

# **Contractor Report to RWM**

## **Knowledge Status on Uranium Hydride**

**November 2020**

Hugh Godfrey and Robin Strange



## **Preface**

Radioactive Waste Management (RWM) carries out Research and Development (R&D) in support of geological disposal of the UK's higher activity radioactive waste. The work presented in this report forms part of our R&D programme and was carried out by NNL on our behalf. This work has been reviewed by RWM and by two independent peer reviewers. RWM accept the data and conclusions in this report.



## Conditions of Publication

This document is made available by Radioactive Waste Management Limited (RWM). RWM is seeking to make information on its activities readily available to enable interested parties to have access to and influence on its future programmes.

RWM is a wholly owned subsidiary of the Nuclear Decommissioning Authority (NDA). All copyright, database rights and other intellectual property rights reside with the NDA.

This document may be freely used for non-commercial purposes provided that the source of this document is acknowledged when it is shared with third parties.

Any commercial use of this document including (but not limited to) sharing, distribution, copying and/or re-publication of this document (and/or any extracts thereof) is prohibited. Accordingly, all commercial use of this document requires express written permission from 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, neither the NDA nor RWM accepts any liability or responsibility for consequences that may arise from its use or reliance by other parties.

© Nuclear Decommissioning Authority 2022. All rights reserved.

## Other Publications

If you would like to see other reports available from RWM, these can be viewed at our website <https://www.gov.uk/rwm>, or please write to us at the address below.

## Feedback

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

RWM Feedback  
Radioactive Waste Management Limited  
Building 329  
Thomson Avenue  
Harwell Campus  
Didcot  
OX11 0GD  
UK

email: [rwmfeedback@nda.gov.uk](mailto:rwmfeedback@nda.gov.uk)



## Knowledge Status on Uranium Hydride

Hugh Godfrey (National Nuclear Laboratory)  
Robin Strange (Galson Sciences Limited)

November 2020



**Galson**  
SCIENCES LTD

5 Grosvenor House, Melton Road, Oakham, Rutland LE15 6AX, UK  
Tel: +44 (1572) 770649 Fax: +44 (1572) 770650 [www.galson-sciences.co.uk](http://www.galson-sciences.co.uk)

## Knowledge Status on Uranium Hydride

### Report History

This document has been prepared by Galson Sciences Limited (GSL) and Orchid partner companies for Radioactive Waste Management Limited (RWM) under the terms of Order No. RWM008826.

Version 1, Draft 1 (dated 29 March 2018) was internally reviewed by Jenny Kent (GSL), Robin Orr (National Nuclear Laboratory, NNL), and Tom Scott (University of Bristol).




Version 1, Draft 2 (dated 11 May 2018) responded to RWM review of Draft 1 by Tom Majchrowski, Amy Shelton and Michelle Cowley. Draft 2 was internally reviewed by Jenny Kent, Robin Orr and Tom Scott. The calculations in Appendix 1 were checked and verified by Robin Orr.

Version 1, Issue 1 (dated 20 June 2018) responded to RWM review of Draft 2 by Tom Majchrowski, Amy Shelton and Michelle Cowley. Issue 1 was internally reviewed by Robin Orr.

Version 1, Issue 1a (dated 2 November 2018) responded to RWM review of Issue 1 by Tom Majchrowski.

Version 1, Issue 2 (dated 14 February 2020) responded to RWM external peer review of Issue 1a by D. Lever and C. Stitt.

Version 1, Issue 2a corrects a textual error and some minor formatting issues in Issue 2.

Knowledge Status on Uranium Hydride				
Report No.:	Date:	Principal Authors:	Reviewed by:	Approved by:
		Hugh Godfrey Robin Strange	Robin Orr	Daniel Galson
1774-4, Version 1, Issue 2a	5 November 2020	Sign pp  Date: 05.11.20	Sign pp  Date: 05.11.20	Sign  Date: 05.11.20



## Executive Summary

This report presents the results of a programme of work to review and collate the current industry knowledge on uranium hydride behaviour and to assess the potential consequences of this behaviour for the geological disposal facility (GDF) safety cases, with particular emphasis on the formation, persistence, and pyrophoric behaviour of uranium hydride.

The UK has a significant inventory of fuels that were manufactured from natural or low-enriched uranium metal:

- Magnox fuel, consisting of a metallic uranium element clad in a magnesium-aluminium-beryllium alloy called Magnox, comprises the majority of this inventory.
- There is a smaller inventory of legacy / research fuels.

Historically, spent Magnox fuel and uranic material associated with wastes generated at reactor stations and reprocessing operations at Sellafield was stored, clad and unclad in ponds and/or silos under a range of different chemical environments. Under some of these conditions, formation of uranium hydride is feasible and some of these materials are due to be disposed of in a GDF.

Uranium hydride is frequently cited as a hazard during the storage and handling of uranium metal owing to its potentially pyrophoric behaviour and the associated risk of fires. Ignition of wastes containing uranium as a result of uranium hydride formation during storage has been implicated in a number of events. These observations, and confusion about where and when uranium hydride could form and how it could react, have historically led to a highly conservative approach to the design of treatment, storage and handling processes for metallic uranium fuel and associated wastes. However, significant progress has been made in understanding the formation and properties of uranium hydride under fuel and waste storage conditions in recent years.

This report focuses on establishing whether uranium hydride formation within waste packages could significantly affect any conclusions of Radioactive Waste Management Limited's (RWM's) 2016 generic Disposal System Safety Case (gDSSC) for a GDF. Further, it also identifies from the perspective of disposability whether there are significant gaps in current understanding that require research. The assessment approach was based on a comprehensive literature review and a workshop with a range of UK experts.

In this report, the results of a literature review are presented followed by an overview of the chemistry and behaviour of uranium hydride, including experience of industry stakeholders. Subsequently, the key claims and arguments of the gDSSC are reviewed with respect to the potential impact of uranium hydride behaviour, and knowledge gaps are identified. The results of a workshop where three scenarios of interest to RWM were developed and assessed against relevant areas of RWM's disposability assessment process are presented in the Appendix to this report.

The following knowledge gaps were identified as work areas of greatest interest to RWM:

- Work to date has identified release fractions for a bed of uranium hydride powder burning in air flow rates of up to 0.5 m/s. Air flows in a GDF are currently expected to exceed 0.5 m/s. There is, therefore, a potential need to investigate the implications of increased air flows below ground and, in the absence of definitive air flow rates from detailed GDF design, to determine air flow rates above which significant release fractions could occur. However, for accident scenarios where uranium hydride remains contained in waste packages, the air flow rates seen by the uranium hydride may be lower than already investigated due to the container restricting air ingress, despite potential higher flow rates around the waste package.
- Data are almost completely absent on hydriding of irradiated uranium metal and the properties of the resulting uranium hydride. The biggest potential impact is on the activity release fractions from burning uranium hydride, although current values used by Sellafield Limited are thought to be representative, or conservative, for irradiated uranium hydride.
- Hydrogen atoms in uranium hydride could act as a built-in moderator. Therefore, the presence of uranium hydride in waste packages could have an impact on criticality safety assessments for a GDF, but the potential scale of the effect is uncertain.

Routes to closure of these knowledge gaps have been identified in this report, i.e. sections on:

- Behaviour of burning active uranium hydride in air flows greater than 0.5 m/s.
- Effects of the modified physical properties of irradiated uranium on the understanding of the hydriding reaction.
- Criticality assessments.

Other knowledge gaps are also identified which are of lesser interest to RWM and these are also documented in the report.

