Corrosion & Expansion of Grouted Magnox

NNL (11) 11524
Issue 3

A report prepared for and on behalf of NDA, RWMD (Customer Task Reference WT 15 05 10)
Corrosion & Expansion of Grouted Magnox

NNL (11) 11524 Issue 3

J Cronin, N Collier – 23 November 2011

KEYWORDS: Corrosion Expansion Magnox Swarf Grout

To assess the evolution of waste packages prior to backfilling and closure of a Geological Disposal Facility, this paper reports the acute and chronic rates of corrosion of unirradiated Magnox encapsulated in a BFS:OPC grout obtained from a series of small-scale trials. These trials were performed over a range of temperatures (25, 40, 60, 75 and 90°C) for curing times of up to 2 1/2 years. Several experimental techniques such as pressure, electrochemical and resistance were investigated to measure Magnox corrosion. Product expansion data and data associated with the expansive forces generated during corrosion were also obtained.

The data for the chronic rate of Magnox corrosion over the temperature range examined were similar to Magnox corrosion datasets from other sources, indicating that the experiments are representative of typical Magnox swarf behaviour in grout.

Structural product degradation starts to develop as the tensile strength of the grout is approached and some deformation of the experimental holding vessels was noted in those experiments that had been undertaken at temperatures of 75°C or above.

Characterisation of the corrosion products at the Magnox/grout interface showed brucite to be the main product of Magnox corrosion. Curing temperature had no detectable effect on the compositions of either the Magnox metal, corrosion product or grout.

This report has been prepared by the National Nuclear Laboratory under contract to the NDA. The report has been reviewed by the NDA, but the views expressed and conclusions drawn are those of the authors and do not necessarily represent those of the NDA.

Conditions of publication

This report is made available under the NDA Transparency Policy. In line with this policy, the NDA is seeking to make information on its activities readily available, and to enable interested parties to have access to and influence on its future programmes. The report may be freely used for non-commercial purposes. However, all commercial uses, including copying and re-publication, require permission from the NDA. All copyright, database rights and other intellectual property rights reside with the NDA. Applications for permission to use the report commercially should be made to the NDA Information Manager.

Although great care has been taken to ensure the accuracy and completeness of the information contained in this publication, the NDA can not assume any responsibility for consequences that may arise from its use by other parties.

© Nuclear Decommissioning Authority 2011. All rights reserved.

Bibliography

If you would like to see other reports available from the NDA, a complete listing can be viewed at our website www.nda.gov.uk, or please write to the Communications Department at the address below or email info@nda.gov.uk.

Feedback

Readers are invited to provide feedback to the NDA on the contents, clarity and presentation of this report and on the means of improving the range of the NDA reports published. Feedback should be addressed to:

Elizabeth Atherton
Head of Stakeholder Engagement and Communications
Nuclear Decommissioning Authority
Radioactive Waste Management Directorate
Building 587
Curie Avenue
Harwell Oxford
Didcot
Oxfordshire OX11 0RH
EXECUTIVE SUMMARY

Magnox fuel cladding will slowly corrode when encapsulated in alkaline cementitious grouts to produce hydrogen gas and an expansive corrosion product. The evolution of hydrogen during waste processing, transport and storage may prove problematic and the development of expansive corrosion products may ultimately lead to expansion and degradation of the wasteform and, if extensive, may deform or even rupture the container.

Over the past 25 years, cementitious grouts based on Blast Furnace Slag and Ordinary Portland Cement (BFS/OPC), have been used in the UK to immobilise ILW Magnox swarf in 500 litre stainless steel drums and currently such wasteforms are in surface storage awaiting geological disposal. The original specification for the required wasteform and package lifetime was for 50 years above ground followed by 50 years below ground. Subsequently, these lifetime requirements have been significantly extended, increasing the risk that these waste forms and containers may not meet these required lifetimes. This risk carries very large liabilities as in some cases it could result in a need to retrieve and repackage such wasteforms. Therefore, the lifetimes of the wasteforms and containers needs further underpinning.

The aim of this project has been to determine the rates of corrosion of Magnox encapsulated in a BFS/OPC grout in a series of small-scale trials and to relate the corresponding dimensional changes in the cemented product to the corrosion that has occurred. The work has consisted of measuring the rate of chronic corrosion of grouted Magnox over a range of temperatures and to measure the expansion and expansive force generated by the Magnox samples as a function of corrosion over a 2\(\frac{1}{2}\) year curing period. Several experimental techniques to monitor the Magnox corrosion rate in grout were used and core samples were taken from cemented products to characterise the corrosion products at the Magnox/grout interface.

The report concludes that:

- Acute and chronic corrosion rates have been determined for Magnox swarf encapsulated in BFS/OPC grout at curing temperatures of 25, 40, 60, 75, and up to 90°C. The data has shown that up to 200 days cure at 25°C is required for the initial acute corrosion phase to decline to provide measurement of steadier longer term chronic corrosion rates.

- Characterisation of the samples has shown the swarf to be well infilled and a close representation of MEP products.

- The chronic rate of Magnox corrosion over the temperature range examined has proved to be compatible with Magnox corrosion datasets obtained from other sources and again this indicates that these data are representative of Magnox swarf behaviour in grout.

- An expansive force generation rate of 0.14 – 0.47 MPa/Wt% corrosion could be taken as a range of expansive force values in modelling of the effects of corrosion product expansion on wasteforms.

- The estimate of the time taken for a typical MEP product to fracture due to the corrosion solely of Magnox is about 350 years for storage at 25°C. However, depending on assumptions about the rate of corrosion, the tensile strength of the grout and the expansive forces generated as a result of corrosion, the onset of the product cracking could range between about 30 and 5800 years.

- Deformation of the restraining vessel caused by Magnox corrosion in 16-litre samples at curing temperatures of 75°C or above was observed and may be useful in validating expansion models.
- No expansion, above the limit of detection of about 1mm as measured with a micrometer, was found for three-litre samples.
- The main phases formed in the grout during curing are calcium silicate hydrate and portlandite with minor quantities of gehlenite. The main component of the corrosion product is brucite. The effect of curing temperature did not affect the composition of either the Magnox metal, corrosion product or grout.
VERIFICATION STATEMENT

This document has been verified and is fit for purpose. An auditable record has been made of the verification process. The scope of the verification was to confirm that :-

- The document meets the requirements as defined in the task specification/scope statement
- The constraints are valid
- The assumptions are reasonable
- The document demonstrates that the project is using the latest company approved data
- The document is internally self consistent

HISTORY SHEET

<table>
<thead>
<tr>
<th>Issue Number</th>
<th>Date</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Issue 1</td>
<td>31 March 2011</td>
<td>Issued to NDA RWMD</td>
</tr>
<tr>
<td>Issue 2</td>
<td>09 October 2011</td>
<td>Comments received from NDA and Nuclear Technologies addressed</td>
</tr>
<tr>
<td>Issue 3</td>
<td>24 November 2011</td>
<td>Comments received from NDA addressed</td>
</tr>
</tbody>
</table>
CONTENTS

1. INTRODUCTION .......................................................................................................................... 11

2. OBJECTIVES .................................................................................................................................. 12

3. SCOPE ........................................................................................................................................... 13

4. DESCRIPTION OF TRIALS ........................................................................................................... 14
   4.1. Trials 1 to 12 - Magnox Corrosion ......................................................................................... 14
   4.2. Trials 18 to 23 - Magnox Corrosion and Dimensional Change ........................................... 15
   4.3. Trials 13 to 15 - Magnox Corrosion, H₂ Gas Sensor Trials ................................................... 15
   4.4. Trials 16 and 17 - Magnox Corrosion, CEION™ Probe Trials ............................................ 16
   4.5. Trials 24 to 29 - Magnox Corrosion and Expansive Forces ................................................ 16
   4.6. Trial 30 - Magnox Corrosion, Product Quality Trial ............................................................ 16

5. EXPERIMENTAL ............................................................................................................................ 17
   5.1. Magnox Corrosion .................................................................................................................. 17
   5.2. Characterisation of the Magnox/Grout Interface and the Corrosion Products .................... 18
   5.3. Soluble Chloride Analysis ...................................................................................................... 20

6. RESULTS ........................................................................................................................................ 21
   6.1. Magnox Corrosion Data (Large top hat trials, 1 to 12) .......................................................... 21
   6.2. Magnox Corrosion Data (H₂ Gas Sensor Trials 13 to 15) .................................................... 23
   6.3. Magnox Corrosion Data (CEION™ Probe, Trials 16 and 17) .............................................. 23
   6.4. Magnox Corrosion Dimensional Expansion Trials Data (Trials 18 to 23) ......................... 23
   6.5. Magnox Corrosion Load Cell Expansion Trials (Trials 24 to 29) ......................................... 24
   6.6. Chronic Corrosion Rate and Effect on Waste Package ........................................................... 24
   6.7. Characterisation of the Magnox/Grout Interface and the Corrosion Products –
        SEM & EDAX .......................................................................................................................... 26
       6.7.1. Trial 1: Magnox Corrosion in Grout at 25°C ................................................................. 26
       6.7.2. Trial 2: Magnox Corrosion in Grout at 40°C ............................................................... 27
       6.7.3. Trial 7: Magnox Corrosion in Grout at 60°C ............................................................... 27
       6.7.4. Trial 8: Magnox Corrosion in Grout at 75°C ............................................................... 28
       6.7.5. Trial 13: Magnox Corrosion in Grout at ~87°C ........................................................... 29
   6.8. Review of Characterisation of the Magnox/Grout Interface Analyses .................................. 29
       6.8.1. Influence of Curing Temperature .................................................................................... 30
       6.8.2. Thickness of Corrosion Layer ....................................................................................... 30
6.8.3. Phases Formed by Corrosion

6.9. Characterisation of the Magnox/Grout Interface and the Corrosion Products – XRD & TGA

7. DISCUSSION

8. CONCLUSIONS

LIST OF TABLES

Table 1: Experimental array of trials .................................................................37
Table 2: Example of Magnox corrosion spreadsheet ........................................38
Table 3: Chloride levels measured in grout powders ........................................39
Table 4: Infill and product quality data for trials 1 to 12 (Large top hats) ..........40
Table 5: Infill data for trials 13 to 15 (hydrogen gas sensor trials) .................41
Table 6: Infill and PQ data for trials 18 to 23 & trial 30 ..................................42
Table 7: Infill and PQ data for trial 24 to 29 (load cell trials) ..........................43
Table 8: Corrosion rates measured for Trials 1 to 12 (gas pressure trials) ......44
Table 9: Magnox Wt% corroded ....................................................................45
Table 10: Product storage times (in years) before product fracture. ...............46
Table 11: Determination of water contents - TGA ........................................47

LIST OF FIGURES

Figure 1: Large top hat containing Magnox swarf prepared for grouting ...........48
Figure 2: Corrosion trial in progress .................................................................48
Figure 3: 3-litre mould containing Magnox swarf ............................................49
Figure 4: Top hat fitted with CEION™ probes ................................................49
Figure 5: Load cell assembly containing Magnox cemented sample ...............50
Figure 6: Trail 30: 3-litre sliced sample maintained at ambient temperature ....50
Figure 7: Typical core sample (Trial 2) ..............................................................51
Figure 8: Corrosion rate with temperature maintained at 25°C .......................52
Figure 9: Corrosion rate with temperature maintained at 40°C .......................53
Figure 10: Corrosion rate with temperature maintained at 60°C .....................54
Figure 11: Corrosion rate with temperature maintained at 75°C .....................55
Figure 12: Large top hat corrosion trials (Trials 1 - 12). Magnox corroded, Wt% against time ..........................................................56
Figure 13: Top hat trial 5 (25°C cure) ...............................................................57
Figure 14: Top hat trial 10 (40°C cure) .............................................................57
Figure 15: Top hat trial 3 (60°C cure) ...............................................................58
Figure 16: Top hat trial 8 (75°C cure) ........................................................................58
Figure 17: Top hat trial 12 (75°C cure) ........................................................................59
Figure 18: Photographs of some top hats cured at temperatures 75 °C and >83 °C ......60
Figure 19: Base of top hat - trial 13 ........................................................................61
Figure 20: Wall of top hat - trial 13 ........................................................................61
Figure 21: Trails 13, 14 and 15 Gas sensor trials. Corrosion rate against time ..........62
Figure 22: Trials 13, 14 and 15 Gas sensor trials. Magnox corroded, Wt% against time63
Figure 23: Arrhenius relationship between Magnox corrosion in grout and temperature64
Figure 24: Data from Magnox corrosion trial 16 (CEION™ probes) .........................65
Figure 25: Data from Magnox corrosion trial 17 (CEION™ probes) .........................65
Figure 26: Small top hat corrosion trials with temperature increased to 60 and 75°C .66
Figure 27: Small top hat corrosion trials (Trials 18 - 23). Magnox corroded, Wt% against
time ................................................................................................................67
Figure 28: 3 Litre product, trial 22 at 2.7 Wt% Magnox corroded ...............................68
Figure 29: 3 Litre product, trial 18 at 7.2 Wt% Magnox corroded ...............................68
Figure 30: 3-litre product, trial 20 at 10.7 Wt% Magnox corroded ...............................69
Figure 31: 3-litre product, trial 25 at 21.7 Wt% Magnox corroded ...............................69
Figure 32: Small scale (Load cell) corrosion trials with temperature increased to 60°C.
Magnox corrosion rate against time ........................................................................70
Figure 33: Small scale (Load cell) corrosion trials with temperature increased to 60°C.
Magnox corroded, Wt% against time ........................................................................71
Figure 34: Trial 24, Expansive force against Magnox corroded ...............................72
Figure 35: Trial 25, Expansive force against Magnox corroded ...............................73
Figure 36: Trial 26, expansive force against Magnox corroded ...............................74
Figure 37: Trial 27, expansive force against Magnox corroded ...............................75
Figure 38: Trial 28, expansive force against Magnox corroded ...............................76
Figure 39: Trial 29, expansive force against Magnox corroded ...............................77
Figure 40: Backscattered SEM micrograph of Trial 1 sample - 25°C .......................78
Figure 41: Backscattered SEM micrograph and EDX trial 1 sample - 25°C ...............79
Figure 42: Backscattered SEM micrograph and EDX trace trial 1 sample - 25°C .........80
Figure 43: Backscattered SEM micrograph and EDX elemental maps trial 1 sample - 25°C
........................................................................................................................81
Figure 44: Backscattered SEM micrograph trial 2 sample - 40°C ...............................82
Figure 45: Backscattered SEM micrograph and EDX traces trial 2 sample - 40°C ......83
Figure 46: Backscattered SEM micrograph and EDXZ trace trial 2 sample - 40°C .......84
Figure 47: Backscattered SEM micrograph and EDX elemental maps trial 2 sample - 40°C
........................................................................................................................85
Figure 48: Backscattered SEM micrograph trial 7 sample - 60°C ...............................86
Figure 49: Backscattered SEM micrograph and EDX traces trial 7 sample - 60°C ......87
Figure 50: Backscattered SEM micrograph and EDX traces trial 7 sample - 60°C ......88
Figure 51: Backscattered SEM micrograph and EDX elemental maps trial 7 sample - 60°C .........................................................89
Figure 52: Backscattered SEM micrograph trial 8 sample - 75°C .................................................................90
Figure 53: Backscattered SEM micrograph and EDX traces trial 8 sample - 75°C ...91
Figure 54: Backscattered SEM micrograph and EDX traces trial 8 sample - 75°C .......92
Figure 55: Backscattered SEM micrograph and EDX elemental maps trial 8 sample - 75°C .................................................................................................................................................................................................93
Figure 56: Backscattered SEM micrograph trial 13 sample - ~87°C .........................................................94
Figure 57: Backscattered SEM micrograph and EDX traces trial 13 sample - ~87°C .....95
Figure 58: Backscattered SEM micrograph and EDX trace trial 13 sample - ~87°C ......96
Figure 59: Backscattered SEM micrograph and EDX elemental maps trial 13 sample - ~87°C .................................................................................................................................................................................................97
Figure 60: Backscattered SEM micrograph and EDX elemental line maps trial 13 sample - ~87°C .................................................................................................................................98
1. Introduction

Magnox fuel cladding will slowly corrode when encapsulated in alkaline cementitious grouts to produce hydrogen gas and an expansive corrosion product. The evolution of hydrogen during waste processing, transport and storage may prove problematic and the development of expansive corrosion products may ultimately lead to expansion and degradation of the wasteform and, if extensive, may deform or even rupture the container.

