720}{T} \right) \mu m \, a^{-1}$$  \hspace{1cm} (3.17)

The corrosion rates predicted by this formula range from 0.9 µm a⁻¹ at 35°C, through 78 µm a⁻¹ at 80°C to 1,700 µm a⁻¹ at 120°C. Back extrapolation to 15°C and 25°C (which are below the range of measurement) gives rates of 0.08 and 0.29 µm a⁻¹ respectively. Corrosion rates in the presence of silicate have been measured at 80°C and above. The rate at 80°C is about 60% higher than that in silicate-free solutions. The lines converge at 60°C and it is uncertain whether any difference is detectable below this temperature. Figure 5 also includes a plot of the post breakaway corrosion in silicate free solutions. This follows the expression,

$$\text{Rate} = 5.9 \times 10^{20} \exp \left( -\frac{14800}{T} \right) \mu m \, a^{-1}$$  \hspace{1cm} (3.18)

which gives 370 µm a⁻¹ at 80°C and 26,000 µm a⁻¹ at 120°C. The rate at 80°C is about five times that before film breakaway, rising to fifteen times at 120°C. The critical film thickness at breakaway falls from 9 µm at 80°C to 0.3 µm at 120°C.
The slope of the plot in Figure 5 gives an activation energy of 89 kJ mol\(^{-1}\) for pre-breakaway corrosion in silicate-free sodium hydroxide solution, compared with 124 kJ mol\(^{-1}\) for post breakaway corrosion and the same for corrosion in silicate-containing solution. The relatively large activation energy suggests that the rate-determining step is either a reaction kinetic one or diffusion through a solid, since aqueous diffusion would have given a smaller value. Though the other two cases have even higher activation energy, this is offset by a larger constant in the Arrhenius equation and the overall corrosion is faster.

### 3.9 Corrosion in reactor station ponds

Corrosion rates can be seen to depend on a variety of factors, including the alloy composition, the pH, the presence of aggressive ions, galvanic coupling, the presence of crevices, the temperature and the thickness of the film. Most of these have not been reproduced from one investigation to another, but there is one environment which is constant, namely the reactor cooling or storage pond. These ponds were used for the holding of irradiated fuel for a 100-day cooling period and there was interest in storage for longer periods either at power stations or at the Sellafield reprocessing plant. The results of a number of measurements are shown in Table 1.

The solutions all contained <2 ppm (Cl\(^-\) + SO\(_4^{2-}\)) to avoid any chance of localised corrosion, since this leads to pitting. Experience with spent fuel stored in ponds [29] has indicated that gamma radiation accelerates the corrosion reactions to a negligible degree.

Specimens that are oxidised under reactor conditions contain carbon throughout the corrosion layer and this can act as a cathode for the evolution of hydrogen with a low overpotential (i.e. create a galvanic couple). The comparison of oxidised and etched specimens in Table 1 show that in general oxidised specimens corrode only two or three times faster than etched ones [29, 38]. The depolarising effect of the carbon may be mitigated by the lack of good electrical contact with the underlying magnesium anode.

The residual general corrosion rate at pH 11.5 (in the range 0.2 to 4 µm a\(^{-1}\)) was insignificant in relation to the cladding thickness (2000 µm), even if the fuel were to be in a pond for 10 years.

A comparison of the measurements at pH 10.5 with all those at 11.5 shows that the corrosion rates fell by roughly an order of magnitude as the pH rose by one unit. This was not the case at 80°C where changes in the pH were observed to have little effect as long as the pH was high [25]. By contrast the concentration of fluoride required to inhibit corrosion is smaller at elevated temperatures than at ambient temperature [28].

The high corrosion rates associated with elevated temperatures, or with high concentrations of chloride ion, have been observed to have linear kinetics and this has been cited as evidence of a barrier layer of constant thickness (and high leakage current) under the corrosion product. Similar observations have been made under storage pond conditions [24, 29] and it has been assumed that the long-term corrosion rate is constant [40]. Most experiments have been made by removing specimens and finding the mass of the corrosion film. This means that each point that is measured represents a new sample and the variability from one specimen to another adds to the scatter of the points. Consequently it is not always certain that another power law might not have been a better fit to the data.

### 3.10 Corrosion in calcium hydroxide

The measurement of the hydrogen evolved is a superior technique for measuring corrosion rate since a number of readings may be taken on one specimen. This was done by Platts et al. [41] as a preliminary to testing Magnox embedded in cement. They found that Magnox specimens in saturated Ca(OH)\(_2\) solutions (pH 12.5) and ones in the same solution plus 100 ppm chloride gave indistinguishable corrosion rates which over 500 days at 25°C followed a parabolic curve thus:
Rate = 3.0 \ t^{-0.45} \text{µm a}^{-1} \quad (3.19)

where \( t \) is in days. The corrosion rates from this equation are 0.38 \text{µm a}^{-1} at 100 days and 0.20 \text{µm a}^{-1} at 400 days. The corresponding depths of corrosion are 0.19 \text{µm} and 0.40 \text{µm}. Saturated calcium hydroxide with 1,500 ppm chloride gave a much faster corrosion rate of 800 \text{µm a}^{-1} (mainly by pitting). This was constant over the later stages of the 48 days of the experiment. Even higher rates were found (7300 \text{µm a}^{-1}) in a very brief experiment at 10,000 ppm chloride. At 80°C the rates were also linear and high: 27 \text{µm a}^{-1} in Ca(OH)\text{)}\text{2} and 42 \text{µm a}^{-1} in Ca(OH)\text{2} + 100 \text{ppm chloride}.

### 3.11 Corrosion in wasteforms

Encapsulation in cement produces an alkaline environment around waste Magnox cladding. This is an advantage in minimising the solubilities of most of the radionuclides which might be released by corrosion of pieces of attached fuel and in preserving a solid matrix to withstand transport and handling accidents. It could also modify the corrosion process, as the layer of porous cement could behave like an exceptionally thick corrosion film and might significantly restrict the permeation of water to the reaction site and the diffusion of hydrogen away from it. The cement would also clamp the corrosion product to the surface of the Magnox and prevent its breakaway, though not its cracking. Since one mole of magnesium hydroxide has a larger volume than one mole of magnesium, there would be a slowly increasing strain on the cement, which would eventually crack.

The corrosion of Magnox in a cement grout is characterised by three phases. The initial “acute” corrosion phase corresponds to a high corrosion rate due to the presence of plentiful free water in the fluid grout and the increase in temperature as the cement hydrates. As the grout solidifies and the passivating corrosion film develops, the availability of water becomes restricted and the temperature decreases, and so the corrosion rate falls; this is the “intermediate” corrosion phase. The “chronic” corrosion phase occurs after longer periods of time, and is characterised by a low, declining corrosion rate.

The corrosion data presented in this section were obtained mainly from reports produced by the Product Evaluation Task Force (PETF) for BNFL during the period 1983–1991. The PETF carried out a major research programme to investigate the effects of grout formulation, water / grout ratio and temperature on the corrosion rate of Magnox encapsulated in grout. A study by Fenton et al. [42] showed that the pore characteristics and permeability of the matrix were similar for several different grout formulations. After initial testing, the formulation of 3:1 BFS/OPC, w/c ratio 0.33 ± 0.2 was adopted in most of the studies. Both inactive and active specimens of Magnox were encapsulated.

Immediately after encapsulation (the “acute” corrosion phase) corrosion rates were determined using a volumetric measurement of gas evolved. At later times (the “chronic” corrosion phase) corrosion rates were measured using mass spectrometry. The corrosion rates were reported as either volume of hydrogen evolved or weight % of metal loss. A large quantity of data is available, but the data are variable which is attributed to the presence of inhomogeneities in the wasteform.

Assuming a specific surface area for the Magnox waste, the corrosion rates can be converted into units of \text{µm a}^{-1}. The resulting corrosion rates can be fitted to a power law of the form:

\[
\text{Rate} = A \ t^n
\]

where

- \( t \) is time (days), and
- \( A, n \) are constants.
3.11.1 Small-scale encapsulation of coupons

Platts et al. [41] performed laboratory experiments in which Magnox coupons were encapsulated in a 10 mm thick layer of 3:1 BFS/OPC cement with a water / cement ratio of 1:3.23 and then exposed at 25°C and 80°C in demineralised water with various additions of chloride ion. At 25°C the total hydrogen produced in each case followed the same parabolic law as the bare coupons:

\[ \text{Rate} = 0.7 t^{-0.45} \mu m \text{ a}^{-1} \]  

(3.21)

though the corrosion rate constant of 0.7 was about five times smaller than the corrosion rate constant measured in saturated Ca(OH)\(_2\) solutions (see Section 3.10). The scatter of the individual results was significant, the constant ranging from 0.4 to 2.5. This suggests that for chloride ion concentrations up to 100 ppm, the cement encapsulant had not introduced a new rate-limiting step. By contrast the corrosion rates for encapsulated coupons in 1,500 ppm chloride were markedly lower than for bare coupons unless the cement covering had fractured, indicating that the cement did act as a physical barrier reducing access of the chloride ion to the surface.

Cement encapsulated coupons exposed to water or humid air at 80°C corroded roughly twice as rapidly as the coupons in Ca(OH)\(_2\) solution at the same temperature and the latter had a much higher corrosion rate than at 25°C. At the end of the experiments all the cement coatings were cracked and it is speculated that this occurred at about 200 days into the runs of 220–500 days. The corrosion rates may have been higher than those for bare coupons on account of the less effective buffering of the pH within a crack. As a consequence some of the Magnox might have been in contact with water of a lower pH.

3.11.2 Small-scale encapsulation of Magnox swarf

Many samples of swarf have been encapsulated in cement in experiments [43–51] at the 0.5 to 2 litre scale as part of the PETF programme. Whilst only a small number of results were published by AEE Winfrith [43, 44] the corrosion of 33 specimens was logged by BNFL Sellafield [45, 46] and 29 small-scale active experiments were conducted at the Windscale Nuclear Laboratories [47–50].

The Windscale Nuclear Laboratories experiments provide the most detailed long-term data with which to calibrate the time variation of the “chronic” corrosion rate. These experiments were at ambient temperature, measured as 21 ± 2°C. The corrosion rates were recorded as volumes of hydrogen evolved during a sample period, and can be converted into units of \( \mu m \text{ a}^{-1} \) by

\[ \text{Rate} = \frac{1}{S} \frac{V_{Mg}^M}{V_H^H} \frac{\Delta V_H}{\Delta t} = \frac{2 \rho_{Mg} h V_{Mg}^M}{M_{Mg} V_H^H} \frac{\Delta V_H}{\Delta t} \mu m \text{ a}^{-1} \]  

(3.22)

where

- \( S \) is the surface area of the Magnox swarf [m\(^2\)];
- \( V_{Mg}^M \) is the molar volume of Magnox, 0.014 L mol\(^{-1}\);
- \( V_H^H \) is the molar volume of hydrogen gas, 24.14 L mol\(^{-1}\) at 1 atm and 21°C;
- \( \Delta V_H \) is the volume of hydrogen released [mL];
- \( \Delta t \) is the sample period [a];
- \( \rho_{Mg} \) is the density of Magnox, about 1740 kg m\(^{-3}\);
- \( h \) is the average thickness of the Magnox swarf, assumed to be 1.6 \( 10^{-3} \) m; and
$M_{Mg}$ is the mass of the Magnox swarf used in the experiment [kg].

All of the data are plotted in Figure 6. This plot shows that there is significant variability in the data. Only some of that variability is due to experimental uncertainty. The rest of the variability implies actual differences between the experiments. For example, the grout used to encapsulate the Magnox is heterogeneous, and therefore the higher corrosion rates could be associated with the presence of more, possibly bigger, voids in the grout.

The corrosion rates measured at times longer than one month were fitted to a power law (Equation (3.20)), and the results are presented in Table 2. (The correlation coefficients indicate the quality of the fits to the original data. A correlation of greater than 0.8 is regarded as strong, whereas a correlation of less than 0.5 is weak.)

### 3.11.3 Magnox swarf encapsulated in cement in 500 litre drums

An important question is whether the results described so far are applicable to the encapsulation of swarf in 500 litre drums for disposal in a repository. In 500 litre drums the swarf will be embedded in a much greater volume of cement, and liquid external to the drum will have access to the matrix only through its vent.

Cumulative data have been published for a number of experiments at the 500 litre scale carried out at Sellafield [46] and Winfrith [44] in Phase 4 Formulation Envelope Corrosion Studies. The five drums used at Sellafield afforded too few data points per drum, but the reviewer has analysed the results for the seven drums monitored at Winfrith. Three experiments were started in 1983 and four from 1987 onwards.

The first experiment used a 560 litre drum filled with swarf encapsulated in 3:1 BFS/OPC, left at ambient temperature (15°C). The drum contained 175 kg of Magnox, and produced a total of 55 litres of hydrogen in 935 days. A good straight line was obtained if the volume of hydrogen was plotted against $t^{0.5}$. Using Equation (3.22), the volumetric equation can be translated to (also, see Figure 7)

$$\text{Rate} = 1.7 t^{-0.5} \mu\text{m a}^{-1} \quad (3.23)$$

The constant lies between those for the encapsulated coupons (0.7) and for the coupons in saturated Ca(OH)$_2$ (3.0). After 935 days the corrosion rate was 0.05 µm a$^{-1}$ and the corrosion film thickness 2.7 µm.

A second experiment used a drum with the same contents, but doped with 10,000 ppm chloride. This would be expected to show linear corrosion kinetics, but a plot of gas volume against time was not linear, nor was one against $t^{0.5}$. The power appeared to be between 0.5 and 1.0. A log-log plot (Figure 7) of the corrosion rate against time revealed that the power law changed abruptly. Up to 57 days the hydrogen evolution followed the expression

$$\text{Rate} = 52.9 t^{-0.5} \mu\text{m a}^{-1} \quad (3.24)$$

This is thirty-one times the rate without chloride doping and at 57 days has a value of 7.0 µm a$^{-1}$. After 57 days the plot was consistent with linear kinetics and corrosion occurred at a constant rate of about 7.8 µm a$^{-1}$. The transition at 57 days might correspond to the cracking of the film under internal stress, since the thickness was in the breakaway range.

The third 500 litre drum contained swarf encapsulated in a sand/OPC grout. The measured corrosion rate (Figure 7) is similar to that for the drum filled with swarf encapsulated in 3:1 BFS/OPC.

Four other drums were part of the programme. Three were 3:1 BFS/OPC blends with water/cement ratios of 0.31, 0.33 and 0.35 and the fourth a 9:1 BFS/OPC blend with a
w/c ratio of 0.35. The samples were kept at 35°C, which was taken to be more typical of the temperature inside a shielded surface store for drums, and monitored for 470 days (by 1989). The corrosion rates were of the order of 0.1% per annum, about ten times the limit of detection. (Some of the data for the early part of the monitoring are taken from reference [43].) The double logarithmic plots are shown in Figure 8. It can be seen that after about 100 days the plots all settle to a constant corrosion rate of about 0.8 µm a⁻¹.

3.11.4 Discussion

Although the early corrosion rate for 9:1 BFS/OPC was notably higher than those for 3:1 BFS/OPC in the experiments at 35°C, all four experiments gave about the same total % corrosion and the same corrosion rates at 400 days. The long-term corrosion rates showed remarkably little scatter about a mean of 0.8 µm a⁻¹, which would mean that 4% corrosion (often estimated as the point at which cracking would occur with slowly applied expansive strains) would be reached after storage for 40 years.

Corrosion at 15°C did not appear to reach a constant rate within the duration of the experiments (900–1000 days) at these temperatures, but adhered to nearly parabolic kinetics. However, the rates at 400 days are within a factor of two of the calculated values (Equation (3.23)) and in any case are small enough to be of no consequence over a 100 year period even if the kinetics became linear.

The corrosion rate power law varies between -0.5 and 0 and it is noticeable that in the experiments at 35°C the pseudo-parabolic part of the curve occurs within the first 100 days and thereafter the kinetics become linear. It is possible that the passive film increases in thickness to begin with, but instead of continuing to do so at an ever decreasing rate it assumes a constant thickness at some point. The thickness of the passive film, which controls the corrosion rate, should be distinguished from that of the layer of corrosion product, which may not reach a constant thickness. At 35°C this transition occurs at about 100 days, but at the lower rates found at ambient temperatures it is possible that it has not been reached even at 1000 days. At the higher corrosion rates associated with high temperatures, with large concentrations of chloride or with lower pH values (as in cooling ponds) the transition time may be too small to be noticed and the kinetics may be recorded as linear.

Whilst there is adequate experimental data on the corrosion of encapsulated swarf at temperatures up to 35°C this is not the case for the extreme repository temperature (80°C). The measurements [25] made on bare coupons in the pH range 11.4 to 13 at 40–120°C were unequivocal in indicating that the corrosion rate would be nearly ninety times higher than at 35°C. This rise would only be mitigated if encapsulation introduced a new rate-limiting step which had a smaller temperature coefficient, such as diffusion in water.

During corrosion a water concentration gradient would be set up in the encapsulant. The length of time needed to consume the free water can be estimated as follows. BFS/OPC grouts are found by drying to contain up to 10% by weight of “free water” so that the 0.4 m³ of grout (800 kg) in a drum would contain up to 80 kg of water. This is sufficient to corrode 53 kg of Magnox or 30% of a typical drum loading. By the time 4% of the Magnox had corroded only 12% of the “free water” would have been used up. At a corrosion rate of 0.1% a⁻¹ (the corrosion rate at 35°C) it would take 300 years to consume all the free water. The rate of corrosion in grout at 35°C is similar to that observed in bulk solutions, indicating that the corrosion rate is not limited by diffusion of water through the grout at these lower temperatures.

It is not clear whether the corrosion rate of Magnox at 80°C at the 500 litre drum scale would be limited by the supply of water, because the necessary experiments have not been carried out. Based on experiments in aqueous solutions, the corrosion rate at 80°C could be 80–400 times faster than at 35°C, depending on whether spalling had occurred. If such high corrosion rates occurred in cement the free water would be consumed within approximately 1 to 4 years.
There are two possible situations: (1) before resaturation the corrosion rate might be limited at the highest temperature by restricted water supply, and (2) after resaturation it is likely that there would be sufficient water present to maintain the corrosion at a high rate, provided the rate of transport of water through the grout, by diffusion or passage through cracks, was sufficiently rapid.

The experimental results on swarf encapsulated in 500 litre drums give no support for a new rate-limiting step, at least up to 35°C, as the corrosion rates are within a factor of two of those observed with bare coupons. It is possible that the projected ninety-fold increase in rate at 80°C would reveal the permeation of water up to the corroding swarf to be a rate-limiting step not seen at lower corrosion rates, but there is no evidence for this. When coupons encapsulated in a 10 mm thickness of cement were exposed at 80°C in demineralised water containing chloride ion, corrosion was rapid and the cement cracked after an estimated 200 days [41]. A final resolution of this uncertainty would require trials at 80°C at the 500 litre drum scale.

In summary, the information from hydrogen evolution experiments on encapsulated Magnox coupons and from full scale tests on 500 litre drums indicates that at ambient temperatures the reaction mechanism follows a parabolic law and that the rates are quite close to those measured for bare coupons in saturated calcium hydroxide. This is true even if 100 ppm chloride is present, but at 1,500 ppm chloride bare coupons corrode quite rapidly whilst an unbroken cement cover acts as a barrier to the diffusion of chloride to the site of corrosion. At 35°C the corrosion follows a linear law and the rate is about ten times greater. Raising the temperature to 80°C causes rapid corrosion of bare and encapsulated coupons and the cement cracks in about 200 days. There is no evidence that this would not happen in 500 litre drums, but only full scale trials at 80°C would resolve this uncertainty.

### 3.12 Conclusions

There is useful information about most aspects of the corrosion of magnesium in alkaline solutions, but it is clear that there are some inconsistencies in the explanations that are given and some points, such as the existence of a barrier film below the corrosion film, and the regimes for parabolic and linear corrosion kinetics are uncertain. The main conclusions are:

- The corrosion of magnesium should lead to the precipitation of Mg(OH)$_2$ at pH values above 10.4.
- A multi-component layer of MgH$_2$/MgO/Mg(OH)$_2$ on the surface of the metal may raise the corrosion potential ($E_{\text{corr}}$) more than 1V above the calculated thermodynamic electrode potential.
- The presence of noble metals (including iron) in contact with the magnesium or the presence of inclusions of iron drives $E_{\text{corr}}$ more positive, as hydrogen is generated with a lower overvoltage, and the rate of corrosion is increased.
- The corrosion rate is also restricted by a passive film on the surface of the metal and any change that increases the leakage current across this film increases the corrosion.
- In alkaline solution the major component of the corrosion film is brucite (Mg(OH)$_2$).
- The corrosion product film appears to be amorphous and does not have the properties expected of a passive film which limits corrosion. Some investigators have postulated the existence of a barrier film of MgO below the corrosion film, but so far it has eluded detection.
- Measurements using H$_2^{18}$O have shown that the film grew at its base (next to the metal) and that its growth rate fell once the film was a few hundred nanometres thick.
A subsequent linear increase in thickness with time is adduced as evidence of a barrier film of constant thickness.

- Fluoride ion inhibits corrosion. At 80°C a concentration of 0.05M will suffice, but at ambient temperatures more than 1M is required. Then a compact film only a few nanometres thick is formed.

- Chloride ion is aggressive and disrupts the passive film. The leakage current is increased and the voltage at which the film undergoes catastrophic breakdown falls towards $E_{corr}$ as the chloride level increases.

- The tolerance levels for chloride are about 1,000 ppm in the presence of 1,000 ppm fluoride, 100 ppm on plain samples, 10 ppm if there is galvanic coupling and 1 ppm if crevices are present.

- At elevated temperatures, or high chloride levels, the corrosion rates are high enough for the film thickness to reach several microns and for breakaway to be seen during the experiments.

- The order of descending aggressiveness is:
  \[ \text{Cl}^- > \text{SO}_4^{2-} > (\text{CO}_3^{2-}, \text{SiO}_3^{2-}) > \text{NO}_3^- \]

- Measurements at elevated temperatures in NaOH solutions show that the corrosion rate increases according to the following expression:

  \[
  \text{Rate} = 1.2 \times 10^{15} \exp\left(-\frac{10720}{T}\right) \mu\text{m a}^{-1}
  \]

  This predicts that the rate will start at about 0.3 $\mu$m a$^{-1}$ at $T = 25^\circ$C and rise through 1.6 $\mu$m a$^{-1}$ at 40°C to reach 78 $\mu$m a$^{-1}$ at 80°C.

- Silicate contamination of the solution leads to higher corrosion rates above 60°C, but delays the breakaway of the film. When this happens in uncontaminated solutions the corrosion rate may increase another five times.

- Coupons in saturated Ca(OH)$_2$ solutions, coupons encapsulated in BFS/OPC and suspended in water, and swarf in 500 litre drums all exhibited the same parabolic corrosion kinetics at ambient temperatures:

  \[
  \text{Rate} \approx A t^{-0.5} \mu\text{m a}^{-1}
  \]

  where $t$ is in days, and $A$ was 3.0, 0.7 and 1.5 in the three cases respectively.

- Chloride at concentrations of 1,500 and 10,000 ppm accelerated the corrosion of coupons, but encapsulation in cement inhibited corrosion until cracking of the cement cover occurred.

- At 80°C encapsulated coupons suspended in water corroded even more rapidly (60 $\mu$m a$^{-1}$) than those in saturated Ca(OH)$_2$ (27–42 $\mu$m a$^{-1}$), possibly because the coatings had cracked and the pH of the water in the crack was not well buffered by contact with the walls.

- There is no evidence for “water starvation” limiting corrosion rates in 500 litre drums at ambient temperature. Although corrosion rates are much larger at 80°C the reserve of “free water” in the BFS/OPC matrix is enough for extensive corrosion to occur.
• Voids in the grout matrix are associated with a significant increase in the corrosion rate, which could be due to increased accessibility of water to the metal surface.
4 Parameterisation of SMOGG Model for Magnox

4.1 SMOGG model

The model implemented in SMOGG [3, 4] specifies the corrosion rate of Magnox as:

\[
\frac{ds}{dt} = -k_a e^{-\frac{t}{t_a}} f_a(T) - k_c e^{-\frac{t}{t_c}} f_c(T) \tag{4.1}
\]

where

- \( s \) is the position of the surface of the Magnox [m];
- \( t \) is the time during which corrosion is occurring [a];
- \( k_a \) is the initial acute corrosion rate (defined at a reference temperature, \( T_{ref} \), for which \( f_a = 1 \) [m a\(^{-1}\)];
- \( t_a \) is a characteristic time for the acute corrosion [a];
- \( f_a \) is a factor that specifies the dependence of the acute corrosion rate on temperature [-];
- \( T \) is the temperature [K];
- \( k_c \) is the initial chronic corrosion rate (defined at a reference temperature, \( T_{ref} \), for which \( f_c = 1 \) [m a\(^{-1}\)];
- \( t_c \) is a characteristic time for the chronic corrosion [a];
- \( f_c \) is a factor that specifies the dependence of the chronic corrosion rate on temperature [-].

This formulation allows separate corrosion rates to be specified for an initial “acute” phase and a later “chronic” phase.

Furthermore, for the purpose of this study the model is simplified by assuming the corrosion rates increase with temperature according to an Arrhenius relationship. That is:

\[
f_a(T) = \exp \left[ -\frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_{ref}} \right) \right] \tag{4.2}
\]

and

\[
f_c(T) = \exp \left[ -\frac{E_c}{R} \left( \frac{1}{T} - \frac{1}{T_{ref}} \right) \right] \tag{4.3}
\]

where

- \( E_a \) is the activation energy for the acute corrosion [J mol\(^{-1}\)];
- \( R \) is the gas constant [J mol\(^{-1}\)K\(^{-1}\)];
$T_{ref}$ is a reference temperature at which $k_a$ and $k_c$ are defined [K]; $E_c$ is the activation energy for the chronic corrosion [J mol$^{-1}$].

Hence, a total of six parameters must be specified to define the corrosion rate of Magnox for a particular corrosive environment:

- two rate constants ($k_a$ and $k_c$, giving the base corrosion rates);
- two characteristic times ($t_a$ and $t_c$, defining the decrease with time); and
- two activation energies ($E_a$ and $E_c$, defining the effect of temperature).