## Abbreviations

ACT:	Accident Conditions of Transport
AWE:	Atomic Weapons Establishment
BEP:	Box Encapsulation Plant
CEGB:	Central Electricity Generating Board
DCIC:	Ductile Cast Iron Container
DF:	Decontamination Factor
ESC:	Environmental Safety Case
FED:	Fuel Element Debris
FEPs:	Features, Events and Processes
FGMSP:	First Generation Magnox Storage Pond
GDF:	Geological Disposal Facility
gDSSC:	Generic Disposal System Safety Case
GNS:	Gesellschaft für Nuklear-Service mbH
HEPA:	High Efficiency Particulate in Air
IP-2:	Industrial Package Type 2
ILW:	Intermediate Level Waste
MBGW:	Miscellaneous Beta / Gamma Waste
MEP:	Magnox Encapsulation Plant
MSSS:	Magnox Swarf Storage Silo
NCT:	Normal Conditions of Transport
NDA:	Nuclear Decommissioning Authority
NNL:	National Nuclear Laboratory
OSC:	Operational Safety Case
PFSP:	Pile Fuel Storage Pond
PIE:	Post-Irradiation Examination

RCT:	Routine Conditions of Transport
RF:	Release Fraction
RWM:	Radioactive Waste Management Limited
SL:	Sellafield Limited
SWTC:	Standard Waste Transport Container
SSB:	Self-Shielded Box
TSC:	Transport Safety Case
UoB:	University of Bristol

## Contents

<b>1</b>	<b>Introduction .....</b>	<b>1</b>
1.1	Background .....	1
1.2	Study Objectives and Assessment Approach .....	3
1.3	Report Structure .....	5
<b>2</b>	<b>Terminology Relevant to the Formation, Form and Reactivity of Uranium Hydride.....</b>	<b>6</b>
2.1	Formation .....	6
2.2	Thermal Behaviour .....	7
2.3	Uranium Hydride Reactivity .....	10
<b>3</b>	<b>Literature Review .....</b>	<b>14</b>
<b>4</b>	<b>Uranium Hydride Chemistry .....</b>	<b>16</b>
4.1	Formation .....	16
4.2	Persistence.....	18
4.3	Reactivity with Atmospheric Oxygen, Water Vapour or Liquid Water ..	19
4.4	$\alpha$ and $\beta$ Uranium Hydride .....	20
4.5	Propagation to Other Material.....	21
4.6	Experience of Industry Stakeholders .....	22
4.7	Summary of the Formation and Behaviour of Uranium Hydride .....	24
<b>5</b>	<b>Impact on RWM Safety Cases .....</b>	<b>27</b>
5.1	Transport Safety Case .....	27
5.1.1	Containment of the radioactive contents .....	29
5.1.2	Control of external radiation levels .....	30
5.1.3	Prevention of criticality .....	30
5.1.4	Prevention of damage caused by heat .....	30
5.2	Operational Safety Case.....	30
5.2.1	Claim OSC.SC1.....	31
5.2.2	Claim OCS.SC2.....	32
5.2.3	Claim OCS.SC3.....	32
5.2.4	Claim OSC.SC4.....	33
5.3	Backfilling.....	34
5.4	Environmental Safety Case .....	34
<b>6</b>	<b>Disposability Assessments.....</b>	<b>36</b>
6.1	Summary .....	36
<b>7</b>	<b>Knowledge Gaps .....</b>	<b>37</b>
<b>8</b>	<b>Conclusions .....</b>	<b>42</b>
	<b>References.....</b>	<b>44</b>
	<b>Appendix 1 - Assessment of Representative Scenarios.....</b>	<b>47</b>
	Magnox FED with Associated Uranium in a Type VI DCIC .....	48

Sealed Fuel Container Containing One Fuel Element from PIE Packaged in a 3 m <sup>3</sup> Box .....	55
FGMSP Bulk Metallic Uranium Fuel Packaged in a Vented SSB.....	60

# Knowledge Status on Uranium Hydride

## 1 Introduction

### 1.1 Background

Magnox fuel\* and a smaller inventory of legacy fuel such as that from the Windscale Piles were manufactured from natural or low-enriched uranium metal. Historically, spent Magnox fuel and uranic material associated with wastes generated at reactor stations and reprocessing operations at Sellafield was stored, clad and unclad in ponds and/or silos under a range of different chemical environments. Under some of these conditions formation of uranium hydride is feasible.

Materials containing uranium metal that might be considered to have the potential to form uranium hydride if hydrogen gas is present include:

- At Sellafield:
  - Magnox swarf encapsulated in the Magnox Encapsulation Plant (MEP).
  - Historic Magnox swarf arisings and miscellaneous beta gamma waste (MBGW) stored in the Magnox Swarf Storage Silo (MSSS) and the Pile Fuel Cladding Silo.
  - Unreprocessed fuel and MBGW stored in the First Generation Magnox Storage Pond (FGMSP), Pile Fuel Storage Pond (PFSP) and the Fuel Handling Plant.
- Other waste streams in the Nuclear Decommissioning Authority (NDA) estate and outwith the estate will also contain uranium metal, albeit in much lower quantities, for example as fragments in Magnox Fuel Element Debris (FED). Other wastes have been identified in the RWM  $^{14}\text{C}$  project inventory assessment [1].

The uranium metal containing material that has been declared as waste is planned to be treated, stored and disposed of in a variety of conditions. Possibilities include encapsulation in cement or storage as raw waste with subsequent finishing at a later date, prior to disposal. Ultimate disposal of the waste will be in a geological disposal facility (GDF).

Bulk accumulations of uranium hydride are known to have the potential to exhibit a highly exothermic oxidation reaction on exposure to liquid water or water vapour and/or atmospheric oxygen (known as pyrophoric behaviour). The reaction with atmospheric oxygen is characterised at its most reactive extreme by high temperatures, red-hot glow, and some particulate release (details are provided in Section 4.3). However, this is not uniformly observed and, dependent on the prior environments the

---

\* Magnox fuel consists of a metallic uranium element clad in a magnesium-aluminium-beryllium alloy called Magnox.

material was exposed to, there may be either little reaction on exposing uranium hydride to atmospheric oxygen, or a delayed reaction.

Historically, the pyrophoric behaviour of uranium hydride has been implicated as the cause of a number of industrial fire and explosion/deflagration incidents involving metallic uranium [2, 3, 4, 5]. In hindsight, and with current understanding, many of these events would have been predicted. For the other events, it is believed that the presence of uranium hydride was unlikely to have been the cause<sup>†</sup>, and incorrectly assigning this as the cause has led to the reputation of uranium hydride behaviour being unpredictable. This history has led to uranium hydride and its subsequent reaction with atmospheric oxygen, water vapour or liquid water being considered a significant hazard which must be avoided, even where uranium hydride is only present in minimal quantities, e.g. small amounts of uranium hydride formed at the uranium metal / corrosion product interface when uranium metal corrodes in water. However, significant progress has been made in understanding the formation and properties of uranium hydride under fuel and waste storage conditions in recent years.

Radioactive Waste Management Limited (RWM) is responsible for delivering solutions for the long-term management of radioactive waste in the UK, including the implementation of a GDF for higher activity waste. Within the inventory for disposal there will be intermediate-level waste (ILW) that contains material originating from metallic uranium which is intrinsic to, but not limited to, historic Magnox fuel. The waste requires packaging, interim storage, and subsequent disposal in a GDF. It is possible that waste packages containing uranium hydride may be consigned to a GDF. Consequently, RWM has acknowledged the necessity to better understand the behaviour of uranium hydride in waste packages consigned to a GDF.

RWM has developed a generic Disposal System Safety Case (gDSSC) for a GDF. The latest version of the gDSSC is the 2016 gDSSC [6]. The 2016 gDSSC is a suite of documents that assesses the safety and environmental implications of the geological disposal of radioactive waste, and it plays a key role in the iterative development of a geological disposal system. The 2016 gDSSC is also a demonstration that a GDF can be implemented safely.

The 2016 gDSSC considers safety in the following phases of the disposal system lifecycle:

- Transport of the waste to the GDF - presented in the generic Transport Safety Case (TSC) [7].
- Construction and operation of the GDF - presented in the generic Operational Safety Case (OSC) [8].
- The long-term period after closure of the GDF - presented in the generic Environmental Safety Case (ESC) [9].

---

<sup>†</sup> It is not possible to identify the actual causes as there was insufficient information recorded at the time of the event. However, in these cases the information that was recorded is incompatible with the current understanding of uranium hydride chemistry.