Over the past 25 years, cementitious grouts based on Blast Furnace Slag and Ordinary Portland Cement (BFS/OPC), have been used in the UK to immobilise ILW Magnox swarf in 500 litre stainless steel drums and currently such wasteforms are in surface storage awaiting geological disposal. The original specification for the required wasteform and package lifetime was for 50 years above ground followed by 50 years below ground. Subsequently these lifetime requirements have been significantly extended, increasing the risk that some of these wasteforms and containers may not meet the new requirement. This risk carries very large liabilities as in some cases it could result in a need to retrieve and repackage such wasteforms. Therefore, the impact of long-term Magnox corrosion on the lifetimes of the waste packages needs further underpinning.

The aim of this project has been to determine the rates of corrosion of Magnox encapsulated in a BFS/OPC grout in a series of small-scale trials and to relate the corresponding dimensional changes in the cemented product to the corrosion that has occurred. The work has consisted of measuring the rate of chronic corrosion of grouted Magnox over a range of temperatures and to measure the expansion and expansive force generated by the Magnox samples as a function of corrosion over a $2^{1/2}$ year curing period. Several experimental techniques were used to monitor the Magnox corrosion rate in grout and core samples were taken from cemented products to characterise the corrosion products at the Magnox/grout interface.

---

1 The production of harmonised European standards for common cement products and their constituents has caused the nomenclature for powders used in ILW encapsulation to change. OPC has been renamed as CEM I, BFS as Ground Granulated Blastfurnace Slag (GGBS) and PFA as Fly Ash (FA). However, the UK nuclear industry uses its own standards for cement powders and these may retain the terms OPC, BFS and PFA to differentiate the powders they specify from those that have only been qualified for compliance to the European Standards. Furthermore, all historical work that pre-dates the current European standards uses the older terms.
2. **Objectives**

The objectives of this project were to:

- Measure the temperature dependence of the rate of corrosion of grouted Magnox swarf and to measure the expansion of grouted Magnox samples as a function of the extent of corrosion,
- Characterise the Magnox/grout interface and the corrosion products and,
- Compare experimental data with published data for the corrosion of Magnox and magnesium in alkaline environments.
3. **Scope**

Small-scale corrosion trials have been carried out on samples of grouted Magnox swarf and coupons. The experimental approach and the array of 30 trials carried out were designed to enable:

- Preparation of encapsulated Magnox samples using vibrogrouting, simulating plant practice in the Magnox Encapsulation Plant (MEP).
- Preparation of different sized cemented products ranging from cylindrical 3-litre unrestrained products to 16 litre cylindrical stainless steel top-hats containing grout infilled Magnox metal.
- Monitoring of corrosion rate and expansive properties of grouted Magnox corrosion products over a curing time approaching 2\(\frac{1}{2}\) years.
- Determination of Magnox corrosion in cemented products initially cured at 25°C primarily by recording hydrogen gas pressure over time at temperatures of 25, 40, 60, 75 and >85°C.
- Evaluation of the performance of alternative experimental methodologies to be assessed such as CEION™ probes manufactured using Al80 Magnox metal and in-line hydrogen gas sensors, as a means to monitor the progress of long-term Magnox corrosion in grout.
- Characterisation of the Magnox/grout interface and corrosion products formed.
- Comparison of the Magnox corrosion data determined in this study with other published data.
4. Description of Trials

The array of 30 trials that were performed for this project is presented in Table 1. The trials were split into four sets. Each set utilised a different sized top hat vessel and or methodology designed to monitor the corrosion and the expansive properties of grouted Magnox swarf products at 25°C and subsequently after an initial curing period at 25°C for some trials, at elevated temperatures approaching 90°C. The top hats used for this project were stainless steel cylindrical vessels with a fitted lid that could ensure a gas tight seal. The lid furniture comprised a pressure transducer to measure evolving hydrogen gas pressure, a thermocouple and automatic and manual gas release valves. Dimensions of the large top hats used in the pressure trials are provided in Table 1.

The preparation of these products simulated closely the conditions experienced by Magnox swarf encapsulated in the Magnox Encapsulation Plant (MEP) at Sellafield to ensure the cemented products had realistic voidage and total water content replicating MEP operating experience. A SD4 colloidal high shear mixer was used to prepare grout at the MEP reference grout formulation (3.44:1 BFS/OPC, W/S 0.35) and Magnox swarf was prepared by splitting new whole unirradiated Magnox fuel cans that had not been exposed to water. The Magnox fuel cans had a dull, slightly dusty surface finish due to surface oxidation. During splitting operations a significant proportion of this dust became detached from the fuel cans. The swarf was then subsequently dewatered and infilled with grout under vibration.

4.1. Trials 1 to 12 - Magnox Corrosion

For these trials, the Magnox swarf was infilled with grout contained within large top hats (16.6 litre volume). These top hats were loaded with dry uncorroded Magnox swarf (4.2 kg) and water, dosed with sodium hydroxide to pH10, was added to cover and condition the Magnox swarf for at least 24 hours. This swarf loading (equivalent to 155kg per 555 litre MEP drum volume) was the maximum loading that could be achieved with the Magnox swarf pieces prepared, typically 30 to 60mm in length. This loading compares to a typical loading per drum on MEP of between 145 -180 kg swarf per drum².

Before being infilled with grout, the Magnox swarf was dewatered using a peristaltic pump. The wetted swarf was carefully taken out of the top hat to determine the mass of residual heel liquor before being returned with the wetted swarf to the top hat. Heel volumes measured ≤0.28 litres and compare closely on scale with heel volumes (≤10 litres) measured on plant. Each top hat was then filled with grout under vibration to leave an ullage volume of ~1.2 litres. Following MEP practice, the top hat was initially vibrated at 26Hz at 0.55g and as grout was added the vibration frequency was gradually reduced to 10Hz. Infill time for each top hat took approximately five minutes. A top hat prepared for infill grouting under vibration is shown in Figure 1. After curing for minimum time of 24 hours at ambient temperature no significant bleed was present, i.e. no more than a couple of mm of residual bleed liquor remained on the majority of the products prepared and this bleed was mostly held in depressions on the product surface. After an initial curing time of up to 48 hours the top hats were transferred to a dedicated curing facility for corrosion monitoring.

² A full size MEP drum (560-litre volume) typically holds between 140 and 180kg dewatered Magnox swarf that is infilled with grout to just cover the AFP (Anti-Flotation Plate) that is fixed at the 510 litre volume level. Subsequently, after cure the drum is filled with capping grout to leave an ullage volume in the drum of ~5 litres.
The lid of each top hat vessel was fitted with a pressure transducer, pressure relief valve, resistance thermistor (inserted to measure the ullage temperature) and a manual gas relief valve that allowed venting of hydrogen gas to atmosphere. The lid was bolted down onto a double ‘o’ ring seal to ensure a gas tight seal and direct heating to the top hat vessels was provided by insulated heating jackets. A top hat vessel prepared for corrosion monitoring is shown in Figure 2. For these trials, Magnox corrosion was calculated using the ideal gas law applied to the increase in gas pressure over time. The pressure relief valve fitted to the top hats restricted pressure build-up to ~1.3 bar absolute (i.e. 0.3 bar “overpressure”) and periodic manual venting of the top hat maintained integrity of the corrosion data being recorded.

4.2. Trials 18 to 23 – Magnox Corrosion and Dimensional Change

For these trials, 3-litre samples were prepared using an assembled mild steel mould to form cylindrical samples for measurement of dimensional change as a function of corrosion. The Magnox swarf (0.82kg) was wetted, dewatered and infilled with grout within the mould under vibration. A photograph of a mould filled with Magnox swarf for infill grouting is shown in Figure 3. After allowing the product to cure for at least 24 hours, the samples were retrieved from their respective moulds and the mass and dimensions of each of the six samples recorded. These samples were placed in smaller sized top hats (12-litre nominal volume) with heating provided by insulated heating jackets. Magnox corrosion was again monitored using the pressure transducer technique. The samples were retrieved for visual inspection, weighing and dimensional measurement at the end of the initial curing period at 25°C, at a total cure time of 500-550 days and at the end of the experiment approaching 900 days. Dimensional measurements were performed using a micrometer.

4.3. Trials 13 to 15 - Magnox Corrosion, H₂ Gas Sensor Trials

For these trials, due to the monitoring temperatures required being above the upper operating range of the pressure transducers (80°C), a more recently developed method was used to measure Magnox corrosion in grout. In these trials, inline hydrogen gas sensors were used to monitor the hydrogen concentration in forced air flows that continuously purged the ullage volume of each of the three large top hats. The gas sensor comprised of an electrochemical cell (GDS Technologies Ltd, 20J JB model) that responded specifically to hydrogen gas over a range of 0 – 2000 ppm. An inlet and outlet port allowed the purged air to flow continuously past the sensor cell where the air purge to each top hat was powered by variable speed diaphragm air pumps and air flow measured using an inline air flow meter. Individual ballast vessels, kept at ambient temperature, were set up in an attempt to condense moisture from the purged air flow and allow trapped liquor to be regularly returned to each top hat. Periodic calibration of the sensor with appropriate hydrogen gas standards allowed the sensor output current to be converted to ppm hydrogen directly; the relationship between voltage output of the sensor and hydrogen concentration being linear. Each large top hat was fitted with a heating jacket and insulation to maintain the top hats at elevated temperatures. During the first few days of curing the corrosion rate of Magnox was monitored at 25°C using the pressure increase method to minimise liquor loss from the curing grout. During subsequent curing at 25°C using the gas sensors to detect hydrogen gas, minimal liquor loss, <100 mls occurred.
4.4. **Trials 16 and 17 - Magnox Corrosion, CEION™ Probe Trials**

The opportunity to assess the performance of another experimental technique to monitor reactive metal corrosion in grout was taken using CEION™ probes, manufactured by Cormon Ltd, West Sussex. These types of probes have found widespread use in the oil industry monitoring the corrosion and erosion of sub sea or sub soil pipelines. Unlike other methods used in this project that enable an average Magnox corrosion rate to be calculated over a specified time interval, these probes combined with their associated electronics provide the opportunity to measure a direct and more sensitive measurement of corrosion rate with time. These probes have been used by NNL to measure the corrosion of aluminium in cement[1].

Two top hats (25-litre internal volume) were near filled with MEP grout and each top hat accommodated two inserted probes, each probe supplied as a stainless steel housing accommodating Magnox AL80 metal in the form of spiral elements. The corrosion of the Magnox metal was monitored by comparing the relative resistance output of the exposed metal spiral with that of an internal "reference" metal spiral protected in epoxy resin within the stainless steel casing. The probes were equipped to measure temperature to ± 0.5°C and can reportedly determine metal loss with a resolution of 1 nm. The manufacturers, Cormon Ltd claim that measurements are unaffected by heating and cooling rates of up to 10°C per hour.

Each probe (length 23 cm, diameter 2 cm) was inserted through the wall of the top hat at mid height with one probe inserted to the centre position (hereafter referred to as ‘inserted’ and the second probe inserted to be flush with the inner vessel wall (hereafter referred to as 'flush'); the two probes were separated by an angle of 30°. A top hat fitted with CEION™ probes is shown in Figure 4.

4.5. **Trials 24 to 29 - Magnox Corrosion and Expansive Forces**

For these trials, similar sized products to those prepared for trials 18 to 23 (3-litre samples) were prepared. The samples were sandwiched between two circular steel plates with the upper plate supporting a load cell (5000 kg capacity) bearing down onto the surface of the standing sample to measure the longitudinal compressive force generated during corrosion. In addition, a clevis pin type load cell (1000 kg capacity) was strapped around the circumference of each product to measure the corresponding circumferential expansive force. These load cell assemblies were placed inside large top hats. Voltage output from both load cells together with measurement of gas pressure and temperature during monitoring was recorded. A load cell assembly complete with a restrained product is shown in Figure 5.

4.6. **Trial 30 – Magnox Corrosion, Product Quality Trial**

For Trial 30, a 3-litre cemented product sample was prepared and stored without monitoring at ambient temperature. After ~3 months storage this sample was sliced using a band saw to assess the effectiveness of infilling the Magnox swarf with grout under the vibration conditions described. A sliced sample shown in Figure 6 demonstrates that the infilling techniques employed during grout infill were satisfactory as no voidage was apparent.
5. Experimental

5.1. Magnox Corrosion

When encapsulated in a cement matrix, Magnox metal reacts with residual pore liquor:

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

The initial relatively high "acute" corrosion rate can last for several days and then begins to decline as the ability of the cement to provide water for corrosion reduces. Through intermediate rates of indefinite timescale the corrosion rate finally reaches a steady long-term "chronic" rate. To monitor the corrosion process in trials that involved measuring hydrogen gas pressure, the corrosion rates were calculated by converting the pressure increase recorded per unit time to moles of hydrogen using the ideal gas law. After correcting for water vapour pressure, the corresponding mass of Magnox swarf corroded per unit time was calculated. As hourly pressure readings were recorded, the corrosion rate data presented is expressed either as a “1-day average” where the average of 24 data points taken equally before and after a point in time is calculated, or as for later trials (Trials 24 to 29) a “5-day average” corrosion rate was calculated taking the average of 120 hourly data points of pressure and temperature. This averaging technique was used as a tool to improve the resolution of the corrosion data. Experience has shown that whilst taking the average of a number of data points over successively shorter time periods will provide a higher degree of resolution, the data noise becomes greater. Conversely, taking the average of a number of data points over longer time periods, the data noise becomes smoother but the resolution decreases. The optimum averaging time period is taken as that which provides the best balance between resolution and associated data noise. An extract taken from an Excel spreadsheet prepared for corrosion monitoring during Trial 1 is shown in Table 2 and the corrosion data plots are shown in Appendix 1.