It is anticipated that Magnox waste generally will be encapsulated in cement in metal containers to form stable and easily movable packages. The conditioned waste then will be transported to a deep underground repository and at an appropriate time surrounded by a cement-based backfill. The Magnox will react with cement porewater to give hydrogen, irrespective of the availability of oxygen. Therefore the two corrosive environments of interest are:

- an alkaline, cementitious environment; and
- after resaturation, an alkaline (pH 12.5–13) porewater which has mixed with groundwater containing chloride ions and various other inorganic salts.

### 4.2 Approach

Given the number of parameters that require calibration, it was decided the approach should be to fit the parameters separately where possible, and then to complete the calibration of the remaining parameters making use of the values that already had been determined. For example, by using the results of experiments at constant temperature, rate constants (for that temperature) and characteristic times can be calibrated without having to fit activation energies simultaneously.

The order in which the parameters can be calibrated depends on the types of experimental data available. In the case of measurements of gas generation from corrosion of Magnox, most of the data are from the PETF programme [43–51], with supplemental data in a few other miscellaneous studies (e.g. [41]). The PETF programme continued over a number of years and considered a range of scenarios for packaged Magnox waste. The data include:

- The variation of hydrogen generation rates over time, both:
  - in the long term; and
  - in the short term, including while the package is subject to temperature variations associated with grout curing.
- Long-term hydrogen generation rates at various temperatures.

Based on initial consideration of the available experimental data, it was decided that the calibration process should consider the long-term behaviour first. Using measurements of gas generation from corrosion of Magnox repeated at regular intervals over an extended time scale, the chronic corrosion rate constant and characteristic time can be calibrated. This is considered in Subsection 4.3.

By comparing the corrosion rates at similar times (~1 year) from a number of experiments performed at different temperatures, the variation with temperature can be determined and the activation energy for the chronic corrosion can be calibrated. This is considered in Subsection 4.4.
Using the calibrated parameters for the chronic corrosion, the more complex behaviour seen in experiments in the short term can be examined. This is considered in Subsection 4.5.

Finally, by comparing the corrosion rates from experiments performed with different concentrations of chloride ions, the effect of the chloride ions can be determined. This is considered in Subsection 4.6.

An important issue for most of the experimental data was the conversion of the reported corrosion rates into the units required by SMOGG. In most cases, the corrosion rates had been reported as a fraction of Magnox corroded per unit time. SMOGG corrosion rates are expressed as a depth of corrosion per unit time. To convert the experimental results into SMOGG units required information about the geometry of the Magnox samples in the experiments, which was not given. However, the Magnox samples used either had been shaped to have the approximate dimensions of Magnox swarf, or, in the case of active experiments, were samples of actual swarf. Magnox swarf can be considered as roughly plate-like, and although there is variation in the effective thicknesses between pieces of Magnox swarf from different sources (i.e. fuel cans from different stations) this is tightly bounded. Therefore, all the experimental results were converted using the assumption that the Magnox is in the form of plates with thickness 1.6 mm (an approximate average of the effective thicknesses of Magnox swarf, taking into account the range of fuel can designs).

### 4.3 Variation of the corrosion rate with time

To determine how the corrosion rate of Magnox varies with time, data are required from long-term, constant temperature experiments in which the corrosion rate has been measured at a large number of times. The objective of most of the long-term experimental studies was to determine a single value (either an average or a maximum) for the long-term corrosion rate, so only a few measurements were made. However, one substantial set of experiments performed under the PETF programme at Windscale [47–50] does provide sufficiently detailed data with which to calibrate the time variation of the chronic corrosion rate. It was decided therefore to calibrate the chronic corrosion rate constant and characteristic time using the results of these experiments, and then to check the consistency of this calibration against the less detailed results from other experiments.

The experimental series to be used for the calibration includes 24 data sets (see Figure 6) with the required constant temperature condition. All of the data sets were from experiments performed at ambient temperature (measured as 21±2°C). The approach to performing the calibration involved using a nonlinear regression computer program [52] to determine a best fit of the SMOGG model:

\[
\frac{ds}{dt} = -k_a e^{-\frac{t}{\tau_a}} - k_c e^{-\frac{t}{\tau_c}}
\]

(4.4)

to the data.

The nonlinear regression algorithm supposes each data point has a measurement error that is independent, random and distributed as a normal distribution around the “true” model. A probability plot\(^{vi}\) may be used to assess this assumption.

To test the assumption of normality, the data were binned into ten distinct time intervals each lasting about 0.5 years. This bin size was chosen as a compromise: the size hopefully was

---

\(^{vi}\) A probability plot is a graphical technique for assessing whether or not a data set follows a given distribution, such as the normal. The data are plotted against a theoretical distribution in such a way that the points should form approximately a straight line. Departures from the straight line indicate departures from the specified distribution.
small enough that the corrosion rate was approximately constant in each bin, but also was
large enough that the bin contained a significant number of data points. Then the data in
each bin were compared against a normal distribution.

The normal probability plot showed a strongly nonlinear behaviour, with the data skewed
right, and so it was concluded that the measurement errors are not distributed normally.
Therefore a right-skewed distribution, such as the lognormal distribution or the Weibull
distribution, is needed to model the measurement errors.

Figure 9 is a lognormal probability plot of the data. The points on this plot mainly form
approximately linear patterns, which suggest that the measurement errors can be modelled
reasonably with a lognormal distribution. Some features of the plot that should be noted are:

- The data for the bin $0.083a < t < 0.5a$ show a nonlinear behaviour, presumably
  because in this bin the corrosion rate is varying also with time; and

- The data for the bins $t > 4a$ appear to have anomalously low corrosion rates. This is
  because specimens which had high hydrogen release rates were not exposed
  beyond 4 years. However, it is more appropriate to use average chronic corrosion
  rates, rather than those for just the “good” encapsulations, since the repository may
  contain a range of packages with a varying quality of encapsulated product.

Therefore it was decided that the SMOGG model should be fitted to the logarithms of the
experimental data, for data points which had been observed at times greater than 0.5a and
less than 4a.

The outcome of the nonlinear regression analysis was that at a temperature of about 20°C:

- $k_a = 2.52 \ \mu m \ a^{-1}$, with a standard deviation of $0.69 \ \mu m \ a^{-1}$;

- $t_a = 0.790a$;

- $k_c = 0.12 \ \mu m \ a^{-1}$, with a standard deviation of $0.51 \ \mu m \ a^{-1}$; and

- $t_c$ is large, and so is assumed to be infinity.

Figure 10 compares the experimental data with a “Preferred” fit, in which $k_a$ and $k_c$ have the
values determined from the regression analysis, and a “Conservative” fit, in which $k_a$ and $k_c$
have been increased from the “Preferred” fit values by about two standard deviations (i.e. this
is the upper end of the 95% confidence interval).

A series of experiments performed under the PETF programme at Winfrith [43, 44] was
examined. This series includes experiments at a number of scales, with different types of
gROUT, at ambient and elevated temperatures, and with the addition of sodium chloride. To
determine the long-term corrosion rate, results from all the experiments that were performed
using BFS/OPC grOUT, at 20°C, and without the addition of sodium chloride were combined.
From this subset of results, to exclude short-term corrosion effects, only measurements taken
after more than a year into the experiments were considered. The range of the corrosion rate
was found to be $0.005–0.027 \ % \ a^{-1}$. This is equivalent to $0.04–0.2 \ \mu m \ a^{-1}$ if it is assumed that
the Magnox is in the form of plates of thickness 1.6 mm (see Subsection 4.2).

Another series of experiments performed under the PETF programme at Sellafield [45, 46]
was also examined. Again, combining only results from those experiments performed at
ambient temperature and without the addition of ions (in this case boron and chromate), and
considering only measurements taken after more than a year into each experiment, the range
of the corrosion rate was found to be $0.0008–0.033 \ % \ a^{-1}$. This is equivalent to $0.006–
0.26 \ \mu m \ a^{-1}$, assuming that the Magnox is in the form of plates of thickness 1.6 mm.
Finally, Platts et al. [41] determined corrosion rates of Magnox from experiments under a range of conditions at various times extending over a period of several years. Based on the results obtained, the authors proposed power-law relationships for the cumulative corrosion of Magnox in a solution of calcium hydroxide and in cement. However, other relationships were shown also to fit the data. In fact, from the plots of the data (Figure 7 of reference [41]) it is not clear there is a reduction in the corrosion rate of Magnox in cement after about half a year. Assuming the corrosion rate after 0.5 a is constant, then from the experiments with Magnox in cement at 25°C and without chloride, the corrosion rate is approximately 0.04–0.26 µm a⁻¹ (calculated from the change in the amount of Magnox corroded from 0.5 a to the end of the experiments).

In summary, the above results consistently indicate that at about 20°C with no addition of ions, a corrosion rate of approximately 0.12 µm a⁻¹ would persist in the long term.

4.4 The effect of temperature

To determine the variation of the corrosion rate with temperature, measurements from experiments performed at a number of temperatures, but otherwise under similar conditions, are required. Two observations suggest the SMOGG model is too simplistic, and so the analysis of the data might not be straightforward:

- In general, following encapsulation of Magnox in grout, the maximum hydrogen release occurs before the peak temperature.
- In experiments where the temperature is cycled from a low value up to a high value and then back down to the original value, typically the corrosion rate does reduce towards the long-term rate, but only gradually (Figure 11).

Consequently, there is not a simple correlation between the corrosion rate and the temperature, as is assumed in SMOGG.

Work performed under the PETF programme at Winfrith [43, 44] provides long-term, approximately constant corrosion rates (thus eliminating the issue of time scale) at several temperatures. The results at 20°C have been discussed already in Subsection 4.3. The corrosion rate was found to be in the range 0.04–0.2 µm a⁻¹. Using the same approach with other experiments from the series that were performed at 60°C gives a corrosion rate of 2.3–19 µm a⁻¹. The series also can provide the corrosion rate for a temperature of 35°C, as the temperature was increased to this value for several of the experiments performed initially at 20°C. Allowing 0.5 a from the time when the temperature was increased for the corrosion rate to reach a constant value, the rate is 0.23–1.2 µm a⁻¹ at 35°C.

The Sellafield PETF work [46] also can provide useful data on the variation of the corrosion rate with temperature. Although the same experiments have not been performed at different temperatures, the temperature was varied during several experiments. There are three sets of experiments of this nature:

- B, C, E and F in which the temperature was increased from ambient to 40°C, and then to 60°C, and subsequently was decreased back to 40°C, and then to ambient;
- 1, 2, 3 and 4 in which the temperature initially was 80°C, and then was decreased to 40°C, and then to ambient; and
- G and J in which the temperature was increased from ambient to 60°C, and then was decreased back to ambient.

In the first of these sets, the time between the variations in temperature is relatively short and the number of measurements too few to provide long-term corrosion rates at elevated temperatures. The second set could provide data for long-term corrosion rates at 40°C and at
ambient temperature. However, it is possible the initial period of rapid corrosion at 80°C would reduce the later long-term corrosion rate at the lower temperatures compared with a case in which Magnox had corroded only at the lower temperatures. Experiments G and J were performed for approximately 600 days at ambient temperature and for a further approximately 600 days at 60°C. This allowed an approximately constant corrosion rate to be established at both temperatures. Taking results from times more than 0.5 a after the start of the experiment and after the change of temperature gives corrosion rates of 0.003–0.04 % a⁻¹ (0.02–0.3 µm a⁻¹) and 0.83–1.4 % a⁻¹ (6.6–11 µm a⁻¹) for ambient temperature and 60°C respectively.

The work of Platts et al. [41] includes results for experiments performed at 80°C, as well as for those at 25°C discussed in Subsection 4.3. The long-term corrosion rate for Magnox in cement at 25°C without chloride was found to be 0.04–0.26 µm a⁻¹. From the results of the equivalent experiments performed at 80°C, making the same assumptions and following the same method as discussed previously, the long-term corrosion rate is approximately 30–70 µm a⁻¹.

For each set of experimental results above, the activation energy can be determined using Equations (4.1) – (4.3). The measured corrosion rates are long-term, constant rates, so the term representing acute corrosion can be set to zero and the exponential decay with time can be ignored (i.e. the characteristic time for the chronic corrosion is infinite). Therefore:

\[
\frac{ds}{dt} = -k_c \exp \left[ -\frac{E_c}{RT} \left( \frac{1}{T} - \frac{1}{T_{ref}} \right) \right] = -k_c \exp \left[ \frac{E_c}{RT_{ref}} \right] \exp \left[ -\frac{E_c}{RT} \right]
\]  

(4.5)

In Equation (4.5) the exponential factor has been separated into a constant part and a part that varies with temperature.

A best fit to the results from all the experiments can be calculated. Equation (4.5) shows that there is a linear relationship between the logarithm of the corrosion rate and the reciprocal of the temperature, allowing a fit to be determined using standard mathematical techniques. The fit is shown in Figure 12, which also includes the data used. The figure plots the logarithm of the averaged corrosion rates against the reciprocal of the temperature to demonstrate the linearity of the relationship. The activation energy given by the best fit is 94 kJ mol⁻¹.

It is worth noting that Francis et al. [53] also calculated an activation energy for the variation of the corrosion rate of Magnox with temperature. In their work, Magnox was corroding under aqueous conditions, so it is less clear whether the results are applicable to the corrosion of Magnox in a cementitious environment. However, their results were for a wider range of temperatures (16–100°C) than those described above, so could be used to support the result obtained here. Francis et al. report a best fit to the activation energy of 64.3 kJ mol⁻¹ (for corrosion in the absence of inhibitors). There is some doubt about this value, since the plot from which it is said to have been calculated appears to indicate a larger activation energy of about 70 kJ mol⁻¹.

### 4.5 Corrosion when the grout is curing

Only a small number of experiments were identified that give detailed results for the short-term corrosion of Magnox. In particular, three of the experiments performed under the PETF programme at Windscale [49, 50] (TPC3–5) provide suitable data against which to calibrate the SMOGG model. Unfortunately, performing a calibration against these
experiments is complicated, as a temperature variation simulating the effect of grout curing was applied to the experiments.

All three experiments were on 2 litre samples containing similar pieces of Magnox in grout of the same formulation, except that the water to solids ratio was slightly lower for TPC3. The effect of this difference is not expected to be significant, and examining other experiments from Windscale [49, 50] there does not appear to be any consistent difference in the corrosion rates between experiments differing only in their water to solids ratio. In all three experiments the temperature was controlled according to a single predefined profile. The intended temperature profile is shown in Figure 13, together with the measured temperatures from the three experiments. The figure shows that the intended temperature profile is reproduced well in experiments TPC3 and TPC5, and the match for experiment TPC4 is reasonable. Based on this similarity of the temperature profiles, a single calibration against the three experiments is considered valid.

After the initial period during which the temperature was varied to simulate the effect of grout curing, the samples were placed in a water bath to hold the temperature at 35°C (±1°C) and the hydrogen release rate was monitored for a further approximately 200 days. Figure 14 is a plot of all the data obtained.

By the end of the experiments, the measured corrosion rates had not achieved a constant long-term value, but the data are not inconsistent with:

- a chronic corrosion rate constant of 0.12 µm a⁻¹, calibrated at 20°C (Subsection 4.3); and
- an activation energy of 94 kJ mol⁻¹ (Subsection 4.4).

These parameters imply that at 35°C the chronic corrosion rate should be 0.78 µm a⁻¹, which is less than most of the values measured during the experiments.

In contrast, the characteristic time inferred from the decline in the experimental data after the samples had been placed in the constant-temperature water bath is 0.232a. This means that the observed corrosion rates decrease more rapidly with time than expected from the characteristic time derived in Subsection 4.3, namely 0.790a. A possible explanation of this behaviour is that a barrier film forms on the surface of the metal, and the film initially increases in thickness, but instead of continuing to do so at an ever decreasing rate it assumes a constant thickness at some point (see the discussion in Subsection 3.11.4). The higher the temperature, the quicker the barrier film would form, and correspondingly the smaller the characteristic time would be. Thus the assumption made in SMOGG that the characteristic time is a constant may be wrong, and actually the characteristic time could depend on the past corrosive environment of the Magnox.

This limitation of the SMOGG corrosion model is noted, but is not considered further because:

- the scope of the current study is to parameterise the existing model;
- there are insufficient short-term corrosion data covering a wide range of temperatures to determine how the characteristic time might vary with corrosive environment; and
- if the above arguments are correct, the use of a constant characteristic time calibrated at 20°C would lead to an overestimate in the corrosion rate of Magnox at higher temperatures, but for only a few years after encapsulation of the metal.

To reiterate, the SMOGG model for the corrosion rate of Magnox (see Equations (4.1) – (4.3)) is:
\[
\frac{ds}{dt} = -k_a e^{-\frac{t}{ta}} \exp\left[-\frac{E_a}{RT}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right] - k_c e^{-\frac{t}{tc}} \exp\left[-\frac{E_c}{RT}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]
\]  
(4.6)

where it has been shown in Subsections 4.3 and 4.4 that:

- \(k_a = 2.52 \mu m a^{-1}\);
- \(t_a = 0.790a\);
- \(T_{ref} = 293.15K\);
- \(k_c = 0.12 \mu m a^{-1}\);
- \(t_c \to \infty\); and
- \(E_c = 94 kJ mol^{-1}\).

The question to be addressed here is the following: Is it possible to calibrate the last unknown parameter, the acute corrosion activation energy \(E_a\), to give a reasonable fit between the model and the measured corrosion rates for experiments TPC3–5?

The outcome of a nonlinear regression analysis was that the activation energy for the acute corrosion is 69 kJ mol\(^{-1}\). (Interestingly, this value is close to the activation energy reported by Francis et al. [53].)

The final fit of the SMOGG corrosion to experiments TPC3–5 is shown in Figure 15. It can be seen that the model predicts a peak corrosion rate that is both smaller than (i.e. about three-quarters of the observed value) and occurs later than the measured maximum. This is consistent with the comment in Subsection 4.4 that following encapsulation of Magnox in grout, the maximum hydrogen release occurs before the peak temperature. The reason for this behaviour is not known, and so it is not clear how the SMOGG model could be modified to improve the fit.

Figure 16 compares the modelled and measured cumulative volumes of hydrogen released. As expected from Figure 15, the model underestimates the amounts of hydrogen released, most of the discrepancy arising during the first day of the experiments.

4.6 The effect of chloride

In SMOGG, the final phase of a waste package life-cycle occurs after resaturation of the repository with groundwater, which may contain a significant concentration of chloride ions. The presence of chloride can damage the protective film. A critical chloride concentration of 70–700 ppm has been observed in 0.01 M NaOH at pH 12. This critical level is reduced to about 10 ppm chloride if there is galvanic coupling to steel, or to about 1 ppm chloride if a crevice is present. After the repository has resaturated, it is quite likely that the levels of chloride will be sufficient to damage the protective film, leading to localised attack or spalling of the film, with substantial increases in the corrosion rate.

The Winfrith PETF work [43, 44] includes experiments with and without the addition of sodium chloride (Figure 7). As discussed in Subsection 4.3, for the experiments that were performed using BFS/OPC grout, at 20°C, and without the addition of sodium chloride, the range of the long-term corrosion rate was found to be 0.005–0.027 % a\(^{-1}\). This is equivalent to 0.04–0.2 \mu m a\(^{-1}\) if it is assumed that the Magnox is in the form of plates of thickness 1.6 mm. Using the same approach for the experiments with the addition of sodium chloride, the range of the long-term corrosion rate was found to be 0.4–1.6 % a\(^{-1}\), or 3–12 \mu m a\(^{-1}\). On average,
this is almost two orders of magnitude larger than the corrosion rate without the addition of sodium chloride.

The work of Platts et al. [41] also considers the effect of chloride on Magnox corrosion. Only one set of results is given for corrosion in a cementitious environment. The results in this case do not show any enhancement of the corrosion rate compared with results from similar experiments containing no chloride. Equivalent results for experiments in calcium hydroxide solution do show an enhancement of the corrosion rate in the presence of chloride. However, only short-term results are provided (i.e. up to about 0.5 a).

### 4.7 Selection of data recommended for use in SMOGG

The objective of this study was to parameterise the corrosion model for Magnox that has been implemented in SMOGG, as given by Equations (4.1) – (4.3). In Subsections 4.3–6, the available data have been identified and interpreted, as far as possible, to give values for the various parameters. This subsection summarises the set of parameters for Magnox corrosion recommended for use in SMOGG.

- The initial acute corrosion rate \( (k_a) \) is 2.52 µm a\(^{-1}\) at 20°C.
- The characteristic time for the acute corrosion \( (t_a) \) is 0.790a.
- The acute corrosion rate increases with temperature according to an Arrhenius relationship:
  \[
  f_a(T) = \exp \left[ -\frac{69000}{8.314472 \left( \frac{1}{T} - \frac{1}{293.15} \right)} \right]
  \]  
  (4.7)
  where \( T \) is the temperature [K]. For example, at the temperatures listed below the initial acute corrosion rate should be scaled by the corresponding factors:

<table>
<thead>
<tr>
<th>Temperature, ( T )</th>
<th>20°C</th>
<th>35°C</th>
<th>50°C</th>
<th>80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor, ( f_a )</td>
<td>1.000</td>
<td>3.967</td>
<td>13.847</td>
<td>122.693</td>
</tr>
</tbody>
</table>

- The initial chronic corrosion rate \( (k_c) \) is 0.12 µm a\(^{-1}\) at 20°C.
- The characteristic time for the chronic corrosion \( (t_c) \) essentially is infinite\(^i\).
- The chronic corrosion rate increases with temperature according to an Arrhenius relationship:
  \[
  f_c(T) = \exp \left[ -\frac{94000}{8.314472 \left( \frac{1}{T} - \frac{1}{293.15} \right)} \right]
  \]  
  (4.8)
  where \( T \) is the temperature [K]. For example, at the temperatures listed below the initial chronic corrosion rate should be scaled by the corresponding factors:

\(^i\) In using the SMOGG model a finite value is required; a value much greater than the duration of the calculation (i.e. at least an order of magnitude greater) should be used.
The corrosion rate is independent of oxygen concentration.

In the presence of significant chloride concentrations, the initial acute and chronic corrosion rates, $k_a$ and $k_c$, increase by a factor of 100. (The corrosion may be limited by local restrictions on the supply of water.)

Calculations of gas generation performed with SMOGG might include variant cases intended to scope the effect of uncertainties in the model parameters. From the experimental results examined here, upper estimates have been determined for some of the parameters of the Magnox corrosion model in SMOGG.

- The initial acute corrosion rate could be increased to 3.87 $\mu$m a$^{-1}$ at 20°C. (This is the upper end of the 95% confidence interval, calculated from the mean and standard deviation given in Subsection 4.3).
- The initial chronic corrosion rate could be increased to 1.11 $\mu$m a$^{-1}$ at 20°C. (This is the upper end of the 95% confidence interval, calculated from the mean and standard deviation given in Subsection 4.3).
- From Figure 12, the uncertainty in the chronic corrosion activation energy (94 kJ mol$^{-1}$) is about 10%, and the range for the parameter is 82–106 kJ mol$^{-1}$.

### 4.8 Discussion

Having derived a parameterisation of the SMOGG model for the corrosion rate of Magnox (Subsection 4.7), it is useful to compare the resulting values with the corrosion rates used previously.

In the *Nirex 97* assessment of gas generation from radioactive wastes [54], the Magnox corrosion rate was assumed to be given by the expression

$$ \text{Rate} = 1.18 \times 10^{21} \exp\left(-\frac{14800}{T}\right) \mu\text{m a}^{-1} $$

(4.9)

This is twice the rate given in Equation (3.18). The consequences of this assumption are:

- The (chronic) corrosion rate is 0.14 $\mu$m a$^{-1}$ at 20°C.
- At the temperatures listed below, the (chronic) corrosion rate should be scaled by the corresponding factors:

<table>
<thead>
<tr>
<th>Temperature, $T$</th>
<th>20°C</th>
<th>35°C</th>
<th>50°C</th>
<th>80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>1.000</td>
<td>11.676</td>
<td>108.520</td>
<td>5311.140</td>
</tr>
</tbody>
</table>

Comparing the two sets of long-term corrosion rates (see Subsection 4.7 and above), the values at 20°C are in good agreement. However, in the *Nirex 97* assessment the corrosion rate was assumed to increase more rapidly with temperature than is now being
recommended. This is because the activation energy used was 123 kJ mol\(^{-1}\) instead of 94 kJ mol\(^{-1}\).

The activation energy of 123 kJ mol\(^{-1}\) was derived from experiments on the corrosion of Magnox in sodium hydroxide solution (at temperatures in the range 40–120°C) after breakaway of the corrosion product film. Before breakaway of the corrosion product film, the activation energy was 89 kJ mol\(^{-1}\) (Subsection 3.8). A priori the latter activation energy would seem more relevant to the long-term corrosion of Magnox encapsulated in cement, and indeed 89 kJ mol\(^{-1}\) is reasonably consistent with the activation energy, 94 kJ mol\(^{-1}\), derived from the experiments performed under the PETF programme.

In conclusion, the activation energy assumed in the Nirex 97 assessment was probably too high, and the chronic corrosion activation energy of 94 kJ mol\(^{-1}\) recommended in Subsection 4.7 is more justified.

Subsequent assessments of gas generation from radioactive wastes have generally reused the Nirex 97 parameterisation of the Magnox corrosion rate [54], except that the Generic Post-closure Performance Assessment [2] assumed additionally that during storage at 35°C local restrictions on the availability of water would limit the Magnox corrosion rate to 0.038 µm a\(^{-1}\). The data acquired from the experiments performed under the PETF programme do not support this assumption.
5 Corrosion Data for Aluminium

The papers and reports that were obtained about the corrosion of aluminium and aluminium alloys can be divided into the following main categories:

- Corrosion of aluminium in bulk aqueous alkaline conditions, e.g. NaOH, KOH, Ca(OH)$_2$, and porewater extracts.
- Corrosion of aluminium in concrete, mortar, cement and other alkaline building materials.
- Corrosion of aluminium in grouts.