In addition to radiological safety considerations, the 2016 gDSSC also considers conventional safety in the operational phase.

The 2016 gDSSC is used as a basis for advice given by RWM to waste producers in packaging waste, and as a basis for assessments of waste package disposability carried out as part of RWM's disposability assessment process [10]. The disposability assessment process aims to give confidence to waste packagers that their proposed waste packages will comply with the eventual needs for transport to, and disposal in, a GDF, and confidence to RWM that the disposal system considered within the 2016 gDSSC will be appropriate to the wastes.

The disposability assessment process includes steps to:

- Establish the packaging properties, via a range of technical evaluations.
- Assess the safety of the packaging concept, by comparing the expected performance of the packaged waste (established by the technical evaluations) against the safety case assessments for transport and the operational and post-closure phases of a GDF (i.e. the 2016 TSC, OSC and ESC).

The presence of uranium hydride may impact the following technical evaluations and safety assessments:

- Wasteform technical evaluation.
- Container integrity and durability technical evaluation.
- Impact accident performance technical evaluation.
- Fire accident performance technical evaluation.
- Criticality technical evaluation.
- Transport safety assessment.
- Operational safety assessment.
- Post-closure safety assessment.

This report presents the results of a programme of work to review and collate the current industry knowledge on uranium hydride behaviour and, with particular emphasis on the formation, persistence, and pyrophoric behaviour of uranium hydride, assess the potential consequences of this behaviour for the 2016 gDSSC. It addresses Task 574 of RWM's Science and Technology Plan.

## **1.2 Study Objectives and Assessment Approach**

This report focuses on establishing whether, based on the current knowledge, the hazards from uranium hydride formation within waste packages are appropriately covered/included in the 2016 gDSSC. Further, it also identifies whether there are

significant gaps in current understanding that require additional research by RWM. Specifically, it looks to:

- Understand if the relevant literature and operational experience have been adequately captured and reviewed.
- Develop and summarise the understanding of conditions required for the formation and persistence of uranium hydride in packaged and/or conditioned waste (assuming waste contains metallic uranium or is of metallic uranium origin).
- Summarise the potential for pyrophoric behaviour of uranium hydride, including where appropriate the:
  - Conditions required.
  - Temperatures generated.
  - Likelihood of propagation to other materials.
  - Release fraction (RF).
  - Duration of the pyrophoric reaction.
  - Reaction products.
- Establish whether uranium hydride formation within waste packages could significantly and adversely compromise the 2016 gDSSC.
- Identify whether in this context there are significant gaps in the current understanding of uranium hydride formation and behaviour that need additional research.

The assessment approach was based on a comprehensive literature review and a workshop with a range of UK experts. The literature review captured existing expertise and experience supporting the NDA estate and general UK and international literature, both industry-based and academic research. A workshop was then held to discuss the formation and behaviour of uranium hydride in waste packages potentially being consigned to a GDF.

The workshop attendees included industry experts from the National Nuclear Laboratory (NNL), Sellafield Limited (SL) and Magnox Limited, academic experts from the University of Bristol (UoB), and RWM technical experts in specialisms of relevance to the disposability of packages containing uranium hydride. The aims of the workshop were:

- 1) To confirm that the literature review captured all relevant industry and academic experience of uranium hydride behaviour.
- 2) To assess potential challenges to the 2016 gDSSC from uranium hydride in waste packages.

The second aim was achieved through the development of three scenarios intended to cover a range of uranium hydride challenges that might be expected if real waste packages were to be assessed through the RWM disposability assessment process. These scenarios were then assessed against the appropriate areas of the disposability

assessment process. The outcome of the workshop was then used to perform a systematic review of the key claims and arguments of the 2016 gDSSC.

### 1.3 Report Structure

The remainder of the report has the following structure:

- Section 2 presents a series of standard definitions relating to uranium hydride reactivity and self-heating terms that are used throughout this report.
- Section 3 presents the methodology used to undertake the literature review.
- Section 4 presents an overview of the chemistry of uranium hydride, including the experience of industry stakeholders. A summary of the important aspects, as agreed by the technical experts involved in the project, RWM and industry stakeholders is also presented.
- Section 5 presents the assessment of the current understanding of uranium hydride behaviour against the 2016 gDSSC. This assessment is based on three scenarios that were identified as part of the project. The detailed assessment of the three scenarios is presented in Appendix 1.
- Section 6 discusses the impact of uranium hydride in wastes on disposability assessments.
- Section 7 summarises the knowledge gaps on uranium hydride properties and behaviour, and proposed paths to closure.
- Section 8 presents conclusions and key findings of the study.
- Appendix 1 describes the outcome of the assessments of the three identified scenarios against the 2016 gDSSC.

## 2 Terminology Relevant to the Formation, Form and Reactivity of Uranium Hydride

When describing uranium hydride formation, behaviour and self-heating events it is helpful to adopt consistent terminology to avoid confusion. This section summarises definitions used in this report and are consistent with those adopted within recent assessments by SL.

### 2.1 Formation

The reaction of uranium metal with hydrogen takes place over four stages [11, 12, 13]:

- An induction period.
- Nucleation and growth of discrete uranium hydride sites.
- Bulk reaction.
- Total conversion of bulk metal to uranium hydride.

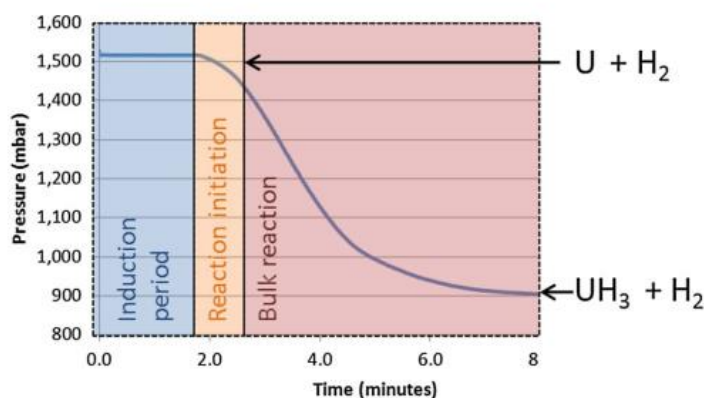
Under normal conditions, the metal surface is covered with a surface passivation layer of oxides, hydroxides, oxycarbides and water [12] which acts as a barrier to hydrogen diffusion [14] and also removes dissociation sites [15]. In the induction period these barriers are being broken down.

Nucleation and growth of discrete uranium hydride sites occurs at the point or points where the surface passivation layer has failed. Initial hydrogen attack is termed as ‘nucleation’. This expression is broadly accepted due to the almost hemispherical way that the sites spread on the metal surface [16]. However, uranium hydride has also been observed forming on the surface in strip-type [17] or filiform-like morphologies [18].

The bulk reaction occurs when the discrete reaction locations coalesce to form a homogeneous reaction front. The transition may be delayed or even not observed depending on the gas purity [19], temperature regime [20] and geometry of the reacting sample [21].

Finally, during conversion of bulk metal to uranium hydride the progression of the hydride reaction front into the metal continues until total consumption occurs, and the reaction slows and eventually ceases.