To determine whether steady state corrosion had been achieved at the end of the initial curing period at 25°C, a time period of ~40 days was selected and a linear trend line fitted. If the ratio of the corrosion rate at the start and at the end satisfied the ratio 1±0.25 then it was judged that steady state corrosion had been achieved and that the temperature could be ramped up to the long-term cure temperatures required. For Trial 1, the linear equation between 100 and 140 days corrosion was:

\[ \text{Magnox corrosion rate (µm/yr)} = -0.0013(\text{Days}) + 0.743 \]

\[ \text{Corrosion rate (µm/yr)} \text{ at day 100: } 0.613 \]

\[ \text{Corrosion rate (µm/yr)} \text{ at day 140: } 0.561 \]

The ratio, 0.613/0.561 = 1.09, satisfied the criteria for subsequent increase in curing temperature where required.

Towards the end of the monitoring period, the final chronic corrosion rate was calculated using a similar technique where the average rate was taken over a significantly longer time period at:

- the end of the near 900 days monitoring period for the low temperature trials where no drying of the sample occurred,
or immediately after the temperature increase for those trials where significant drying occurred.

- Or the closest point to either of the above where a reasonably stable rate was measured.

For the chronic rates a standard deviation was calculated over the same range of data as the average.

Corrosion data have been presented as “μm/yr” or as Wt% Magnox corroded; the surface area of the Magnox swarf taken as 1m²/kg[2].

For the dimensional stability trials (Trials 18 - 23) where a 3-litre sized product was contained within a 12-litre top hat, the resolution of the corrosion data was enhanced by filling the excess ullage volume with sand.

5.2. Characterisation of the Magnox/Grout Interface and the Corrosion Products

To characterise the Magnox/grout interface and the corrosion products, core samples (2 inch diameter) were taken from one large top hat in each series of long-term cure temperature giving five cores samples in total.

Core samples were taken from the following top hats:

- Trial 1 – 25°C, Trial 2 – 40°C, Trial 7 – 60°C, Trial 8 – 75°C and Trial 13 – ~87°C.

Figure 7 shows a typical core sample from Trial 2. As coring of the top hats was a wet operation (water provides lubrication and cooling) and dry samples were required for Thermogravimetric Analyses (TGA) samples were taken using a dry sampling technique from different but equivalent top hat samples with respect to long-term cure temperature.

Samples for TGA were taken from:


It was intended that samples would be taken from a range of positions such as from voids, well-infilled areas, etc. However, on visual examination of the core samples taken not all these features were apparent as good quality products were prepared.

The samples retrieved enabled internal samples to be taken for:

- Measurement of thickness, elemental composition and morphology of the corrosion layer and surrounding metal and grout, using Environmental Scanning Electron Microscopy (ESEM) with Energy Dispersive Analysis by X-ray (EDAX).
- Mineralogical characterisation by X-ray Diffractometry (XRD) of the corrosion products and the grout at the interface to determine the composition of any crystalline material present.
- Thermogravimetric Analysis (TGA) of the grout at the interface and the bulk of the matrix to provide data on the free and bound water content of the grout during the chronic corrosion stage.

Analysis by environmental scanning electron microscopy (ESEM) was performed in both secondary electron imaging (SEI) mode, using a detector called a Large Field Detector (LFD), and in backscattered electron imaging (BEI) mode, using a BSED (Backscattered
Electron Detector) detector. Due to the capability of the microscope to operate without the need for high vacuum within the analysis chamber, the samples did not require coating, although where necessary charging was reduced by forming a conductive path between the sample surface and the microscope stage using adhesive aluminium tape. Analysis was performed using a FEI Quanta 200 Mark 2 Field Emission Gun Environmental Scanning Electron Microscope, fitted with an Oxford Instruments Inca 250 Energy Dispersive X-Ray (EDX) Spectrometer. This equipment is capable of imaging and analysing moist and non-conducting samples without coating or other pre-treatment.

Each sample was studied at a number of locations throughout the microstructure to investigate the elemental composition and elemental distribution of:

- the hardened composite cement paste in proximity to the Magnox metal,
- the Magnox corrosion layer.

Cracking and damage of the microstructure, which may have been caused by Magnox corrosion, was also investigated, and a visual examination of the porosity of the samples was made. The elemental information obtained was used to infer the possible compositions of the phases present.

In order to be consistent in the interpretation of results, the magnification of all the micrographs obtained was similar. This allowed an estimated comparison of corrosion layer thickness to be obtained.

For all samples, an overall micrograph of the samples was obtained in both SEI and BEI mode. This showed that very little effective information could be obtained in SEI mode, so all subsequent analysis was performed in BEI mode. This provided very useful data because in BEI mode all micrographs obtained are representative of the elemental composition of the sample, i.e.

- elements with low atomic number appear dull in the micrographs,
- pores where no elements are present appear as black,
- elements with high atomic number appear as bright points in the micrographs.

Therefore, this provides indicative information on phase composition.

Elemental information was obtained using the EDX spectrometer and was represented in the form of graphical plots of X-ray energy (keV) associated with the elements detected against intensity. This identified which elements were present in an area of sample as well as providing information on the relative quantity of each element in the area being analysed. Elemental maps were also obtained for areas of interest to investigate the distribution of the elements present in order to infer which phases were likely to be present in the samples.

XRD analysis was carried out using a Co tube operating at 30 kV and 30 mA on an Inel Equinox 1000. A solid-state detector that measured all angles simultaneously over a 2 theta spread of 110 degrees was used with a data collection time of 30 minutes. Analysis was carried out using the Match software package.

For Thermogravimetric Analysis (TGA), each of the five top hats selected provided two grout samples for analyses. To minimise the potential for carbonation of the first sample, this was retrieved from the bulk of the matrix using a 5mm diameter drill bit to dry drill a hole to a depth of ~50mm beneath the surface of the matrix and a sub-sample taken from the bulk of the grout adhering to the retrieved drill bit for analysis. Whilst this technique attempted to minimise carbonation, it is recognised that a finely divided
A powdered sample would be very vulnerable to carbonation and the TGA traces do show that some carbonation took place before the samples were analysed. However, as the sole intention of TGA was to estimate free and bound water, carbonation of the samples was subsequently thought not to be detrimental. The second sample was taken from near the matrix surface at the interface between an unexposed piece of Magnox swarf and surrounding grout.

5.3. **Soluble Chloride Analysis**

The water soluble chloride content of the grout was determined as much of the chloride present would be fixed as calcium chloro-aluminate and would have no significant effect on the Magnox swarf chronic corrosion rates measured. A single sample of powdered grout (~50g) taken from the surface of a product was supplied to UK Analytical Ltd for percent water soluble chloride analysis. The result received stated that the grout formulation prepared for these corrosion trials contained 0.031 wt% soluble chloride. Sellafield Ltd (SL) Specification for ordinary Portland cement (OPC) currently has a maximum (total) chloride content of 0.05wt% and is manufactured specifically for the nuclear industry. CEM I Portland produced for the construction and other industries typically contains up to 0.07wt% chloride, whereas BS EN 197-1 CEM I can contain up to 0.1wt% total chloride.

The total chloride levels in the cementitious powders supplied to Sellafield Ltd have been recorded and are summarised in Table 3. Due to problems associated with determining whether any chloride present is soluble or insoluble there appears to be little agreement on the relative amounts of either in cement grouts and no literature quantitatively assessing the release of chloride from the cement during mixing/hydration into the pore solution of the hardened cement has been identified.

Other than purposeful addition of chloride to matrix grout to enhance Magnox corrosion, no specific studies to study the effect of soluble chloride on Magnox corrosion could be found.
6. Results

Infill data for all top hats prepared for corrosion monitoring are presented in:

- Table 4 for the large top hats trials (Trials 1 - 12),
- Table 5 for the gas sensor trials (Trial 13 - 15),
- Table 6 for the small top hat dimensional stability trials (Trials 18 - 23) and Trial 30, and
- Table 7 for the load cell expansion trials (Trials 24 - 29).

To ensure that the infill cement grout had hydrated under realistic but controlled conditions for the purpose of these trials, all products that were destined for curing at elevated temperatures above 25°C were initially cured at 25°C for a period of time. This initial cure temperature was selected as a reflection of the range of ambient temperatures that MEP stores experience and which could be maintained during this project during the summer months. For the purpose of this project it was important to maintain a steady temperature during the initial curing period to ensure that the condition of the products were comparable before curing temperatures were increased. This also allowed early Magnox corrosion to stabilise and chronic corrosion to be established before curing temperatures were increased. This initial curing time took between 86 and 200 days where it was judged that stable corrosion rates for all top hat trials had been measured for at least 40 days. At this point in time the curing temperature was increased to that selected for each trial. Long-term cure temperatures maintained were 25, 40, 60 and 75°C for the gas pressure trials and between 80 and 90°C for the gas sensor trials. Corrosion monitoring was maintained for a period approaching 900 days.

Graphs showing corrosion rate against curing time are presented for each trial in Appendix 1. In this appendix two plots are presented, the first showing a profile of corrosion rate against curing time over the lifetime of each trial and the second a similar plot focused towards the end of each trial where it was judged that a steady corrosion rate had been established. For this steady corrosion rate, a linear relationship is calculated between corrosion rate and the timescale over which it is considered to be valid to generate an average corrosion rate. The treatment method applied to the data has been explained in Section 5. The data presented in Appendix 1 has been used to construct the comparative graphs presented in this report.

6.1. Magnox Corrosion Data (Large top hat trials, 1 to 12)

Corrosion monitoring for these trials commenced immediately after grouting and graphs showing the progress of Magnox corrosion with curing time are presented in Figure 8 to Figure 12. As seen in Table 8, the steady corrosion rates measured at 25°C at a moment in time before enhanced curing temperatures were controlled, typically after 41 to 142 days initial curing, were 0.19 to 0.59 µm/yr. The corrosion rate data shown in Figure 10 and Figure 11, illustrate that enhanced corrosion rates for these trials were, for those curing at 75°C in particular, maintained for 100 or less days before they steadily declined to similar corrosion rates measured for lower temperature trials (Figure 8 and Figure 9) as curing time progressed.

The combined dataset data presented in Figure 12 provides a visual presentation of total Magnox swarf corroded under the four temperature curing conditions that were maintained. As seen in Table 9, the mass of Magnox swarf corroded after curing for near 900 days at 25°C is 0.1 to 0.16wt%, whilst at 75°C between 10.3 to 30.8wt% original Magnox had corroded.
Figure 13 to Figure 17 show the upper surfaces of some of the products at the ends of the trials after curing. The majority of the products that had been cured at 75°C and above showed a surface layer, at least 2cm in depth, formed of a powdery mass of grout and loose swarf. In some cases the product volume had expanded to near fill the available ullage volume.

During retrieval of the top hats from the curing facility in preparation for coring, it was also noted that some of the large top hats, most notably those that had been subjected to temperatures of 75°C and above, had suffered noticeable distortion. Generally the flat base of the top hat vessels had slightly domed such that the top hats could be spun on their vertical axes. Also noted was the deformation of the vessel walls where noticeable expansion and/or undulations along the vessel wall could be seen or felt. Photographs of all the top hats that showed noticeable deformation are presented in Figure 18, Figure 19 and Figure 20. The largest deformations recorded were 20mm at a central point of a top hat base and an increase of 22mm in circumference along a significant length of the vessel wall. For top hats that exhibited noticeable deformation, the expansive volumes that would theoretically be produced, based on Wt% Magnox corroded, is calculated to be 1 to 2 litres. The magnitude of this volume increase when compared to the extent of the vessel deformations noted, strongly suggested that the increase in vessel volumes observed could be attributable to the expansive corrosion products produced when Magnox corrodes.
6.2. **Magnox Corrosion Data (H₂ Gas Sensor Trials 13 to 15)**

The data from these trials are shown in Figure 21 and Figure 22.

In Figure 21, the Magnox corrosion rates are seen to decrease over the first 150 days of curing at 25°C and, typically, over this period corrosion rates are then seen to decrease from between 0.3 and 30µm/yr to <0.2 µm/yr. During curing at 25°C, Magnox swarf corroded was calculated to be <0.1wt%. Increasing temperature to 60°C caused a rapid rise in corrosion rate such that after ~170 total days corrosion, the amount of Magnox corroded was calculated to be 3, 9 and 12wt% for Trials 13, 14 and 15 respectively.

Increasing the curing temperature to ~87°C for the last 300 days of monitoring caused corrosion rates to rise and these elevated corrosion rates were maintained for ~25 days with rates peaking at ~7000 µm/yr. Thereafter, the rates steadily declined to measure below 7µm/yr, thought largely due to liquor loss as increasing the temperature from 60 to ~87°C caused an increase in grout pore liquor being collected in the ballast vessels with up to 1 litre of liquor from each trial being collected during the first few days. As before, this liquor was returned to each respective top hat but this procedure was maintained with diminishing return in liquor volume due to liquor losses from the system. On reflection it is considered that a more efficient experimental design to keep the products at high humidity during air purge could have prevented much of the liquor loss occurring. The sensitivity of this technique has resulted in relatively noisy traces of corrosion rate against time when compared to such traces constructed from trials employing the gas pressure technique using sealed vessels. Nevertheless, the Arrhenius plot shown in Figure 23 shows that these data showed good agreement with corrosion rate data generated by the gas pressure technique. The data shown in Figure 23 are discussed later in Section 6.6.

6.3. **Magnox Corrosion Data (CEION™ Probe, Trials 16 and 17)**

These two trials were monitored for a curing time approaching 350 days. The profile of metal loss against time measured for Trial 16 is shown in Figure 24 and similarly for Trial 17 in Figure 25. The data shown for Trial 16 suggests that the “FLUSH” probe attained a steady rate of corrosion fairly early on during the trial, while the “INSERTED” probe exhibited a decreasing resistance signal that only started to recover after curing for 150 days. Once this signal had stabilised for a few days, at 250 days cure, the temperature of the Top Hat was increased to 85°C. Shortly after increasing temperature, the outputs from both probes started to provide non numeric data and were judged to have failed. For the two probes in Trial 17, the “FLUSH” probe continued to provide a positive output with time indicating a metal loss of ~1600nm after curing at 25°C for 320 days. The performance of the “INSERTED” probe has proved disappointing with signal output being erratic and continuing to decrease with time. Owing to the unsatisfactory performance these trials were discontinued.

6.4. **Magnox Corrosion Dimensional Expansion Trials Data (Trials 18 to 23)**

Corrosion data measured from the six smaller scale top hat trials performed to measure dimensional stability on 3-litre products are presented in Figure 26 and Figure 27. These corrosion data are consistent with the corrosion data corresponding to the larger top hat trials also cured at 60°C (Trials 3, 7 & 11) with 2 to 8 Wt% Magnox swarf being corrod
during the lifetime of these trials as shown in Table 6. Towards the end of the trials, the curing temperature for Trials 20, 22 and 23 was increased to 75°C in an attempt to increase the degradation experienced and widen the corrosion rate dataset from these trials.