5.1 Corrosion in aqueous solutions

5.1.1 Overview

Although aluminium is a reactive metal it can nevertheless be used for many practical applications because of the adherent, protective oxide and hydroxide films which develop on its surface. However, as the oxides are amphoteric, aluminium is not resistant to corrosion in acidic and alkaline conditions, because the protective films dissolve. The overall behaviour of aluminium can be summarised by the Pourbaix diagram, as shown in Figure 17 [55, 56]. This diagram shows the stability of aluminium as a function of the pH and potential. It is based on thermodynamic data for the reactions which are believed to occur during the corrosion of aluminium in aqueous solutions. At high pH values the stable form of aluminium is AlO$_2^-$.

The regions of corrosion, immunity and passivation are shown in Figure 18. The E-pH diagram has been extended by Giminez et al. [57] for the alloy 5086 to take account of pitting which occurs in the passive range in the presence of chloride (Figure 19), and Lowson [58] has produced a 3-dimensional E-pH-T diagram to demonstrate the effect of temperature on the stability of aluminium oxide phases. The corrosion of a wide range of aluminium alloys in alkaline environments has been investigated and the compositions of the most common alloys tested are given in Table 3. A more detailed summary of the composition of aluminium alloys is given in reference [59]. Throughout this review the following conversion factors have been used to normalise the corrosion rates of aluminium:

$$1 \text{ µA cm}^{-2} = 0.805 \text{ mg dm}^{-2} \text{ d}^{-1} (i.e. \text{ mdd}) = 0.1 \text{ litres (at NTP)} \text{ H}_2 \text{ m}^{-2} \text{ d}^{-1} = 10.9 \text{ µm a}^{-1}$$

When aluminium is immersed in highly alkaline conditions the air-formed oxide (amorphous Al$_2$O$_3$ [9]) is dissolved and the metal is activated [60]. The corrosion potential then drops to -1250 mV NHE, compared to the equilibrium thermodynamic potential of -1676 mV NHE associated with the anodic corrosion reaction [61]:

$$\text{Al} \rightarrow \text{Al}^{3+} + 3e^- \quad (5.1)$$

In alkaline conditions the aluminium ion reacts with hydroxide ions to form aluminium hydroxide:

$$\text{Al}^{3+} + 3\text{OH}^- \rightarrow \text{Al(OH)}_3 \quad (5.2)$$

* The physical parameters required for the conversion are: the density, 2700 kg m$^{-3}$; the molar mass, 26.98 g mol$^{-1}$; and the number of electrons in the reaction, 3.
However at high pH the hydroxide film dissolves to form a soluble aluminate ion:

$$\text{Al(OH)}_3 + \text{OH}^- \rightarrow \text{AlO}_2^- + 2\text{H}_2\text{O} \quad \text{(or, equivalently, Al(OH)$_4^-$)} \quad (5.3)$$

At high pH the cathodic reaction to balance anodic dissolution is the reduction of water:

$$3\text{H}_2\text{O} + 3\text{e}^- \rightarrow 3\text{OH}^- + \frac{3}{2}\text{H}_2 \quad (5.4)$$

The overall reaction is therefore:

$$\text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + \frac{3}{2}\text{H}_2 \quad (5.5)$$

or if the hydroxide film dissolves:

$$\text{Al} + \text{H}_2\text{O} + \text{OH}^- \rightarrow \text{AlO}_2^- + \frac{3}{2}\text{H}_2 \quad (5.6)$$

The aluminium corrosion reaction can also be balanced by the reduction of oxygen:

$$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \quad (5.7)$$

### 5.1.2 Corrosion in sodium and potassium hydroxide solutions

Since the porewater in grout will contain sodium and potassium hydroxides, the literature on the corrosion of aluminium in such solutions has been reviewed. Early work, dating from the first half of the last century, has been summarised by Straumanis [62, 63]. These studies indicated that the rate of dissolution of aluminium in sodium hydroxide was either directly proportional to the concentration of the alkali or proportional to the square root of the concentration. In order to clarify these relationships Straumanis measured the hydrogen evolution rate, and hence by calculation the dissolution rate, of 99.998% pure aluminium in a series of alkaline solutions including KOH, NaOH and Ca(OH)$_2$. Tests lasted for 28–30 hours. At low concentrations (less than 0.5–1.0N) the corrosion rate was proportional to the cube root of concentration for monovalent bases and proportional to the square root for the divalent bases. At higher concentrations the corrosion rate was directly proportional to the concentration. The corrosion rate was higher in NaOH than in KOH.

Other workers [56, 64, 65] have shown that the corrosion rate is at a minimum at pH 6, corresponding to a minimum in the solubility of the aluminium oxides, as shown in Figure 20. The slope of the relationship between pH and corrosion rate is different on each side of pH 6. Pryor and Keir [66] showed that at pHs in the range 2–12 the corrosion rate is increased by increasing the amount of dissolved oxygen in the test solution, indicating that corrosion proceeds by reduction of both oxygen and water.

Tabrizi et al. [67] summarised the corrosion rate data given in more recent literature; data for pH 10 are given in Table 4. The same authors also carried out longer-term measurements (up to 80 days) using commercially pure aluminium in sodium hydroxide solutions at pH values in the range 8–12, at temperatures of 30 and 60°C. As expected the corrosion rate increased with pH. At pH 10 and 11 the corrosion rate decreased slightly with increasing immersion time; long-term data were not obtained for pH 12, presumably because the corrosion rate was so rapid.

#### (a) Effect of temperature

The corrosion rate at a given pH increases with increasing temperature. Tabrizi et al. [67] found that after 40 days exposure the corrosion rates of aluminium in sodium hydroxide at
pH 11, at 30°C and 60°C, were approximately 100 µm a⁻¹ and 300 µm a⁻¹ respectively. At pH 12 the corrosion rate was 540 µm a⁻¹ at 30°C, after 20 days exposure.

Mansour et al. [68] used a thermometric technique to measure the corrosion rate of 99.9% aluminium and Al-5%Mg alloy in sodium hydroxide solutions in the concentration range 0.5 to 2.75M. The corrosion rate was related to the concentration of hydroxide, C (N) by:

\[
\text{Rate} = K C^n
\]  

(5.8)

where K is a constant and n had values of 0.46 at 31.5°C, 0.7 at 33.5°C and 0.91 at 35.5°C. The reason given for the increase in the value of n with temperature was that the oxide film initially present on the surface dissolved more quickly at higher temperatures. The activation energy for corrosion was roughly 9–12 kcal mole⁻¹ for Al-Mg alloys and 7.3–17.4 kcal mole⁻¹ for pure aluminium.

(b) Effect of chloride

Tabrizi et al. [67] observed that at 30°C the addition of 1,000 ppm chloride had little effect on the corrosion rate at pH 10, whereas at 60°C a similar addition reduced the corrosion rate by about two thirds. McKee and Brown [69] found that the corrosion rate of aluminium in sodium hydroxide solutions in the pH range 9–14 (quiescent, room temperature, two-day tests, solution changed every 24 hours) was not affected by the addition of sodium chloride at concentrations up to 1M.

(c) Effect of flow

Prazak and Eremias [70] used a rotating disc electrode to investigate the effect of laminar flow on the corrosion rate of aluminium in sodium hydroxide in the presence of carbonate, borate and phosphate ions. The degree of acceleration of the corrosion rate was related to the pH. At pH 12 the corrosion rate was unaffected by rotation of the disc because, it was proposed, the corrosion product was soluble and there were no mass transport limitations on the supply of reactant, hydroxide ions, to the surface of the aluminium. At pH 11 rotation of the disc led to an acceleration of the corrosion rate, because it was controlled by the rate of transport of corrosion product away from the surface of the aluminium. Borate and phosphate ions decreased the corrosion rate compared to carbonate.

(d) Electrochemical measurements

Detailed electrochemical investigations of aluminium in sodium hydroxide solutions were reported by Narayan and Sheriff [71] and Chandra et al. [72]. The techniques used included Tafel slope measurements, AC impedance and cyclic voltammetry. The main features of these measurements are summarised in Table 5. Armstrong and Braham [73] investigated the electrochemical mechanism of aluminium corrosion in weakly alkaline solutions (up to pH 11 was studied) and showed that the rate of the cathodic reaction was a function of electrode potential but not pH. The reaction rate is independent of film thickness, suggesting that the electron reacts with water at the surface of the metal and is incorporated into the anodic film. The slow step in the anodic reaction is the formation of aluminate from the anodic film on the electrode surface, that is:

\[
\text{Al} + 4\text{OH}^- \Rightarrow \text{Al(OH)}_4^- + 3\text{e}^-
\]  

(5.9)

Hurlen and Haug [74] investigated the electrochemical behaviour of aluminium in mildly alkaline ammonium acetate solutions (pH 7.2 to 9.9). A minimum in the passive current density was measured at a pH of about 8; at higher pH the passive current increased. The addition of oxygen acted as an inhibitor by moving the rest potential into the passive range. The steady state evolution of hydrogen showed a typical Butler-Volmer potential dependence (i.e. the log of the current is proportional to the overpotential [75]), but no pH dependence.
Hydrogen evolution measurements

Onuchukwu and Adamu [76] investigated hydrogen evolution rates from aluminium in an alkaline medium. They treated the generation of hydrogen as a two-step process:

\[ 4\text{Al} + 3\text{H}_2\text{O} \rightarrow 3\text{Al-H}_{\text{ad}} + \text{Al(OH)}_3 \]  \hspace{1cm} (5.10)

\[ 2\text{Al-H}_{\text{ad}} \rightarrow 2\text{Al} + \text{H}_2 \]  \hspace{1cm} (5.11)

A similar mechanism was proposed by Paramasivam and Iyer [77]. In a further paper Onuchukwu [78] also used gas evolution measurements to investigate the effect of organic inhibitors on the corrosion rate of aluminium in 0.15M KOH. The uninhibited gas evolution rate was approximately 1152 litres H\(_2\) m\(^{-2}\) d\(^{-1}\). A similar technique was used by Abd-el-nabey et al. [79] to study the effect of adding organic components, such as ethanol, methanol and glycol, to aqueous alkaline solutions on the corrosion rate of 99.9% pure aluminium in 0.5M and 0.1M NaOH at 25°C. In the absence of any organic material the gas evolution rate was 5904 litres H\(_2\) m\(^{-2}\) d\(^{-1}\). A linear relationship between elapsed time and the volume of hydrogen produced was observed. It was concluded that the corrosion of aluminium in an alkaline medium was determined by the rate of mass transfer of AlO\(_2^-\) from the metal surface to the bulk solution, in agreement with Prazak’s observation on the effects of flow (see Subsection (c) above). MacDonald et al. [80] reported that the hydrogen evolution rate for 99.99% aluminium in 4M KOH at 50°C was 10454 litres H\(_2\) m\(^{-2}\) d\(^{-1}\).

Abd-el-nabey et al. [81] also studied the corrosion of Al-Mg alloys containing 0.4–5% Mg, with a range of annealing treatments, in 0.5M NaOH. Gas evolution rates were highest for pure aluminium, although within the set of Al-Mg alloys those with the highest magnesium content had the highest hydrogen generation rate. The gas evolution rates were related to the effect of alloying additions and heat treatment on the microstructure of the alloy.

Onuchukwu and Trasatti investigated the permeation of hydrogen produced by corrosion through a membrane of alloy 1060 [82]. The work demonstrated that some of the hydrogen produced by reduction of water can be absorbed by the metal, viz.

\[ \text{Al} + 2\text{OH}^- \rightarrow \text{AlO}_2^- + \text{H}_2 \]  \hspace{1cm} (5.12)

\[ \text{H}_2\text{O} + \text{e}^- \rightarrow [\text{H}] + \text{OH}^- \]  \hspace{1cm} (5.13)

\[ \text{Al} + [\text{H}] \rightarrow \text{Al-H}_{\text{ad}} \rightarrow \text{Al-H}_{\text{ab}} \text{ or } \rightarrow \text{Al} + \text{H}_2 \]  \hspace{1cm} (5.14)

The diffusion constant for hydrogen in aluminium was dependent on the texture and composition of the test samples. The presence of NO\(_2^-\), S\(^2-\) and CN\(^-\) all increased the corrosion rate of aluminium [83].

Frid et al. [84] measured gas hydrogen generation rates for three aluminium alloys in simulated coolant sprays at pH 5 and 9 and temperatures of 50, 100 and 150°C. The results given in Frid’s paper are summarised in Table 6.

Corrosion in calcium hydroxide solutions

Takatani and co-workers investigated the corrosion behaviour of aluminium and a range of aluminium alloys in saturated calcium hydroxide solution at 30°C, with and without sodium chloride present [85, 86] for alloys 1050, 5052, 6063, 3003, 7072 and 2017. Measurements of passive current density and weight loss were used to determine the corrosion rate as a function of immersion time and chloride concentration. A good correlation was obtained
between the two techniques. The pitting potential was derived from the polarisation curve measurements. The main conclusions from this work were as follows:

- The corrosion rate decreased with immersion time. The corrosion decreases in roughly inverse proportion to time, i.e. corrosion rate $\approx 1000 \ t^{-1} \ \mu m \ a^{-1}$, where $t$ is in days.

- For alloy 1050 (99.6% Al) the corrosion rate after a period of 40 days immersion was in the region of 2 $\mu A \ cm^{-2}$ (22 $\mu m \ a^{-1}$).

- Different alloys corroded at different rates. The weight loss for the aluminium alloys decreased in the order Al-Mg-Si >> Al-Zn > Al-Mg ~ Al > Al-Mn > Al-Cu.

- The addition to calcium hydroxide of chloride in the concentration range up to 0.5M did not significantly increase the corrosion rate compared to that in chloride-free solutions.

- The pitting potential became closer to the corrosion potential with increasing chloride concentrations, i.e. chloride increased the risk of pitting.

- Initially the corrosion potential of a range of aluminium alloys was approximately -1500 mV vs. Ag/AgCl. The corrosion potential became more positive with immersion, but the behaviour differed between alloys. In the presence of chloride the potentials became positive more rapidly.

- For a given chloride concentration the pitting potential became more positive with increasing immersion time.

Cook et al. [87] used the hydrogen evolution and AC impedance techniques to measure the corrosion rate of 99% aluminium in pore fluid extracted from OPC, 3:1 PFA/OPC, and 9:1 BFS/OPC grouts with a water:solids ratio of 0.35. OPC porewater was also simulated using a mixture of NaOH and Ca(OH)$_2$ at a pH of 13.6. Tests were carried out at ambient temperature. Further tests were carried out in sodium hydroxide solutions in the pH range 10 to 14 and in saturated solutions of Ca(OH)$_2$ whose pH was adjusted by adding sodium hydroxide, at temperatures of 20, 40 and 60°C. The rate of hydrogen evolution for aluminium in the porewaters is shown in Figure 21. It can be seen that as expected the corrosion rate in alkaline conditions increases with increasing pH. Complete corrosion of the aluminium in the simulated OPC porewater occurred within 5 hours, but for the 3:1 PFA/OPC and 9:1 BFS/OPC pore solutions, and for the saturated solutions of Ca(OH)$_2$, the corrosion rate decreased with time due to the build up of a corrosion product film, in agreement with Takatani's results. Good agreement was obtained between the AC impedance and hydrogen evolution measurements.

Straumanis [63] found that in Ca(OH)$_2$ the rate of dissolution of aluminium fell rapidly during the first 30 minutes of reaction, then diminished steadily, to reach a constant level during the 60–360 minute reaction period; the corrosion rate had halved again after 1500 minutes. After the tests a white tenacious porous layer was present on the surface which was presumed to be a mixture of calcium aluminate and aluminium hydroxide.

5.1.4 Corrosion products formed on aluminium in alkaline solutions

In sodium and potassium hydroxides at pHs below 12 aluminium tends to be covered with a protective film of oxide. A range of crystal structures are possible, but they are all soluble at higher pHs (see Figure 20). The composition and density of the most common aluminium oxides and hydroxides are shown in Table 7. The corrosion product in alkali metal hydroxide solutions initially consists of an aluminium hydroxide gel, but this ages to form boehmite, pseudo-boehmite, bayerite or hydrargillite [56]. The exact composition of the corrosion product depends on the temperature, composition of the solution, pH, and the time of immersion [9, 67]. In weakly alkaline solutions (pH 7–10) the oxide film consists of an
adherent, inner, thin oxide barrier layer, which is probably alumina in the form of pseudo-boehmite or gelatinous-boehmite, and an outer non-barrier, bayerite layer [67, 76]. At pH 12 it is more difficult to form an extensive coverage of bayerite because of the high solubility of the Al\(^{3+}\). The corrosion rate appears to be controlled by competitive film growth and dissolution processes.

Nanova et al. [88] tested aluminium-silicon alloy Al-10 in saturated calcium hydroxide and observed a flaky corrosion product; EDAX showed Al and Ca in the proportions 20%/80%. Cook [87] used X-ray diffraction (XRD) to characterise the corrosion product formed on aluminium in calcium hydroxide solutions. The main components were aluminium hydroxide and calcium aluminate. A carbonated calcium aluminate was also identified, presumably as a result of reaction with carbon dioxide in the air. Walton et al. [89] used XRD to identify the corrosion product formed on aluminium in calcium hydroxide as 3CaO.Al\(_2\)O\(_3\).8–12H\(_2\)O and the corrosion product formed in a slurry of Portland cement as Al\(_2\)O\(_3\).6CaO.3SO\(_3\).32H\(_2\)O.

5.1.5 Galvanic corrosion of aluminium in alkaline solutions

Japanese workers [90] looked at the effect of the contact between iron and aluminium in mortar. It was found that although contact with iron increased the corrosion rate of aluminium the rate of hydrogen evolution actually fell, suggesting that some corrosion was occurring by oxygen reduction rather than water reduction. Their work also demonstrated the rapid corrosion rate which aluminium undergoes initially on contact with cement.

Pryor and Keir [65] studied the effect of pH and oxygen concentration on the rate of galvanic corrosion for aluminium-steel couples in 1N NaCl, over the pH range of 0 to 14. This extended earlier work carried out on the galvanic corrosion of aluminium-steel couples in neutral sodium chloride. Coupling to steel caused an increase in the weight loss of the aluminium, while the steel was cathodically protected, over the whole pH range. Weight loss increased with pH, for both coupled and uncoupled electrodes. The corrosion rate of the aluminium was controlled by the size of current that could be sustained at the steel cathode, although at high pH substantial increases in the weight loss were due partly to local cell action, rather than just to the current passing to the steel cathode.

The corrosion potential of the aluminium-steel couple fell to very negative values at high pH; the potential of the couple was controlled by the potential of the aluminium. Above pH 12 hydrogen bubbles were visible at the steel cathode. The potential of the couple was well below the thermodynamically reversible potential for hydrogen reduction (-0.83 vs. NHE at pH 14). The oxide films on the steel coupled to the aluminium were reductively dissolved within a day at pH 12 and within a few seconds at pH 14, after which corrosion and hydrogen evolution occurred at an essentially film-free iron surface.

Winkel and Childs [91] developed a galvanic series for a range of alloys in alkaline conditions (0.05M sodium carbonate, pH 11.3, 29°C). For a couple between aluminium alloy 5083 and uranium (¾ wt% Ti) the corrosion rate of aluminium was approximately 6000 µm a\(^{-1}\).

5.1.6 Inhibition of corrosion in alkaline conditions

Several groups have investigated the use of organic inhibitors to reduce the corrosion rate of aluminium in alkaline solutions, with particular reference to the use of aluminium as an anode in alkaline batteries. The use of such inhibitors would be impractical in the radioactive waste disposal situation; they may also introduce a nutrient supply to support microbial activity and thus enhance microbiologically-induced corrosion and/or the formation of breakdown products such as acids. Inorganic inhibitors such as chromate, bicarbonate, borate, nitrite, silicate, molybdate, and phosphate have also been evaluated [92, 93]. Generally speaking inhibition effectiveness decreased in the order borate > bicarbonate > chromate > silicate > molybdate. The effectiveness depended on the concentration. Some compounds, for example sodium nitrite and sodium phosphate, accelerated corrosion. Oguzie et al. [94] investigated the use of methylene blue for alkaline corrosion of aluminium; Meena et al. [95] investigated the use
of various organic acids (e.g. tartaric, citric, maleic and malic acids) as corrosion inhibitors for aluminium.

In a series of papers Matsuo and co-workers [96–98] investigated the efficiency of LiNO₃ as an inhibitor for the hydrogen generation by corrosion of aluminium in cement. Gas generation measurements in the absence of inhibitor (25°C, cement paste) showed that the period of rapid production of gas decreased [98] after about 20 hours.

5.2 Corrosion in building materials

5.2.1 Introduction

A number of authors have reported their experiences of using aluminium in contact with alkaline building materials [60, 89, 99–104]. Many of the reports refer to long-term exposure (up to 27 years) and they are therefore a useful analogue for predicting the long-term performance of grouted aluminium waste. The free moisture in wet concrete, i.e. porewater, provides an aqueous medium which facilitates transport of soluble species such as oxygen and chlorides towards the metal. It also increases the electrical conductivity of the concrete, thus increasing the likelihood of corrosion. The porewater in concrete is essentially a mixture of sodium, potassium and calcium hydroxides. The exact pH depends on a number of factors including the type of cement used, the water-solids ratio, the extent of hydration, the extent of drying or wetting, and the possible leaching out of the alkali.

Hydrogen generated by the corrosion of aluminium powder additions is sometimes used to form a cellular structure in aerated lightweight building blocks, or if present in smaller amounts to provide a slight expansion in bedding base plates for machinery [104].

5.2.2 Laboratory experiments

The corrosion behaviour of a range of aluminium alloys in concrete, mortar and cement has been described in a series of papers by Japanese authors, most notably Takatani [105-110]. The papers build on Takatani’s earlier work (see Subsection 5.1.3) on the corrosion of aluminium alloys in saturated calcium hydroxide solutions.

Electrochemical and weight loss experiments on aluminium alloy coupons cast into mortar and concrete [106, 107] showed that in the absence of chloride the corrosion of the alloys was controlled by the accumulation of corrosion products. This behaviour was similar to that observed in calcium hydroxide solution. The change in corrosion rate with time can be described approximately by:

\[
\text{Rate} \approx 1000 \, t^{-1} \, \mu m \, a^{-1}
\]  

where \( t \) is in days.

(a) Effect of chloride

Takatani found that when chloride was present in mortar [106] the corrosion rate remained constant, i.e. passivation did not occur within the 100 day duration of the experiment. Rincon et al. [111] used the linear polarisation resistance technique to measure the corrosion rate of aluminium in mortar, with and without chlorides present, after 28 days in a high humidity environment. It was found that the corrosion rate increased with increasing concentration of chloride in the mortar, in agreement with Takatani’s results. In chloride-free mortar the

\[\text{Rate} \approx 1000 \, t^{-1} \, \mu m \, a^{-1}\]  

\[\text{(5.15)}\]

---

\[\text{xi} \] These papers are mainly in Japanese but have English abstracts and figure captions; full translations were not obtained.
corrosion rate was 305 µm a\(^{-1}\), but for 0.1 and 0.3% chloride, at the highest porosity tested (23.5%), the corrosion rates increased to 480 and 1120 µm a\(^{-1}\) respectively. Decreasing the mortar porosity decreased the corrosion rate. Mortar containing 0.1% chloride had not cracked after 3 years, but mortars with 0.3% and 0.5% chloride cracked after 8 months for 23.5% porosity and 18 months for 16% porosity. It was concluded that high porosity, coupled with an increase in the chloride ion concentration, resulted in a higher corrosion rate.

However for wet concrete, as opposed to mortar, both with and without chloride, Takatani [108] found that the corrosion rate continued to decrease with time, although the rate was slightly higher in the presence of chloride. This agrees with measurements in bulk calcium hydroxide solutions containing chloride, in which chloride was not found to significantly affect the corrosion rate or hinder passivation.

Escudero et al. [112] used electrochemical techniques to study the effect of carbonation, relative humidity and chloride content on the corrosion of aluminium in mortar. Initial corrosion rates were greater than 1000 µm a\(^{-1}\) during the curing process, but the rate decreased by more than an order of magnitude after 1 day, and after 6 months the highest corrosion rate was less than 10 µm a\(^{-1}\). The effects of carbonation and low humidity reduced the corrosion rate to less than 1 µm a\(^{-1}\). It was also found that there was a strong relationship between the conductivity of the concrete and the corrosion rate.

It appears that the corrosion behaviour of aluminium in chloride-contaminated mortar is different to that in chloride-contaminated concrete and calcium hydroxide solutions. The detailed chemical reasons for these differences are not clear at present, but the observation shows the importance of chloride for aluminium corrosion in grouts.

(b) Effect of sodium and calcium ions

The corrosion rates of aluminium alloys in mortars containing additions of 3% CaCl\(_2\) and 3% NaCl were measured by Takatani et al. [109] using weight loss and electrochemical measurements. The corrosion rate was higher in the presence of sodium ions and it was concluded that sodium ions tend to accelerate corrosion, whereas calcium ions decrease the corrosion rate. This is due to the different compositions and protective capabilities of the corrosion product films that are formed (see Subsection 5.2.5). Some groundwaters may contain high concentrations of sodium ions that could accelerate aluminium corrosion following resaturation of the near field following repository closure.

(c) Corrosion potentials and cathodic processes

Takatani found that the corrosion potentials measured for aluminium alloys in mortar were similar to those measured in calcium hydroxide solution, ranging from approximately -1540 mV (vs. SCE) for alloys 1050 and 6063, to approximately -1240 mV (vs. SCE) for alloy 2017 [106]. The potential of the alloys became more anodic after approximately 40 days. Similar values were obtained by Walton et al. [89]. These can be compared to typical values for steel of -400 to -950 mV (vs. SCE).

The cathodic polarisation behaviour was also investigated by Takatani et al. [110] using cyclic voltammetry. It was concluded that in the absence of chloride the cathodic reaction changed from hydrogen evolution initially to oxygen evolution in the longer term, but with chloride present hydrogen evolution was the only cathodic reaction.