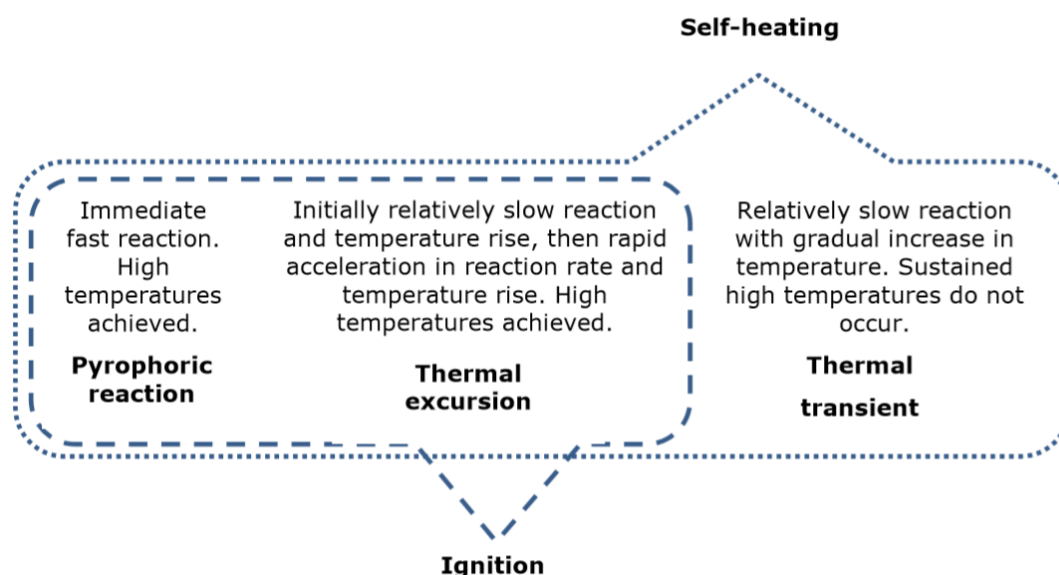
An illustration of the first three stages is shown in Figure 1.



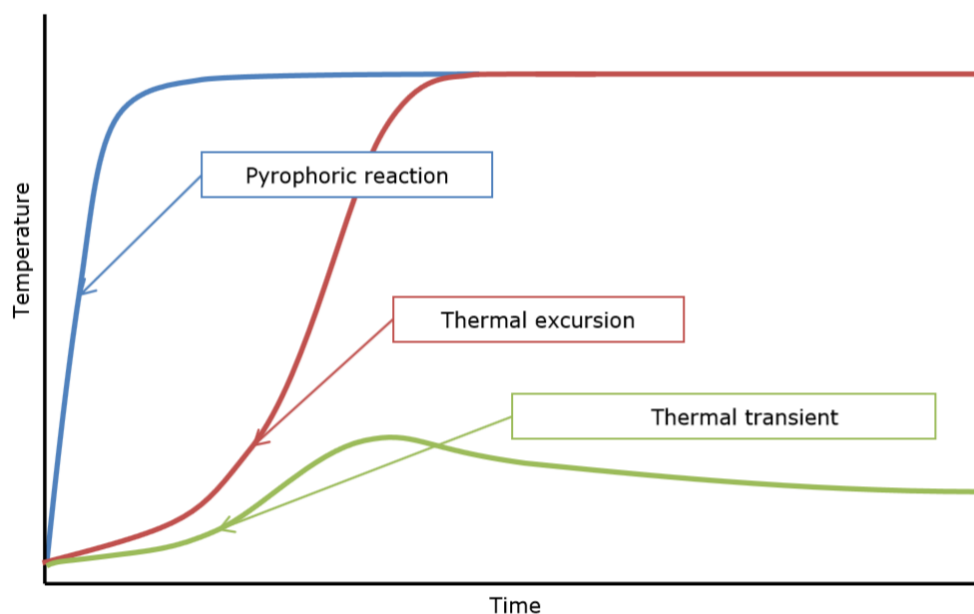
**Figure 1:** Stages of uranium hydriding reaction (the reaction was carried out with a fixed volume of hydrogen gas hence the pressure decrease with time) [22].

## 2.2 Thermal Behaviour

Five terms are defined with respect to thermal behaviour: three are relatively specific, i.e. pyrophoricity, thermal excursion, and thermal transient, and two are more general terms, i.e. self-heating and ignition. The relationship between these five terms is summarised in Figure 2, and the qualitative temperature vs time dependence is described graphically in Figure 3.



**Figure 2:** Summary and interrelationship between self-heating terms [23].



**Figure 3:** Schematic graph showing the difference in relationship between temperature and time depending on the nature of an event; decay heat from radiogenic processes is neglected. In all cases the temperature would eventually decay as uranium (or oxidant) was consumed [23].

### Self-heating

Self-heating results from the exothermic reaction of a material which causes the bulk temperature of the material to rise without the addition of heat from an external source. Self-heating implies nothing about the timescale or magnitude of the heating. The degree of heating is strongly dependent on the quantity and spatial distribution of material involved, surrounding materials and the ambient temperature. Depending on the material and context, this process may or may not be associated with emission of electromagnetic radiation in the visible spectrum (i.e. visible light) and could lead to ignition. Thermal transient and ignition (either from a thermal excursion or pyrophoric reaction) are subsets of self-heating which reflect the different peak temperatures and rate of temperature rise observed.

### Thermal transient

A thermal transient results from the exothermic reaction of a material which causes the bulk temperature of the material to rise relatively slowly without the addition of heat from an external source. The temperature rise is relatively small, too low for ignition to occur, and then cools over time as the reactants are consumed. The degree of heating is strongly dependent on the quantity and spatial distribution of material involved, surrounding materials and the ambient temperature. This may occur because the rate of reaction is too low to cause ignition, or the quantity of reactant is too small and exhausted before ignition can take place.

## Ignition

Ignition is the onset of a rapid temperature rise caused by the rate of heat generation by an exothermic reaction of a substance exceeding the rate of dissipation of heat to its surroundings. This imbalance leads to ignition, the reaction rate increases rapidly until it is limited by the supply of reacting material, either oxidant or the material being oxidised. At this point the material is said to be burning or to have ignited. Ignition of a material requires a change in its ambient environment that causes the material to move from a stable low temperature thermal equilibrium to an unstable system approaching thermal runaway.

Typical initiating events could be:

- Removal of a large heat sink (e.g. water).
- Exposure of a sample, previously in an inert atmosphere, to oxygen.
- An external heat source (e.g. sparks).
- A change in geometry of the materials that reduces the dissipation of heat to the surroundings, e.g. through mechanical shock.
- An increase in the ambient temperature. Ignition could be a multi-stage process, involving more than one exothermic reaction mechanism.

Two temperature-time cases for the approach to ignition can be differentiated: a thermal excursion and a pyrophoric reaction. It is useful to draw a distinction between these cases because the ability to control and respond to the scenarios is quite different, and the types of materials involved in each case are also often quite different. These two cases are detailed below.

### Thermal excursion

A thermal excursion is a route to ignition that initially involves a relatively slow initial reaction at ambient temperature, and thus a slow initial rate of temperature rise, but which gradually accelerates as the temperature rises until thermal runaway occurs. The balance between heat production from oxidation and dissipation to the surroundings determines whether a thermal excursion will take place and, if so, the temperature at which it occurs. It will not, however, affect the maximum rate of reaction as this is controlled by the supply of oxidant.

### Pyrophoricity and hypergolic reactions

A pyrophoric material is defined as a material that ignites immediately on exposure to atmospheric oxygen, i.e. there is no initial stage where there is a relatively slow rate of reaction. A hypergolic reaction is where two materials ignite spontaneously on contact; hence the reaction of uranium hydride with water can be hypergolic. Pyrophoric or hypergolic behaviours are not intrinsic properties of a material. They depend mainly on its surface area to mass ratio, with other factors having some influence too. These include:

- Quantity of material.

- Spatial distribution.
- Surrounding materials.
- Oxygen concentration and rate of supply.
- Ambient temperature.

For example, uranium hydride may or may not exhibit pyrophoric or hypergolic behaviour depending on the factors outlined above. However, some other materials, e.g. aluminium oxide, will not show pyrophoric or hypergolic behaviour under any conditions. It is important to recognise that it is generally incorrect to say that “*uranium hydride is pyrophoric or hypergolic*”. In some documents pyrophoric materials are also defined as those that spark on scratching. However, this is not part of the definition used here as scratching is not relevant in the context of a bed of uranium hydride powder.

In general, a pyrophoric reaction and thermal excursion will result in uranium hydride reacting at the same temperature, with the difference being the time taken to reach this temperature. This is because the maximum rate of reaction in both cases is limited by the rate of oxygen transport to the reaction site and this is the same in both cases.

Uranium hydride ignition and any subsequent propagation is a “nuclear material” fire (consistent with the definition used by the Office for Nuclear Regulation) as it is not the result of a criticality or other nuclear process (i.e. a nuclear fire).