Photographs of some of the 3-litre cemented products are presented in Figure 28 to Figure 31 to provide a visual assessment of product quality with Wt% Magnox corroded. The presence of cracking and product degradation steadily worsened as Magnox corrosion progressed.

For products which had remained intact with no significant external cracking no expansion above the limit of detection of about 1mm using a micrometer was measured. This limit of detection is this high as it was difficult to place the micrometer in exactly the same place due to the unevenness of one face of the samples. For those samples that had suffered significant degradation accurate measurements of product dimensions could not be made.

6.5. Magnox Corrosion Load Cell Expansion Trials (Trials 24 to 29)

These six trials incorporating 3-litre products progressed at 60°C after curing at 25°C for up to 183 days. The corrosion rate data are shown in Figure 32 and Figure 33 and the expansive forces measured for the six trials are presented in Figure 34 to Figure 39. The trend lines were generated from best fit lines over the range selected.

The corrosion rates measured show broad compatibility to those measured on the other top hat trials maintained at 60°C, although higher cumulative Magnox corroded values, approaching a maximum of 34wt% Magnox corroded was achieved with these restrained products. In all trials a steady increase in longitudinal expansion force was measured as Magnox corrosion progressed at the elevated curing temperature of 60°C. Difficulties in all but one trial were experienced with recording the voltage output from the circumferential load cells but as no significant circumferential expansion was measured, as indicated by the data recorded for Trial 25, the remaining trials were not disturbed unnecessarily to resolve this issue.

The longitudinal expansion profiles are characterised by a steady more or less linear increase in expansion as corrosion proceeds and then, but not before at least 5 to 10 Wt% Magnox has corroded, appear to lose momentum and become static and irregular as corrosion continues to higher levels. This observation could be indicative of the restrained products starting to suffer structural degradation and transferring less of the expansion force to the load cell. Linear trend lines fitted to appropriate data suggest that the unit increase in longitudinal force per Wt% Magnox corroded, before product degradation starts to develop, generally lies between 0.14 and 0.47 MPa/Wt% Magnox corroded. The magnitude of the longitudinal forces experienced by the products suggests that the levels at which structural degradation starts, i.e. 1.1 to 2.6 MPa, is related to the tensile strength of cement grout which is generally quoted in the literature to lie between 1 and 4 MPa. Previous project work\(^5\) that measured the mechanical properties of four cemented Magnox swarf samples (100mm cubes) determined the tensile strength to be between 2 and 3 MPa.

6.6. Chronic Corrosion Rate and Effect on Waste Package

The Arrhenius plot in Figure 23 shows the corrosion rate data taken from all these trials. Where the corrosion rate reduced with time due to drying out only the rate immediately
after the sample had been heated to temperature is used. Historic corrosion data from all trials carried out within the UK using Magnox swarf or fin in saturated grout systems is included for comparison. These historic data are taken from a recent review completed for the NDA to derive corrosion rate datasets for reactive metals that can be used as a standard reference, within the nuclear industry, to predict lifetime behaviour of grouted wasteform packages. It can be seen in Figure 23 that the corrosion rate data generated in this project aligns closely with that of the historic data.

Two Arrhenius corrosion rate equations are shown:-

The first equation has been derived from the corrosion data generated by this study:-

\[ \text{Equation 1} \quad \text{Ln Corrosion rate (µm/yr)} = -14748/T(\text{K}) + 47.273 + \text{Ln}(4997390) \]

Whilst the second Arrhenius equation shown below is that taken from the historic data that also included the corrosion data generated from this study:-

\[ \text{Equation 2} \quad \text{Ln Corrosion rate (µm/yr)} = -13362/T(\text{K}) + 27.489 + \text{Ln}(4997390) \]

The standard deviation associated with Equation 2 is 0.84.

Note 1: The addition of Ln (4997390) to each rate equation shown above converts the corrosion rate from m³/m²/hour to microns per year.

Note 2: The replacement of Ln (4997390) with Ln (871045) to each rate equation shown above converts the corrosion rate from m³/m²/hour to Wt% per year.

Using equation 2 as the chosen corrosion rate equation, the following calculation shows how the data can be used to predict storage times when an MEP type product fractures i.e. exceeds product tensile strength.

Assumptions: Cure temperature: 25°C Tensile Strength: 3 MPa

Tensile strength development = 0.33 MPa/Wt% Magnox corroded and corrosion rate of Magnox derived from equation 2 = 2.62E-02 Wt%/yr.

\[
\text{Time to product fracture} = \frac{(3/0.33)/2.62E-02}{2.62E-02} = 347 \text{ years}
\]

From the data presented in Figure 34 to Figure 39 for the 3-litre product load cell expansion force trials (Trials 24 to 29) it is seen that tensile stress develops at a rate between 0.14 and 0.47 MPa/Wt% Magnox corroded where an average (typical) rate is calculated to be 0.33 MPa/Wt%. Taking these values to represent lower, upper and typical values for tensile stress development respectively, Table 10 provides calculated storage times at 25°C for an MEP type product to fracture. Times are shown for a cement matrix having tensile strengths of 2, 3 and 4 MPa and for average and upper- and lower-bound calculated corrosion rates.
6.7. Characterisation of the Magnox/Grout Interface and the Corrosion Products – SEM & EDAX

6.7.1. Trial 1: Magnox Corrosion in Grout at 25°C

A low magnification micrograph typical of a grouted Magnox fin, presented in Figure 40, shows a corrosion layer between the surface of the Magnox metal and the surrounding grout. The microstructure of the grout appeared to be randomly arranged and was typical of a hydrated BFS:OPC composite cement. The pores of the grout appeared to be randomly arranged and grout porosity did not appear to be highest close to the grout/Magnox interface. The corrosion layer appeared darker than both the Magnox metal and the grout matrix which indicated that the solid material in the corrosion layer contained elements with a lower atomic number, or that porosity was higher than in the Magnox metal or in the grout. No micro or macro-cracks were distinguishable.

At higher magnification, shown in Figure 41, the contrast between the Magnox metal, the corrosion layer and the grout is more discernible and a distinct band of corrosion layer can be seen. Due to the sample preparation process used, a small amount of particle carry over was observed, with small particles of brighter material, either particles of Magnox metal or grout, present on the surface of the corrosion layer. The main element detected by EDX in the Magnox metal was magnesium, and an extremely minor peak for oxygen was also present. Minor peaks for aluminium, silicon and calcium reflect the levels of these materials in Magnox. The EDX trace for the corrosion layer showed that the main elements present were magnesium and oxygen, suggesting that this layer was principally magnesium hydroxide (brucite) formed during Magnox corrosion. Again, minor aluminium, calcium and silicon peaks are seen.

The elemental composition of the grout was typical of a hydrated BFS:OPC cement with major EDX peaks for calcium, silicon and oxygen due to the presence of calcium-silicate-hydrate, [CSH] formed during hydration of both BFS and OPC and also possibly due to the presence of portlandite (Ca(OH)\(_2\)) formed from hydration of OPC. A peak for aluminium is likely to be due to unreacted gehlenite (2CaO.Al\(_2\)O\(_3\).SiO\(_2\), \([C_2AS]\) present in BFS. The strongest peak of all in the grout is for magnesium. Although there may be a small quantity of magnesium in the BFS and OPC powders the intensity of the peak suggests that magnesium present in the Magnox corrosion layer may have dissolved into solution and migrated away from the corrosion layer into the body of the grout. Other EDX data, presented in Figure 42, shows that the intensity of the magnesium peak in the grout at a position further away from the interface was significantly reduced compared to that close to the Magnox/grout interface. A small peak for carbon in the grout suggests the presence of calcite (CaCO\(_3\)) that is likely to be formed from the carbonation of any portlandite present. Minor peaks for sulphur, potassium and titanium were detected in the grout for the minor phases present in both BFS and OPC powders.

The elemental distribution in the Magnox/grout interface region is shown in Figure 43. This shows that the concentration of magnesium was highest in the Magnox metal and was significantly less in the corrosion layer. It also suggests that the concentration of magnesium in the grout reduced as the distance away from the corrosion layer increased. The concentration of oxygen was highest in the corrosion layer which again suggests that this corrosion layer is mainly brucite. Most of the calcium was present in the grout although small quantities were detected in the corrosion layer and the Magnox due either to the levels present in Magnox or from contamination by grout during sample preparation. Virtually all the silicon and aluminium present was present in the grout. The elemental maps obtained for potassium, carbon and sulphur showed that their presence was very minor and it was not possible to associate their presence with any specific regions due to their pervasive location within the whole microstructure. However, there was a slightly higher concentration of carbon in the grout when compared to that in the
Magnox and corrosion layer which suggests that there may be a small amount of carbonate present in the grout (possibly calcite).

**6.7.2. Trial 2: Magnox Corrosion in Grout at 40°C**

A low magnification micrograph of a sample taken from trial 2, Figure 44, shows similar features to the micrograph obtained for trial 1. A corrosion layer between the Magnox metal and the encapsulating grout is seen and grout porosity appeared to be random although regions of slightly higher porosity were observed close to areas that appeared to have thicker corrosion layers than other areas. The corrosion layer again appeared to contain solid material with low atomic number and higher porosity than either in the Magnox metal or the grout.

Analysis at higher magnification, Figure 45, reveals significant differences in the elemental composition of the Magnox metal, the corrosion layer and the grout and a distinct band of corrosion layer is seen. Pockets of higher porosity appear to be particle carry over. The main element detected by EDX in the Magnox metal was magnesium, and the main elements detected in the corrosion layer were magnesium and oxygen, again suggesting the presence of brucite. Minor calcium, silicon and aluminium peaks in both EDX traces for the Magnox metal and the corrosion layer are again found. The elemental composition of the grout showed major EDX peaks for calcium, silicon and oxygen (likely to be due to CSH and portlandite) as well as a peak for aluminium which again is probably due to gehlenite. The intensity of the peak for magnesium in the grout suggests that some magnesium from the corrosion layer may have dissolved in the pore water and migrated from the Magnox/grout interface in to the body of the grout. The micrograph shown in Figure 46 shows that the intensity of the magnesium peak is still extremely high in an area of grout between two Magnox fins. Minor peaks for sulphur and potassium were detected in the grout.

As expected, analysis of the elemental distribution, Figure 47, shows that the concentration of magnesium was highest in the Magnox metal compared to the corrosion layer and magnesium may be migrating from the corrosion layer in to the grout. The higher concentration of oxygen in the corrosion layer suggests again that brucite is the main phase present in the corrosion layer and virtually all the silicon and aluminium are present in the grout. As with the results in Figure 43, the relative intensity of the elemental maps obtained for potassium, carbon and sulphur was low compared to all other elements and showed that minor quantities were present and their pervasive location across the whole microstructure suggested that they were not associated with any specific microstructural regions.

**6.7.3. Trial 7: Magnox Corrosion in Grout at 60°C**

The low magnification micrograph for a sample taken from Trial 7 shown in Figure 48 shows a broad corrosion layer between the Magnox metal and the encapsulating grout. No micro- or macro-cracks were observed in the grout, and grout porosity appeared to be random with regions of slightly higher porosity. The contrast in elemental concentration, indicated by the brightness of the areas of microstructure, showed that the solid material contained elements with lower atomic number than in either the Magnox metal and the grout, and the corrosion layer porosity was higher than in the Magnox or the grout.

At higher magnification, Figure 49, the elemental differences between the Magnox metal, the corrosion layer and the grout are highlighted and the band of corrosion layer is
distinct. Typically, the main element detected in the Magnox was magnesium, and those in the corrosion layer being magnesium and oxygen, suggesting brucite. Minor peaks due to the presence of calcium, silicon and aluminium are also present. The elemental composition of the grout again showed major EDX peaks for calcium, silicon and oxygen (probably due to CSH and portlandite) and a peak for aluminium (probably due to gehlenite). The peak for magnesium in the grout is very strong which again suggests the possibility of some magnesium migration from the corrosion layer into the body of the grout. The EDX trace shown in Figure 50 shows that the intensity of the magnesium peak further away from the Magnox/grout interface was less intense. Minor amounts of sulphur and potassium were detected in the grout probably from the BFS and OPC powders.

The elemental distribution, presented in Figure 51, shows that the magnesium concentration was highest in the Magnox metal and was less in the corrosion layer than in the metal. Little magnesium appeared to be present in the grout of this sample when compared to the previous samples analysed. Again, brucite was the main phase in the corrosion layer. Nearly all the calcium detected was present in the grout as was virtually all the silicon and aluminium. As in trial 1, the elemental maps for potassium, carbon and sulphur (not presented here) showed these elements to be pervasive across the whole sample microstructure and very minor quantities were present and did not appear to be associated with any specific regions of the microstructure.

6.7.4. Trial 8: Magnox Corrosion in Grout at 75°C

This sample was difficult to prepare as given the extensive corrosion the grout material within the core samples was not now well adhered to the surface of the Magnox metal. This is shown in the typical low magnification micrograph produced for this sample in Figure 52 where a broad corrosion layer between the Magnox metal and the encapsulating grout was observed and where cracking was apparent in the grout. Grout porosity appeared to be random and regions of slightly higher porosity were observed. From this micrograph it was apparent that the corrosion layer contained elements with a lower atomic number and higher porosity than in the Magnox metal and the grout.

When analysed at higher magnification, as shown in Figure 53, the elemental differences in the three main regions were easily discernible and the Magnox corrosion layer was distinct. Areas of higher porosity were observed in the corrosion layer and the grout. Magnesium was the main element present in the Magnox, and the main elements detected in the corrosion layer again suggested the major presence of brucite. Very minor traces of calcium and silicon were again detected in the corrosion layer. The elemental composition of the grout suggests the presence of CSH and possibly portlandite, and gehlenite. Again the presence of a strong EDX peak for magnesium in the grout suggests the possibility of magnesium migration from the Magnox corrosion layer into the body of the grout, although the intensity of this magnesium peak was much diminished further away from the Magnox/grout interface as shown in Figure 54. Minor amounts of sulphur and potassium in the grout suggests the presence of relic material from the BFS and OPC.

The elemental maps, shown in Figure 55, show that the magnesium concentration was less in the corrosion layer than in the Magnox metal, and little magnesium was present in the grout. The highest oxygen concentration was in the area of the corrosion layer suggesting that brucite was the main phase in the region. Nearly all the calcium, silicon and aluminium detected were in the grout and only very minor quantities of potassium, carbon and sulphur were present (as seen in Figure 43 for trial sample 1) and were pervasive across the whole sample microstructure making it difficult to associate their presence with any other elements.
6.7.5. Trial 13: Magnox Corrosion in Grout at \( \sim 87^\circ C \)

A typical low magnification micrograph produced for this sample, shown in Figure 56, shows a broad corrosion layer between the Magnox metal and the encapsulating grout and no micro or macro-cracking of the grout was apparent. Grout porosity was random and regions of slightly higher porosity were observed. It was evident from this micrograph that the corrosion layer again contained elements with lower atomic number and higher porosity than in either the Magnox metal or the grout.