5.2.3 Long-term corrosion rates in building materials

The reported long-term corrosion rates for aluminium in alkaline building materials are summarised in Table 8. The lowest reported rate was 1.3 µm a\(^{-1}\), averaged over 27 years. Most attack occurs immediately after casting, when the concrete or mortar is still wet. At this stage hydrogen is freely evolved and superficial etching of the surface occurs. Generally speaking, in dry chloride-free concrete at ambient temperature, very low corrosion rates are
observed in the long-term. The attack is self-limiting because the corrosion product films have a limited solubility and are protective.

The Building Research Establishment (BRE) carried out a detailed ten-year test programme on the corrosive effect of various building materials on a range of aluminium alloys [113, 114]. The building materials examined, with measured or predicted porewater pH given in parentheses, included cement-sand mortar (13.6–14), cement-lime-sand mortar (13.6–14), high calcium lime plaster (12.4), Magnesian lime (9.9), and two plasters based on calcium sulphate, namely hemi-hydrate (10.0) and Keene’s (5.2) plaster. Only the cement-based mortars, and possibly the high calcium lime plaster, have pHs comparable to those of Nirex Reference Vault Backfill (NRVB). The test samples were mounted either outdoors, or indoors while half immersed in wet sand, and examined after periods of 1, 2, 5 and 10 years. Slight cracking of all the test samples occurred within a few months, owing to the stresses generated in the concrete by the formation of corrosion products.

The weight losses for the various alloys tested in sand-cement or sand-lime-cement mixtures, for both outdoor and indoor exposure, are shown in Figure 22 and Figure 23. The weight losses between five and ten years exposure were very small, and in some cases a weight gain was measured. (Note that this refers to measurements made on different specimens tested under the same conditions.) Taking the weight change between two different specimens over the 5 and 10 year period as the basis for calculating the corrosion rate gives the values shown in Table 9. Despite the experimental variation observed, it appears that the long-term corrosion rate for all four test conditions, for all the alloys investigated, was below 10 µm a\(^{-1}\). Post-test analysis of the mortars showed that some leaching of the alkali metal hydroxides occurred during the test programme, as a result of flushing by rainwater and atmospheric moisture. This would have reduced the corrosiveness of the environment. Leaching of NRVB is predicted to occur over a much longer timescale than that experienced in the BRE tests. Cracking of the test matrix may also have allowed carbonation to proceed, reducing the pH of the porewater in contact with the aluminium and hence reducing the corrosion rate.

The highest corrosion rates were observed for alloy NE7, both in the plain and anodised states. This alloy contained the highest concentration of magnesium (6.7 wt%). All the specimens suffered considerable cracking, except for those containing the leanest mixture (i.e. the least cement). All outdoor tests cracked within 2 years; all indoor tests lasted for at least 10 years.

(a) Effect of chloride content, alkali content and humidity

(i) Chloride content

Most work has concentrated on the effects of calcium chloride, because it is used as a concrete curing accelerator. Monfore and Ost [102] investigated the corrosion of aluminium 6061 in concrete as a function of both calcium chloride content and alkali content, at two values of humidity. The results are shown in Table 10. At the higher alkali content (0.89% Na\(_2\)O) the corrosion rate was lower with 2% calcium chloride present, but no significant effect was observed at the lower alkali content (0.22% Na\(_2\)O). Wright et al. [99] and Walton et al. [89] also found that calcium chloride additions to concrete did not accelerate the corrosion. Because calcium chloride accelerates the curing rate it may affect the corrosion behaviour through limiting the availability of “free water”. Walton and co-workers found that sodium chloride did not have a significant effect either, although this does not agree with the laboratory tests of Takatani (Subsection 5.2.2 (b)), who found that the presence of sodium ions tended to increase the corrosion rate.

(ii) Alkali content

Several groups have found that the corrosion rate of aluminium in concrete increases with increasing free alkali content. These include Wright et al. [99] and Monfore and Ost [102] (Table 10) who carried out one year and 6 month tests respectively. Similarly, Endtinger and Weber [60] reproduced data from earlier work by Tronstad and Bukowiecki
showing that corrosion rate increased with increasing pH of the porewater in various building materials. In the BRE work, mortar which contained lime resulted in a lower corrosion rate than the standard mortar mixes, owing to the lower concentration of free alkali metal hydroxides in the porewater. This behaviour is not unexpected in view of the relationship between pH and corrosion rate in bulk alkaline solutions (see Subsection 5.1.2).

(iii) Humidity

In the BRE work the corrosion rate for the blocks exposed indoors was rather lower than for outdoor exposure (see Figures 22 and 23), although the tests were not strictly comparable because different size blocks of cement were used and the reserves of alkali metal hydroxides were therefore different. Monfore and Ost [102] showed that a moist atmosphere caused higher corrosion rates than a dry atmosphere, even over periods of a few days (Table 10). Earlier work by Tronstad also showed that atmospheric humidity affected corrosion rate. However, in contrast, Walton et al. [89] showed that the corrosion rate of aluminium embedded in concrete was not significantly affected by the volume of the concrete block in which it was mounted or on the availability of water at the periphery of the block.

5.2.4 Galvanic corrosion of aluminium in building materials

Several cases of severe corrosion have been reported for aluminium in buildings as a result of galvanic coupling to steel reinforcement [115]. Galvanic coupling leads to a foam-like gelatinous aluminium corrosion product, which may crack the surrounding concrete. The main conclusions from the experimental work carried out by Wright [115, 116], Walton et al. [89], Monfore and Ost [102] and Copenhagen and Costello [103] were as follows:

- In the absence of chloride, galvanic corrosion is negligible.
- In chloride-free mortar the galvanic corrosion current passing between coupled aluminium-mild steel electrodes is unaffected by the ratio of the areas of the metals.
- In chloride-free mortar the distance between the electrodes does not have a significant effect on the corrosion rate, suggesting that the resistance at the metal-mortar interface is the most important parameter.
- Galvanic currents are highest when the cement is periodically or continuously wet.
- The corrosion rate of coupled steel-aluminium electrodes in mortar is considerably higher at the air-mortar interface than in the bulk mortar.
- Addition of CaCl₂ to concrete causes an increase in the electrical conductivity of the concrete and if moisture is present it increases the likelihood of galvanic corrosion between connected metals.
- The addition of chloride (CaCl₂ or NaCl) to the mortar increases the galvanic corrosion current, but not the uncoupled corrosion rate. The galvanic corrosion rate increases as the calcium chloride content increases. The maximum effect for NaCl was observed at 1 wt%.
- In chloride-containing cement the galvanic corrosion rate is proportional to the ratio of the areas of the aluminium-steel couples.
- In chloride-containing cement the rate of galvanic corrosion is proportional to the distance between the metals, if externally coupled, or the distance from the point of contact, if internally coupled.
- The galvanic corrosion rate increases with the alkali content of the mortar.
• The galvanic corrosion rate decreases with time.

5.2.5 Corrosion products formed on aluminium in building materials

(a) Composition of corrosion products

The corrosion products formed on aluminium alloys in mortar and concrete were analysed by Takatani and co-workers [117, 118] using electron microprobe analysis and X-ray diffraction. In mortar the corrosion product has a duplex structure, with an inner hydrated sodium aluminate gel (NaAl(OH)$_4$ and Al$_2$O$_3$.3H$_2$O), approximately 20 µm thick, in which sodium and chloride ions are concentrated, and an outer crystalline layer, approximately 80 µm thick, with a flake-like structure and a composition of CaO.Al$_2$O$_3$.yH$_2$O. The thickness of the layers depends on the immersion time and whether or not sodium chloride is present. X-ray diffraction analysis of the corrosion products in mortar detected bayerite, hydrargillite and nordstrandite. In concrete the corrosion product was hydrargillite only. Significant quantities of magnesium were observed in the corrosion product, particularly close to the metal-oxide interface.

Jones and Tarleton [113] proposed that the initial corrosion product formed on aluminium in mortar was a gel, which probably initially consisted of boehmite. This then aged to bayerite and then to gibbsite. In the presence of cement or lime this could then react to form calcium aluminates. The corrosion products were generally poorly crystalline, owing to the presence of gelatinous alumina. Traces of calcite and aragonite (both CaCO$_3$) were also found where atmospheric carbon dioxide had reacted with the corrosion product.

Walton et al. [89] found that the white corrosion product formed during galvanic corrosion experiments with aluminium in a mortar containing calcium chloride had a composition of 40% Al and 20% Cl.

(b) Effect of sodium and calcium chloride on composition of corrosion product

Takatani et al. [119] used electron microprobe analysis to examine the distribution of elements in the corrosion product films formed on the aluminium samples. In the presence of 3% CaCl$_2$ the corrosion product consisted of 3CaO.Al$_2$O$_3$.8H$_2$O, but when both 3% NaCl and 3% CaCl$_2$ were present the corrosion product was Al$_2$O$_3$.3H$_2$O. Sodium and chloride were concentrated in the inner layer, whereas calcium was concentrated in the outer layer. The higher the concentration of calcium in the outer layer the lower the corrosion rate and the higher the concentration of sodium in the inner layer the lower the concentration of calcium in the outer layer. It was proposed that high concentrations of sodium aluminate could accelerate the formation of tri-hydrated aluminium oxide and maintain the strong alkaline conditions at the surface, leading to higher corrosion rates.

The presence of sodium chloride in the concrete or mortar resulted in the predominance of bayerite over hydrargillite. The maximum in the ratio of the peak intensities of bayerite to hydrargillite corresponded to a maximum in the corrosion rate.

On the basis of the corrosion product analyses described above Takatani proposed the corrosion mechanism that is summarised in Figure 24.

(c) Effect of corrosion product expansion

The corrosion product formed on aluminium occupies a larger volume than the original metal and this can lead to cracking of the concrete [60, 100]. This is particularly likely if galvanic coupling causes high corrosion rates. However, the volume of the corrosion product for aluminium is less than for magnesium, and so aluminium has sometimes been preferred as a cathodic protection anode for use in concrete [111].

Monfore and Ost [102] measured the pressures developed in concrete blocks by the corrosion of aluminium, using strain gauges. As an illustration, the maximum pressures
developed for low and high alkali cement for aluminium coupled to steel, with chloride present, were 17.9 and 20.7 MPa respectively.

The amount of expansion will be related to a number of factors such as the composition, crystallographic structure, porosity and mechanical properties (e.g. plasticity) of the corrosion product.

5.3 Corrosion in wasteforms

5.3.1 Introduction

Most of the research within the nuclear industry has concentrated on the effect of aluminium corrosion on waste encapsulation grouts and on the integrity of wasteforms and consequently much of the data is derived from relatively short-term experiments. Although literature information regarding the corrosion of aluminium in alkaline building materials can provide guidance about the likely performance in grouted waste, account must also be taken of the actual water chemistries that will arise both before and after saturation in the repository, when pH and other ionic concentrations will be significantly different to those experienced in conventional civil engineering applications.

5.3.2 Corrosion rates and hydrogen evolution rates in grout

The experimental data from the Product Evaluation Task Force (PETF) programme was summarised in 1989 by Lee and Wilding [120]. The review was based mainly on references [121–124]. It included hydrogen evolution measurements for aluminium in 9:1 BFS/OPC, 3:1 BFS/OPC, OPC, PFA/OPC, PFA/HAC, BFS/Na₂SO₄ and considered the effect of water-solids ratio, the composition of the alloys, and surface preparation. Initial corrosion rates (0–24 hours) ranged from 1,620 to 22,000 µm a⁻¹ with the lowest corrosion rates observed for 9:1 PFA/OPC and 3:1 PFA/HAC. Longer term corrosion rates fell below 800 µm a⁻¹ and generally below 325 µm a⁻¹ for the OPC-based systems. The lowest corrosion rates for B41 cladding simulant in 9:1 BFS/OPC and 9:1 PFA/OPC were 16 and 20 µm a⁻¹, after 40 and 48 days respectively. The longest duration of the tests was 107 days. The main conclusions from this work were:

- The higher the proportion of OPC the higher the corrosion rate.
- The higher the water-solids ratio the greater the quantity of hydrogen produced.
- The corrosion rate is determined by water availability and the permeability of the grout.
- Waste compaction reduces the surface area of aluminium in contact with the grout and hence the rate of hydrogen generation.
- The corrosion rate in porewater simulants is higher than in grouts.
- Different alloys produce gas at different rates.

These conclusions are consistent with those reported in previous subsections for the corrosion behaviour of aluminium in building materials.

White, Jefferis and Associates [125] also reviewed the available information about the corrosion of aluminium in alkaline conditions and the composition of the corrosion products. Experimental work to monitor the evolution of hydrogen from aluminium coupons embedded in grouts of various compositions resulted in initial measured corrosion rates of 4,000 µm a⁻¹, which decreased to less than 10 µm a⁻¹ after 28 days. It was concluded that the decrease in corrosion rate could be due to passivation and/or depletion of water. The major corrosion
products were gibbsite, bayerite and nordstrandite. There was no evidence for calcium aluminate films.

A programme of generic research on the hydrogen evolution from aluminium corrosion in grout matrices has been carried out by the PETF [126, 127]. The test media included various grouts and a filtrate from BFS/OPC mixed with water. The gas evolution behaviour showed the typical features of high initial rates which decreased with time as the protective calcium aluminate film formed. Most tests lasted for only 30 days. The corrosion rates increased in the order 9:1 BFS/OPC < 3:1 BFS/OPC < OPC < 3:1 PFA/OPC. Aluminium hydroxide and calcium aluminates were the main corrosion products. The long-term corrosion rate was lower at 50°C compared to 20°C, although initially it was higher. After 55 days in 3:1 PFA/OPC the corrosion rate had reached 9 µm a⁻¹ and was still decreasing.

Naish et al. [128] used acoustic emission, hydrogen evolution and electrochemical measurements to monitor the corrosion of both Magnox and aluminium, in 3:1 BFS/OPC, with and without chloride. Good agreement was obtained between all three techniques. The typical pattern of high initial corrosion rates followed by a rapid fall was observed. The emphasis of the work was on validating the applicability of the acoustic emission technique, rather than on generating long-term corrosion rate data.

The long-term corrosion of aluminium at elevated temperatures in 3:1 BFS/OPC, 9:1 BFS/OPC and 3:1 PFA/OPC (with and without chloride additions) at 25, 50 and 80°C, was investigated by Thomas et al. [129,130] using the hydrogen evolution and AC impedance techniques to measure the corrosion rates. Initially the corrosion rates were high (1000 to 13000 µm a⁻¹ at 25°C for the first 30 hours) but fell with time to ~100 µm a⁻¹ after 400 hours (16.7 days), ~10 µm a⁻¹ after 900–1800 hours, 1–2 µm a⁻¹ after 4000–5000 hours, and 0.1-0.5 µm a⁻¹ after 16000 hours (667 days). The corrosion rates decreased according to a relationship of the form:

\[ \text{Rate} = A \cdot t^{-n} \mu\text{m} \ \text{a}^{-1} \]

where \( A = 1000 \text{ to } 13000 \), \( t \) is time in days, and \( n \) is ~1.5–1.7 for 3:1 PFA/OPC at 25, 50 and 80°C. Slightly lower long-term corrosion rates were observed at higher temperatures. The addition of 15,000 ppm chloride did not increase the corrosion rate. Resaturation of one test sample caused a peak in the corrosion rate which did not decay back to the previously low corrosion rate – the corrosion rate remained above 1 µm a⁻¹ for the remainder of the experiment. It is possible that the corrosion rate in the other specimens was limited by the supply of water.

5.3.3 Effect of aluminium corrosion on grout-metal interface

The effect of hydrogen generation on the morphology of the aluminium-grout interface was investigated in detail by Dalton and Fenton [131]. Tubes of aluminium were filled with 3:1 PFA/OPC (0.42 w/s ratio) and the corrosion rate measured after 1 and 16 days by weight loss. A detailed microscopic analysis of the interface was made. This indicated that the voidage produced was approximately \( 2.1 \times 10^{-4} \text{ m}^3 \text{ per m}^2 \) of exposed aluminium. A region approximately 1 mm thick around the metal surface was affected. This region contained three zones: voidage caused by hydrogen evolution, a “porous region” containing aluminium corrosion products and grout, and a discrete layer next to the metal surface, 40–50 µm thick, with a high aluminium content. The presence of voidage near the metal surface may be beneficial because it could accommodate the formation of expansive corrosion products.

Large scale trials (560 litres) using various loadings of B41 cladding in 9:1 BFS/OPC [122, 132] have been carried out to determine the upper limit of aluminium that can be successfully encapsulated in grout. Increased porosity at the metal-grout interface was observed, but this was not regarded as sufficiently serious to jeopardise the monolithic nature of the wasteform. The peak hydrogen generation rates were initially in the range 2.7 to 4.0 litres h⁻¹ kg⁻¹ Al, falling to 0.07 to 0.22 litres h⁻¹ kg⁻¹ Al after 24 hours. After 48 hours
some products produced no detectable hydrogen. These values correspond to peak corrosion rates of 10,000 to 15,300 µm a\(^{-1}\) falling to 33 to 360 µm a\(^{-1}\) after 48 hours.

### 5.3.4 Galvanic corrosion of aluminium in grout

Thomas et al. [133] investigated the galvanic corrosion of aluminium coupled with uranium in 3:1 PFA/OPC grout at 25, 50 and 80°C by measuring the currents passing between coupled electrodes. Initially corrosion of the aluminium predominated, particularly at 25°C, but in some cases the direction of the current changed during the course of the experiment, i.e. the polarity of the galvanic cell switched during the course of the experiment.

### 5.3.5 Inhibition of corrosion in wasteforms

It is possible that a lack of available water within the grout matrix will inhibit the corrosion rate but as yet no measurements have been made. This may limit the corrosion rate of aluminium during repository resaturation.

### 5.3.6 Effect of radiation on aluminium corrosion

Kumar et al. [134] investigated the effect of radiation on the corrosion of aluminium in brackish water (pH 8.95). It was found that the presence of radiation consumed oxygen and reduced the corrosion potential below the pitting potential.

### 5.4 Atmospheric corrosion

The atmospheric corrosion of aluminium will not be discussed in detail as it is peripheral to the main topic of gas generation by the corrosion of aluminium in cementitious environments. However, it is should be noted that prior to encapsulation, aluminium in the waste streams will be subject to atmospheric corrosion conditions which will determine the nature of the initial corrosion product on the surface of the aluminium. This is particularly relevant to ungrouted or supercompacted wastes, which may not come into contact with alkaline aqueous conditions until repository resaturation occurs. Graedel [135] has reviewed the chemistry of the atmospheric corrosion of aluminium and listed the range of compounds which may be formed through corrosion of aluminium; they can be divided into oxides-hydroxides (21), sulphates (34), chlorides (16), nitrates (2) and carbonates (3). Corrosion rates are typically 0.4–0.6 µm a\(^{-1}\) in a marine atmosphere and 0–0.01 µm a\(^{-1}\) in a rural environment.

Friel [136] has also studied the composition of the corrosion products formed by atmospheric corrosion of aluminium coatings in marine and industrial atmospheres over a nine year period. The main components were hydrated aluminium sulphate and hydrated Al\(_2\)O\(_3\). The detailed weathering behaviour has been reviewed by Sowinski and Sprowls [137]; curve fitting to long-term data resulted in equations of the form:

\[
D = A t^b \tag{5.15}
\]

where \(D\) is the corrosion damage measured at time \(t\), and \(A\) and \(b\) are constants.

### 5.5 Conclusions

The main conclusions regarding the corrosion of aluminium in alkaline environments are as follows:

- At high pHs the stable form of aluminium is AlO\(_2\)^{2-}.
• In conditions of free corrosion (i.e. no galvanic coupling), hydrogen generation is the predominant cathodic reaction at high pH, although oxygen reduction can occur simultaneously.

• On immersion in alkaline conditions the air-formed oxide film is dissolved, the metal is activated and the potential falls to approximately -1250 mV vs. NHE.

• In sodium and potassium hydroxide solutions the corrosion rate increases with increasing pH. Very little decrease with time occurs because the corrosion product is soluble.

• At a given pH the corrosion rate in sodium and potassium hydroxide solutions increases with temperature.

• Chloride does not affect the general corrosion rate in sodium, potassium or calcium hydroxide solutions although it does increase the risk of pitting.

• At pH 12 the corrosion rate of aluminium in potassium hydroxide is not affected by the flow conditions.

• Some of the hydrogen generated by corrosion permeates into the bulk metal. The diffusion constant depends on the metallurgical structure.

• In calcium hydroxide solutions the corrosion rate of aluminium decreases with time.

• The corrosion of aluminium alloys decreases in the order Al-Mg-Si >> Al-Zn > Al-Mg ~ Al > Al-Mn > Al-Cu.

• Below pH 12, the corrosion product in alkali metal hydroxide solutions initially consists of an aluminium hydroxide gel, but the gel ages to form boehmite, pseudo-boehmite, bayerite or hydrargillite. The exact composition of the corrosion product depends on the temperature, composition of the solution, pH, and the time of immersion. At pHs above 12 the corrosion product is too soluble to form a stable film.

• In calcium hydroxide the corrosion product film is composed predominantly of aluminium hydroxide and calcium aluminate.

• Galvanic coupling with steel greatly accelerates the corrosion rate of aluminium.

• In the absence of chloride the corrosion rate of aluminium in mortar and concrete decreases with time.

• There is contradictory evidence about the effect of chloride on the corrosion rate of aluminium in building materials. In concrete aluminium passivates in the presence of chloride, but in mortar chloride appears to prevent passivation. The detailed chemical reasons for this difference remain to be resolved.

• Sodium ions tend to increase the corrosion rate, whereas calcium ions reduce it.

• There is a long history of using aluminium in building materials. Long-term corrosion rates may fall to less than 1 µm a⁻¹.

• Calcium chloride does not increase the corrosion rate in concrete.

• The intensity of attack in concrete is increased by a higher alkali content, higher humidity (although there is some contradictory evidence), a higher concrete porosity, and the duration of drying.
Galvanic corrosion of aluminium coupled to steel has been widely reported. The main conclusions are:

- In the absence of chloride, galvanic corrosion is negligible.
- In chloride-free mortar the galvanic corrosion current passing between coupled aluminium-mild steel electrodes is unaffected by the ratios of the areas of the metals.
- In chloride-free mortar the distance between the coupled electrodes does not have a significant effect on the corrosion rate, suggesting that the resistance at the metal-mortar interface is the most important parameter.
- Addition of CaCl$_2$ to concrete causes an increase in the electrical conductivity of the concrete and if moisture is present it increases the likelihood of galvanic corrosion between connected metals.
- Galvanic currents are highest when the cement is periodically or continuously wet.
- The corrosion rate of coupled steel-aluminium electrodes in mortar is considerably higher at the air-mortar interface than in the bulk mortar.
- The addition of chloride (CaCl$_2$ or NaCl) to the mortar increases the galvanic corrosion current, but not the uncoupled corrosion rate. The galvanic corrosion rate increased as the calcium chloride content increases. The maximum effect for NaCl was observed at 1 wt%.
- In chloride-containing cement the galvanic corrosion rate is inversely proportional to the ratio of the areas of the aluminium-steel couples.
- In chloride-containing cement the rate of galvanic corrosion is proportional to the distance between the metals, if externally coupled, or the distance from the point of contact, if internally coupled.
- The galvanic corrosion rate increases with the alkali content of the mortar.
- The galvanic corrosion rate decreases with time.

The main conclusions regarding the corrosion of aluminium in grouts are as follows:

- The corrosion product in building materials has a duplex structure consisting of an outer calcium aluminate film and an inner sodium aluminate / aluminium hydroxide film. The crystal structure, composition and relative thicknesses depend on the concentration of sodium. Calcium aluminate was also observed in the corrosion product formed in cement grouts used for waste encapsulation.
- Most corrosion rate data for aluminium in grout porewaters are for relatively short periods (<150 days).
- The corrosion rate increases with the proportion of OPC in the grout.
- The corrosion rate is determined by water availability and the permeability of the grout.
- The corrosion rate in porewater simulators is higher than in grouts, possibly because of water supply limitations.
- Different alloys produce gas at different rates.
• In laboratory tests corrosion rates for aluminium in 3:1 BFS/OPC and 3:1 PFA/OPC grouts fell to 0.1–0.5 μm a\(^{-1}\) after 16,000 hours\(^{\text{xii}}\).
6 Parameterisation of SMOGG Model for Aluminium

From the information summarised in Section 5 it appears that initially the corrosion rate of aluminium in grout will be rapid, but the rate will reduce with time, so that by the time the wasteform is emplaced in a repository the rate will be slow.

The limited data available for temperatures above ambient indicate that the long-term (or “chronic”) corrosion rate does not increase with temperature\textsuperscript{\textcopyright}. However, there are a number of other factors which could affect the corrosion rate of aluminium in a repository. These include:

- Alloy composition. Different aluminium alloys corrode at different rates.
- pH. The corrosion rate of aluminium in alkaline solutions is pH dependent.
- Chloride concentration. The corrosion rate of aluminium in grout is controlled by the protective film on the metal surface, which could be disrupted by chloride. In fact the information in the literature suggests that the corrosion rate is unchanged by the addition of chloride.
- Galvanic coupling with steel. Galvanic interactions, especially with steel and in the presence of chlorides, accelerate the corrosion rate of aluminium.

6.1 SMOGG model

The model implemented in SMOGG [3, 4] specifies the corrosion rate of aluminium as:

\[
\frac{ds}{dt} = -k_a e^{-\frac{t}{t_a}} f_a(T) - k_c e^{-\frac{T}{T}} f_c(T)
\]  

(6.1)

where

- \(s\) is the position of the surface of the aluminium [m];
- \(t\) is the time during which corrosion is occurring [a];
- \(k_a\) is the initial acute corrosion rate (defined at a reference temperature, \(T_{ref}\), for which \(f_a = 1\) [m a\(^{-1}\)]);
- \(t_a\) is a characteristic time for the acute corrosion [a];
- \(f_a\) is a factor that specifies the dependence of the acute corrosion rate on temperature [-];
- \(T\) is the temperature [K];
- \(k_c\) is the initial chronic corrosion rate (defined at a reference temperature, \(T_{ref}\), for which \(f_c = 1\) [m a\(^{-1}\)]);
- \(f_c\) is a factor that specifies the dependence of the chronic corrosion rate on temperature [-].