## 2.3 Uranium Hydride Reactivity

Uranium hydride displays a wide range of reactivity depending on the degree to which it has been oxidised [23]. This is illustrated in Figure 4, which shows how the reaction rate of uranium hydride with oxygen, liquid water or water vapour changes with reaction extent. Initially the reaction rate for uranium hydride is very fast and in an appropriate environment, ignition can take place. The reaction rate then rapidly reduces to an intermediate stage, by about 15 % reaction extent, where the reaction rate remains fairly constant. Finally, at about 80 % reaction extent the reaction rate decreases rapidly with reaction extent<sup>‡</sup>. This results in some surface oxidised uranium hydride remaining, even after months or years exposure to oxygen, liquid water or water vapour at ambient temperature.

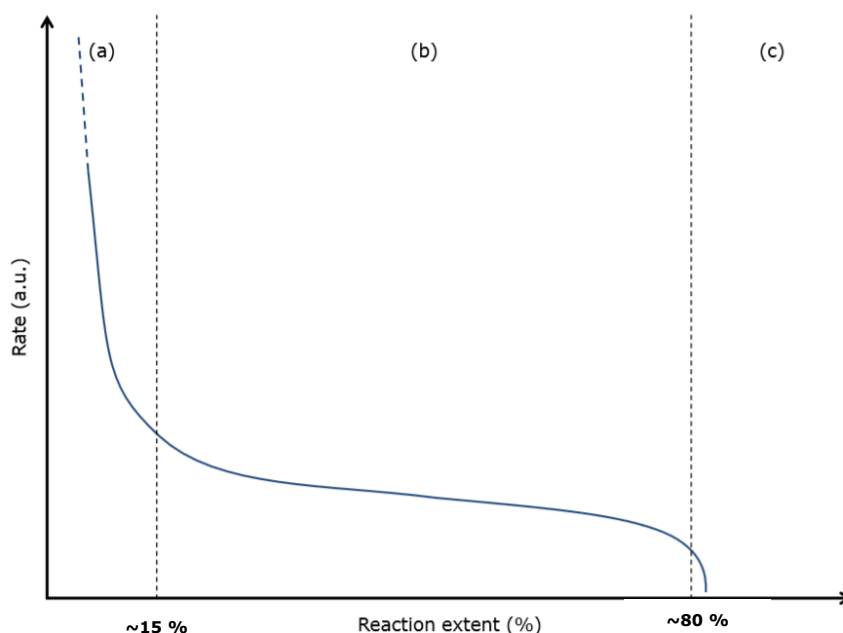
The large variation of the reaction rate of uranium hydride with oxidation extent means that it is useful to differentiate uranium hydride that has not had prior oxidation from that which has. In the past, uranium hydride that had been partially oxidised was often been described as “**passivated**”, while un-oxidised uranium hydride was referred to as “**pyrophoric**” uranium hydride. However, these terms were misleading and frequently misinterpreted as the “passivated” term implied that the uranium hydride was in a stable form, and therefore would not ignite. This has been shown to be incorrect in numerous

---

<sup>‡</sup> This is a phenomenological observation and the physical cause has not been determined.



laboratory studies and events during plant process operations [23]. Use of the term “passivated uranium hydride” is therefore no longer recommended.



**Figure 4:** Schematic illustration of the effect of uranium hydride reaction extent on reaction rate for oxygen, liquid water and water vapour. (a) initial phase - active uranium hydride, (b) intermediate phase, and (c) final phase which are both surface oxidised uranium hydride [23]. a.u. = arbitrary units.

The following definitions of “**active uranium hydride**” and “**surface oxidised uranium hydride**,” are recommended to distinguish the key types of uranium hydride reactivity.

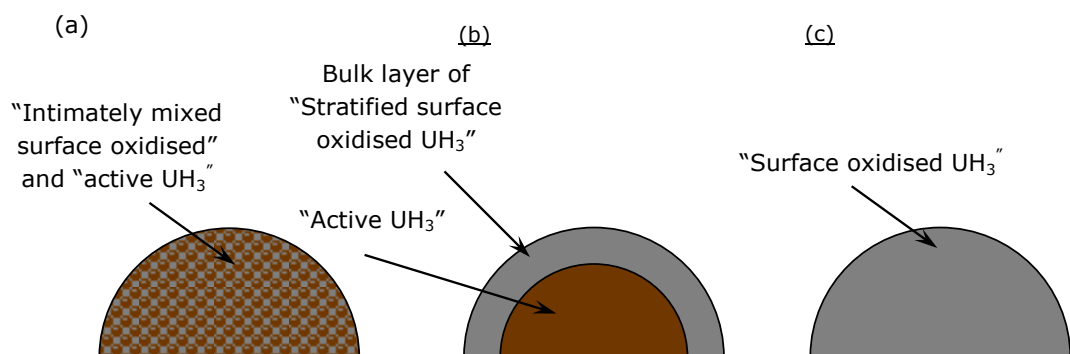
“**Active uranium hydride**” is defined as uranium hydride that has undergone very limited prior oxidation and is in the “initial phase” of the uranium hydride oxidation process illustrated in Figure 4 [23]. As it has had limited oxidation there will be no, or at most a very thin, oxide layer. The high reaction rate means it will undergo a rapid oxidation reaction immediately and spontaneously on exposure to atmospheric oxygen, water vapour or liquid water, generating uranium oxides (the exact stoichiometry depending on the reactants and temperature), hydrogen gas and heat; i.e. in air it usually demonstrates pyrophoric behaviour and in water a violent hypergolic reaction occurs unless the ratio of uranium hydride to water is small. Active uranium hydride can be expected to persist only in environments where no oxidants have been present to react with the uranium hydride, i.e. in a sealed system.

“**Surface oxidised uranium hydride**” is defined as the remaining uranium hydride after the rest has been oxidised and formed an oxide layer on the surface of the uranium hydride particles [23]. This form of uranium hydride may still self-heat on exposure to atmospheric oxygen, water vapour or liquid water but it shows a much-reduced reactivity in comparison to active uranium hydride. Hence, surface oxidised uranium hydride may not be pyrophoric, but could still ignite through gradual self-heating or from mechanical disturbance or external heating.

In some contexts, e.g. when considering the effects of mechanical disturbance on uranium hydride, it may be important to consider that a mixture of surface oxidised and active uranium hydride could be present. The difference between surface oxidation of all the particles of uranium hydride in the accumulation of uranium hydride, and a bulk layer of oxidised uranium hydride surrounding the external surface of an accumulation of uranium hydride in corrosion products should be recognised. This leads to the need for a distinction to also be drawn between:

- Accumulations of “**intimately mixed surface oxidised**” and “**active uranium hydride**”.
- Accumulations with a layer of “**stratified surface oxidised uranium hydride**” surrounding a core of “**active uranium hydride**”.
- Accumulations of corrosion products containing only “**surface oxidised uranium hydride**”.

For clarity these cases are illustrated schematically below in Figure 5.



**Figure 5:** Potential distributions of active (brown) and surface oxidised (grey) uranium hydride: (a) accumulation of “intimately mixed surface oxidised” and “active uranium hydride”, (b) accumulation of uranium hydride with a “stratified surface oxidised uranium hydride” surface layer and core of “active uranium hydride” and (c) accumulation of “surface oxidised uranium hydride” [23].

In general:

- Surface oxidised uranium hydride intimately mixed with active uranium hydride would be expected to ignite on exposure to atmospheric oxygen, without mechanical disturbance [23].
- A stratified surface oxidised uranium hydride layer and a core of active uranium hydride particles may only undergo a thermal excursion if the surface oxidised uranium hydride covering is disturbed and the active uranium hydride is exposed to atmospheric oxygen [23]. That is, the surface oxidised layer may provide a diffusion barrier that prevents rapid reaction of the underlying active uranium hydride, unless that barrier is disturbed. If this occurs, it would not require vigorous disturbance of the accumulation of uranium hydride; just sufficient force to disturb the powder bed.