At higher magnification shown in Figure 57, the elemental differences in the three main regions were easily discernible and the Magnox corrosion layer was distinct. Porous areas were observed in the corrosion layer and to a lesser extent in the grout. Magnesium was the main element present in the Magnox, and the main elements detected in the corrosion layer (magnesium and oxygen) suggested the presence of much brucite. Very minor amounts of calcium and silicon were detected in the corrosion layer. The elemental composition of the grout suggested the presence of CSH and possibly portlandite, and gehlenite. The presence of a very strong EDX magnesium peak in the grout, as seen in Figure 58, again suggests that magnesium present in the corrosion layer may have dissolved in the pore water and migrated into the body of the grout, although the intensity of this magnesium peak was diminished further away from the Magnox/grout interface. Minor amounts of sulphur and potassium in the grout suggested the presence of relic material from the BFS and OPC.

From the elemental maps shown in Figure 59 it was evident that magnesium concentration was less in the corrosion layer than in the Magnox metal and much less magnesium was present in the grout. The highest oxygen concentration was in the corrosion layer suggesting the presence of much brucite in this region. Nearly all the calcium, silicon and aluminium detected were in the grout and only very minor quantities of potassium, carbon and sulphur were present (as for trial 1 in Figure 43) the location of which were pervasive and could not be associated with any other elements in order to hypothesise on possible phase composition.

In Figure 60, an elemental line scan across the interface region shows that magnesium is by far the most abundant element detected along this line and that the concentration of magnesium reduces significantly but gradually along the line, with the most abrupt reductions at the interface between the Magnox metal and the corrosion layer, and at the interface between the corrosion layer and the grout. However, it is interesting to note that the concentration of magnesium in the grout is not significantly less than that in the corrosion layer, and that areas of high magnesium content are present in the grout. The other data from these line maps show that the highest oxygen concentration is in the area of the corrosion layer, and that the relative concentration of aluminium and silicon is low compared to that of calcium, oxygen and magnesium, particularly the latter.

6.8. Review of Characterisation of the Magnox/Grout Interface Analyses

At times it was difficult to compare results obtained for each sample because the adherence of the grout to the Magnox metal was sometimes poor, making it hard to produce consistent samples. In some of the samples, such as those prepared for Trial 8 (Figure 52 to Figure 55), the grout did not stay adhered to the surface of the Magnox metal during sample preparation and gave what could be taken as false impressions on the amount of porosity present.

The microstructures of all five samples appeared to be very similar and no significant differences were observed between them when analysed by SEM. Similarly, the elemental composition of all samples when investigated by SEM also appeared to be very
similar which suggests that the phases formed in each sample were similar to each other. These observations are also confirmed by the XRD trace data that indicated similar crystalline phases were identified in the samples examined.

Although no major microstructural or compositional differences were observed between samples, a number of subtle differences are detailed below.

6.8.1. Influence of Curing Temperature

The progressive increase in curing temperature as experienced by these samples should create an upward trend in the amount of porosity capable of being observed in the grout of each sample examined, as the increase in temperature will cause the release of pore water as well as the removal of hydrate water in certain high water-containing phases. Calcium-silicate-hydrate (CSH) for example is reported to lose hydrate water between 50 and 550°C. Although not measured quantitatively, a trend in grout porosity to increase with curing temperature was observed in the micrographs obtained with samples cured at 40°C and above showing progressively higher amounts of porosity in the grout, although this was difficult to discern at times. This tends to confirm that water was being lost from samples cured at higher temperatures and that this was the cause of the observed reduction in corrosion rate with time.

The rise in curing temperature appeared to have no effect on the porosity of the Magnox metal at all or on the porosity of the corrosion layer at curing temperatures of 25°C and 40°C. However, at 60°C and above, areas of porosity were present in the corrosion layer, particularly in the layer that appeared to be external to where the original surface of the Magnox metal used to be before corrosion took place. This is best observed in Figure 58 which has a hypothetical line drawn where it is thought the original surface of the Magnox metal lay. The corrosion layer on the inside of this line is dense, whereas outside this line the corrosion layer contains significant areas of porosity. This suggests that corrosion of the Magnox metal in grout produces a dense inner layer of corrosion as well as a more porous outer corrosion product. The EDX results obtained suggest that the composition of these two areas of corrosion product was very similar for all samples.

From the cores samples that originated from coring the restrained products in the large top hats, the increase in curing temperature appeared to have little or no effect on sample cracking at least that could be seen at the micro level. This contrasts with the observed behaviour with the unrestrained 3-litre products where at the macro level significant product degradation was achieved at higher curing temperatures.

6.8.2. Thickness of Corrosion Layer

Although not directly measured, it was seen from the SEM micrographs that the thickness of the corrosion layer appeared to be similar in the samples cured at 25 and 40°C, but at temperatures at 60°C and above the thickness of this layer appeared to increase with temperature reflecting the increased corrosion that had occurred. However, the corrosion layer thickness was not consistent throughout each sample and varied within a sample. The apparent thickness also varies depending on the angle at which the sample is cut in relation to the fin, i.e. a shallow angle of cut will produce a thicker apparent layer than a steep cut angle.

Pockets of corrosion on the surface of the Magnox metal were observed in some samples. This is shown in Figure 44 (Trial 2, 40°C) where there is a pocket of corrosion product on
the lower surface of the lower Magnox fin. It is likely that such pockets of surface corrosion are caused by defects or pitting on the surface of the Magnox metal.

6.8.3. Phases Formed by Corrosion

The elemental composition of the grout in each sample was typical of a hydrated BFS:OPC composite cement with oxygen, calcium and silicon being detected. The main phases that these (but not all) elements are likely to be in are CSH and portlandite. A smaller amount of aluminium is also present in the grout in each sample which is either likely to be in gehlenite, incorporated into the CSH, or present in ettringite (3CaO.Al₂O₃.3CaSO₄.26H₂O) or monosulphate (3CaO.Al₂O₃.CaSO₄.12H₂O), although the presence of the latter two phases is unlikely due to the low sulphur content. In all the areas of grout analysed by EDX, significant quantities of magnesium were detected resulting in significant EDX peaks which at times indicated quantities greater than that of calcium or silicon. Minor EDX peaks for carbon suggested that some atmospheric carbonation of the samples had occurred, probably resulting in the formation of calcite (CaCO₃). Very minor quantities of potassium, sodium, titanium and iron were probably relics from the composite cement powders. Curing temperature did not appear to affect the elemental composition of the grouts.

The EDX results for the Magnox metal showed no difference in elemental composition resulting from the increase in curing temperature, with magnesium being the principal element detected. Minor EDX peaks for oxygen, calcium, aluminium and silicon were probably due to the presence of minor grout particles on the surface of the Magnox caused by carry over during sample preparation.

The principal elements detected by EDX in the corrosion layer of all samples were magnesium and oxygen suggesting the formation of brucite. The intensity of the oxygen peak in the corrosion layer in all samples was approximately half that of the magnesium peak which gives evidence to suggest that brucite (Mg(OH)₂) was the main phase formed from corrosion of the Magnox metal. The oxygen peak in the EDX results for the corrosion layers in each sample was significantly more intense than that in the Magnox metal of each sample, giving evidence to the formation of brucite during corrosion. What was thought to be carry over from the grout to the surface of the corrosion layer was evident in each sample, although some of the cement hydrates may have been combined with the corrosion layer during the expansive formation of the latter (the density of magnesium is 1,740 kg/m³ whereas that of brucite is 2,390 kg/m³). From the elemental maps for all samples, aluminium appeared to be associated with magnesium and oxygen in the area of each corrosion layer, although the quantity of aluminium appeared to be only very small. There was no elemental evidence to suggest that different phases were forming in the corrosion layer due to differences in the curing temperature.

6.9. Characterisation of the Magnox/Grout Interface and the Corrosion Products – XRD & TGA

X-Ray diffraction (XRD) traces were performed on sub-samples taken from the cored samples to determine the structure of crystalline phases present in the corrosion product between the Magnox swarf and adhering grout. The recorded traces showing the assigned peaks for the individual traces can be seen in Appendix 2. Generally the reflections assigned support the observations made from the SEM/EDAX data in that the most intense reflections recorded are for brucite and the more minor reflections for magnesite (magnesium carbonate) and calcite, the latter probably indicating the
presence of grout. The broad amorphous hump noted in sample 1 (Trial 1 – 25°C) and sample 2 (Trial 2 -40°C) at the lower end of the spectrum probably indicates the presence of more grout contamination. However, the absence of any gehlenite that was detected in the SEM/EDAX data probably suggests that these samples had relatively low grout contamination. The less noisy trace recorded for sample 13 (Trial 13 - ~87°C) indicates a very well ordered material, i.e. brucite and no presence of calcite or magnesite which may be due to the higher curing temperature or just to less contamination of the corrosion product given the larger volumes of corrosion product generated. Overall, it is considered that the differences observed between the traces recorded are not necessarily due to changes in cure temperature but are due to difficulties associated with the scraping of the metal surface to remove just corrosion product for the less corroded samples.

Little chemical interaction was observed between the Magnox corrosion product and the cement phases as the phases detected were largely either brucite or magnesite from the corrosion product or C-S-H phases or calcite from the grout. There was evidence that a small amount of the magnesium had combined with cement through the presence of hydrotalcite.

The TGA profiles recorded can be seen in Appendix 3 and were used solely to estimate the free (evaporable) water and bound (non-evaporable) water contents of the grout samples taken. The free water content was taken to be approximated by the weight loss experienced at 105°C. The bound water content was taken to be approximated by the weight loss experienced between 105 and 300°C and is generally considered to correspond to water loss from amorphous hydrated calcium-silicate-hydrate (CSH) gel that is formed during cement hardening from the reaction between water and tricalcium silicate.

The water content values based on the TGA analysis are listed in Table 11. Whilst the absolute values of free and bound water in the samples could be debated and the relevance of the temperature ranges chosen, these results clearly show that the reduction in Magnox corrosion rate measured at the two higher curing temperatures, 75 & ~87°C, was due to these samples reaching very low or negligible free water contents. The difference in water content determined between the bulk matrix samples and those of the interface between Magnox and grout is not thought to be significant.
7. Discussion

The cemented products for these corrosion trials were prepared using the Magnox Encapsulation Plant (MEP) grout formulation. MEP procedures were simulated as closely a possible to ensure products were representative of those prepared on plant, including vibrogrouting to ensure good infilling of the Magnox swarf. A 3-litre cemented product prepared and subsequently sliced confirmed that no visible voidage was present and provided confidence that the infilling technique had produced well-infiltrated products for subsequent corrosion monitoring. This is confirmed by the:

- corrosion data that are similar to other well infilled corrosion rates\(^6\) rather than the higher rates experienced by poorly infilled samples.
- later coring and analysis of the samples confirming good infilling.
- Grout fluidities measured exceed 200 mm Colflow that is considered in the MEP Product Parameters report to be the minimum flow required for MEP to produce an acceptable product.

Therefore, these samples can be taken to be a close representation of those produced by MEP.

Chronic corrosion rates of Magnox encapsulated in BFS/OPC grout have been successfully determined over a range of curing temperatures using the gas pressure transducer technique and hydrogen gas sensors to monitor changes in hydrogen gas evolution. The data has shown that up to 200 days of curing time at 25°C is required to allow the initial acute corrosion rates to approach a steady corrosion rate.

As expected, once the initial acute corrosion phase had passed, there were rapid rises in Magnox corrosion rates in response to the curing temperatures being increased. Over the short-term, the highest peak corrosion rates approached 3000 µm/yr at curing temperatures above 60°C, but these steadily declined to be comparable to the rates measured at lower temperatures. At lower temperatures consistent corrosion rates were measured over the lifetime of the trials that approached 900 days cure. Comparison of the corrosion rate data with historic data\(^6\) as shown in Figure 23, suggest strongly that the corrosion rates derived in this study are typical of those associated with encapsulated Magnox swarf and confirms that the experiments are closely representative of Magnox swarf behaviour in grout.

Thermogravimetric analyses on selected top hat samples indicates that the samples monitored at high temperatures, 75°C and above, had effectively dried out during corrosion monitoring. This was despite repeated capture and return of liquor loss back to the cemented products during the gas sensor trials.

The load cell expansion trials have indicated that typically at 1.2 – 2.6 MPa longitudinal force structural degradation starts to develop as the tensile strength of cement grout is approached. The relationship between longitudinal expansive force and Wt% Magnox corrosion appears to follow a two stage development process where the initial higher rate of increase in longitudinal force is followed by a lower rate that is seen to be maintained until finally the restrained products suffer significant degradation. After this, any force generated by corrosion can be applied in other unconstrained directions rather than to the load cell. In a wasteform that is completely constrained by the container this cannot occur unless there is some voidage available for the fractured wasteform to expand into. It is likely that in the fully constrained case the earlier rates of force generation would continue. However if there is voidage available for expansion to occur after fracture then the force generated is likely to be very small until the voidage is filled. At this point the force generated will revert to the initial higher levels. The expansive force generation rate of 0.14-0.47 MPa/Wt% corrosion is suggested as a pessimistic value of expansive force to use in modelling applications to test effects of corrosion product expansion on wasteforms.
It is understood that typical storage temperatures within the Encapsulation Stores, EPS1 and ESP2, at Sellafield are seasonal and range between 10 and 30°C; with vault extract temperatures controlled to be less than 35°C in EPS1 and less than 30°C in ESP2. For the purpose of calculating storage times before product starts to fracture, a storage temperature of 25°C was taken. The data presented in Table 10 show that for assumed tensile strengths of the matrix grout ranging between 2 and 4MPa and a range of corrosion rates, the MEP type product could be stored for between about 30 to 5800 years before a product started to fracture. A typical estimate, assuming the matrix grout has a tensile strength of 3MPa and the Magnox corrodes at an average rate of 2.62 x10⁻² Wt% per year would be about 350 years.

The deformation of the top hat vessels caused by Magnox corrosion, particularly noticeable for those trials cured at 75°C and above, are estimated to approach 20mm at the base of the vessel. Measurement of vessel deformations experienced during these trials may be useful in validating any expansion models.

The observation of expansion of the 16-litre samples is not necessarily inconsistent with the absence of measurable expansion in the 3-litre expansion samples. The expansion samples were three litres in volume and the degree of corrosion at the end of the experiment was only half as much or less than the 16 litre samples. This would give a much smaller volume change that would be on the limit of detection.