\textsuperscript{\textcopyright} The chronic corrosion rate appears to decrease slightly as the temperature increases, based on the data obtained. A possible explanation of this behaviour is that competing hydration reactions use water at the expense of the aluminium corrosion reaction, and hence limit the corrosion rate.


t\text{c} \quad \text{is a characteristic time for the chronic corrosion [a];}

f_{\text{c}} \quad \text{is a factor that specifies the dependence of the chronic corrosion rate on temperature [-].}

This formulation allows separate corrosion rates to be specified for an initial "acute" phase and a later "chronic" phase.

The model simplifies because the corrosion rates are assumed to be independent of temperature, based on the available information. That is:

\[ f_{\text{a}}(T) = 1 \]  
\[ (6.2) \]

and

\[ f_{\text{c}}(T) = 1 \]  
\[ (6.3) \]

Hence, a total of four parameters must be specified to define the corrosion rate of aluminium for a particular corrosive environment:

- two rate constants (k_{\text{a}} and k_{\text{c}}, giving the base corrosion rates); and
- two characteristic times (t_{\text{a}} and t_{\text{c}}, defining the decrease with time).

It is assumed that aluminium waste generally will be encapsulated in cement in metal containers to form stable and easily movable packages. The conditioned waste then will be transported to a deep underground repository and at an appropriate time surrounded by a cement-based backfill. The aluminium will react with cement porewater to give hydrogen, irrespective of the availability of oxygen. Therefore the two corrosive environments possibly of interest are:

- an alkaline, cementitious environment; and
- after resaturation, an alkaline (pH 12.5–13) porewater which has mixed with groundwater containing chloride ions and various other inorganic salts.

However, the information in the literature (e.g. [129, 130]) suggests that the presence of chloride will not affect the corrosion rate of aluminium in grout. In other words, the two environments are indistinguishable as regards aluminium corrosion.

### 6.2 Approach

The approach to performing the calibration was to use a nonlinear regression computer program [52] to determine a best fit of the SMOGG model:

\[ \frac{ds}{dt} = -k_{\text{a}} e^{\frac{t}{t_{\text{a}}}} - k_{\text{c}} e^{\frac{t}{t_{\text{c}}}} \]  
\[ (6.4) \]

to the data.

In the case of measurements of gas generation from corrosion of aluminium, the most relevant data [122, 132, 138] are from the PETF programme, with supplemental data in a few other miscellaneous studies (e.g. [129, 130]).
The PETF programme considered a range of scenarios for packaged aluminium waste. The data include measurements of hydrogen evolution from corrosion of aluminium in trial wasteforms. However, the emphasis was on the consequences of hydrogen generation for the integrity of the grout matrix, rather than on hydrogen evolution in a waste store or repository. Intermediate scale (70 litres) and large scale (560 litres) experiments using various loadings of B41 cladding in 9:1 BFS/OPC were carried out to determine the upper loading limit of aluminium that can be encapsulated in grout successfully. The longest duration of these tests was less than 100 days.

Based on initial consideration of the available experimental data, it was decided that the calibration process should consider only the data [122, 132, 138] from the PETF programme. Using measurements of gas generation from corrosion of aluminium repeated at regular intervals over an extended time scale, the corrosion rate constants and characteristic times can be calibrated. This is considered in Subsection 6.3.

### 6.3 Variation of the corrosion rate with time

Three large-scale and four intermediate-scale measurements of the corrosion rate of aluminium (see Figure 25) were used for the calibration.

The SMOGG model (Equation (6.4)) was fitted to the logarithms of the experimental data.

Although most data on aluminium corrosion have been obtained from short-term experiments (i.e. 100 – 200 days duration), the general view (e.g. [139]) is that the initial period of rapid corrosion is followed by a period during which the corrosion rate appears to be reaching a more constant value in the range 1–10 µm a\(^{-1}\). To ensure the SMOGG model exhibits this behaviour, that is an underlying constant corrosion rate which persists in the long-term, the characteristic time for the chronic corrosion was taken to be large (i.e. \(t_c \rightarrow \infty\)).

With this assumption, the outcome of the nonlinear regression analysis was that:

- \(k_a = 15,300 \ \mu\text{m a}^{-1}\), with a standard deviation of 4,600 \(\mu\text{m a}^{-1}\);
- \(t_a = 0.001\text{a}\); and
- \(k_c = 24.5 \ \mu\text{m a}^{-1}\), with a standard deviation of 3.4 \(\mu\text{m a}^{-1}\).

Note that these values depend on the composition of the aluminium alloy and the formulation of the grout. Also the lack of sufficient long-term data means the value calculated for the initial chronic corrosion rate, \(k_c\), could be rather conservative.

Figure 26 compares the experimental data with a “Preferred” fit, in which \(k_a\) and \(k_c\) have the values determined from the regression analysis, and a “Conservative” fit, in which \(k_a\) and \(k_c\) have been increased from the “Preferred” fit values by about two standard deviations (i.e. this is the upper end of the 95% confidence interval).

### 6.4 Selection of data recommended for use in SMOGG

The objective of this study was to parameterise the corrosion model for aluminium that has been implemented in SMOGG, as given by Equation (6.4). In Subsection 6.3, the available data have been identified and interpreted, as far as possible, to give values for the various parameters. This subsection summarises the set of parameters for aluminium corrosion recommended for use in SMOGG.

- The initial acute corrosion rate is 15,300 \(\mu\text{m a}^{-1}\).
• The characteristic time for the acute corrosion is 0.001a.

• The acute corrosion rate is independent of temperature.

• The initial chronic corrosion rate is 24.5 µm a\(^{-1}\).

• The characteristic time for the chronic corrosion is infinite\(^{xiv}\), by assumption.

• The chronic corrosion rate is independent of temperature.

• The corrosion rate is independent of oxygen and chloride concentrations.

Calculations of gas generation performed with SMOGG might include variant cases intended to scope the effect of uncertainties in the model parameters. From the experimental results examined here, upper estimates have been determined for some of the parameters of the aluminium corrosion model in SMOGG.

• The initial acute corrosion rate could be increased to 24,400 µm a\(^{-1}\). (This is the upper end of the 95% confidence interval, calculated from the mean and standard deviation given in Subsection 6.3).

• The initial chronic corrosion rate could be increased to 31.2 µm a\(^{-1}\). (This is the upper end of the 95% confidence interval, calculated from the mean and standard deviation given in Subsection 6.3).

6.5 Discussion

Having derived a parameterisation of the SMOGG model for the corrosion rate of aluminium (Subsection 6.4), it is useful to compare the resulting values with the corrosion rates used previously.

In the Nirex 97 assessment of gas generation from radioactive wastes [54], the aluminium corrosion rate was assumed to be 30 µm a\(^{-1}\). This is comparable to the long-term constant corrosion rate, 24.5 µm a\(^{-1}\), now being recommended.

Subsequently [140], a temperature-dependence for the corrosion rate of aluminium was derived by making the following assumptions:

• The aluminium corrosion rate in the Nirex 97 assessment, 30 µm a\(^{-1}\), is for a temperature of 50°C.

• The aluminium corrosion rate increases by a factor of 9 when the temperature increases from 30°C to 60°C\(^{xv}\).

\(^{xiv}\) In using the SMOGG model a finite value is required; a value much greater than the duration of the calculation (i.e. at least an order of magnitude greater) should be used.

\(^{xv}\) This is stated to be based on the data obtained by Tabrizi et al. [67], who measured the corrosion rates of aluminium after 80 days exposure in sodium hydroxide at pH 11, at 30°C and 60°C (see Subsection 5.1.2 (a)). However, re-examination of the data suggests that the factor of 9 is roughly double what it ought to be.
The variation of the aluminium corrosion rate with temperature is given by an approximate form of the Arrhenius equation, i.e.

\[
\text{Rate} \left( T \right) = \text{Rate} \left( T_{\text{ref}} \right) \times \exp \left[ - \frac{E}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right] \approx \text{Rate} \left( T_{\text{ref}} \right) \times \exp \left( \alpha \left( T - T_{\text{ref}} \right) \right)
\]

Hence, the corrosion rate of aluminium was taken to be:

<table>
<thead>
<tr>
<th>Temperature, ( T )</th>
<th>35°C</th>
<th>50°C</th>
<th>80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrosion rate</td>
<td>10 µm a(^{-1})</td>
<td>30 µm a(^{-1})</td>
<td>270 µm a(^{-1})</td>
</tr>
<tr>
<td>Factor</td>
<td>0.333</td>
<td>1.000</td>
<td>9.000</td>
</tr>
</tbody>
</table>

These corrosion rates vary more rapidly with temperature than is now being recommended. Some reasons for the change of view include:

- The previous analysis used data from an experiment on aluminium corrosion in sodium hydroxide solution, rather than in grout. The limited data available for temperatures above ambient indicate that the long-term corrosion rate of aluminium in grout does not increase with temperature.

- The previous analysis estimated the variation in corrosion rate with temperature by comparing a single point at 30°C with a single point at 60°C. This approach is likely to be subject to significant experimental error. In addition, it seems the ratio of the corrosion rates at the two temperatures may have been calculated incorrectly.

Subsequent assessments of gas generation from radioactive wastes generally reused this parameterisation, except that the Generic Post-closure Performance Assessment [2] assumed additionally that during storage at 35°C local restrictions on the availability of water would limit the aluminium corrosion rate to 1.0 µm a\(^{-1}\). There is no clear experimental evidence to support this assertion.

In conclusion, the aluminium corrosion rate used in the Nirex 97 assessment is comparable to the long-term constant corrosion rate, 24.5 µm a\(^{-1}\), now being recommended. However, the variation of this corrosion rate with temperature assumed in subsequent assessments is not substantiated by the information in the literature.
7 Corrosion Data for Uranium

7.1 Introduction

Uranium metal, originating mainly from the fuel elements of Magnox reactors, is present in some waste streams. This section provides an overview of the corrosion mechanisms, and corresponding corrosion rates, of uranium in the environments that are likely to arise during the disposal of radioactive wastes.

7.1.1 Corrosive environments

During the waste disposal process the uranium could be exposed to a range of environments, ranging from humid air prior to encapsulation in grout, to an alkaline porewater with a pH in the region of 12.5 to 13 after encapsulation. In cements with a low proportion of water the uranium may be exposed to a humid gaseous environment, particularly if separation occurs at the cement-uranium interface. Both gaseous and aqueous environments are likely to become deoxygenated over time, so the effect of oxygen on the corrosion behaviour of uranium is important. The effect of temperature is also an important variable, since it may vary from ambient during storage to 80°C in the repository. In order to allow for the corrosion of uranium in models such as SMOGG, it is necessary to compile corrosion rates for both aerobic and anaerobic conditions, so that both the rate of metal consumption and the rate of gas generation can be calculated.

7.1.2 Reviews

Literature searches were carried out in the following databases: INIS (1976-2006), Nuclear Science Abstracts (1948-2006), Chemical Abstracts (1967-2006) and Metals Abstracts (1966-2006). The keywords used were: uranium, corrosion, oxidation, alkaline and cement.

Interest in the corrosion of uranium began during the wartime years and Waber has reviewed this early work [141, 142]. The main focus of attention at this time was on the gaseous oxidation of uranium, rather than on corrosion in bulk aqueous conditions. This interest continued after the war during the further development of nuclear weapons and the early development of nuclear power in the 1950s and 1960s. Uhlmann [143] has produced a bibliography of abstracts relating to uranium corrosion studies for the period 1952-1963. In recent years the corrosion of uranium during storage and waste disposal has become of interest. Until the 1970s most corrosion studies involved measurements of weight change and gas production rates, combined with X-ray diffraction and electron diffraction to identify the corrosion products. Very few investigations have been conducted with modern electrochemical instrumentation or materials characterisation equipment.

Brief overviews of the corrosion behaviour of uranium can be found in references [144-146], and more extensive reviews, covering both gaseous oxidation and aqueous corrosion, have been published by Totemeier [147, 148] and Haschke [149]. The latter three papers are concerned with the risk of pyrophoric reactions during the storage of uranium. The most recent review by Hilton [150] reanalysed existing data to derive rate equations for uranium oxidation under different conditions (i.e. in oxygen, water vapour and water). The paper was produced for the US Department of Energy to provide a rationale for predicting the general corrosion behaviour of metallic spent nuclear fuel.

This section is based on papers which contain information relevant to assessing the rate of metal consumption and the rate of gas generation under waste disposal conditions. An overview of the corrosion mechanisms involved and the nature of the corrosion products is presented, but a comprehensive review of all aspects of the corrosion behaviour of uranium is
not intended. This section, for example, does not cover the effects of alloying on corrosion, since waste uranium is mainly unalloyed.

7.2 Corrosion in aqueous solutions

7.2.1 Thermodynamic stability of uranium

The thermodynamic stability of uranium in aqueous environments is summarised in the Pourbaix diagrams for uranium [56], as shown in Figure 27. These diagrams show the regions of potential and pH in which two different sets of solid uranium compounds are thermodynamically stable. Ritchie [151] believes Figure 27 (b) is more realistic because it allows for the presence of the more thermodynamically stable UO$_3$·2H$_2$O and UH$_3$. More accurate thermodynamic data have been produced since Pourbaix constructed the initial diagram and revised versions have been calculated by Paquette and Lemire [152] and Inoue and Tochiyama [153]. Llewelyn Leach and Nehru investigated the corrosion of uranium in alkaline conditions using a reflection interference technique [154] and proposed that under alkaline conditions the following phases are formed on moving from negative to positive potentials: U, U(OH)$_4$, U$_4$O$_9$, U$_3$O$_7$, U$_3$O$_8$ and UO$_3$.

Pourbaix diagrams do not provide any information about the formation kinetics for the various substances. In addition to the substances shown, various uranium complexes can be formed, for example with organic acids. These may be important for the repository safety case but are not considered further here in relation to the corrosion behaviour of uranium. The domain of stability of uranium oxide is below the water reduction potential, implying that at low potentials, for example in de-aerated conditions, there is a strong tendency to reduce water to form hydrogen and uranium oxide. In general, uranium dissolves in acidic or neutral environments, but forms an oxide film in alkaline conditions. Uranium hydride is unstable in air and it reduces water violently to form UO$_2$ and hydrogen. It also reacts violently with hydrogen peroxide. Alkalis have little effect on hydride [155].

7.2.2 The electrochemical mechanism for aqueous corrosion of uranium

The early work on the corrosion of uranium in water was reviewed by Hopkinson [156] and the most extensive subsequent investigations of corrosion of uranium in water were reported by Baker et al. [157, 158]. The corrosion of uranium is sensitive to temperature, oxygen concentration and pH. Proton reduction does not occur until low pHs are reached, so aerobic corrosion normally proceeds by oxygen reduction. In oxygenated conditions the reaction product has been identified as UO$_3$·0.8 H$_2$O [144].

Uranium reacts with de-aerated water to produce hydrogen and non-stoichiometric uranium oxide. Oxygen inhibits the uranium-water reaction and makes uranium susceptible to crevice attack and pitting [145]. Oxygen inhibition is most marked at low temperatures, when oxygen solubility is highest [145]. The overall corrosion reaction with de-aerated water can be summarised as [159]:

$$ U + (2 + x) H_2O \rightarrow UO_{2+x} + (2 + x) H_2 $$ (7.1)

where $x$ is between 0.2 and 0.4. Uranium hydride is also formed to a lesser extent (~9%) and in some circumstances it is only a transitory species which reacts with water to produce uranium dioxide and hydrogen.

Baker et al. [157] proposed the following reaction mechanism for the corrosion of uranium in de-aerated water. At the oxide surface:

$$ H_2O \rightarrow H^+ \text{(hydrated)} + OH^- $$ (7.2)
Then, at the uranium-uranium oxide interface:

\[ \text{U} \rightarrow \text{U}^{4+} + 4e^- \quad (7.3) \]

\[ \text{OH}^- \rightarrow \text{O}^{2-} + \text{H}^+ \quad (7.4) \]

\[ \text{H}^+ + e^- \rightarrow \text{H}^+ \quad (7.5) \]

The hydrogen atom, H*, is very reactive and it may attack uranium directly to form uranium hydride at the interface between the metal and the oxide, by the following reaction:

\[ 3\text{H}^* + \text{U} \rightarrow \text{UH}_3 \quad (7.6) \]

In some instances fingers of hydride penetrating into the uranium metal have been observed. Alternatively, H* may diffuse away from the metal-oxide interface and recombine to form molecular hydrogen at the oxide-solution interface:

\[ 2\text{H}^* \rightarrow \text{H}_2 \quad (7.7) \]

Some of the uranium hydride formed is expected to react with water according to the following reaction:

\[ 2\text{UH}_3 + 4\text{H}_2\text{O} \rightarrow 2\text{UO}_2 + 7\text{H}_2 \quad (7.8) \]

It has been postulated that the corrosion rate is controlled by the diffusion of the hydroxide formed at the surface of the oxide (Equation (7.2)) through the film to oxidise the uranium at the metal-oxide interface [160]. Experiments using isotopically labelled water combined with SIMS analysis [161] have confirmed this premise by demonstrating that fresh oxide is produced at the metal-oxide interface and that oxygen in some form diffuses through the oxide layer to react with the underlying metal. These experiments also showed that oxygen inhibition occurs at the metal-oxide interface and not by blocking water adsorption at the oxide-solution interface.

Baker et al. [157] and Waber [162] reported the generation of small quantities of methane, arising from the reaction between water and carbide impurities in the uranium.

### 7.2.3 The electrochemistry of uranium

The anodic reaction in the aqueous corrosion of uranium is generally considered to be:

\[ \text{U} \rightarrow \text{U}^{4+} + 4e^- \quad (7.9) \]

although Ward and Waber [163] have proposed that the reaction proceeds firstly by rapid oxidation to U3+:

\[ \text{U} + \text{H}_2\text{O} \rightarrow \text{UO}^+ + \text{H}_2 + e^- \quad (7.10) \]

followed by a slower oxidation to U4+:

\[ \text{UO}^+ + \text{H}_2\text{O} \rightarrow \text{UO}_2 + \text{H}_2 - e^- \quad (7.11) \]
In de-aerated water the oxidation reaction is balanced by the cathodic reduction of water:

\[ \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^- \] (7.12)

If oxygen is present the cathodic reaction is:

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \] (7.13)

Ward and Waber [163] observed hydrogen peroxide as an intermediate species.

Corrosion is generally considered to occur under anodic control. A passive film forms when oxygen is present, when the cathodic reaction is the reduction of oxygen. In de-aerated water, uranium actively corrodes at low potentials, due to the reduction of water and the formation of hydrogen and hydroxide ions. Hydride formation by the reaction of water and uranium may also be part of the reaction.

(a) Corrosion potentials in aerated aqueous conditions

In aerated 0.1M KClO\textsubscript{4} at pH 7 and 35°C the open circuit potential (E\textsubscript{o.c.}) has been measured as 0.143 V (vs. SCE) [163]. Bullock \textit{et al.} [164, 165] reported open circuit potential measurements in air-equilibrated solutions at pH 14 of ~-400 mV (vs. SCE). At these potentials no hydrogen would be evolved. The addition of chloride to neutral, aerated conditions makes the corrosion potentials more active (i.e. more negative).

(b) Corrosion potentials in de-aerated aqueous conditions

Jenks [166] measured the open circuit potential of uranium in de-aerated 0.1M K\textsubscript{2}SO\textsubscript{4} solutions, in the pH range 5 to 10, and in 0.1N and 1N H\textsubscript{2}SO\textsubscript{4}. E\textsubscript{o.c.} falls with decreasing oxygen partial pressure and in fully de-aerated water it is ~-1100 mV (vs. SCE). The potential-oxygen concentration behaviour follows the Nernst equation [163] and decreases linearly with increasing pH according to the equation:

\[ \text{E}_{\text{o.c.}} = -0.059 \text{pH} + \text{constant} \] (7.14)

Bullock \textit{et al.} [164, 165] observed that the potential fell to between -600 and -1000 mV (vs. SCE) in de-aerated conditions. In oxygen-free neutral solutions Ward and Waber [163] measured initial rest potentials of ~-300 mV (vs. SCE), which lies in the UO\textsubscript{2} region of the Pourbaix diagram and corresponds to the passive state near the transpassive region, but after a time the potential fell to between -1100 and -1200 mV (vs. SCE), which lies on the UO\textsubscript{2} / UH\textsubscript{3} boundary in the Pourbaix diagram and would be sufficiently negative to allow hydrogen formation by reduction of water.

(c) Correlation with Pourbaix diagrams

From the experimental electrochemical results and an analysis of thermodynamic data in the Pourbaix diagrams, Jenks drew the following conclusions for the pH range 0–6:

- UH\textsubscript{3} forms by reaction between U and H\textsubscript{2}O below potentials corresponding to the UH\textsubscript{3} / UO\textsubscript{2} equilibrium;
- A passive film of UO\textsubscript{2} forms on uranium above the potential for UH\textsubscript{3} / UO;
- The passive film is removed at potentials above the UO\textsubscript{2} / UO\textsubscript{3} equilibrium and corrosion rates increase;
- Above the transpassive potential, pitting occurs due to the formation of soluble UO\textsubscript{3}. 

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UO₂ is more soluble than UO₃ – its solubility depends on the degree of hydration and it is more soluble in acidic conditions;

UO₂ dissolves in alkali conditions containing hydrogen peroxide;

UO₂ is slowly oxidised to UO₃ in oxygenated water.

Bullock et al. [164, 165] reviewed the literature on the oxide films formed on uranium. At pH 14 for potentials less than 0.0V the oxide was UO₂, and for potentials greater than 0.0V the film was UO₂ plus possibly U₃O₈ or UO₃·2H₂O. Leach and Nehru [167] found evidence of U₃O₇, U₃O₈ and probably U(OH)₄.

(d) Polarisation behaviour

Bullock et al. [164, 165] carried out potentiodynamic scans in argon-purged 1N KOH at pH 13.7. Two regions of active-passive behaviour were observed, one between about -1100 mV and -400 mV (vs. SCE) and a second between -300 mV and +100 mV (vs. SCE). The second, more positive peak was quite reproducible and was attributed to UO₂ oxidation to UO₃, whereas the lower one was sensitive to small changes in surface preparation and solution composition and was attributed to the oxidation of U(IV) species in solution produced by the chemical dissolution of UO₂.

Ritchie [151] summarised the polarisation curve behaviour, observed by various investigators, for uranium in de-aerated aqueous solutions as follows. As the potential is increased above the corrosion potential (~-1.2V (vs. SCE)) the current increases rapidly, up to a peak at ~-0.7V (vs. SCE), when the current falls and remains constant over the range -500 mV to +200 mV (vs. SCE), after which it increases in the transpassive region. The difference between the corrosion rates in the active and passive regions is relatively small. In the active and passive regions UO₂ is formed, whereas UO₃ or uranates species are formed in the transpassive region, depending on pH. Oxidising inhibitors increase the potential into the passive region and so reduce corrosion, but very strong oxidising agents, such as peroxide, raise the potential into the transpassive region and hence accelerate corrosion.

7.2.4 Corrosion rates in aqueous solutions

Most authors have reported corrosion rate data for uranium in terms of mg U cm⁻² h⁻¹. 1 mg U cm⁻² h⁻¹ is equivalent to a corrosion rate of 4.597 µm a⁻¹ or, assuming 1 mole of uranium produces 2 moles of hydrogen, 16,487 litres (at NTP) H₂ m⁻² a⁻¹. 1 µm a⁻¹ is equivalent to 3.586 litres (at NTP) H₂ m⁻² a⁻¹.

(a) Aerated aqueous conditions

After an initial period the corrosion rate in aerated aqueous conditions is constant. When all the available oxygen has been consumed the corrosion rate reverts to that of the uranium-water reaction and hydrogen production commences. In aerated conditions the corrosion rate is ~30–100 times less than in de-aerated conditions. A summary of literature corrosion rate data for uranium in aerated aqueous conditions is presented in reference [150]. The degree of oxygen inhibition is linearly related to the oxygen pressure [168].

The galvanic corrosion for various couples with uranium in aqueous solutions has been reviewed by Levy and Zabielski [169] and investigated by Winkel and Childs [170] and McIntyre et al. [171]. The data will not be discussed in detail here as wide variations are observed depending on the exact conditions of metal composition and pH.

(b) De-aerated aqueous conditions

In de-aerated solutions, the oxidation of uranium and the resulting hydrogen generation follow linear kinetics [157]. Arrhenius plots give activation energies varying from 50 to 70 kJ mol⁻¹ [157]. No effect of hydrogen pressure on the reaction rate has been found, up to
6 atmospheres overpressure [157]. In the pH range 2 to 14 a slight decrease (10–15%) in corrosion rate with increasing pH is observed, but a 10-fold decrease is observed at pH <2. No effect of the identity of the anion or cation on the corrosion is observed, indicating that the corrosion rate is determined by the balance of hydroxide and hydrogen ions only. The one exception to this is that carbonate ions reduced the corrosion rate to about 50% [157], possibly by the formation of uranyl carbonates [162]. The hydrogen deficiency in the reaction is 1–13%, with the remainder forming uranium hydride.

The oxide does not form a protective layer due to the large difference in the density and lattice parameter between the oxide and the metal (11 and 19 gm cm$^{-3}$ respectively), and the disruptive effect of hydrogen formation. During corrosion there is continuous spallation of the oxide, although a thin continuous layer is present next to the metal surface.

Tyfield [160] investigated the corrosion of reactor grade uranium in de-aerated sodium hydroxide over a range of pHs. The corrosion rates were monitored by measuring the pressure increase caused by the production of hydrogen inside sealed autoclaves and also by analysing the amount of caesium-137 released from irradiated uranium fuel into the test solutions. The hydrogen production rate was found to be generally constant, but at <60°C an induction period was observed; the length of which decreased with increasing temperature. The induction period was thought to be due to the presence of an adsorbed molecular oxygen layer, which inhibited the uranium-water reaction. It lasted for only a few 10s of hours and it is unlikely to be significant in the waste disposal context. The mass of hydrogen produced did not match exactly the volume of uranium corroded, because of the formation of uranium hydride and the non-stoichiometry of the oxide; x in Equation (7.1) was estimated to be <0.1. Increasing the pH from ~6 to 11.5, measured at 25°C, reduced the hydrogen evolution rate at 90°C by about 50% for both un-irradiated fuel and irradiated fuel. Little difference in corrosion rate was observed between pH 11.5 and 12.5.