- Surface oxidised uranium hydride may ignite if is aggressively disturbed. Based on practical laboratory experience this required mechanical grinding in a pestle and mortar [23]. This is thought to cause a breakdown of the surface oxide layer on particles that leads to local rapid reactions and heating. However, there may also be an effect from frictional heating or static discharge. A more precise description is not possible with current information.

In practice active and surface oxidised uranium hydride are qualitative definitions that allow a concise description of the different possible types of behaviour that could occur for uranium hydride in a waste stream, rather than a quantitative classification based on a specific reaction extent. This is, in part, because ignition depends on additional factors (the total mass of uranium hydride, its geometry, ambient temperature, etc.) and not just the reaction rate. More importantly, in most cases the exact history of the environments that wastes have been exposed to are unknown, therefore predicting whether and when uranium hydride has formed, and the extent of subsequent oxidation, cannot be achieved with any precision: it is only possible to identify the potential for uranium hydride to form, not whether it actually will occur in all cases.

### 3 Literature Review

This project builds on previous work by NNL and UoB over the past decade. The literature on uranium hydride has been reviewed by NNL for waste management projects within SL, such as the MSSS Reactive Materials project and Box Encapsulation Plant (BEP) project, as well as development of the SL Uranium Technical Guide [23]. UoB have also carried out regular reviews of the literature and have recently produced a public domain review article on the formation of uranium hydride [22]. The following sources and methods were used to identify relevant literature:

- Searches in the public domain using an internet browser.
- Searches of published scientific literature using the Scopus database.
- Goldfire<sup>§</sup> searches.
- Searches of the NNL / British Nuclear Fuels Limited / Magnox internal literature.
- Searches of the US Department of Energy literature.
- Reviews of references supplied in journal articles and books.
- Contacts with current and retired experts in NNL, SL, Magnox Limited, the Atomic Weapons Establishment (AWE) and other companies and national laboratories; both in the UK and the United States.
- Searches were also carried out using the French, German Spanish, Russian, Indian Chinese and Japanese equivalents to “uranium hydride” provided by Google Translate.

There is therefore a high degree of confidence that all the important literature relevant to this project has been captured.

This literature was re-examined in the context of assessing of the potential consequences of uranium hydride formation, in relation to the 2016 gDSSC, for disposal of waste packages containing waste of metallic uranium origin. The following specific topics were considered:

- Conditions required for the formation of uranium hydride, including likely amounts of uranium hydride formed.
- Persistence of uranium hydride.
- Pyrophoric / self-heating behaviour of uranium hydride, including:
  - Conditions required.
  - Temperature generated.

---

<sup>§</sup> IHS Goldfire is an extremely powerful software platform for technical knowledge discovery and problem solving which uses semantic searching of both the internet and information held internally by NNL.

- Likelihood of propagation to other materials.
  - RFs.
  - Duration of the pyrophoric reaction.
  - Reaction products.
- The potential for uranium hydride fires to propagate to other wastes and materials in the same waste package.
- Previous experience of uranium hydride pyrophoric reactions.

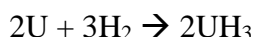
The outcome of the review was that no additional references were identified above those that have already been captured in the SL Uranium Technical Guide [23] and the UoB review article [22].

## 4 Uranium Hydride Chemistry

A comprehensive and up-to-date description of the chemistry of uranium hydride can be found in the SL Uranium Technical Guide [23] and a review article by the UoB [22]. The following sections, based on these two documents, outline the key aspects of the chemistry of uranium hydride that are relevant to assessment of its impact on the 2016 gDSSC.

### 4.1 Formation

The hydriding reaction is as follows:



#### Bulk hydriding

A hydrogen gas overpressure in contact with uranium metal is required to form significant quantities of uranium hydride from uranium metal. Usually this hydrogen gas results from the corrosion of other metals such as Magnox, but it can also result from the corrosion of metallic uranium itself. Once bulk hydriding has been initiated then the ongoing reaction is relatively fast compared with typical waste storage timescales, as long as sufficient hydrogen gas is available. For example, a piece of uranium metal with the diameter of a Magnox fuel element (~28 mm) will typically take several months to hydride at room temperature.

Before bulk hydriding is initiated there is an induction period. Under typical ambient conditions (i.e. room temperature and 101 kPa hydrogen pressure) and without special preparation of the sample surface, the duration of the induction period before the hydriding starts can exceed hundreds of hours. The duration of the induction period typically depends on the [22]:

- Thickness of the pre-existing surface oxide layer. Thicker layers inhibit hydrogen reaching the surface of the metal which extends the duration of the induction period.
- Hydrogen overpressure with higher pressures reducing the duration of the induction period.
- Presence of competing gases such as oxygen or water vapour. These can adsorb onto the oxide surface preventing access of the hydrogen and hence extend the duration of the induction period.
- Presence of defects and surface strain that can allow more ready access of hydrogen to the uranium. These can provide shortcuts through the oxide layer for the hydrogen, thereby reducing the duration of the induction period.
- Over time the target fuel composition of Magnox fuel has changed, with later fuel low-alloyed by addition of increasing levels of aluminium and iron on

average. This resulted in uranium metal that was more resistant to oxidation and hydriding.\*\*

- Increased levels of carbides and nitrides as impurities in the uranium, which can also reduce the duration of the induction period.
- Pre-existing uranium hydride. This can provide a shortcut through the oxide layer for the hydrogen, thereby reducing the duration of the induction period.

Depending on the precise conditions any, or all, of these effects may be important and in some cases these conditions will be changed by factors such as the encapsulant and packaging. For most scenarios involving metallic uranium wastes the conditions and history will not be sufficiently understood, or controlled, to be able to predict which, if any, of these factors dominate and hence the duration of any induction period will be uncertain.

Given the long timescales of the waste management lifecycle, if at any time metallic uranium waste is exposed to a significant hydrogen gas overpressure for a sustained period, then it should be assumed that uranium hydride can be formed. Consequently, assessment of the potential presence of uranium hydride in a wasteform will need to assume it can form and consider the potential for subsequent oxidation reactions to surface oxidise it and reduce its reactivity.

### **Formation during corrosion in water or grout**

Bulk hydriding is difficult to achieve underwater. In the event that bulk hydriding is somehow achieved the persistence of active uranium hydride is generally prevented by the ready access of water to react with it. Small amounts, i.e. a few percent, of surface oxidised uranium hydride, which are insignificant in terms of self-heating on exposure to atmospheric oxygen or water, can be found when uranium metal has corroded in water without a significant hydrogen overpressure. The hydriding reaction has the potential to accelerate the corrosion reaction if sufficient hydrogen is available in the system for bulk hydriding to be initiated.

Trials within academia and industry have demonstrated that pinholing of clad fuel elements in water or grout can result in significant hydrogen partial pressures with little oxygen in the cladding, leading to bulk active uranium hydride formation [24, 25, 26]. In contrast, unclad uranium encapsulated in cement for over ten years at up to ~50 °C has not been found to cause bulk hydriding; experimental results were consistent with 0.3 % w/w of the corrosion products being surface oxidised uranium hydride with the remainder being uranium dioxide [27].

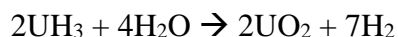
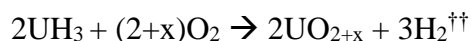
A thin 3 nm to 5 nm layer of uranium hydride is formed at the interface between the uranium metal and the oxide corrosion product [22]. This is continuously generated and then reacts with the water so remains very thin. This layer is not significant in terms of heat generation and self-heating.

---

\*\* Although still not significant on the timescales that apply during the waste management lifecycle.

## 4.2 Persistence

Uranium hydride can be lost by two processes: thermal decomposition or reaction with atmospheric oxygen or water. The reactions are:



Thermal decomposition requires temperatures  $>350^\circ\text{C}$ . Hence, at the temperatures expected during normal waste storage, transport and disposal, the thermal decomposition of uranium hydride to uranium metal and hydrogen gas is insignificant. This is because the equilibrium partial pressure of hydrogen is very low at these low temperatures and the presence of low concentrations of hydrogen will prevent uranium hydride decomposing. Even if no hydrogen is present then the rate of decomposition is insignificant at low temperatures. Therefore, the decomposition of uranium hydride to form finely divided uranium metal and hydrogen need not be considered, apart from in accident scenarios where heating occurs.