The characterisation of the Magnox grout interface suggests that the main phases formed in the grout in all samples were calcium silicate hydrate and portlandite with minor quantities of gehlenite present in the BFS. As expected, the composition of the corrosion layer was mainly magnesium hydroxide, and it was difficult to identify any other phases such as magnesium silicate material. The effect of curing temperature did not appear to have any effect on elemental composition of either the Magnox metal, corrosion layer or grout. There was little chemical reaction between the grout and the corrosion product. However, in some samples the concentration of magnesium in the grout decreased with distance from the corrosion layer and this suggests that a migration of magnesium ions into the bulk of the grout is associated with some dissolution of magnesium ions from the parent metal and from the corrosion product.
8. CONCLUSIONS

- Acute and chronic corrosion rates have been determined for Magnox swarf encapsulated in BFS/OPC grout at curing temperatures of 25, 40, 60, 75, and up to 90°C. The data has shown that up to 200 days cure at 25°C is required for the initial acute corrosion phase to decline to provide measurement of steadier longer term chronic corrosion rates.

- Characterisation of the samples has provided confidence that the swarf was well infilled during the grouting process and given that the preparation of the products closely reflected that carried out in MEP, the samples are considered to be closely representative of Magnox swarf encapsulated by MEP.

- The chronic rate of Magnox corrosion over the temperatures examined has proved to be compatible with Magnox corrosion datasets obtained from other sources of information and again this indicates that these data are representative of Magnox swarf behaviour in grout.

- The load cell expansive trials indicate that structural product degradation starts to develop as the tensile strength of the grout, typically 1.2 – 2.6 MPa is approached.

- An expansive force generation rate of 0.14 – 0.47 MPa/Wt% corrosion could be taken as a range of expansive force values in modelling of the effects of corrosion product expansion on wasteforms.

- An estimate of the time taken for a typical MEP product to fracture due to the corrosion solely of Magnox is about 350 years for storage at 25°C.

- Depending on assumptions about the rate of corrosion, the tensile strength of the grout and the expansive forces generated as a result of corrosion, the extent of the product cracking could range between about 30 and 5800 years.

- No expansion above the limit of detection of about 1mm, as measured with a micrometer was measured in the three litre samples.

- The deformation of the restraining vessel caused by Magnox corrosion at curing temperatures of 75°C or above may be useful in validating expansion models.

- The main phases formed in the grout during curing are calcium silicate hydrate and portlandite with minor quantities of gehlenite. The main component of the corrosion product is brucite. The effect of curing temperature did not affect the composition of either the Magnox metal, corrosion product or grout.
References


2. Calculated data based on dimensions and weights from Data Manual – FEDO Memo 84/1235.


5. Preparation, Dimensions and Mechanical Properties of Simulated Cemented ILW Sample Packages Prepared for the JGC Corporation and the TOYO Corporation of Japan. RDR 670, I. H. Godfrey and E. Miller.

Table 1: Experimental array of trials

<table>
<thead>
<tr>
<th>Trial</th>
<th>Magnox Type</th>
<th>Target Temperature/°C After Initial Curing Period @ 25°C.</th>
<th>Corrosion Monitoring Technique</th>
<th>Top Hat Internal Volume / Litre</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Swarf</td>
<td>25</td>
<td>Pressure</td>
<td>16.6</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Swarf</td>
<td>25</td>
<td>Pressure</td>
<td>16.6</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Swarf</td>
<td>25</td>
<td>Pressure</td>
<td>16.6</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Swarf</td>
<td>40</td>
<td>Pressure</td>
<td>16.6</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Swarf</td>
<td>40</td>
<td>Pressure</td>
<td>16.6</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Swarf</td>
<td>40</td>
<td>Pressure</td>
<td>16.6</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Swarf</td>
<td>60</td>
<td>Pressure</td>
<td>16.6</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Swarf</td>
<td>60</td>
<td>Pressure</td>
<td>16.6</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Swarf</td>
<td>60</td>
<td>Pressure</td>
<td>16.6</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Swarf</td>
<td>75</td>
<td>Pressure</td>
<td>16.6</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Swarf</td>
<td>75</td>
<td>Pressure</td>
<td>16.6</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Swarf</td>
<td>75</td>
<td>Pressure</td>
<td>16.6</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Swarf</td>
<td>83 – 90</td>
<td>Gas flow</td>
<td>16.6</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Swarf</td>
<td>83 – 90</td>
<td>Gas flow</td>
<td>16.6</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Swarf</td>
<td>83 – 90</td>
<td>Gas flow</td>
<td>16.6</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Coupon</td>
<td>25</td>
<td>CEION probe</td>
<td>25</td>
<td>2 probes</td>
</tr>
<tr>
<td>17</td>
<td>Coupon</td>
<td>83-90</td>
<td>CEION probe</td>
<td>25</td>
<td>2 probes</td>
</tr>
<tr>
<td>18</td>
<td>Swarf</td>
<td>60 then either 40 or 75</td>
<td>Pressure</td>
<td>12.7</td>
<td>Dimensional change, L&amp;C*</td>
</tr>
<tr>
<td>19</td>
<td>Swarf</td>
<td>60 then either 40 or 75</td>
<td>Pressure</td>
<td>12.7</td>
<td>Dimensional change, L&amp;C*</td>
</tr>
<tr>
<td>20</td>
<td>Swarf</td>
<td>60 then either 40 or 75</td>
<td>Pressure</td>
<td>12.7</td>
<td>Dimensional change, L&amp;C*</td>
</tr>
<tr>
<td>21</td>
<td>Swarf</td>
<td>60 then either 40 or 75</td>
<td>Pressure</td>
<td>12.7</td>
<td>Dimensional change, L&amp;C*</td>
</tr>
<tr>
<td>22</td>
<td>Swarf</td>
<td>60 then either 40 or 75</td>
<td>Pressure</td>
<td>12.7</td>
<td>Dimensional change, L&amp;C*</td>
</tr>
<tr>
<td>23</td>
<td>Swarf</td>
<td>60 then either 40 or 75</td>
<td>Pressure</td>
<td>12.7</td>
<td>Dimensional change, L&amp;C*</td>
</tr>
<tr>
<td>24</td>
<td>Swarf</td>
<td>60 then either 40 or 75</td>
<td>Pressure</td>
<td>19</td>
<td>Load cells L&amp;C*</td>
</tr>
<tr>
<td>25</td>
<td>Swarf</td>
<td>60 then either 40 or 75</td>
<td>Pressure</td>
<td>19</td>
<td>Load cells L&amp;C*</td>
</tr>
<tr>
<td>26</td>
<td>Swarf</td>
<td>60 then either 40 or 75</td>
<td>Pressure</td>
<td>19</td>
<td>Load cells L&amp;C*</td>
</tr>
<tr>
<td>27</td>
<td>Swarf</td>
<td>60 then either 40 or 75</td>
<td>Pressure</td>
<td>19</td>
<td>Load cells L&amp;C*</td>
</tr>
<tr>
<td>28</td>
<td>Swarf</td>
<td>60 then either 40 or 75</td>
<td>Pressure</td>
<td>19</td>
<td>Load cells L&amp;C*</td>
</tr>
<tr>
<td>29</td>
<td>Swarf</td>
<td>60 then either 40 or 75</td>
<td>Pressure</td>
<td>19</td>
<td>Load cells L&amp;C*</td>
</tr>
<tr>
<td>30</td>
<td>Swarf</td>
<td>Ambient</td>
<td></td>
<td>3 litre sample for examination of product quality.</td>
<td></td>
</tr>
</tbody>
</table>

* L = Longitudinally, C = Circumferential
### Table 2: Example of Magnox corrosion spreadsheet

<table>
<thead>
<tr>
<th>Col 1</th>
<th>Col 2</th>
<th>Col 3</th>
<th>Col 4</th>
<th>Col 5</th>
<th>Col 6</th>
<th>Col 7</th>
<th>Col 8</th>
<th>Col 9</th>
<th>Col 10</th>
<th>Col 11</th>
<th>Col 12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Age / Days</td>
<td>Pressure bar.a</td>
<td>Temp °C</td>
<td>Vapour Pressure bar.a</td>
<td>Corrected Pressure atm</td>
<td>No of H2 Moles</td>
<td>H2 evolved per cycle</td>
<td>Cumulative Moles H2 evolved</td>
<td>Mx Corroded g</td>
<td>g Mx/day</td>
<td>mg Mx/day/m²</td>
<td>um/yr</td>
</tr>
<tr>
<td>Row 1</td>
<td>0.04</td>
<td>1.0554</td>
<td>32.7</td>
<td>0.0494</td>
<td>0.9928</td>
<td>0.0459</td>
<td>0.0023</td>
<td>0.0023</td>
<td>0.055</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Row 2</td>
<td>0.08</td>
<td>1.1208</td>
<td>34.0</td>
<td>0.0531</td>
<td>1.0538</td>
<td>0.0485</td>
<td>0.0026</td>
<td>0.0049</td>
<td>0.119</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Row 3</td>
<td>0.13</td>
<td>1.1826</td>
<td>34.4</td>
<td>0.0545</td>
<td>1.1133</td>
<td>0.0511</td>
<td>0.0053</td>
<td>0.0075</td>
<td>0.183</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Row 4</td>
<td>0.17</td>
<td>1.2272</td>
<td>34.3</td>
<td>0.0542</td>
<td>1.1576</td>
<td>0.0532</td>
<td>0.0073</td>
<td>0.0096</td>
<td>0.233</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Row 5</td>
<td>0.21</td>
<td>1.2659</td>
<td>34.3</td>
<td>0.0542</td>
<td>1.1959</td>
<td>0.0550</td>
<td>0.0091</td>
<td>0.0114</td>
<td>0.276</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Row 6</td>
<td>0.25</td>
<td>1.0610</td>
<td>34.1</td>
<td>0.0534</td>
<td>0.9944</td>
<td>0.0457</td>
<td>0.0008</td>
<td>0.0121</td>
<td>0.295</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Row 7</td>
<td>0.29</td>
<td>1.0914</td>
<td>33.8</td>
<td>0.0527</td>
<td>1.0251</td>
<td>0.0472</td>
<td>0.0014</td>
<td>0.0136</td>
<td>0.330</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Row 8</td>
<td>0.33</td>
<td>1.1176</td>
<td>33.5</td>
<td>0.0518</td>
<td>1.0518</td>
<td>0.0485</td>
<td>0.0027</td>
<td>0.0141</td>
<td>0.342</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Row 9</td>
<td>0.38</td>
<td>1.1412</td>
<td>33.3</td>
<td>0.0512</td>
<td>1.0757</td>
<td>0.0496</td>
<td>0.0039</td>
<td>0.0152</td>
<td>0.370</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Row 10</td>
<td>0.42</td>
<td>1.1610</td>
<td>33.1</td>
<td>0.0505</td>
<td>1.0960</td>
<td>0.0506</td>
<td>0.0048</td>
<td>0.0162</td>
<td>0.394</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Row 11</td>
<td>0.46</td>
<td>1.1806</td>
<td>32.8</td>
<td>0.0498</td>
<td>1.1159</td>
<td>0.0515</td>
<td>0.0058</td>
<td>0.0172</td>
<td>0.417</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Row 12</td>
<td>0.50</td>
<td>1.1974</td>
<td>32.6</td>
<td>0.0491</td>
<td>1.1332</td>
<td>0.0524</td>
<td>0.0066</td>
<td>0.0180</td>
<td>0.437</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Row 13</td>
<td>0.54</td>
<td>1.2120</td>
<td>32.4</td>
<td>0.0485</td>
<td>1.1482</td>
<td>0.0531</td>
<td>0.0074</td>
<td>0.0187</td>
<td>0.455</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Row 14</td>
<td>0.58</td>
<td>1.2271</td>
<td>32.1</td>
<td>0.0479</td>
<td>1.1638</td>
<td>0.0539</td>
<td>0.0081</td>
<td>0.0195</td>
<td>0.474</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Row 15</td>
<td>0.63</td>
<td>1.2385</td>
<td>31.9</td>
<td>0.0473</td>
<td>1.1756</td>
<td>0.0544</td>
<td>0.0087</td>
<td>0.0201</td>
<td>0.488</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Row 16</td>
<td>0.67</td>
<td>1.2513</td>
<td>31.7</td>
<td>0.0466</td>
<td>1.1888</td>
<td>0.0551</td>
<td>0.0094</td>
<td>0.0207</td>
<td>0.504</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Row 17</td>
<td>0.71</td>
<td>1.2615</td>
<td>31.5</td>
<td>0.0462</td>
<td>1.1993</td>
<td>0.0556</td>
<td>0.0099</td>
<td>0.0212</td>
<td>0.516</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Row 18</td>
<td>0.75</td>
<td>1.2723</td>
<td>31.3</td>
<td>0.0457</td>
<td>1.2105</td>
<td>0.0562</td>
<td>0.0104</td>
<td>0.0218</td>
<td>0.530</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Row 19</td>
<td>0.79</td>
<td>1.2825</td>
<td>31.1</td>
<td>0.0452</td>
<td>1.2210</td>
<td>0.0567</td>
<td>0.0110</td>
<td>0.0223</td>
<td>0.542</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Row 20</td>
<td>0.83</td>
<td>1.2907</td>
<td>31.0</td>
<td>0.0449</td>
<td>1.2295</td>
<td>0.0571</td>
<td>0.0114</td>
<td>0.0227</td>
<td>0.553</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Row 21</td>
<td>0.88</td>
<td>1.3008</td>
<td>30.8</td>
<td>0.0445</td>
<td>1.2399</td>
<td>0.0576</td>
<td>0.0119</td>
<td>0.0233</td>
<td>0.565</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Row 22</td>
<td>0.92</td>
<td>1.3079</td>
<td>30.7</td>
<td>0.0441</td>
<td>1.2472</td>
<td>0.0580</td>
<td>0.0123</td>
<td>0.0236</td>
<td>0.574</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Row 23</td>
<td>0.96</td>
<td>1.0583</td>
<td>30.3</td>
<td>0.0433</td>
<td>1.0017</td>
<td>0.0466</td>
<td>0.0002</td>
<td>0.0238</td>
<td>0.578</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Row 24</td>
<td>1.00</td>
<td>1.0707</td>
<td>30.1</td>
<td>0.0428</td>
<td>1.0144</td>
<td>0.0473</td>
<td>0.0066</td>
<td>0.02442</td>
<td>0.593</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Row 25</td>
<td>1.04</td>
<td>1.0800</td>
<td>30.0</td>
<td>0.0424</td>
<td>1.0241</td>
<td>0.0477</td>
<td>0.0011</td>
<td>0.02490</td>
<td>0.605</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Notes:**
- **Col 1:** Cure Time / Days
- **Col 2:** Recorded Pressure
- **Col 3:** Recorded Temperature
- **Col 4:** Water vapour pressure calculated at recorded temperature (Col 2)
- **Col 5:** Moles hydrogen gas from n=PV/RT (T = Col 2+273.1)
- **Col 6:** Gas Const @ Mass Mx /g
- **Col 7:** Cumulative Moles H2 evolved = linked summations of Col 6
- **Col 8:** Column *24.3
- **Col 9:** 1st Corrosion rate calculated = (Col 9, Row 25 - Col 9, Row 1)/(Col 1, Row 25 - Col 1, Row 1)
- **Col 11:** Col 10*4200*1000
- **Col 12:** Col 11/1000*210 (g/m²/day = 210 μm/yr)
**Table 3: Chloride levels measured in grout powders**