Tyfield [160] determined that the activation energy for the hydrogen evolution rate in the range 75–140°C was ~60 kJ mol$^{-1}$. Good agreement was observed between the reactor grade uranium, which contained 0.6–2 kg/t aluminium, and the corrosion data reported by Baker et al. [157] for $\alpha$-uranium, which did not contain aluminium. Iron impurities did not appear to affect the corrosion rate significantly. The corrosion rate of irradiated uranium was found to be enhanced compared to that of un-irradiated uranium due to an increase in its surface area as a result of void formation. Weight loss measurements yielded higher corrosion rates because of the loss of some particles of un-corroded uranium.

Various authors have derived equations for the corrosion rate of uranium in aqueous conditions. Hilton [150] reanalysed all available uranium/water reaction rate data up to 1999, and gives the following equation for the corrosion rate of uranium in de-aerated water:

$$\text{Rate} = 5.03 \times 10^9 \exp\left(\frac{-66400 \pm 2000}{RT}\right) \text{mg U cm}^{-2}\text{h}^{-1}$$

(7.15)

where

- \( R \) is the gas constant [J mol$^{-1}$K$^{-1}$]; and
- \( T \) is the absolute temperature (K).

### 7.2.5 Effect of radiation on uranium corrosion

Radiolysis has the effect of producing various reactive species such as free radicals, nitric acid and hydrogen peroxide which can affect the corrosion behaviour of metals [172]. Uranium is attacked fairly readily by hydrogen peroxide at a considerably faster rate than in water. The rate is constant with time and peaks at a hydrogen peroxide concentration of ~12%, with a maximum corrosion rate of 0.37 mg U cm$^{-2}$h$^{-1}$, about 10$^2$ times greater than in pure water. It is believed that a hydrated uranium peroxide $\text{UO}_2\cdot x\text{H}_2\text{O}$ is formed. On the
other hand, other work has shown that the corrosion rate of uranium in water is unaffected by a \( \gamma \)-radiation dose of \( \sim 72 \, \text{Mrad} \) at 30°C [157].

7.2.6 Corrosion products formed on uranium in aqueous solutions

The exposure of uranium to water or water vapour results in a rapid darkening. When the adherent surface film reaches a certain thickness, spalling occurs, producing an outer friable layer [160]. Corrosion occurs fairly uniformly, although prolonged reaction results in roughening, but no deep pitting. Colmenares [173] has reviewed the physico-chemical properties of uranium oxides in detail, and has produced a phase diagram of the various uranium oxides as a function of the uranium-oxide ratio.

Ward and Waber [163] observed a sharp X-ray pattern for crystalline \( \text{UO}_2 \) formed under aerated conditions. The small crystallites had a Face Centred Cubic fluorite structure and a lattice spacing corresponding to \( \text{UO}_2 \cdot 2.1 \). In de-aerated conditions the solid product was an amorphous, finely divided black powder with a surface area of 30 m\(^2\)g\(^{-1}\) [157]. When it was brought into contact with oxygen, oxidation to \( \text{UO}_2 \cdot 2.2 \cdot 0.1 \) occurred. 2-9% \( \text{UH}_3 \) was present in the corrosion product. Tyfield [160] and Ward and Waber [162] observed a layer of uranium hydride under the uranium dioxide and fingers of uranium hydride penetrating into the metal surface.

Fuller \textit{et al}. [174, 175] examined the oxide formed on uranium metal in water vapour and water, using a diffuse reflectance infra-red spectroscopy technique. Layers of corrosion product (lamellae), which spalled off when the strain in the oxide became sufficiently high, were observed. This process may be accelerated in liquid water by bubble generation.

7.2.7 Reaction of uranium hydride

Uranium hydride is formed during the uranium-water reaction, with the quantity varying with relative humidity, temperature and the metallurgical state of the uranium. Uranium hydride may form through reaction between the metal and free hydrogen produced at the metal surface as a result of corrosion, or as an intermediate in the uranium-water reaction. In gaseous oxidation, the quantity of hydride is greatly reduced by a reduction in the relative humidity but changes little with temperature and is unaffected by large changes in the external hydrogen pressure.

Uranium hydride is a black powder, which reacts with water according to the reaction:

\[
2\text{UH}_3 + 4\text{H}_2\text{O} \rightarrow 2\text{UO}_2 + 7\text{H}_2
\]

A proportion of the hydride remains un-reacted, due to the protection afforded by the oxide. This reaction ceases at \( \sim 83\% \) completion [157]. If oxygen is present a rapid reaction ensues, yielding water.

Haschke [149] has considered the risks associated with the corrosion of uranium and the pyrophoric nature of uranium hydrides. He proposed that the solid corrosion product is actually an oxide hydride, with a stoichiometry of \( \text{UO}_{1.2}\text{H}_{0.6} \), rather than a mixture of \( \text{UO}_2 \) and \( \text{UH}_3 \). The rate of reaction between the hydride and water is quoted as being:

\[
\text{Rate} = 2.20 \times 10^5 \exp\left(\frac{-53400}{RT}\right) \, \text{mg U cm}^{-2}\text{h}^{-1}
\]

This kinetics may apply only to small amounts of uranium hydride, as larger volumes may enter a violently pyrophoric regime if they are suddenly immersed in water.

Uranium hydride can also react directly and violently with oxygen [176]:

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7.3 Rates for gaseous oxidation

The oxidation of uranium in gaseous environments is relevant because uranium will be exposed to a gaseous environment during storage and through voids that may arise in the grout surrounding the waste after encapsulation. Oxidation has been studied in three main environments, namely dry air or oxygen, pure water vapour, and mixtures of air or oxygen and water vapour. Several review papers have been published on the oxidation of uranium, most notably by Ward and Waber [162] and Wilkinson [168], and more recently by Orman [177], Ritchie [178], Colmenares [173], Weirick [144], Haschke [179, 180] and Hilton [150]. Various techniques have been used to measure the oxidation rate, including weight change and, for the uranium-water reaction, hydrogen generation.

Ritchie [178] derived mathematical relationships to predict the oxidation of uranium based on data in the literature. Literature data were converted to mg U cm\(^{-2}\) hr\(^{-1}\), assuming stoichiometric reactions, but the error introduced by assuming stoichiometry was estimated to be less than the experimental error in the measurements. Linear kinetics was most commonly observed, although the initial stages of reaction often exhibited a non-linear dependence on time. The relative rates of corrosion in oxygen, water vapour-oxygen mixtures, and water vapour increase in the approximate ratio 1 : 20 to 50 : 3000 to 5000 [177, 181].

7.3.1 Uranium oxidation in oxygen

In air or oxygen the corrosion reaction [178] is:

\[ \text{U} + (2 + \frac{1}{2} \times) \text{O}_2 \rightarrow \text{UO}_{2+x} \]  

(7.19)

Up to 200°C the oxide formed is hyper-stoichiometric uranium dioxide, with \(x\) in the range 0.2 to 0.4. At temperatures greater than 275°C \(\text{U}_3\text{O}_8\) also forms. Oxidation in dry oxygen at temperatures up to 100°C produces a tightly adherent oxide and a fine loose powder [173].

At low oxygen pressures the oxidation rate is a function of pressure, in a way related to a Langmuir isotherm, but above a certain threshold, pressure has no effect. On the basis of literature data for the temperature range 40°C to 300°C reported before 1981, Ritchie [178] produced the following Arrhenius expression to describe the oxidation rate in dry oxygen:

\[
\text{Rate} = 7.59 \times 10^8 \exp\left(-\frac{76600}{RT}\right) \text{mg U cm}^2\text{h}^{-1}
\]  

(7.20)

where 
- \(R\) is the gas constant [J mol\(^{-1}\)K\(^{-1}\)]; and
- \(T\) is the absolute temperature (K).

Pearce and co-workers [182, 183] reassessed earlier work on the oxidation of uranium in oxygen and water vapour and combined it with new data. Although Pearce reviewed the world body of literature, he recommended Arrhenius expressions for the reaction rate constants based solely on his own data.
Hilton [150] reviewed and reanalysed the available data in Pearce’s report [183]. That reanalysis produced an Arrhenius expression that was virtually identical to the results of other recent regression analyses. The temperature dependence determined for the reaction rate of uranium oxidation in oxygen (for the temperature range 38°C to 300°C) was:

$$\text{Rate} = 1.09 \times 10^8 \exp\left(\frac{-71300 \pm 2100}{RT}\right) \text{mg U cm}^{-2}\text{h}^{-1}$$ (7.21)

### 7.3.2 Uranium oxidation in water vapour

The uranium-water vapour reaction is:

$$\text{U} + (2 + x) \text{H}_2\text{O} \rightarrow \text{UO}_{(2+x)} + (2 + x) \text{H}_2$$ (7.22)

where the corrosion product is hyper-stoichiometric uranium dioxide. The degree of hyper-stoichiometry is less than in oxygen, with x between 0.0 and 0.1. $\text{U}_4\text{O}_{9-y}$ may also be present [173]. The efficiency of hydrogen evolution increases as the water vapour pressure falls, reaching ~99% of the theoretical value at 20% RH, then remaining constant [157]. The deficiency in hydrogen factor is probably due to the formation of uranium hydride. The access of water is believed to be determined by the passage of condensed water vapour through micropores in the oxide, although it is independent of vapour pressure when several monolayers of water have adsorbed on the surface [157]. The reaction rate increases to that of bulk water as saturation is reached; the corrosion rate at 100°C and 100% RH is the same as under full immersion conditions. The injection of oxygen into a system containing only uranium and water vapour brings the production of hydrogen to an abrupt halt [184].

Hilton [150] performed a regression analysis of the reaction rate data reported up to 1999. That analysis evaluated the uranium/water vapour oxidation rates for the temperature range 20°C to 302°C, and determined a temperature dependence of:

$$\text{Rate} = 9.75 \times 10^5 \exp\left(\frac{-46600 \pm 700}{RT}\right) p^{0.5} \text{mg U cm}^{-2}\text{h}^{-1}\text{kPa}^{-0.5}$$ (7.23)

where

$R$ is the gas constant [J mol$^{-1}$K$^{-1}$];

$T$ is the absolute temperature (K); and

$p$ is the water vapour pressure [kPa].

### 7.3.3 Uranium oxidation in oxygen and water vapour

Uranium reacts with oxygen in water vapour [144] according to the reaction:

$$4\text{U} + 4\frac{1}{2} \text{O}_2 \rightarrow \text{U}_4\text{O}_9$$ (7.24)

In the presence of oxygen a more highly oxidised $\text{UO}_{2+x}$ product is formed than in water vapour only, with x = 0.2 to 0.4. In normal air or saturated water vapour at >90%RH a yellow trioxide ($\text{UO}_3\cdot0.8\text{H}_2\text{O}$) is formed soon after exposure [168] and this may become brown-black or green-black after further exposure. The reaction product is compact and adherent. Baker et al. [158] observed a black oxide under non-condensing conditions, with a composition of $\text{UO}_{2.2-2.4}$, which formed as a result of the oxidation of the initial $\text{UO}_{2.06}$. There is more than a 15% mismatch in the lattice parameters between the uranium and the oxide, hence stresses build up and spalling is likely [168].
Virtually no hydrogen is produced in the presence of oxygen at concentrations >0.1%, except under saturated conditions [158]. Below the threshold, corrosion produces hydrogen and the corrosion rate approaches that in pure water. When all the oxygen in a sealed system is consumed, hydrogen generation commences immediately and water is consumed [158].

Ritchie [178] and McGillivray et al. [185] have developed mathematical relationships for the oxidation rate of uranium. For moist air the corrosion behaviour can be divided into three regions:

- At low water vapour pressure (0%–2% RH), the oxidation rate increases strongly with relative humidity. Up to monolayer coverage the corrosion rate is proportional to the amount of water adsorbed [168].
- At 2%–90% RH, the oxidation rate is constant. Below about 90% RH the net result is the consumption of oxygen, with the formation of uranium dioxide. Virtually no hydrogen is produced, but the oxide is derived from the water vapour.
- At >90% RH, the oxidation rate increases weakly up to 100% RH. 100% RH is seen as being close to the pure water situation. The reaction product changes from being UO$_2$ to UO$_3$ and the evolution of hydrogen gas occurs.

Ritchie derived the following equations for the reaction rates:

$$\text{Rate} = 4.8 \times 10^{13} \exp\left(\frac{-104700}{RT}\right) \text{mg U cm}^{-2}\text{h}^{-1} \text{ at } 40°C < T < 130°C \text{ and 2%–90% RH} \quad (7.25)$$

$$\text{Rate} = 4.6 \times 10^9 \exp\left(\frac{-74500}{RT}\right) \text{mg U cm}^{-2}\text{h}^{-1} \text{ at } 25°C < T < 100°C \text{ and 100% RH} \quad (7.26)$$

where

- $R$ is the gas constant [J mol$^{-1}$K$^{-1}$]; and
- $T$ is the absolute temperature (K).

McGillivray and co-workers modelled the effects of water vapour at low relative humidity (<4% RH) by Langmuir kinetics for temperatures between 0°C and 350°C. The model is based on the Langmuir adsorption equation, where the rate is determined by the surface water concentration. In the absence of water vapour the oxidation rate is determined by the oxygen concentration. A plateau in the oxidation rate is reached when one monolayer of adsorbed water has developed. The observed oxidation rate is given by:

$$\text{Rate} = D + \frac{k_1 p}{1 + k_2 p} \quad (7.27)$$

where

- $D$ is the oxidation rate in dry oxygen; and
- $k_1$ and $k_2$ are temperature dependent constants.

Hilton [150] re-evaluated the existing data up to 1999 for the reaction of uranium with oxygen-water vapour at intermediate and at 100% RH relative humidity. Arrhenius expressions for the two relative humidity ranges were determined by linear regression analysis of the literature data. The temperature dependence of the reaction rate was determined as:
The reaction rate of uranium in water-saturated oxygen (100% RH) is around an order of magnitude higher than in dry oxygen; however it is one to two orders of magnitude less than the reaction rate in anoxic water vapour or water immersion.

7.3.4 Effect of irradiation history on uranium corrosion

The effects of irradiation on the reaction rate of uranium with oxygen and moist oxygen were investigated by Bennett and co-workers [186–188] and reviewed by Totemeier [147] and Hilton [150]. The uranium metal was irradiated in Magnox reactors. The surface area, swelling and open porosity of the irradiated samples were determined by standard techniques.

For less than 22% swelling, the oxidation rate is less than a factor of two greater for irradiated uranium than for unirradiated uranium in the temperature range 100°C–250°C. Above 22% swelling, the oxidation rate increased exponentially with swelling. Bennett et al. modelled the increase in reaction rate due to irradiation at temperatures of 100°C–350°C as an exponential function of swelling and inverse temperature [188]. The enhancement factor was given as:

\[
\text{Enhancement factor} = \exp\left(\frac{19400 S}{T} \right)
\]  

(7.30)

where
\begin{itemize}
  \item \( S \) is the per cent swelling for the irradiated fuel [-]; and
  \item \( T \) is the absolute temperature (K).
\end{itemize}

Hilton [150] assumed the reaction rate was independent of temperature and related only to swelling. He reanalysed Bennett’s data for temperatures between 100°C and 300°C and determined an enhancement factor of:

\[
\text{Enhancement factor} = 0.444 \exp\left(0.0786 S\right)
\]  

(7.31)

In summary, irradiation does not increase the intrinsic oxidation rate of uranium metal. The enhancement factor due to irradiation is defined as an exponential function of swelling and is attributed to the associated increase in surface area. The oxidation rate of metal fuel irradiated to low burn-up, which has negligible swelling, is expected to be similar to that of unirradiated uranium metal.

7.4 Corrosion in wasteforms

There are very few published data for the corrosion of uranium in cementitious environments.

During decanning of Magnox fuel some uranium is carried over with the Magnox fuel cans, so the possible galvanic corrosion of uranium and Magnox has been investigated [189]. Uranium in calcium hydroxide adopted a free corrosion potential of -0.25V (vs. SCE), compared to Magnox at -1.3V (vs. SCE). In BFS/OPC the Magnox and uranium potentials were -1.0V and -0.15V (vs. SCE) respectively. When the two metals were coupled the potential was -0.225V (vs. SCE), so that on the basis of the Pourbaix diagram the corrosion
products were expected to be UO$_2$, UO$_3$, and UH$_3$. Varying pH in range 11–13 had little effect on the corrosion rate of the uranium, which was measured as 10 µA/cm$^2$ (~100 µm a$^{-1}$) at pH 13. The authors reported that there was evidence that UO$_2$ and UO$_3$ can form a number of hydrated calcium uranates and uranium-substituted calcium silicate hydrates in BFS/OPC.

Curwen [190] considered the effect of the corrosion of uranium in packaged waste from the Sellafield Drypack Process plant. Most waste uranium was expected to have corroded to uranium dioxide prior to packaging, but some un-corroded fuel was also anticipated. In alkaline liquor at 26°C the corrosion rate was expected to be 40 mdd (77 µm a$^{-1}$, or 275 litres (at NTP) H$_2$ m$^{-2}$ a$^{-1}$), but 576 mdd for highly swollen irradiated fuel. For 28 kg of uranium (the amount present in an individual puck) the surface area was expected to be 0.77 dm$^2$ kg$^{-1}$ and the predicted hydrogen evolution rate was 191 ml per day. The authors expected this to fall because of corrosion product formation, although this seems unlikely in view of the linear kinetics that has been described in previous sections. The predicted corrosion rate is comparable with information in the literature. It is possible that corrosion may be limited by the supply of water and some corrosion may proceed by oxygen rather than water reduction, until anaerobic conditions have been established.

In trials for the BNFL Big Box package it was found that the corrosion rate for uranium decreased rapidly with time, from initial corrosion rates of ~80 mdd (153 µm a$^{-1}$) to the limit of detection, due to limitations on the water supply [191]. Such low corrosion rates would not be expected to persist in a repository after resaturation had occurred.

Thomas et al. [133] investigated the corrosion rates of uranium and uranium-aluminium couples in an aerobic cementitious grout. Electrochemical measurements indicated that the corrosion rate of uncoupled uranium was initially of the order of 60 µm a$^{-1}$, falling to 12 µm a$^{-1}$ after 2 months. No gas evolution was detected during the experiments, suggesting that, as expected, the uranium was corroding by cathodic reduction of the oxygen, rather than reduction of water.

Blackwood and Farmilo [192] and Farmilo and Simmons [193] used electrochemical techniques to measure the corrosion rate of uranium as function of time, temperature and humidity in both 0.1M sodium hydroxide solution and 3:1 PFA/OPC cement grout. The corrosion rates of uranium encapsulated in cement seemed to be dependent on the availability of water. The measured corrosion rates fell from their initial values to less than 0.1 µm a$^{-1}$. When subsequently the specimens were irrigated with distilled water, the corrosion rates increased dramatically, with values of 5 µm a$^{-1}$ and 160 µm a$^{-1}$ being determined at ambient temperature and 80°C respectively. In the case of uranium encapsulated in cement doped with 10,000 ppm of chloride however, the long-term corrosion rates were erratic and showed no clear variation with exposure time.

More recent studies by BNFL [194, 195] investigated the corrosion behaviour of uranium metal encapsulated in a BFS/OPC cement grout. Twenty trials determined the corrosion rate of uranium by measuring the pressure increases in sealed reactor vessels due to the hydrogen evolved from the corrosion reaction. Each reactor vessel was charged with a known surface area of metal. Eight grout formulations were assessed, with each formulation cured at a nominal constant temperature (e.g. 25°C or 50°C). The corrosion rate was determined by measuring the change in pressure caused by hydrogen evolution via pressure transducers in each reactor vessel lid.

Hayes et al. [194] found that over the time period studied the corrosion behaviour of uranium is characterised by an incubation period followed by linear corrosion kinetics, with the duration of the incubation period reducing with increasing temperature. Once corrosion has initiated, temperature has a significant effect on the corrosion rates measured. Thus, constant rates of 30–80 mdd$^{xvi}$ were observed in trials conducted at 25°C. In comparison, trials conducted at

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$xvi$ 1 mdd = 1.93 µm a$^{-1}$

73
30–35°C showed linear corrosion rates of 130–300 mdd. Neither BFS/OPC ratio nor water content had a statistically significant effect on the uranium corrosion rates.

Godfrey et al. [195] found that the corrosion rate of uranium encapsulated in BFS/OPC cement is very similar to that in water (see Equation 7.15), and can be predicted using the equation:

\[
\text{Rate} = 3.32 \times 10^{11} \exp\left(-\frac{77300}{RT}\right) \text{mg U cm}^{-2}\text{h}^{-1} \quad (7.32)
\]

where

- \( R \) is the gas constant \([\text{J mol}^{-1}\text{K}^{-1}]\); and
- \( T \) is the absolute temperature \((\text{K})\).

The activation energy is 77 kJ mol\(^{-1}\).

### 7.5 Conclusions

The main conclusions from this review of the effects of uranium corrosion on gas generation during radioactive waste disposal are as follows:

- Under aerobic conditions uranium corrodes to form non-stoichiometric uranium dioxide or hydrated uranium trioxide. Hydrogen will not be produced until \(<~0.1\%\) oxygen is present, after which anaerobic corrosion of uranium will produce hydrogen. This corresponds to a fall to highly negative corrosion potentials (<1V vs. SCE).

- Uranium exhibits active-passive transitions, corresponding to the various oxide phases described in Pourbaix diagrams.

- Small quantities of methane are produced by the corrosion of carbides in the uranium metal.

- The uranium corrosion rate in anaerobic aqueous conditions is 30–100 times higher than in aerated conditions.

- In deoxygenated conditions the temperature dependence of the corrosion rate is given by the Arrhenius Equation.

- No effect of hydrogen pressure has been observed for the anaerobic corrosion of uranium.

- The corrosion rate is only weakly dependent on pH in the range 2–13.

- No effect of cation or anion type has been observed for the anaerobic corrosion of uranium, with the possible exception of carbonate ions.

- The relative rates of corrosion in oxygen, water vapour-oxygen mixtures and water vapour increase according to the ratio 1 : 20 to 50 : 3000 to 5000.

- Mathematical relationships are available for the corrosion of uranium in de-aerated water, oxygen, water vapour and oxygen-water vapour mixtures. Kinetics is generally linear. Spalling of the oxide is observed due to the lattice mismatch between the metal and the oxides.

- Very few data are available for the corrosion of uranium in cement, particularly under anaerobic conditions.
8 Parameterisation of SMOGG Model for Uranium

From the information summarised in Section 7, it appears that once conditions have become anaerobic corrosion of uranium metal will generate hydrogen. The timing of this will depend on, for example:

- whether the container is vented;
- whether the vent has been blocked (e.g. by backfill);
- how easily air can circulate in the container; and
- whether corrosion of other metals in the waste package has caused the environment to become anaerobic.

The rate of hydrogen generation will increase significantly with temperature, while the build-up of corrosion product and limitations on the supply of water could reduce the rate. Since uranium metal will generate hydrogen, a model for its corrosion is included in SMOGG.

8.1 SMOGG model

The model implemented in SMOGG [3, 4] specifies the corrosion rate of uranium as:

\[
\frac{ds}{dt} = -k_a e^{\frac{t_a}{t_c}} f_a(T) - k_c e^{\frac{t_c}{t_c}} f_c(T)
\]

(8.1)

where

- \(s\) is the position of the surface of the uranium [m];
- \(t\) is the time during which corrosion is occurring [a];
- \(k_a\) is the initial acute corrosion rate (defined at a reference temperature, \(T_{ref}\), for which \(f_a = 1\)) [m a\(^{-1}\)];
- \(t_a\) is a characteristic time for the acute corrosion [a];
- \(f_a\) is a factor that specifies the dependence of the acute corrosion rate on temperature [-];
- \(T\) is the temperature [K];
- \(k_c\) is the initial chronic corrosion rate (defined at a reference temperature, \(T_{ref}\), for which \(f_c = 1\)) [m a\(^{-1}\)];
- \(t_c\) is a characteristic time for the chronic corrosion [a];
- \(f_c\) is a factor that specifies the dependence of the chronic corrosion rate on temperature [-].

This formulation allows separate corrosion rates to be specified for an initial “acute” phase and a later “chronic” phase.
Furthermore, for the purpose of this study the model is simplified by assuming the corrosion rates increase with temperature according to an Arrhenius relationship. That is:

\[ f_a(T) = \exp \left[ - \frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_{ref}} \right) \right] \]  

(8.2)

and

\[ f_c(T) = \exp \left[ - \frac{E_c}{R} \left( \frac{1}{T} - \frac{1}{T_{ref}} \right) \right] \]  

(8.3)

where

- \( E_a \) is the activation energy for the acute corrosion [J mol\(^{-1}\)];
- \( R \) is the gas constant [J mol\(^{-1}\)K\(^{-1}\)];
- \( T_{ref} \) is a reference temperature at which \( k_a \) and \( k_c \) are defined [K];
- \( E_c \) is the activation energy for the chronic corrosion [J mol\(^{-1}\)].

Hence, a total of six parameters must be specified to define the corrosion rate of uranium for a particular corrosive environment:

- two rate constants (\( k_a \) and \( k_c \), giving the base corrosion rates);
- two characteristic times (\( t_a \) and \( t_c \), defining the decrease with time); and
- two activation energies (\( E_a \) and \( E_c \), defining the effect of temperature).

Uranium corrodes under aerobic conditions to produce uranium oxides according to:

\[ U + 0.5 \,(2+x) \,O_2 \Rightarrow UO_{2+x} \quad (0.2 < x < 0.4) \]  

(8.4)

Although this reaction occurs without the production of gas, it is included in SMOGG because it may reduce the inventory of uranium available for the subsequent production of gas under the anaerobic conditions that will develop after repository closure.