In fire accidents, or when uranium hydride has ignited, the heat generated may be sufficient to decompose the uranium hydride to finely divided uranium metal and hydrogen, which can then go on and rapidly react. In this situation, whether the uranium hydride ignites itself, or decomposes due to the fire accident, is only of academic interest as there are no significant differences in the consequences in the two scenarios.

The persistence of uranium hydride is also dependent on the absence of suitable oxidants in the short-term. In the scenarios of concern for waste management the oxidants are liquid water, water vapour or atmospheric oxygen. In the longer-term the large reduction in the oxidation reaction rate means that the persistence of uranium hydride becomes controlled by the slow oxidation reaction kinetics, even if a ready supply of oxidant is available.

Unless the system is sealed there will usually be sufficient water present or there will be a ready supply of atmospheric oxygen so that any uranium hydride that may be present will be surface oxidised. Therefore, for active uranium hydride to persist, a sealed system is generally required, i.e. oxidant access is limited.

It follows that, in general, uranium hydride could be present in a waste package from two routes. First, if uranium hydride has formed in a sealed container before conditioning of the waste for disposal then, provided the container has not been disrupted during conditioning, any uranium hydride already formed will remain.

---

<sup>††</sup> Note: the hydrogen may react further with oxygen to form water and x reflects the addition oxidation that may take place depending on the temperature reached during the reaction. The oxides formed include,  $\text{UO}_2$ , ( $x = 0$ ),  $\text{U}_4\text{O}_9$  ( $x = \frac{1}{4}$ ),  $\text{U}_3\text{O}_7$  ( $x = \frac{1}{3}$ ),  $\text{U}_3\text{O}_8$  ( $x = \frac{2}{3}$ ),  $\text{UO}_3$  ( $x = 1$ ).



Second, if uranium hydride has not already formed in a sealed container of uranium metal before conditioning to a wasteform then, provided the container is not disturbed and conditions are suitable within the container, uranium hydride will still have the potential to form within the wasteform. There is little practical difference between these cases. A further possibility is that the waste container becomes a sealed package if venting is inadequate or fails, promoting uranium hydride formation.

### **4.3 Reactivity with Atmospheric Oxygen, Water Vapour or Liquid Water**

#### **Atmospheric oxygen at low temperatures**

As shown in Figure 4, the reactivity of uranium hydride changes significantly with oxidation extent. Initially, the reaction rate for active uranium hydride is very fast and ignition can take place unless the supply of oxygen is deliberately controlled. The reaction rate rapidly reduces to an intermediate stage where the reaction rate remains fairly constant. Finally, at about 80 % reaction extent, the reaction rate decreases rapidly with reaction extent. This results in some surface oxidised uranium hydride remaining even after extended periods. However, this surface oxidised uranium hydride will not undergo ignition, unless it is broken down by aggressive measures such as grinding.

#### **Atmospheric oxygen at high temperatures**

Experiments in which active uranium hydride was ignited have been used to measure the particulate release rate, which can then be used to determine the non-volatile RFs in simulated scenarios. In these experiments air was passed over up to 100 g of uranium hydride at a velocity of ~0.5 m/s [28, 29]. As the burning rate is limited by oxygen diffusion to the reacting interface of uranium hydride the amount of particulate released is largely independent of the mass of uranium hydride and mainly depends on the air-exposed surface area of the bulk mass rather than the surface area of the particulate. This allows the work to be scaled to larger accumulations.

At a typical burning temperature of 600 °C to 700 °C in air, which for  $\geq 100$  g uranium hydride can last for tens of minutes, the maximum release fraction (RF) (the mass fraction that becomes airborne beyond the local area of the reacting material) under static bed condition was  $1.5 \times 10^{-4}$ . In a more vigorous reaction where a bed is disturbed so that all the uranium hydride powder was physically displaced from the sample container during burning the particulate RF was still only  $4 \times 10^{-4}$ .

Given the high temperature reached during burning, volatile radionuclides, such as ruthenium and caesium, can be released in addition to the non-volatile release of particulates.

When considering a waste package containing metallic uranium containing waste encapsulated in a cement matrix under non-accident conditions, the burning rate will be significantly affected by the waste package filters, etc. restricting oxygen ingress. The release of activity will be similarly hindered due to the restricted release pathways through the grout matrix even if some degradation, i.e. cracking, etc. has occurred.

## Water Vapour and Liquid Water

The reaction of uranium hydride with water vapour shows an initial reaction rate limited by the supply of water vapour that quickly decreases with reaction extent up to about 10 % to 15 %. Thereafter, the reaction rate decreases gradually up to about 80 % reaction extent. At this point the reaction rate becomes very low.

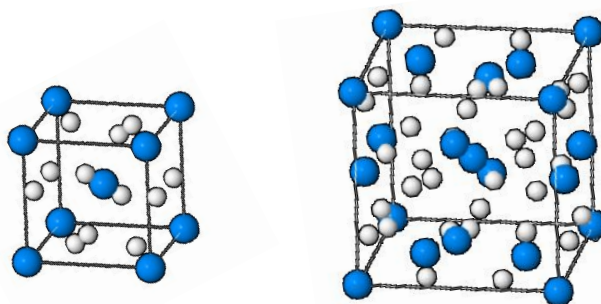
Less information is available on the behaviour of active uranium hydride on addition of liquid water. In the absence of air, different behaviour has been noted between small and large volumes of water added to uranium hydride. Small volumes result in vigorous reactions, because the heat of reaction is not dissipated, causing ignition and the production of water vapour that acts as a carrier for particulate. Large volumes of water added to uranium hydride can quickly quench the reaction, so that a vigorous reaction does not occur. When submerged in water the reaction rate decreases with reaction extent, similar to the reaction in water vapour.

When adding water to uranium hydride that has already ignited and is burning in air, the burn rate is rapidly increased and the release of particulate is enhanced. Trials have shown that the addition of 2.6 mL to 7.2 mL of water, starting at approximately one minute after ignition of ~100 g of uranium hydride in air, gave RFs in the range  $7.8 \times 10^{-4}$  to  $6.6 \times 10^{-3}$  for an air flow rate of 0.5 m/s [28, 29]. This is significantly higher than for the reaction in air, due to the more rapid reaction caused by the concentrated oxidant source and evaporation of water entraining more particulate into the air. Additional work is being considered by SL to expand the RF data to include the release from sudden under-water failure of a bottle containing active uranium hydride.

## 4.4 $\alpha$ and $\beta$ Uranium Hydride

Uranium hydride can form with one of two crystal structures, denoted  $\alpha$  [30, 31] and  $\beta$  [32]. The  $\alpha$ -form is more prevalent at ambient temperatures. The  $\beta$ -phase tends to remain as the major component in reactions at temperatures above ~100 °C, whereas the  $\alpha$ -phase is only found in significant amounts in reactions at temperatures below ~100 °C [31, 33].

The  $\alpha$ -phase has unit cell with two uranium hydride formula units whilst the  $\beta$ -phase has eight uranium hydride formula units. The densities of the  $\alpha$ -phase and  $\beta$ -phase are 11.1 g/cm<sup>3</sup> and 10.91 g/cm<sup>3</sup>, respectively. The  $\alpha$ -phase has a body centred cubic structure, with unit cell dimension of 4.153 Å [31, 33], whilst the  $\beta$ -phase has a more complex unit cell structure, with unit cell dimension of 6.63 Å [34] (Figure 6).



**Figure 6:** Single unit cell of  $\alpha$ - $\text{UH}_3$  (left) and  $\beta$ - $\text{UH}_3$  (right); uranium atoms are shown as blue spheres whereas hydrogen atoms are shown as white spheres.