<table>
<thead>
<tr>
<th>Powder</th>
<th>Total chloride level, Wt%</th>
<th>Time Period years over which levels were recorded</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min</td>
<td>Max</td>
<td>Mean</td>
</tr>
<tr>
<td>OPC</td>
<td>0.015</td>
<td>0.05</td>
</tr>
<tr>
<td>BFS</td>
<td>0.020</td>
<td>0.020</td>
</tr>
<tr>
<td>MEP Wastwater Supply</td>
<td>Typically 6 ppm (0.0006 wt%)</td>
<td></td>
</tr>
</tbody>
</table>
Table 4: Infill and product quality data for trials 1 to 12 (Large top hats)

<table>
<thead>
<tr>
<th>Trial</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target Temperature /°C</td>
<td>25</td>
<td>40</td>
<td>60</td>
<td>75</td>
<td>25</td>
<td>40</td>
<td>60</td>
<td>75</td>
<td>25</td>
<td>40</td>
<td>60</td>
<td>75</td>
</tr>
<tr>
<td>Magnox swarf / kg</td>
<td>4.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Residual water /kg:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Swarf water /kg</td>
<td>0.24</td>
<td>0.24</td>
<td>0.33</td>
<td>0.30</td>
<td>0.27</td>
<td>0.28</td>
<td>0.28</td>
<td>0.34</td>
<td>0.30</td>
<td>0.35</td>
<td>0.28</td>
<td>0.24</td>
</tr>
<tr>
<td>Heel water /kg</td>
<td>0.28</td>
<td>0.15</td>
<td>0.04</td>
<td>0.03</td>
<td>0.08</td>
<td>0.12</td>
<td>0.11</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0.06</td>
<td>0.07</td>
</tr>
<tr>
<td>Grout added / kg</td>
<td>23.4</td>
<td>23.8</td>
<td>24.0</td>
<td>24.1</td>
<td>24.2</td>
<td>24.0</td>
<td>23.8</td>
<td>24.2</td>
<td>23.0</td>
<td>23.4</td>
<td>24.3</td>
<td>22.9</td>
</tr>
<tr>
<td>Grout added / litres</td>
<td>12.0</td>
<td>12.2</td>
<td>12.3</td>
<td>12.4</td>
<td>12.2</td>
<td>12.1</td>
<td>12.0</td>
<td>12.2</td>
<td>11.9</td>
<td>12.1</td>
<td>12.6</td>
<td>11.9</td>
</tr>
<tr>
<td>Grout fluidity/ mm</td>
<td>380</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Final Wt% Magnox Corroded.</td>
<td>0.26</td>
<td>0.69</td>
<td>1.9</td>
<td>20.5</td>
<td>0.12</td>
<td>0.42</td>
<td>5.9</td>
<td>30.8</td>
<td>0.13</td>
<td>0.39</td>
<td>2.6</td>
<td>10.3</td>
</tr>
<tr>
<td>Description of product surface at end of trial.</td>
<td>Product surface slight damp</td>
<td>Intact</td>
<td>Intact</td>
<td>Friable surface distortion to top hat</td>
<td>Product surface slight damp</td>
<td>Intact</td>
<td>Intact</td>
<td>Friable surface distortion to top hat</td>
<td>Product surface slight damp</td>
<td>Intact</td>
<td>Intact</td>
<td>Friable surface distortion to top hat</td>
</tr>
</tbody>
</table>
### Table 5: Infill data for trials 13 to 15 (hydrogen gas sensor trials)

<table>
<thead>
<tr>
<th></th>
<th>Trial</th>
<th>13</th>
<th>14</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Target Temperature, °C</strong></td>
<td></td>
<td></td>
<td></td>
<td>25 then 83 – 90</td>
</tr>
<tr>
<td><strong>Magnox swarf / kg</strong></td>
<td></td>
<td></td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td><strong>Residual water / kg:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Swarf water</td>
<td>0.15</td>
<td>0.13</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>Heel water</td>
<td>0.10</td>
<td>0.19</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td><strong>Grout added, kg</strong></td>
<td>24.6</td>
<td>24.4</td>
<td>24.6</td>
<td></td>
</tr>
<tr>
<td><strong>Grout added, litres</strong></td>
<td>12.6</td>
<td>12.5</td>
<td>12.7</td>
<td></td>
</tr>
<tr>
<td><strong>Grout fluidity, mm</strong></td>
<td></td>
<td></td>
<td>590</td>
<td></td>
</tr>
<tr>
<td><strong>Final Wt% Magnox Corroded.</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Description of product surface at end of trial.</strong></td>
<td>All top hats had noticeable distortion to base and wall</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trial</td>
<td>18</td>
<td>19</td>
<td>20</td>
<td>21</td>
</tr>
<tr>
<td>-------</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Target temperature after initial 25°C cure, °C</td>
<td>60°C</td>
<td>60°C</td>
<td>60°C</td>
<td>60°C</td>
</tr>
<tr>
<td>then</td>
<td>then</td>
<td>then</td>
<td>then</td>
<td>then</td>
</tr>
<tr>
<td>75°C</td>
<td>75°C</td>
<td>75°C</td>
<td>75°C</td>
<td>75°C</td>
</tr>
<tr>
<td>Magnox swarf, kg</td>
<td>0.82</td>
<td>0.82</td>
<td>0.82</td>
<td>0.82</td>
</tr>
<tr>
<td>Residual water (total), kg</td>
<td>0.095</td>
<td>0.095</td>
<td>0.085</td>
<td>0.110</td>
</tr>
<tr>
<td>Grout fluidity, mm</td>
<td>520</td>
<td>520</td>
<td>520</td>
<td>520</td>
</tr>
<tr>
<td>Properties of the cemented product before curing:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density, kg/m³:</td>
<td>1.909</td>
<td>1.928</td>
<td>1.916</td>
<td>1.929</td>
</tr>
<tr>
<td>Dimensions, mm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Height (avg):</td>
<td>152.0</td>
<td>153.2</td>
<td>152.7</td>
<td>152.5</td>
</tr>
<tr>
<td>Diameter:</td>
<td>165.4</td>
<td>165.4</td>
<td>165.4</td>
<td>165.9</td>
</tr>
<tr>
<td>Properties of the cemented product at end of initial curing at 25°C:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density, kg/m³:</td>
<td>1.910</td>
<td>1.924</td>
<td>1.910</td>
<td>1.872</td>
</tr>
<tr>
<td>Dimensions, mm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Height (avg):</td>
<td>154.1</td>
<td>153.7</td>
<td>152.4</td>
<td>154.5</td>
</tr>
<tr>
<td>Diameter:</td>
<td>164.7</td>
<td>165.1</td>
<td>165.2</td>
<td>165.9</td>
</tr>
<tr>
<td>Properties of the cemented product after curing at 60°C:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Days Curing:</td>
<td>550</td>
<td>500</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>Mass, kg:</td>
<td>5.997</td>
<td>6.005</td>
<td>5.991</td>
<td>6.050</td>
</tr>
<tr>
<td>Final Wt% Magnox Corroded:</td>
<td>7.2</td>
<td>7.4</td>
<td>10.7</td>
<td>2.6</td>
</tr>
<tr>
<td>Description of product surface at end of trial.</td>
<td>Several cracks but remained intact</td>
<td>Several cracks but remained intact</td>
<td>Crumbled upon retrieval</td>
<td>Several cracks but remained intact</td>
</tr>
<tr>
<td>Trial</td>
<td>24</td>
<td>25</td>
<td>26</td>
<td>27</td>
</tr>
<tr>
<td>-------</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Target temperature after initial 25°C cure, °C</td>
<td>60°C</td>
<td>60°C</td>
<td>60°C</td>
<td>60°C</td>
</tr>
<tr>
<td>Magnox swarf, kg</td>
<td>0.82</td>
<td>0.82</td>
<td>0.82</td>
<td>0.82</td>
</tr>
<tr>
<td>Residual water (total), kg</td>
<td>0.095</td>
<td>0.095</td>
<td>0.085</td>
<td>0.110</td>
</tr>
<tr>
<td>Grout fluidity, mm</td>
<td>520</td>
<td>520</td>
<td>520</td>
<td>520</td>
</tr>
<tr>
<td>Properties of the cemented product before curing:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density, kg/m³</td>
<td>1.911</td>
<td>1.860</td>
<td>1.919</td>
<td>1.923</td>
</tr>
<tr>
<td>Dimensions, mm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Height (avg):</td>
<td>155.3</td>
<td>154.9</td>
<td>152.7</td>
<td>158.5</td>
</tr>
<tr>
<td>Diameter:</td>
<td>165.4</td>
<td>165.4</td>
<td>165.4</td>
<td>165.9</td>
</tr>
<tr>
<td>Final Wt% Magnox Corroded.</td>
<td>4.9</td>
<td>21.7</td>
<td>22.8</td>
<td>33.4</td>
</tr>
<tr>
<td>Description of product surface at end of trial.</td>
<td>Few cracks remained intact</td>
<td>Intact but very fragile</td>
<td>Intact but very fragile</td>
<td>Crumbled upon retrieval</td>
</tr>
</tbody>
</table>

Table 7: Infill and PQ data for trial 24 to 29 (load cell trials)
### Table 8: Corrosion rates measured for Trials 1 to 12 (gas pressure trials)

<table>
<thead>
<tr>
<th>Trial (Elevated cure temperature)</th>
<th>Chronic Magnox corrosion rate at 25°C prior to elevation in cure temperature, where applicable, (µm/yr). Mean rate ± σ</th>
<th>Chronic Magnox corrosion, (µm/yr) Mean rate ± σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trial 1 (25°C)</td>
<td>0.59 ± 0.17</td>
<td>0.50 ± 0.11</td>
</tr>
<tr>
<td>Trial 5 (25°C)</td>
<td>0.28 ± 0.03</td>
<td>0.22 ± 0.06</td>
</tr>
<tr>
<td>Trial 9 (25°C)</td>
<td>0.32 ± 0.04</td>
<td>0.21 ± 0.05</td>
</tr>
<tr>
<td>Trial 2 (40°C)</td>
<td>0.40 ± 0.07</td>
<td>1.6 ± 0.4</td>
</tr>
<tr>
<td>Trial 6 (40°C)</td>
<td>0.29 ± 0.07</td>
<td>1.2 ± 0.1</td>
</tr>
<tr>
<td>Trial 10 (40°C)</td>
<td>0.19 ± 0.03</td>
<td>0.80 ± 0.05</td>
</tr>
<tr>
<td>Trial 3 (60°C)</td>
<td>0.32 ± 0.04</td>
<td>Temperature went above 100°C</td>
</tr>
<tr>
<td>Trial 7 (60°C)</td>
<td>0.19 ± 0.03</td>
<td>28 ± 1</td>
</tr>
<tr>
<td>Trial 11 (60°C)</td>
<td>0.58 ± 0.06</td>
<td>7 ± 1</td>
</tr>
<tr>
<td>Trial 4 (75°C)</td>
<td>0.24 ± 0.10</td>
<td>31 ± 2</td>
</tr>
<tr>
<td>Trial 8 (75°C)</td>
<td>0.21 ± 0.08</td>
<td>50 ± 12</td>
</tr>
<tr>
<td>Trial 12 (75°C)</td>
<td>0.42 ± 0.11</td>
<td>134 ± 2</td>
</tr>
</tbody>
</table>
### Table 9: Magnox Wt% corroded

<table>
<thead>
<tr>
<th>Trial (Elevated cure temperature)</th>
<th>Magnox corroded at end of trial, Wt%.</th>
<th>External dimensions of top hat vessel, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Expansion measured at base of top hat (maximum)</td>
</tr>
<tr>
<td>Trial 1 (25°C)</td>
<td>0.26</td>
<td>Zero</td>
</tr>
<tr>
<td>Trial 5 (25°C)</td>
<td>0.12</td>
<td>Zero</td>
</tr>
<tr>
<td>Trial 9 (25°C)</td>
<td>0.13</td>
<td>Zero</td>
</tr>
<tr>
<td>Trial 2 (40°C)</td>
<td>0.69</td>
<td>Zero</td>
</tr>
<tr>
<td>Trial 6 (40°C)</td>
<td>0.42</td>
<td>Zero</td>
</tr>
<tr>
<td>Trial 10 (40°C)</td>
<td>0.39</td>
<td>Zero</td>
</tr>
<tr>
<td>Trial 3 (60°C)</td>
<td>1.9</td>
<td>Zero</td>
</tr>
<tr>
<td>Trial 7 (60°C)</td>
<td>5.9</td>
<td>Zero</td>
</tr>
<tr>
<td>Trial 11 (60°C)</td>
<td>2.6</td>
<td>Zero</td>
</tr>
<tr>
<td>Trial 4 (75°C)</td>
<td>20.5</td>
<td>12</td>
</tr>
<tr>
<td>Trial 8 (75°C)</td>
<td>30.8</td>
<td>8</td>
</tr>
<tr>
<td>Trial 12 (75°C)</td>
<td>10.3</td>
<td>22</td>
</tr>
<tr>
<td>Trial 13 (~87°C) max</td>
<td>28.2</td>
<td>10</td>
</tr>
<tr>
<td>Trial 14 (~87°C max)</td>
<td>14.7</td>
<td>10</td>
</tr>
<tr>
<td>Trial 15 (~87°C max)</td>
<td>21.8</td>
<td>12</td>
</tr>
</tbody>
</table>

* Measured circumference of new top hats: 860 – 865mm.
Table 10: Product storage times (in years) before product fracture.