Under anaerobic conditions, uranium corrodes to produce hydrogen according to:

\[ U + (2 + x) \,H_2O \Rightarrow UO_{2+x} + (2+x) \,H_2 \quad (0.2 < x < 0.4) \]  

(8.5)

For the purpose of the simplified model in SMOGG, the parameter \( x \) in the equation for uranium corrosion is set cautiously (as far as maximising hydrogen generation from a given mass of uranium corroding anaerobically is concerned) to the value \( x = 0.4 \).

It is assumed that uranium waste generally will be encapsulated in cement in metal containers to form stable and easily movable packages. The conditioned waste then will be transported to a deep underground repository and at an appropriate time surrounded by a cement-based backfill. Therefore the three corrosive environments possibly of interest are:

- an aerobic, cementitious (alkaline) environment;
- an anaerobic, cementitious (alkaline) environment; and
• after resaturation, an alkaline (pH 12.5–13) porewater which has mixed with groundwater containing chloride ions and various other inorganic salts.

However, the information in the literature (see Section 7) suggests that the presence of chloride will not affect the anaerobic corrosion rate of uranium metal in grout. In other words, the last environment is not distinct as regards uranium corrosion.

8.2 Approach

There is diversity in the results obtained from the different studies of uranium metal corrosion in a cementitious environment. The early studies show corrosion profiles characteristic of Magnox and aluminium corrosion, i.e. an initial “acute” phase that declines to a “chronic” phase with a corrosion rate of less than 1 μm a⁻¹. In contrast, more recent studies [194, 195] show profiles characterised by a brief “incubation period” (during which oxygen is reduced in preference to water) followed by a constant corrosion rate which is similar to that in de-aerated water.

In the absence of reliable data, it is suggested that the reaction rates of uranium metal should be based on the recent, comprehensive review and analyses by Hilton [150], who has derived the following rate equations for uranium oxidation.

• In oxygen and water vapour (at 100% RH):

\[
\text{Rate} = 8.65 \times 10^9 \exp\left(-\frac{76900 \pm 7000}{RT}\right) \text{mg U cm}^{-2} \text{h}^{-1} \quad (8.6)
\]

• In water:

\[
\text{Rate} = 5.03 \times 10^9 \exp\left(-\frac{66400 \pm 2000}{RT}\right) \text{mg U cm}^{-2} \text{h}^{-1} \quad (8.7)
\]

where

\[ R \quad \text{is the gas constant [J mol}^{-1} \text{K}^{-1}] ; \text{ and} \]
\[ T \quad \text{is the absolute temperature (K).} \]

These reaction rates are not affected greatly either by pH (in the range 3–14) or by the presence of anions and cations, but are affected by temperature. A further enhancement of the reaction rates occurs if the uranium is high burn-up material, which has an increased effective surface area (see Subsection 7.3.4). For the purpose of this report, an enhancement factor of 2 will be used to accommodate the effect of irradiated metal fuel.

Hence, the aerobic corrosion rate of uranium metal, including an enhancement factor of 2, is determined as:

\[
\text{Rate} = 7.95 \times 10^{13} \exp\left(-\frac{76900 \pm 7000}{RT}\right) \mu\text{m a}^{-1} \quad (8.8)
\]

and the anaerobic corrosion rate as:

\[
\text{Rate} = 4.62 \times 10^{13} \exp\left(-\frac{66400 \pm 2000}{RT}\right) \mu\text{m a}^{-1} \quad (8.9)
\]
8.3 Selection of data recommended for use in SMOGG

The objective of this study was to parameterise the corrosion model for uranium that has been implemented in SMOGG, as given by Equation (8.1). In Subsection 8.2, the available data have been identified and interpreted, as far as possible, to give values for the various parameters. This subsection summarises the set of parameters for uranium corrosion recommended for use in SMOGG.

8.3.1 Aerobic conditions

- There is no identifiable phase of acute corrosion.
- The initial chronic corrosion rate (including an enhancement factor of 2 to accommodate the effect of irradiated metal fuel) is 1.58 µm a⁻¹ at 20°C.
- The characteristic time for the chronic corrosion essentially is infinite\textsuperscript{xvii}.
- The chronic corrosion rate increases with temperature according to an Arrhenius relationship:

\[ f_c(T) = \exp\left(-\frac{76900}{8314472} \left(\frac{1}{T} - \frac{1}{293.15}\right)\right) \quad (8.10) \]

where \( T \) is the temperature [K]. For example, at the temperatures listed below the initial chronic corrosion rate should be scaled by the corresponding factors:

<table>
<thead>
<tr>
<th>Temperature, ( T )</th>
<th>20°C</th>
<th>35°C</th>
<th>50°C</th>
<th>80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor, ( f_c )</td>
<td>1.000</td>
<td>4.645</td>
<td>18.709</td>
<td>212.801</td>
</tr>
</tbody>
</table>

Calculations of gas generation performed with SMOGG might include variant cases intended to scope the effect of uncertainties in the model parameters. In particular, the uncertainty in the chronic corrosion activation energy (76.9 kJ mol⁻¹) is about 9%, and the range for the parameter is 69.9–83.9 kJ mol⁻¹.

8.3.2 Anaerobic conditions

- There is no identifiable phase of acute corrosion.
- The initial chronic corrosion rate (including an enhancement factor of 2 to accommodate the effect of irradiated metal fuel) is 68.2 µm a⁻¹ at 20°C.
- The characteristic time for the chronic corrosion essentially is infinite\textsuperscript{xvii}.

\textsuperscript{xvii} In using the SMOGG model a finite value is required; a value much greater than the duration of the calculation \( i.e. \) at least an order of magnitude greater should be used.
The chronic corrosion rate increases with temperature according to an Arrhenius relationship:

\[ f_c(T) = \exp\left[-\frac{6640}{8.314472} \left(\frac{1}{T} - \frac{1}{293.15}\right)\right] \]  

(8.11)

where \( T \) is the temperature [K]. For example, at the temperatures listed below the initial chronic corrosion rate should be scaled by the corresponding factors:

<table>
<thead>
<tr>
<th>Temperature, ( T )</th>
<th>20°C</th>
<th>35°C</th>
<th>50°C</th>
<th>80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor, ( f_c )</td>
<td>1.000</td>
<td>3.766</td>
<td>12.542</td>
<td>102.355</td>
</tr>
</tbody>
</table>

Calculations of gas generation performed with SMOGG might include variant cases intended to scope the effect of uncertainties in the model parameters. In particular, the uncertainty in the chronic corrosion activation energy (66.4 kJ mol\(^{-1}\)) is about 3%, and the range for the parameter is 64.4–68.4 kJ mol\(^{-1}\).

### 8.4 Discussion

Having derived a parameterisation of the SMOGG model for the corrosion rate of uranium (Subsection 8.3), it is useful to compare the resulting values with the corrosion rates used previously.

The Generic Post-closure Performance Assessment [2] is the only assessment to have considered gas generation from uranium corrosion. This assessment assumed that the uranium corrosion rate would be 1 µm a\(^{-1}\) under storage conditions (i.e., aerobic environment at 35°C), and 100 µm a\(^{-1}\) at other times. The justification for these corrosion rates were the following assumptions:

- waste conditioning will inhibit corrosion; and
- during storage, corrosion will be limited by local restrictions on the supply of water.

It was acknowledged however that “data from experiments on the anaerobic corrosion of uranium immersed in aqueous solutions give much higher corrosion rates”, and also “show a significant temperature dependence” [196].

In contrast, more recent studies of uranium metal corrosion in a cementitious environment [194, 195] show profiles characterised by a brief “incubation period” (during which oxygen is reduced in preference to water) followed by a constant corrosion rate which is similar to that in de-aerated water. As a result of this experimental evidence, the uranium corrosion rates which are now being recommended, i.e.:

<table>
<thead>
<tr>
<th>Corrosion Rates at Different Temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condition</td>
</tr>
<tr>
<td>Storage (aerobic)</td>
</tr>
<tr>
<td>Other (anaerobic)</td>
</tr>
</tbody>
</table>

are significantly higher than those used in the Generic Post-closure Performance Assessment.
9 Summary

The reactive metals Magnox, aluminium and uranium may be present in some cement encapsulated wastes, and will corrode under aerobic and anaerobic alkaline conditions. Magnox and aluminium will corrode and generate hydrogen, and under anaerobic conditions uranium also will produce hydrogen.

This report identifies the various corrosive environments that could be experienced by these encapsulated metal wastes during their long-term management (i.e. during surface storage and transportation, and then in a deep geological repository, both before and after resaturation with a groundwater that could have a high chloride concentration). For each environment, relevant corrosion rate data for Magnox, aluminium and uranium have been compiled from the literature. The effects on the corrosion rates of a number of variables (including oxygen concentration, temperature and chloride concentration) have been considered.

These experimental data have been reviewed critically, and, where appropriate, used to calibrate the SMOGG corrosion model. From this information, parameters recommended for use in the SMOGG corrosion model for the reactive metals Magnox, aluminium and uranium are selected.

The following subsections summarise the conclusions of the literature survey for each of the reactive metals, and the standard set of parameters that should be used in SMOGG (see also Table 11).

9.1 Magnox

9.1.1 Overview

The corrosion of magnesium in alkaline solution involves two electrochemical reactions in balance, namely the cathodic reduction of water to form hydrogen and the anodic dissolution of magnesium to form magnesium hydroxide. The presence of iron as an impurity in the magnesium, or galvanic coupling to a steel component, shifts the potential in a positive direction and tends to increase the corrosion rate. The rate of dissolution of magnesium appears to be limited by a protective corrosion film consisting of a layer of small randomly oriented crystals of brucite, Mg(OH)$_2$. The film also contains water, appears to be porous and has a low electrical resistance, so that it does not have the characteristics required of a protective film. If a true protective film does exist it has been deduced to be below the outer film and less than 100 nm thick. This thin protective film could be MgO or in some circumstances MgH$_2$.

Fluoride ions have been found to be an effective corrosion inhibitor at high temperatures, where a concentration of 0.05M will suffice, but much higher concentrations (~1M) are needed at low temperatures. Chloride, on the other hand, damages the protective film, increasing the leakage current through it and reducing the potential required for breakdown.

Corrosion rates in NaOH solutions at pH 11.5 rise rapidly with temperature (activation energy 89 kJ mol$^{-1}$), so that rates which are acceptable at ambient temperature in a cooling pond (1–2 µm a$^{-1}$) would become high enough at 80°C (80 µm a$^{-1}$) to lead to breakaway of the protective film in a short time and to a further acceleration of corrosion. There is no evidence that the corrosion kinetics are changed by covering the corroding surface with a layer of cement. The layer may slow the diffusion of chloride ions to the surface, so mitigating their acceleration of the corrosion rate. At ambient temperatures the corrosion rates eventually appear to become constant. Linear kinetics are associated also with the high corrosion rates induced by elevated temperatures or high chloride ion concentrations. There is no evidence
that encapsulation introduces a new rate-limiting step, but high corrosion rates might expose such a limit.

9.1.2 Parameterisation of SMOGG model

The parameters recommended for use in SMOGG for Magnox corrosion are:

- An initial acute corrosion rate of 2.52 µm a\(^{-1}\) at 20°C.
- A characteristic time for the acute corrosion of 0.790a.
- An acute corrosion rate that increases with temperature according to an Arrhenius relationship:

\[
\exp\left[-\frac{69000}{8.314472}\left(\frac{1}{T} - \frac{1}{293.15}\right)\right]
\]  
(9.1)

where \(T\) is the temperature [K]. For example, at the temperatures listed below the initial acute corrosion rate should be scaled by the corresponding factors:

<table>
<thead>
<tr>
<th>Temperature, (T)</th>
<th>20°C</th>
<th>35°C</th>
<th>50°C</th>
<th>80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor, (f_a)</td>
<td>1.000</td>
<td>3.967</td>
<td>13.847</td>
<td>122.693</td>
</tr>
</tbody>
</table>

- An initial chronic corrosion rate of 0.12 µm a\(^{-1}\) at 20°C.
- A characteristic time for the chronic corrosion that essentially is infinite.
- A chronic corrosion rate that increases with temperature according to an Arrhenius relationship:

\[
\exp\left[-\frac{94000}{8.314472}\left(\frac{1}{T} - \frac{1}{293.15}\right)\right]
\]  
(9.2)

where \(T\) is the temperature [K]. For example, at the temperatures listed below the initial chronic corrosion rate should be scaled by the corresponding factors:

<table>
<thead>
<tr>
<th>Temperature, (T)</th>
<th>20°C</th>
<th>35°C</th>
<th>50°C</th>
<th>80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor, (f_c)</td>
<td>1.000</td>
<td>6.536</td>
<td>35.885</td>
<td>700.871</td>
</tr>
</tbody>
</table>

- A corrosion rate that is independent of oxygen concentration.
- Initial acute and chronic corrosion rates that increase in the presence of significant chloride concentrations by a factor of 100. (The corrosion may be limited by local restrictions on the supply of water.)
9.1.3 Discussion

In the Nirex 97 assessment of gas generation from radioactive wastes [54], the Magnox corrosion rate was assumed to be given by the expression

\[
\text{Rate} = 1.18 \times 10^{21} \exp\left(-\frac{14800}{T}\right) \mu m \text{ a}^{-1}
\]  

(9.3)

The consequences of this assumption are:

- The (chronic) corrosion rate is 0.14 µm a\(^{-1}\) at 20°C.
- At the temperatures listed below, the (chronic) corrosion rate should be scaled by the corresponding factors:

<table>
<thead>
<tr>
<th>Temperature, (T)</th>
<th>20°C</th>
<th>35°C</th>
<th>50°C</th>
<th>80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>1.000</td>
<td>11.676</td>
<td>108.520</td>
<td>5311.140</td>
</tr>
</tbody>
</table>

Comparing the two sets of long-term corrosion rates (see Subsection 9.1.2 and above), the values at 20°C are in good agreement. However, in the Nirex 97 assessment the corrosion rate increases more rapidly with temperature than is now being recommended. This is because the activation energy used was 123 kJ mol\(^{-1}\) instead of 94 kJ mol\(^{-1}\).

The activation energy of 123 kJ mol\(^{-1}\) was derived from experiments on the corrosion of Magnox in sodium hydroxide solution (at temperatures in the range 40–120°C) after breakaway of the corrosion product film. Before breakaway of the corrosion product film, the activation energy was 89 kJ mol\(^{-1}\) (Subsection 3.8). A priori the latter activation energy would seem more relevant to the long-term corrosion of Magnox encapsulated in cement, and indeed 89 kJ mol\(^{-1}\) is reasonably consistent with the activation energy, 94 kJ mol\(^{-1}\), derived from the experiments performed under the PETF programme.

In conclusion, the activation energy assumed in the Nirex 97 assessment probably was too high, and the chronic corrosion activation energy of 94 kJ mol\(^{-1}\) recommended in Subsection 9.1.2 is more justified.

Subsequent assessments of gas generation from radioactive wastes generally reused the Nirex 97 parameterisation of the Magnox corrosion rate [54], except that the Generic Post-closure Performance Assessment [2] assumed additionally that during storage at 35°C local restrictions on the availability of water would limit the Magnox corrosion rate to 0.038 µm a\(^{-1}\). The data acquired from the experiments performed under the PETF programme do not support this assumption.

9.2 Aluminium

9.2.1 Overview

For the corrosion of aluminium both oxygen reduction and water reduction are possible cathodic reactions but the latter predominates at pHs greater than approximately 12. The corrosion rate passes through a minimum at pH 6, corresponding to a minimum in the solubility of the oxides. In alkali metal hydroxide solutions the corrosion rate depends logarithmically on the pH, on either side of pH 6, but it is insensitive to chloride concentration. At pH 12 and 30°C the corrosion rate is approximately 500 µm a\(^{-1}\). The corrosion rate depends on the alloy composition. Galvanic coupling to steel increases the corrosion rate
although it does not necessarily increase the gas generation rate if corrosion occurs by oxygen reduction.

In cementitious environments, in which the porewaters contain sodium, potassium and calcium hydroxides, a protective calcium aluminate film is gradually formed, so that after an initial burst of rapid corrosion when the concrete/mortar is wet the corrosion rate decays to low values. In dry chloride-free concrete at ambient temperature, low long-term corrosion rates are observed (~1 µm a\(^{-1}\)). In humid and wet conditions the corrosion rate increases. At high temperatures the corrosion rate is initially higher than at lower temperatures but eventually this situation reverses. The presence of sodium and chloride ions in mortar appears to hinder passivation, because of the formation of an un-protective, hydrated sodium aluminate film, but the addition of calcium chloride to mortar decreases the corrosion rate compared to mortar with no chloride added. However, in contrast, chloride in concrete does not prevent passivation as it does in mortar. The detailed chemical reasons for the differences between the effect of chloride on the corrosion of aluminium in mortar and concrete are still to be resolved.

The corrosion rate in cementitious materials is also affected by the alkali content, the porosity of the cement, the external humidity, duration of drying, differential aeration and the conductivity of concrete. In long-term experiments on uncoupled aluminium in grout, corrosion rates of the order of 1 µm a\(^{-1}\) were measured after 16,000 hours at temperatures up to 80°C. In this case the addition of chloride did not increase the corrosion rate significantly. Resaturation caused an initial increase in corrosion rate which decayed with time but did not re-attain as low a corrosion rate as before resaturation.

Gas generation by corrosion of aluminium causes voidage at the grout/metal interface and this may have the beneficial effect of allowing expansion due to the formation of corrosion product. The permissible loading of aluminium in the wasteform will depend on the thickness of the individual pieces of aluminium. Galvanic coupling with steel reinforcement leads to severe corrosion and cracking of the surrounding concrete. The rate of galvanic corrosion is proportional to chloride concentration, distance between the coupled metals, and the steel to aluminium area ratio.

The corrosion product on aluminium in cementitious building materials has a two-layer structure with an inner hydrated sodium aluminate gel (NaAl(OH)\(_4\).Al\(_2\)O\(_3\)·3H\(_2\)O), which may also contain sodium and chloride ions, and an outer crystalline layer, with a flake-like structure, with a composition of CaO.\(\text{Al}_2\text{O}_3\cdot y\text{H}_2\text{O}\).

### 9.2.2 Parameterisation of SMOGG model

The parameters recommended for use in SMOGG for aluminium corrosion are:

- An initial acute corrosion rate of 15,300 µm a\(^{-1}\).
- A characteristic time for the acute corrosion of 0.001a.
- An acute corrosion rate that is independent of temperature.
- An initial chronic corrosion rate of 24.5 µm a\(^{-1}\).
- A characteristic time for the chronic corrosion that is infinite, by assumption.
- A chronic corrosion rate that is independent of temperature.
- A corrosion rate that is independent of oxygen and chloride concentrations.
9.2.3 Discussion

In the *Nirex 97* assessment of gas generation from radioactive wastes [54], the aluminium corrosion rate was assumed to be 30 µm a\(^{-1}\). This is comparable to the long-term constant corrosion rate, 24.5 µm a\(^{-1}\), now being recommended.

Subsequently a temperature-dependence for the corrosion rate of aluminium was derived [140], and the corrosion rate of aluminium was taken to be:

<table>
<thead>
<tr>
<th>Temperature, (T)</th>
<th>35°C</th>
<th>50°C</th>
<th>80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrosion rate</td>
<td>10 µm a(^{-1})</td>
<td>30 µm a(^{-1})</td>
<td>270 µm a(^{-1})</td>
</tr>
<tr>
<td>Factor</td>
<td>0.333</td>
<td>1.000</td>
<td>9.000</td>
</tr>
</tbody>
</table>

These corrosion rates vary more rapidly with temperature than is now being recommended. Some reasons for the change of view include:

- The previous analysis used data from an experiment on aluminium corrosion in sodium hydroxide solution, rather than in grout. The limited data available for temperatures above ambient indicate that the long-term corrosion rate of aluminium in grout does not increase with temperature.

- The previous analysis estimated the variation in corrosion rate with temperature by comparing a single point at 30°C with a single point at 60°C. This approach is likely to be subject to significant experimental error. In addition, it seems the ratio of the corrosion rates at the two temperatures may have been calculated incorrectly.

Subsequent assessments of gas generation from radioactive wastes generally reused this parameterisation, except that the Generic Post-closure Performance Assessment [2] assumed additionally that during storage at 35°C local restrictions on the availability of water would limit the aluminium corrosion rate to 1.0 µm a\(^{-1}\). There is no clear experimental evidence to support this assertion.

In conclusion, the aluminium corrosion rate used in the *Nirex 97* assessment is comparable to the long-term constant corrosion rate, 24.5 µm a\(^{-1}\), now being recommended. However, the variation of this corrosion rate with temperature assumed in subsequent assessments is not substantiated by the information in the literature.

9.3 Uranium

9.3.1 Overview

In aerated conditions uranium corrodes by oxygen reduction, with negligible hydrogen production, but in de-aerated conditions anaerobic corrosion proceeds by water reduction to form hydrogen, non-stoichiometric uranium dioxide and a small amount of uranium hydride (<10%). Small quantities of methane are generated by the corrosion of carbide impurities in the metal.

The corrosion mechanism involves diffusion of hydroxide through the corrosion product layer where it reacts with the uranium metal at the metal-corrosion product interface. Hydrogen gas is evolved at the oxide-liquid interface by recombination of nascent hydrogen atoms. A range of uranium oxides can form, depending on the surface potential and the pH. Spalling is likely, due to the large mismatch in the lattice parameters between the oxide and the metal. Uranium exhibits an active-passive transition in polarisation curves. In de-aerated conditions
the corrosion potential falls into an active region, corresponding to the generation of hydrogen.

Aqueous corrosion rates from the literature have been summarised. The corrosion rate reduces by 10–15% over the pH range 2–14. Carbonate ions weakly inhibit corrosion in alkaline conditions. Hydrogen peroxide causes an increase in the corrosion rate, peaking at a concentration of ~12%. There are a number of published mathematical relationships for the corrosion rate of uranium in de-aerated aqueous conditions, all of which show an exponential increase in the corrosion rate with temperature. There is significant variability in the constants applied in the mathematical relationships.

The oxidation rates of uranium in oxygen, water vapour-oxygen mixtures and water vapour increase in the ratio 1 : 20 to 50 : 3000 to 5000 respectively. Mathematical equations describing the oxidation rates of uranium in these environments as a function of temperature have been presented.

Very few data have been published for the corrosion of uranium in cement-based wasteforms. The more recent studies [194, 195] show profiles characterised by a brief “incubation period” (during which oxygen is reduced in preference to water) followed by a constant corrosion rate which is similar to that in de-aerated water. The corrosion rate in waste packages may be limited by the availability of water.

9.3.2 Parameterisation of SMOGG model

The parameters recommended for use in SMOGG for uranium corrosion are:

(a) **Aerobic conditions**

- There is no identifiable phase of acute corrosion.
- An initial chronic corrosion rate (including an enhancement factor of 2 to accommodate the effect of irradiated metal fuel) of 1.58 µm a\(^{-1}\) at 20°C.
- A characteristic time for the chronic corrosion that essentially is infinite.
- A chronic corrosion rate that increases with temperature according to an Arrhenius relationship:

\[
\exp\left[\frac{76900}{8.314472 \left(\frac{1}{T} - \frac{1}{293.15}\right)}\right]
\]

(9.4)

where \(T\) is the temperature [K]. For example, at the temperatures listed below the initial chronic corrosion rate should be scaled by the corresponding factors:

<table>
<thead>
<tr>
<th>Temperature, (T)</th>
<th>20°C</th>
<th>35°C</th>
<th>50°C</th>
<th>80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor, (\phi_c)</td>
<td>1.000</td>
<td>4.645</td>
<td>18.709</td>
<td>212.801</td>
</tr>
</tbody>
</table>

(b) **Anaerobic conditions**

- There is no identifiable phase of acute corrosion.
- An initial chronic corrosion rate (including an enhancement factor of 2 to accommodate the effect of irradiated metal fuel) of 68.2 µm a\(^{-1}\) at 20°C.
• A characteristic time for the chronic corrosion that essentially is infinite.

• A chronic corrosion rate that increases with temperature according to an Arrhenius relationship:

\[
\exp\left[-\frac{66400}{8.314472}\left(\frac{1}{T} - \frac{1}{293.15}\right)\right]
\]

where \( T \) is the temperature [K]. For example, at the temperatures listed below the initial chronic corrosion rate should be scaled by the corresponding factors:

<table>
<thead>
<tr>
<th>Temperature, ( T )</th>
<th>20°C</th>
<th>35°C</th>
<th>50°C</th>
<th>80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor, ( f_c )</td>
<td>1.000</td>
<td>3.766</td>
<td>12.542</td>
<td>102.355</td>
</tr>
</tbody>
</table>

9.3.3 Discussion

The Generic Post-closure Performance Assessment [2] is the only assessment to have considered gas generation from uranium corrosion. This assessment assumed that the uranium corrosion rate would be 1 µm a\(^{-1}\) under storage conditions (i.e. aerobic environment at 35°C), and 100 µm a\(^{-1}\) at other times. The justification for these corrosion rates were the following assumptions:

• Waste conditioning will inhibit corrosion; and

• During storage, corrosion will be limited by local restrictions on the supply of water.

It was acknowledged however that “data from experiments on the anaerobic corrosion of uranium immersed in aqueous solutions give much higher corrosion rates”, and also “show a significant temperature dependence” [196].

In contradistinction, more recent studies of uranium metal corrosion in a cementitious environment [194, 195] show profiles characterised by a brief “incubation period” (during which oxygen is reduced in preference to water) followed by a constant corrosion rate which is similar to that in de-aerated water. As a result of this experimental evidence, the uranium corrosion rates which are now being recommended, i.e.:

<table>
<thead>
<tr>
<th>Corrosion Rates at Different Temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condition</td>
</tr>
<tr>
<td>Storage (aerobic)</td>
</tr>
<tr>
<td>Other (anaerobic)</td>
</tr>
</tbody>
</table>

are significantly higher than those used in the Generic Post-closure Performance Assessment.
10 References


98 T. Matsuo, T. Nishi, T. Izumida and M. Matsuda, Influence of Increased Temperature from Cement Hydration on Aluminium Corrosion Prevention When LiNO₃ is Added to the Cement, Nuclear Technology 125, 332, 1999.


<table>
<thead>
<tr>
<th>Reference</th>
<th>Title</th>
</tr>
</thead>
</table>


Table 1  Corrosion rates for Magnox in station pond conditions

<table>
<thead>
<tr>
<th>Reference</th>
<th>Metal condition*</th>
<th>Environment</th>
<th>Temp. (°C)</th>
<th>Duration (days)</th>
<th>Corrosion (µm a⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Masterson and Harrison [38]</td>
<td>Untreated</td>
<td>pH 10.5</td>
<td>Ambient</td>
<td>–</td>
<td>~17</td>
</tr>
<tr>
<td></td>
<td>Oxidised</td>
<td>pH 10.5</td>
<td></td>
<td>–</td>
<td>~15</td>
</tr>
<tr>
<td></td>
<td>Untreated</td>
<td>pH 11.5</td>
<td>&quot;</td>
<td>–</td>
<td>~1</td>
</tr>
<tr>
<td></td>
<td>Oxidised</td>
<td>pH 11.5</td>
<td>&quot;</td>
<td>–</td>
<td>~15</td>
</tr>
<tr>
<td>Case and Hilton [29]</td>
<td>–</td>
<td>Station ponds</td>
<td>pH &gt;11.5</td>
<td>20–30</td>
<td>1–2</td>
</tr>
<tr>
<td></td>
<td>Etched</td>
<td>pH 11.5</td>
<td>Ambient</td>
<td>120</td>
<td>~4</td>
</tr>
<tr>
<td></td>
<td>Oxidised</td>
<td>pH 11.5</td>
<td></td>
<td>120</td>
<td>~8</td>
</tr>
<tr>
<td>Robbins [24]</td>
<td>Etched / oxidised</td>
<td>pH 11.5</td>
<td>~20</td>
<td>365</td>
<td>0.2</td>
</tr>
<tr>
<td>Carney and Marsh [20]</td>
<td>Oxidised</td>
<td>pH 12.5</td>
<td>~40</td>
<td>400</td>
<td>1–2</td>
</tr>
</tbody>
</table>

* 'Untreated' refers to specimens which had no pre-formed oxide film; 'Oxidised' refers to specimens which had been treated to simulate the corrosion of Magnox in a carbon dioxide reactor coolant; 'Etched' refers to specimens which had been treated to remove the oxide produced during exposure in the reactor.
Table 2  Corrosion rates for Magnox encapsulated in grout. Data from the experiments in the PETF AB series [50] are fitted to the expression
Rate = A t^n, where t is the time (days), and A, n are constants.

<table>
<thead>
<tr>
<th>Experiment ID†</th>
<th>Rate constant, A</th>
<th>Exponent, n</th>
<th>Correlation coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB1</td>
<td>0.02</td>
<td>-0.09</td>
<td>0.15</td>
</tr>
<tr>
<td>AB2</td>
<td>324.13</td>
<td>1.32</td>
<td>0.82</td>
</tr>
<tr>
<td>AB3</td>
<td>5.52</td>
<td>0.89</td>
<td>0.82</td>
</tr>
<tr>
<td>AB4</td>
<td>0.02</td>
<td>-0.10</td>
<td>0.03</td>
</tr>
<tr>
<td>AB5</td>
<td>582.79</td>
<td>1.14</td>
<td>0.75</td>
</tr>
<tr>
<td>AB6</td>
<td>33.37</td>
<td>0.86</td>
<td>0.56</td>
</tr>
<tr>
<td>AB7</td>
<td>20.08</td>
<td>0.76</td>
<td>0.69</td>
</tr>
<tr>
<td>AB8</td>
<td>8.52</td>
<td>0.57</td>
<td>0.45</td>
</tr>
<tr>
<td>AB10</td>
<td>107.24</td>
<td>1.12</td>
<td>0.72</td>
</tr>
<tr>
<td>AB11</td>
<td>30.93</td>
<td>0.45</td>
<td>0.78</td>
</tr>
<tr>
<td>AB12</td>
<td>101.59</td>
<td>0.61</td>
<td>0.48</td>
</tr>
<tr>
<td>AB13</td>
<td>31.17</td>
<td>0.35</td>
<td>0.61</td>
</tr>
<tr>
<td>AB14</td>
<td>141.68</td>
<td>0.77</td>
<td>0.84</td>
</tr>
<tr>
<td>AB15</td>
<td>1385.72</td>
<td>1.40</td>
<td>0.85</td>
</tr>
<tr>
<td>AB16</td>
<td>689.62</td>
<td>1.20</td>
<td>0.83</td>
</tr>
<tr>
<td>AB17</td>
<td>366.97</td>
<td>0.92</td>
<td>0.84</td>
</tr>
<tr>
<td>AB18</td>
<td>35.89</td>
<td>0.42</td>
<td>0.63</td>
</tr>
<tr>
<td>AB19</td>
<td>0.77</td>
<td>0.15</td>
<td>0.09</td>
</tr>
<tr>
<td>AB20</td>
<td>621.74</td>
<td>0.96</td>
<td>0.81</td>
</tr>
<tr>
<td>AB21</td>
<td>115.07</td>
<td>1.18</td>
<td>0.81</td>
</tr>
<tr>
<td>AB22</td>
<td>25.65</td>
<td>0.83</td>
<td>0.84</td>
</tr>
<tr>
<td>AB23</td>
<td>38.36</td>
<td>0.87</td>
<td>0.79</td>
</tr>
<tr>
<td>AB24</td>
<td>35.06</td>
<td>0.96</td>
<td>0.77</td>
</tr>
</tbody>
</table>

† Note that specimen AB9 included considerable void spaces, and so is excluded.
Table 3  Composition of aluminium alloys for which corrosion data have been reported (wt%)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>BS equiv.</th>
<th>Cu</th>
<th>Fe</th>
<th>Mg</th>
<th>Mn</th>
<th>Si</th>
<th>Cr</th>
<th>Zn</th>
<th>Ti</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>3S-H14</td>
<td></td>
<td>0.4</td>
<td>1.2</td>
<td>0.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>bal.</td>
</tr>
<tr>
<td>3S-F</td>
<td></td>
<td>0.4</td>
<td>1.2</td>
<td>0.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>bal.</td>
</tr>
<tr>
<td>50S-T5</td>
<td></td>
<td>0.3</td>
<td>0.65</td>
<td>0.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>bal.</td>
</tr>
<tr>
<td>65S-T6</td>
<td></td>
<td>0.3</td>
<td>0.35</td>
<td>0.95</td>
<td>0.6</td>
<td>0.25</td>
<td></td>
<td></td>
<td></td>
<td>bal.</td>
</tr>
<tr>
<td>L34</td>
<td>E1C/E1B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.2</td>
</tr>
<tr>
<td>DTD 297</td>
<td>NE7</td>
<td></td>
<td></td>
<td>6.68</td>
<td>0.14</td>
<td>0.12</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DTD 346</td>
<td>HE30</td>
<td></td>
<td></td>
<td>0.74</td>
<td>0.80</td>
<td>0.88</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6L1</td>
<td>HE14/HE1</td>
<td>4.38</td>
<td>0.47</td>
<td>0.62</td>
<td>0.46</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.03</td>
</tr>
<tr>
<td>DTD 363</td>
<td>AW16</td>
<td>2.05</td>
<td>2.48</td>
<td>0.53</td>
<td>0.24</td>
<td>&lt;0.05</td>
<td></td>
<td>5.13</td>
<td>&lt;0.02</td>
<td>bal.</td>
</tr>
<tr>
<td>L33</td>
<td>LM6</td>
<td>0.03</td>
<td></td>
<td></td>
<td></td>
<td>&lt;0.05</td>
<td>11.7</td>
<td></td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>1050 (Al)</td>
<td></td>
<td>0.005</td>
<td>0.31</td>
<td>0.001</td>
<td>0.002</td>
<td>0.10</td>
<td>trace</td>
<td>0.002</td>
<td>0.012</td>
<td>bal.</td>
</tr>
<tr>
<td>1100</td>
<td></td>
<td>0.12</td>
<td>0.54</td>
<td>trace</td>
<td>0.01</td>
<td>0.11</td>
<td>trace</td>
<td>0.01</td>
<td>0.03</td>
<td>bal.</td>
</tr>
<tr>
<td>5052 (Al-Mg)</td>
<td></td>
<td>0.06</td>
<td>0.23</td>
<td>2.51</td>
<td>0.03</td>
<td>0.11</td>
<td>0.21</td>
<td>trace</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>6063 (Al-Mg-Si)</td>
<td></td>
<td>0.03</td>
<td>0.18</td>
<td>0.57</td>
<td>0.01</td>
<td>0.46</td>
<td>0.02</td>
<td>0.01</td>
<td>0.02</td>
<td>bal.</td>
</tr>
<tr>
<td>3003 (Al-Mn)</td>
<td></td>
<td>0.15</td>
<td>0.64</td>
<td>trace</td>
<td>1.07</td>
<td>0.21</td>
<td>trace</td>
<td>0.01</td>
<td>0.02</td>
<td>bal.</td>
</tr>
<tr>
<td>7072 (Al-Zn)</td>
<td></td>
<td>0.02</td>
<td>0.26</td>
<td>trace</td>
<td>0.01</td>
<td>0.08</td>
<td>trace</td>
<td>1.07</td>
<td>0.01</td>
<td>bal.</td>
</tr>
<tr>
<td>2017 (Al-Cu)</td>
<td></td>
<td>4.07</td>
<td>0.22</td>
<td>0.45</td>
<td>0.43</td>
<td>0.32</td>
<td>0.45</td>
<td>0.02</td>
<td>0.02</td>
<td>bal.</td>
</tr>
<tr>
<td>57S-H</td>
<td></td>
<td></td>
<td></td>
<td>0.20</td>
<td>0.25</td>
<td></td>
<td>0.10</td>
<td>0.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3S-1/2-H</td>
<td></td>
<td></td>
<td></td>
<td>0.40</td>
<td>1.20</td>
<td>0.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3S-F</td>
<td></td>
<td></td>
<td></td>
<td>0.40</td>
<td>1.20</td>
<td>0.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50S-A33</td>
<td></td>
<td></td>
<td></td>
<td>0.30</td>
<td>0.65</td>
<td>0.40</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>65S-T</td>
<td></td>
<td>0.3</td>
<td>0.35</td>
<td>0.95</td>
<td>0.60</td>
<td>0.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## Table 4  Summary of corrosion rates of aluminium in alkaline solutions

<table>
<thead>
<tr>
<th>Reference</th>
<th>Environment</th>
<th>Corrosion rate (µm a⁻¹)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>[62, 63]</td>
<td>NaOH up to 5N. 25°C.</td>
<td>0.5N: 15.6±4.6 mm² H₂/cm² of surface in the period 1–6 hours (~400 µm a⁻¹).</td>
<td>High purity aluminium used. Corrosion rate determined by hydrogen evolution measurements. Specimen mounted on a rotating shaft (120 rpm). Variations in the gas evolution rate caused by inhomogeneities in material.</td>
</tr>
<tr>
<td>[67]</td>
<td>NaOH, pH 10.</td>
<td>25°C: 55–232 60°C: 248</td>
<td>All rates were obtained in short term tests (&lt;7 days).</td>
</tr>
<tr>
<td>[95]</td>
<td>Aerated. 0.1N NaOH</td>
<td>RT: 2250</td>
<td>Corrosion rates measured using Tafel slope extrapolation.</td>
</tr>
<tr>
<td>[77]</td>
<td>0.04M NaOH</td>
<td>RT: 243.5 mm a⁻¹ (grade 2S) 365.4 mm a⁻¹ (grade 3S) 102.5 mm a⁻¹ (grade 26S) 97.01 mm a⁻¹ (grade 57S)</td>
<td>Corrosion rates measured using weight loss measurements.</td>
</tr>
<tr>
<td>[94]</td>
<td>2M KOH</td>
<td>30°C: 23 mm a⁻¹ 60°C: 42 mm a⁻¹</td>
<td>Corrosion rates measured using weight loss measurements.</td>
</tr>
</tbody>
</table>

## Table 5  Summary of electrochemical measurements on aluminium in alkaline solutions

<table>
<thead>
<tr>
<th>Reference</th>
<th>Environment; metal</th>
<th>Corrosion rate (µm a⁻¹)</th>
<th>Open circuit potential (mV SCE)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>[71]</td>
<td>0.1M NaCl; NaOH to adjust to pH 10; 99.99% pure Al</td>
<td>210</td>
<td>-1,320</td>
<td>Corrosion rate measured using AC impedance.</td>
</tr>
<tr>
<td>[72]</td>
<td>NaOH/NaCl, pH 9–12; 98.5% Al</td>
<td>1,090 at pH 10 10,900 at pH 12</td>
<td>-980 at pH 9 -1,460 at pH 12</td>
<td>Polarisation curve measurements</td>
</tr>
</tbody>
</table>
Table 6  Corrosion of aluminium in alkaline cooling spray solutions [84]

<table>
<thead>
<tr>
<th>Aqueous solution</th>
<th>Temperature (ºC)</th>
<th>Corrosion rate</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15M NaOH + 0.28M H₃BO₃ with/without 0.064M Na₂S₂O₃</td>
<td>55</td>
<td>3.3–4.8 mm a⁻¹ in spray 1.1–2.2 mm a⁻¹ submerged</td>
<td>From a paper by Griess</td>
</tr>
<tr>
<td>Deionised water, pH 5–8, aerated and de-aerated</td>
<td>50</td>
<td>60 µm a⁻¹</td>
<td>Chalky film; from a paper by Berzins</td>
</tr>
<tr>
<td>Deionised water, pH 5 and 9, aerated and de-aerated</td>
<td>50, 100, 150</td>
<td>De-aerated, pH 5: 46 max De-aerated, pH 9: 40 max Aerated, pH 9: 80 max</td>
<td>The gas generation rate decreased with time</td>
</tr>
<tr>
<td>PWR water, 0.15M NaOH/0.28M H₃BO₃, pH 9.7 at ambient</td>
<td>150</td>
<td>63–570 mm a⁻¹, depending on the alloy</td>
<td></td>
</tr>
</tbody>
</table>

PWR water, 0.15M NaOH/0.28M H₃BO₃, pH 9.7 at ambient
Table 7  Oxides formed on aluminium [9]

<table>
<thead>
<tr>
<th>Name</th>
<th>Composition</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gibbsite</td>
<td>$\alpha$-$\text{Al}_2\text{O}_3.3\text{H}_2\text{O}$</td>
<td>3.0</td>
</tr>
<tr>
<td>(also known as Hydrargillite)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bayerite</td>
<td>$\beta$-$\text{Al}_2\text{O}_3.3\text{H}_2\text{O}$</td>
<td>2.5</td>
</tr>
<tr>
<td>Boehmite</td>
<td>$\alpha$-$\text{Al}_2\text{O}_3.\text{H}_2\text{O}$ or $\text{AlO.OH}$</td>
<td>3.0</td>
</tr>
<tr>
<td>Pseudo-boehmite</td>
<td>$\text{Al}_2\text{O}_3.x\text{H}_2\text{O}$</td>
<td>3.4</td>
</tr>
<tr>
<td>Gamma Alumina</td>
<td>$\gamma$-$\text{Al}_2\text{O}_3.3\text{H}_2\text{O}$</td>
<td>4.0</td>
</tr>
</tbody>
</table>
Table 8  Summary of corrosion rates of aluminium in mortar, concrete and buildings

<table>
<thead>
<tr>
<th>Reference</th>
<th>Environment</th>
<th>Corrosion rate (µm a(^{-1}))</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>[99]</td>
<td>57S-H, 3S-(1/2)H, 3S-F, 50S-A33, 65S-T alloys in concrete mixes</td>
<td>10–110</td>
<td>Measurements made after 1 year in various OPC-based concretes. Cracking of the concrete matrix was observed in some tests. Even in wet conditions the corrosion was slight.</td>
</tr>
<tr>
<td>[100]</td>
<td>57S-H, 3S-(1/2)H, 3S-F, 50S-A33, 50S-T5, 3S-H14, 65S-T alloys in concrete and mortar mixes</td>
<td>Concrete dry: 2.5–5 atmosphere: 0–7 wet: 2.5–7 wet soil: 4.5–11.4 Mortar atmosphere: 0.25–1.3</td>
<td>Continuation of Wright [99]. Ten year results. Various cements and concrete investigated. Inspected after 10 years. Concrete was 1:3:3 cement : sand : crushed stone.</td>
</tr>
<tr>
<td>[89]</td>
<td>alloy 3003 in OPC-based mortar and concrete in 100% RH at 52 C</td>
<td>Corrosion rate was very high for the first few hours (&gt;1000 µm a(^{-1})) falling to 50 µm a(^{-1}) after 6 months</td>
<td>Concrete sandwiched by metal test coupons. Both coupled and uncoupled specimens were tested.</td>
</tr>
<tr>
<td>[89]</td>
<td>8 years indoors, industrial, seacoast</td>
<td>5.4–7.6 (averaged over 8 year period)</td>
<td></td>
</tr>
<tr>
<td>[89]</td>
<td>27 years industrial atmosphere</td>
<td>1.3 (averaged over 27 year period)</td>
<td></td>
</tr>
<tr>
<td>[101]</td>
<td>1100, 2024, 5056, 6061 alloys in concrete</td>
<td>60–100</td>
<td>One year tests.</td>
</tr>
</tbody>
</table>
Table 9  Range of corrosion rates for aluminium in various mortars over 5–10 year period, for all alloys \[113\]

<table>
<thead>
<tr>
<th>Environment</th>
<th>Range of corrosion rates ((\mu\text{m a}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>cement-sand, outdoors</td>
<td>-3.0 to 3.3</td>
</tr>
<tr>
<td>cement-sand, indoors</td>
<td>-9.8 to 1.6</td>
</tr>
<tr>
<td>cement-lime-sand, outdoors</td>
<td>-2.7 to 3.0</td>
</tr>
<tr>
<td>cement-lime-sand, outdoors</td>
<td>-3.6 to 1.7</td>
</tr>
</tbody>
</table>

Table 10  Effect of alkali and chloride on the corrosion of aluminium conduit embedded in concrete prisms (4" × 4" × 12") \[102\]

<table>
<thead>
<tr>
<th>Cement</th>
<th>Alkali content (%Na(_2)O)</th>
<th>Chloride content (%CaCl(_2))</th>
<th>Exposure conditions</th>
<th>Corrosion rate ((\mu\text{m a}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>RH</td>
<td>Temp. (°C)</td>
</tr>
<tr>
<td>A</td>
<td>0.22</td>
<td></td>
<td>50</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>50</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td>&quot;</td>
</tr>
<tr>
<td>B</td>
<td>0.89</td>
<td></td>
<td>50</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>50</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td>&quot;</td>
</tr>
</tbody>
</table>
### Table 11 Parameters recommended for use in the SMOGG corrosion model
(based on an assessment of literature data and a calibration exercise)

<table>
<thead>
<tr>
<th>Stage in SMOGG model</th>
<th>Magnox</th>
<th>Aluminium</th>
<th>Uranium</th>
</tr>
</thead>
<tbody>
<tr>
<td>grout, aerobic, low chloride</td>
<td>Arrhenius variation of $k_a$: $k_a = 2.52 , \mu m , a^{-1}$ at 20°C, activation energy 69 kJ mol$^{-1}$ $t_a = 0.790a$ No dependence on temperature: $k_a = 15,300 , \mu m , a^{-1}$ $t_a = 0.001a$</td>
<td>No acute corrosion phase</td>
<td></td>
</tr>
<tr>
<td>chronic</td>
<td>Arrhenius variation of $k_c$: $k_c = 0.12 , \mu m , a^{-1}$ at 20°C, activation energy 94 kJ mol$^{-1}$ $t_c = \infty$</td>
<td>No dependence on temperature: $k_c = 24.5 , \mu m , a^{-1}$ $t_c = \infty$</td>
<td>Arrhenius variation of $k_c$: $k_c = 1.58 , \mu m , a^{-1}$ at 20°C, activation energy 76.9 kJ mol$^{-1}$ $t_c = \infty$</td>
</tr>
<tr>
<td>grout, anaerobic, low chloride</td>
<td>No dependence on oxygen availability</td>
<td>No dependence on oxygen availability</td>
<td>No acute corrosion phase</td>
</tr>
<tr>
<td>chronic</td>
<td>No dependence on oxygen availability</td>
<td>No dependence on oxygen availability</td>
<td>No dependence on oxygen availability</td>
</tr>
<tr>
<td>grout, anaerobic, high chloride</td>
<td>Arrhenius variation of $k_a$: $k_a = 252 , \mu m , a^{-1}$ at 20°C, activation energy 69 kJ mol$^{-1}$ $t_a = 0.790a$</td>
<td>No dependence on chloride</td>
<td>No dependence on chloride</td>
</tr>
<tr>
<td>chronic</td>
<td>Arrhenius variation of $k_c$: $k_c = 12 , \mu m , a^{-1}$ at 20°C, activation energy 94 kJ mol$^{-1}$ $t_c = \infty$</td>
<td>No dependence on chloride</td>
<td>No dependence on chloride</td>
</tr>
</tbody>
</table>

**Notes:**

1. In using the SMOGG model a finite value is required; a value much greater than the period of the calculation (e.g. $10^6$ years) should be used.
Figure 1  Pourbaix diagram for magnesium [56], showing regions of stability as a function of pH and potential (V vs. standard hydrogen electrode, SHE)
Figure 2  Electrochemistry of magnesium in aqueous solutions

(This is from the paper by Fabjan et al. [17] and relates to pH 13. The anodic current flowing at the site of oxidation (dotted line) and the cathodic current flowing at the site of reduction (solid line) are plotted on a logarithmic axis against the applied potential. The anodic and cathodic currents are of opposite sign, but it is conventional to plot them on the same side of the axis to make it easier to see when they are equal. The rest potential and currents will settle at the intersection of the anodic and cathodic curves.)
Figure 3  Typical current-potential curve obtained in cyclic voltammetry
Figure 4 Variation of pre-breakaway isothermal corrosion rates in NaOH solutions and NaOH solutions containing dissolved silica [25]. (The references shown in the figure refer to the original work [25], and not to the current report.)
Figure 5  Variation of isothermal post-breakaway corrosion rates in NaOH solutions [25]. (The references shown in the figure refer to the original work [25], and not to the current report.)
Figure 6  Corrosion rates for Magnox encapsulated in grout. Data from the experiments in the PETF AB series [50] (BFS / OPC small scale trials performed at ambient temperature, measured as 21±2°C) are shown.
Figure 7 Corrosion rates for Magnox encapsulated in grout. Data from the 500 litre scale experiments carried out at Winfrith [43] are shown.
Figure 8 Corrosion rates for Magnox encapsulated in grout. Data from the 500 litre scale experiments carried out at Winfrith [44] in Phase 4 Formulation Envelope Corrosion Studies are shown.
Figure 9  Lognormal probability plot for data from the experiments in the PETF AB series [50]. The data are binned into ten distinct time intervals lasting about 0.5 years, and then the data in each bin are compared against a lognormal distribution.
Figure 10  SMOGG model for corrosion rates of Magnox encapsulated in grout fitted to data from the experiments in the PETF AB series [50] (BFS / OPC small scale trials performed at ambient temperature, measured as 21±2°C).
Figure 11  Corrosion rates of Magnox encapsulated in grout from two experiments performed under the PETF programme at Sellafield [46]. Reducing the temperature causes a subsequent decrease in corrosion rate, but the decrease is gradual.
Figure 12 Arrhenius plot showing the variation in the long-term corrosion rate of Magnox in grout with temperature.
Figure 13  Comparison of measured temperatures with target temperature for experiments TPC3–5 [49, 50].
Figure 14  Corrosion rates for Magnox encapsulated in grout. Data from experiments in the PETF TPC series are shown [49, 50]. (A temperature variation simulating the effect of grout curing was applied to the experiments. The predefined temperature profile is shown in Figure 13.)
Figure 15  SMOGG model for corrosion rates of Magnox encapsulated in grout fitted to data from the experiments in the PETF TPC series [49, 50].
(A temperature variation simulating the effect of grout curing was applied to the experiments. The predefined temperature profile is shown in Figure 13.)
Figure 16  SMOGG model for volume of hydrogen released compared to data from the experiments in the PETF TPC series [49, 50]. (A temperature variation simulating the effect of grout curing was applied to the experiments. The predefined temperature profile is shown in Figure 13.)
Figure 17 Pourbaix diagram for aluminium [56], showing regions of stability as a function of pH and potential (V vs. standard hydrogen electrode, SHE)
Figure 18  Pourbaix diagram for aluminium [56], showing regions of corrosion, passivation and immunity as a function of pH and potential (V vs. standard hydrogen electrode, SHE)
Figure 19  Experimental E–pH diagram for 5086 aluminium alloy in a chloride-containing environment with extrapolation to pHs <4 and >9. Thermodynamic data is shown in dotted lines [57]. The diagram shows regions of stability as a function of pH and potential (V vs. standard calomel electrode, SCE).
Figure 20  Relationship between solubility of aluminium oxides and pH [56]
Figure 21  Hydrogen evolution for aluminium in solutions of various pH [87]
Figure 22  Weight loss of aluminium alloys in cement-sand mortar as a function of time [113]. Full lines = 6” cube outdoors, dotted lines = 4” cube indoors.

Figure 23  Weight loss of aluminium alloys in cement-lime-sand mortar as a function of time [113]. Full lines = 6” cube outdoors, dotted lines = 4” cube indoors.
Figure 24  Proposed corrosion mechanism for aluminium in mortar [117]
Figure 25 Corrosion rates for aluminium encapsulated in grout. Data from various experiments in the PETF programme [122, 132, 138] are shown.
Figure 26 SMOGG model for corrosion rates of aluminium encapsulated in grout fitted to data from various experiments in the PETF programme [122, 132, 138].
Figure 27  Pourbaix diagram for the uranium-water system [56], showing regions of stability as a function of pH and potential (V vs. standard hydrogen electrode, SHE): (a) where the solid substances present are U, UO, U₂O₃, UO₂, U₃O₈ and anhydrous UO₃; (b) where the solid substances present are UH₃, U, UO, U₂O₃, UO₂, U₃O₈ and anhydrous UO₃.2H₂O