Storage temperature, 25°C

<table>
<thead>
<tr>
<th>Assumed Tensile Grout Strength</th>
<th>Upper Bound Expansion Force (0.47 MPa/Wt%)</th>
<th>Typical Case Expansion Force (0.33 MPa/Wt%)</th>
<th>Lower Bound Expansion Force (0.14 MPa/Wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lower Avg Upper</td>
<td>Lower Avg Upper</td>
<td>Lower Avg Upper</td>
<td></td>
</tr>
<tr>
<td>2 MPa</td>
<td>872 162 30</td>
<td>1242 231 43</td>
<td>2927 545 102</td>
</tr>
<tr>
<td>3 MPa</td>
<td>1308 244 45</td>
<td>1863 347 65</td>
<td>4390 818 152</td>
</tr>
<tr>
<td>4 MPa</td>
<td>1744 325 61</td>
<td>2483 463 86</td>
<td>5854 1091 203</td>
</tr>
<tr>
<td>Trial</td>
<td>Curing Temperature</td>
<td>Sample Location</td>
<td>Evaporable Water, Wt%</td>
</tr>
<tr>
<td>-------</td>
<td>-------------------</td>
<td>----------------</td>
<td>-----------------------</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>Interface</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>Bulk</td>
<td>9</td>
</tr>
<tr>
<td>10</td>
<td>40</td>
<td>Interface</td>
<td>9</td>
</tr>
<tr>
<td>10</td>
<td>40</td>
<td>Bulk</td>
<td>7</td>
</tr>
<tr>
<td>11</td>
<td>60</td>
<td>Interface</td>
<td>5</td>
</tr>
<tr>
<td>11</td>
<td>60</td>
<td>Bulk</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>75</td>
<td>Interface</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>75</td>
<td>Bulk</td>
<td>1</td>
</tr>
<tr>
<td>15</td>
<td>~87</td>
<td>Interface</td>
<td>3</td>
</tr>
<tr>
<td>15</td>
<td>~87</td>
<td>Bulk</td>
<td>1</td>
</tr>
</tbody>
</table>
Figure 1: Large top hat containing Magnox swarf prepared for grouting

Figure 2: Corrosion trial in progress
Figure 3: 3-litre mould containing Magnox swarf

Figure 4: Top hat fitted with CEION™ probes
Figure 5: Load cell assembly containing Magnox cemented sample

Figure 6: Trail 30: 3-litre sliced sample maintained at ambient temperature
Figure 7: Typical core sample (Trial 2)
Trials 1, 5 & 9
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature maintained at 25°C

Figure 8: Corrosion rate with temperature maintained at 25°C
Trials 2, 6 & 10

Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout

Temperature increased from 25°C to 40°C

Figure 9: Corrosion rate with temperature maintained at 40°C
Trials 3, 7 & 11
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature increased from 25°C to 60°C

Figure 10: Corrosion rate with temperature maintained at 60°C
Trials 4, 8 & 12
Corrosion of Magnox Swarf in 3:1 BFS/OPC, W/S 0.35 Grout
Temperature increased from 25°C to 75°C

Figure 11: Corrosion rate with temperature maintained at 75°C
Figure 12: Large top hat corrosion trials (Trials 1 - 12). Magnox corroded, Wt% against time
Figure 13: Top hat trial 5 (25°C cure)

Figure 14: Top hat trial 10 (40°C cure)
Figure 15: Top hat trial 3 (60°C cure)

Figure 16: Top hat trial 8 (75°C cure)
Figure 17: Top hat trial 12 (75°C cure)
Figure 18: Photographs of some top hats cured at temperatures 75 °C and >83 °C
Figure 19: Base of top hat - trial 13

Figure 20: Wall of top hat - trial 13
Figure 21: Trails 13, 14 and 15 Gas sensor trials. Corrosion rate against time.
Trials 13, 14 and 15
Gas Sensor Trials
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature increased from 25°C to 60°C then ~87°C

Temperature increased from 60°C to ~87°C

Temperature increased from 25°C to 60°C

Figure 22: Trials 13, 14 and 15 Gas sensor trials. Magnox corroded, Wt% against time
**Arrhenius Relationship between Magnox Corrosion in grout and temperature**

Ln Corrosion rate (µm/year) = -14748x + 47.273 [This report]

Ln Corrosion rate (µm/year) = -13362x + 27.489 [All Magnox Swarf/fin data including data from this report]

![Figure 23: Arrhenius relationship between Magnox corrosion in grout and temperature](image)
Figure 24: Data from Magnox corrosion trial 16 (CEION™ probes)

Figure 25: Data from Magnox corrosion trial 17 (CEION™ probes)
Trials 18 to 23 (3 litre dimensional stability trials)
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature increased from 25°C to 60°C, then 75°C (for Trials 22 & 23)

Temperature increased to 75°C for Trials 22 & 23

All Trials increased to 60°C

Figure 26: Small top hat corrosion trials with temperature increased to 60 and 75°C
Trials 18 to 23 (3 litre dimensional stability trials)
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout

Temp increased from 60°C to 75°C (Trials 22 & 23)

Temp increased from 25°C to 60°C

Figure 27: Small top hat corrosion trials (Trials 18 - 23). Magnox corroded, Wt% against time
Figure 28: 3 Litre product, trial 22 at 2.7 Wt% Magnox corroded

Figure 29: 3 Litre product, trial 18 at 7.2 Wt% Magnox corroded
Figure 30: 3-litre product, trial 20 at 10.7 Wt% Magnox corroded

Figure 31: 3-litre product, trial 25 at 21.7 Wt% Magnox corroded
Figure 32: Small scale (Load cell) corrosion trials with temperature increased to 60°C. Magnox corrosion rate against time.
Trials 24 to 29
(3 litre products)

Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature 60°C

Figure 33: Small scale (Load cell) corrosion trials with temperature increased to 60°C. Magnox corroded, Wt% against time
Figure 34: Trial 24, Expansive force against Magnox corroded
Figure 35: Trial 25, Expansive force against Magnox corroded
Figure 36: Trial 26, expansive force against Magnox corroded
Figure 37: Trial 27, expansive force against Magnox corroded
Figure 38: Trial 28, expansive force against Magnox corroded
Figure 39: Trial 29, expansive force against Magnox corroded
Figure 40: Backscattered SEM micrograph of Trial 1 sample - 25°C
Figure 41: Backscattered SEM micrograph and EDX trial 1 sample - 25°C
Figure 42: Backscattered SEM micrograph and EDX trace trial 1 sample - 25°C
Figure 43: Backscattered SEM micrograph and EDX elemental maps trial 1 sample - 25°C
Figure 44: Backscattered SEM micrograph trial 2 sample - 40°C
Figure 45: Backscattered SEM micrograph and EDX traces trial 2 sample - 40°C
Figure 46: Backscattered SEM micrograph and EDZ trace trial 2 sample - 40°C
Figure 47: Backscattered SEM micrograph and EDX elemental maps trial 2 sample - 40°C
Figure 48: Backscattered SEM micrograph trial 7 sample - 60°C
Figure 49: Backscattered SEM micrograph and EDX traces trial 7 sample - 60°C
Figure 50: Backscattered SEM micrograph and EDX traces trial 7 sample - 60°C
Figure 51: Backscattered SEM micrograph and EDX elemental maps trial 7 sample - 60°C
Figure 52: Backscattered SEM micrograph trial 8 sample - 75°C
Figure 53: Backscattered SEM micrograph and EDX traces trial 8 sample - 75°C
Figure 54: Backscattered SEM micrograph and EDX traces trial 8 sample - 75°C
Figure 55: Backscattered SEM micrograph and EDX elemental maps trial 8 sample - 75°C
Figure 56: Backscattered SEM micrograph trial 13 sample - ~87°C
Figure 57: Backscattered SEM micrograph and EDX traces trial 13 sample - \( \sim 87^\circ C \)
Figure 58: Backscattered SEM micrograph and EDX trace trial 13 sample - ~87°C
Figure 59: Backscattered SEM micrograph and EDX elemental maps trial 13 sample - ~87°C
Figure 60: Backscattered SEM micrograph and EDX elemental line maps trial 13 sample - ~87°C
Appendix 1: Magnox corrosion graphs

Trial 1
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature 25°C

Trial 1
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature 25°C

\[ y = 2E^{-0.05x} + 0.485 \]
\[ \pm 2\sigma, \sigma = 0.11 \]
Trial 2
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature increased from 25°C to 40°C

Corrosion Rate vs Days Cure

Trial 2
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature 40°C

Corrosion Rate vs Days Cure

\[ y = -2.76E-04x + 1.78E+00 \]
\[ \pm 2\sigma, \sigma = 0.402 \]
Trial 3
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature increased from 25°C to 60°C

Temperature >100°C for ~4 days

Trial 3
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature 60°C
Trial 4
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature increased from 25°C to 75°C

![Graph showing corrosion rate and temperature over days of cure.]

Trial 4
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC. W/S 0.35 Grout
Temperature 75°C

![Graph showing corrosion rate and linear regression.]

\[ y = -7.816E-05x + 8.330E-01 \]
\[ \pm 2\sigma, \sigma = 0.56 \]
Trial 5
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature 25°C

Trial 5
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature 25°C

\[ y = -1.06E-04x + 3.00E-01 \]
\[ \pm 2\sigma, \sigma = 0.056 \]
Trial 6
Corrosion of Magnox Swarf in 3.44:1 BFS:OPC, W/S 0.35 Grout
Temperature increased from 25°C to 40°C

![Graph showing corrosion rate and temperature over days of cure.]

Trial 6
Corrosion of Magnox Swarf in 3.44:1 BFS:OPC, W/S 0.35 Grout
Temperature 40°C

![Graph showing corrosion rate and linear trend analysis.]

\[ y = -1.298E-04x + 1.30E+00 \]

\[ \pm 2\sigma, \sigma = 0.07 \]
Trial 7
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature increased from 25°C to 60°C

Trial 7
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature 60°C

\[ y = 7.57 \times 10^{-3} x + 9.30 \times 10^{-3} \]
\[ + 2\sigma, \sigma = 0.97 \]
Trial 8
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature increased from 25°C to 75°C

Trial 8
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature 75°C

\[
y = -5.43E-04x + 9.30E-01 \\
\pm 2\sigma, \sigma = 0.71
\]
Trial 9
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature 25°C

Trial 9
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature 25°C

\[ y = -6.32E+05 x + 2.69E-01 \]
\[ \pm 2\sigma, \sigma = 0.05 \]
Trial 10
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature increased from 25°C to 40°C

- Corrosion Rate - Temperature

Trial 10
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature 40°C

\[ y = -1.540E-04x + 9.28E-01 \]
\[ \pm 2\sigma, \delta = 0.05 \]
Trial 11
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature increased from 25°C to 60°C

Trial 11
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature 60°C

y = -4.72E-04x + 7.76E+00
±2σ, σ = 1.04
Trial 12
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature increased from 25°C to 75°C

Trial 12
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature 75°C

\[ y = -2.118E-03x + 2.550E+00 \pm 20, \sigma = 0.54 \]
Trial 13
Gas Sensor Trial
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature increased from 25°C to 60°C then ~87°C

![Graph showing corrosion rate and temperature over time.]

Trial 13
Gas Sensor Trial
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature increased from 25°C to 60°C then ~87°C

![Graph showing stress-strain relationship for corroded material.]

- Corrosion Rate
- Temperature

- Magnox Corroded
- Corrosion rate
**Trial 14**
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature increased from 25°C to 60°C then ~67°C

**Trial 14**
Gas Sensor Trial
Corrosion of Magnox in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature increased from 25°C to 60°C then 75°C
Trial 15
Gas Sensor Trials
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature increased from 25°C to 60°C then ~87°C

![Graph showing corrosion rate and temperature over time.]

Trial 15
Gas Sensor Trial
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature increased from 25°C to 60°C then ~87°C

![Graph showing weight percent Magnox corroded and corrosion rate over time.]

Trial 18
[3 litre product]
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature increased from 25°C to 60°C

Trial 18
[3 litre product]
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature 60°C

\[ y = 0.26x - 0.03 + 1.53 \times 10^1 \pm 2\sigma, \sigma = 4.4 \]
Trial 19 [3 litre product]
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature increased from 25°C to 60°C

Trial 19 [3 litre product]
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature 60°C

\[ y = 3.410 \times 10^{-5} x + 1.883 \times 10^{1} \pm 20, \sigma = 2.2 \]
Trial 20
[3 litre product]
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature increased from 25°C to 60°C then 75°C

Trial 20
[3 litre product]
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature 60°C

\[ y = 4.28E-04x + 1.68E+01 \pm 2\sigma, \sigma = 3.8 \]
Trial 21
[3 litre product]
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature increased from 25°C to 60°C

Trial 21
[3 litre product]
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature 60°C

\[ y = 6.213 \times 10^{-3}x + 8.300 \times 10^{-1} \pm 2\sigma, \sigma = 1.9 \]
Trial 23
[3 litre product]
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature increased from 25°C to 60°C then 75°C

Trial 23
Corrosion of Magnox Swarf in BFS/OPC Grout
3.44:1 BFA/OPC, W/S 0.35
Temperature 60°C

\[ y = 1.05E-02x + 1.57E+01 \pm 2\sigma, \sigma = 4.0 \]
**Trial 24**

Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout

Temperature increased from 25° to 60°C

![Graph](image1)

- Days Cure
- 1 Day Avg
- Temperature, °C

**Trial 24**

Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout

Temperature increased from 25° to 60°C

![Graph](image2)

\[ y = 2.18E-02x + 4.60E-01 \pm 2\sigma, \sigma = 17.6 \]
Trial 25
[3 litre product]
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature increased from 25° to 60°C

Trial terminated and product examined at 340 days
Trial 26
[3 litre product]
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature increased from 25°C to 60°C

Days Cure
- Corrosion Rate vs. Temperature

Trial 26
[3 litre product]
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature 60°C

γ = 8.47E-02x + 5.81E+01
±2σ, σ = 129.0

Days Cure
- Corrosion Rate
- ±2σ
- Linear (Corrosion Rate)
Trial 27
[3 litre product]
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature increased from 25°C to 60°C

Trial 27
[3 litre product]
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature 60°C

\[ y = -3.113E-04x + 7.203E+01 \]
\[ \pm 20, \sigma = 10.9 \]
Trial 28
[3 litre product]
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature increased from 25° to 60°C

Days Cure
- Corrosion Rate  - Temperature, °C

Trial 28
[3 litre product]
Corrosion of Magnox Swarf in 3.44 BFS/OPC, W/S 0.35 Grout
Temperature 60°C

Days Cure
- Corrosion Rate  - 2σ  - Linear (Corrosion Rate)
Trial 29
[3 litre product]
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature increased from 25° to 60°C

Days Cure
- Corrosion Rate - Temperature

Trial 29
[3 litre product]
Corrosion of Magnox Swarf in 3.44:1 BFS/OPC, W/S 0.35 Grout
Temperature 60°C

Days Cure
- Corrosion Rate ±2σ - Linear (Corrosion Rate)
Appendix 2: XRD Traces

XRD Trace – Trial 1 Sample
XRD Trace – Trial 2 Sample (Inner – sample scraped from close to Magnox metal surface)
XRD Trace – Trial 2 Sample (Outer - sample taken from region between two fins – not adjacent to surface of Magnox and more contaminated with grout)
XRD Trace – Trial 7 Sample
XRD Trace – Trial 8 Sample
XRD Trace – Trial 13 Sample
Appendix 3: TGA Traces

TGA Trace – Trial 5 Sample (Interface)

TGA Trace – Trial 5 Sample (Interface)
TGA Trace – Trial 10 Sample (Interface)

TGA Trace – Trial 10 Sample (Bulk)
TGA Trace – Trial 11 Sample (Interface)

TGA Trace – Trial 11 Sample (Bulk)
TGA Trace – Trial 4 Sample (Interface)

TGA Trace – Trial 4 Sample (Bulk)
TGA Trace – Trial 15 Sample (Interface)

TGA Trace – Trial 15 Sample (Bulk)
## DISTRIBUTION

<table>
<thead>
<tr>
<th>Name</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>S Williams</td>
<td>NDA RWMD</td>
</tr>
<tr>
<td>NNL Document Controller</td>
<td></td>
</tr>
</tbody>
</table>