There is a difference in reactivity between the two forms. However, this is not usually significant with respect to ignition when compared to the difference in reactivity between active and surface oxidised uranium hydride. In terms of persistence, the  $\alpha$  form of uranium hydride, formed at lower temperatures, has faster oxidation rates. While this leads to different outcomes on short timescales it is not relevant to persistence over extended storage or disposal scenarios. Therefore, whether the  $\alpha$  or  $\beta$  form is formed need not be considered in disposability assessments.

It is also possible that amorphous uranium hydride might form. As there are few data on the relative proportions of  $\alpha$  or  $\beta$  uranium hydride (or amorphous material) formed at ambient temperatures, the relative proportions that could be formed under a given set of conditions cannot be well defined.

## 4.5 Propagation to Other Material

Propagation of burning from uranium hydride to other waste materials would have a significant impact on the consequences of an incident. Propagation requires:

- Adequate proximity of the uranium hydride and surrounding materials so that thermal transfer to that material is effective.
- Sufficient heating power to heat the surrounding material and balance the dissipation of heat.
- Sufficient total energy to ignite these materials.

Meeting these conditions for uranium hydride is actually quite demanding for most wastes.

Detailed assessment is beyond the scope of the discussion here, but physical isolation of the uranium hydride source in a container and cement immobilisation of waste provide substantial barriers to heat transfer. For unencapsulated waste, even in the absence of a container or cement immobilisation, the reaction also has insufficient energy and/or power to ignite Magnox swarf (from decanning spent fuel) or bulk uranium metal unless a situation is contrived where particulate of gradually increasing

particle size is arranged<sup>††</sup>. In addition, there is generally poor heat transfer between items of waste which will minimise the potential for propagation. Hence, propagation from active uranium hydride that has ignited can be shown to be extremely unlikely. Other flammable wastes materials may be ignited by uranium hydride and the risks and consequences would need to be assessed based on knowledge of the inventory of materials, the ignition and burning properties and the spatial distribution of wastes.

## 4.6 Experience of Industry Stakeholders

This section collates relevant experience provided by industry stakeholders, which includes practical experience of events that have occurred, technical work sponsored by these organisations and experience of developing technical and safety cases for handling materials/wastes that contain, or potentially contain, uranium hydride.

### Magnox Limited

Magnox Limited has operational experience of handling spent fuel and the development of safety cases to manage handling materials potentially containing uranium hydride:

- Post-irradiation examination (PIE) operations at Berkeley Laboratories of nominally dry, bottled failed fuel, i.e. with some water carry-over.
- The safety case for retrievals and packaging of waste from the Hunterston A vaults, containing Magnox ends and furniture with some uranium.
  - The safety case was based on evidence that a propagating fire in FED (mixed Magnox and uranium metal waste) could not occur. This meant that the vault retrievals could be carried out in air rather than an argon atmosphere, which has associated costs and conventional safety hazards.
  - Packaging of the resulting ILW in vented Type VI Ductile Cast Iron Containers (DCICs) (Gesellschaft für Nuklear-Service mbH (GNS) Yellow Boxes) or six cubic metre concrete boxes was considered to be safe as long as the boxes were not reopened.

Magnox Limited has not undertaken experimental programmes on uranium hydride behaviour, although some limited experimental work on uranium metal oxidation under hydrogen-water vapour mixtures and associated uranium hydride formation was completed by its predecessor organisation the Central Electricity Generating Board (CEGB) in the 1980s. This information has been included in the SL Uranium Technical Guide [23] together with information on a plant ignition event during PIE operations on bottle fuel.

All of the assumptions used by Magnox Limited are consistent with the understanding of uranium hydride behaviour described previously and presented in the Uranium Technical Guide [23] and the UoB review [22]. It was noted that the safety case did not

---

<sup>††</sup> It is theoretically possible to ignite the large piece of Magnox by firstly igniting a small Magnox particle as “kindling” which then ignites a slightly larger particle and so on until the large particle is ignited. This is not considered credible in practical scenarios.

distinguish between “passive” or surface-oxidised uranium hydride and active uranium hydride layered with uranium dioxide, but that if the distinction could be made, then there may be an opportunity to reduce conservatism.

### **Sellafield Limited**

SL has wide ranging experience of uranium hydride covering both on-plant experience, experimental programmes and technical/safety assessments. Only representative examples are possible here. Events in decanning and PIE of fuel stored in fuel bottles are the most notable that have occurred. These historical thermal events have provided information on uranium hydride self-heating behaviour and activity release. SL has also commissioned extensive experimental studies carried out recently by NNL and UoB. In addition, there has been some less systematic but important historical research.

The main current projects / plants / processes where uranium hydride has been of concern include the following:

- BEP, which will treat wastes from the FGMSP and PFSP where a cemented product will be produced within a vented 3 m<sup>3</sup> stainless-steel box container to allow hydrogen removal, so uranium hydride should not be produced from non-containerised uranium during storage. Uranium hydride may be present within sealed containers received by BEP, but if it is exposed during handling operations and it ignites, the consequences are manageable on site as this will not have sufficient energy to ignite co-located Magnox cladding or fuel elements. Once containerised in the 3m<sup>3</sup> box, oxygen transfer is slower and there is no potential for propagation.
- MSSS, where waste will be retrieved into skips for interim storage, noting that within the facility there is scope for anoxic conditions and that sealed cans are present. During on-site transport, there was concern that if active uranium hydride ignited then the reaction could propagate through the bulk waste. Experiments were conducted where a high surface area magnesium source was ignited using a blowtorch and propagation was not observed through the adjacent waste simulant for the waste compositions expected in the MSSS.
- For both the BEP and the MSSS, sealed and unbreached cans could be included in the waste that is placed into interim storage.

For the BEP and the MSSS, any thermal events that may result from the ignition of active uranium hydride are tolerable and are within the design basis for the various processes.

SL’s work on uranium corrosion and uranium hydride, in support of safety cases for MSSS retrievals, the BEP and a range of other projects has been documented in the Uranium Technical Guide [23]. The Uranium Technical Guide is planned to be updated annually.

All of the assumptions used by SL are consistent with the understanding of uranium hydride behaviour described previously and presented in the Uranium Technical Guide [23] and the UoB review [22].

## AWE

At AWE, the focus is on initiation of uranium hydride formation for clean uranium metal. Therefore, most of their work is not relevant to RWM's areas of concern.

## Dounreay Site Restoration Limited

Dounreay Site Restoration Limited has not performed any research and development on uranium hydride properties and behaviour but they do have some information collected during a number of operational events where burning of uranium fuel occurred. This includes measurements of the activity collected in ventilation systems and the performance of cells during operations to declad and repackage Dounreay Fast Reactor fuel into cans for shipment and reprocessing, where ignition events resulting from uranium hydride reactions were observed. These data have been included in the SL Uranium Technical Guide [23] and hence are captured in this assessment. Also, the low consequence of these events, and hence minimal response by the operators, highlights the pragmatic approach that should be applied to the potential for uranium hydride to form and react within managed nuclear facilities.

## 4.7 Summary of the Formation and Behaviour of Uranium Hydride

The following position statements were agreed by the attendees at a workshop<sup>§§</sup> held to discuss the formation and behaviour of uranium hydride in waste packages potentially being consigned to a GDF as a suitable high-level description of the behaviour of uranium hydride, based on the uranium hydride behaviour previously described and assessments carried out by SL and Magnox Limited. These behaviours provide a basic set of principles on which to base subsequent assessments:

- For the formation of active uranium hydride an overpressure of hydrogen gas directly in contact with the metal is needed. In general, the higher the hydrogen gas overpressure the faster the rate of reaction.
- For significant quantities of active uranium hydride to persist, atmospheric oxygen, water vapour or liquid water access must be limited, i.e. a sealed system. Any of these oxidants having access to the active uranium hydride will react to form surface oxidised uranium hydride.
- It would be possible for active uranium hydride to be transferred into, and to persist within, a waste product, i.e. it is possible that a waste management process can take place during which any uranium hydride present in the waste is not exposed to any oxidants. This means that any active uranium hydride present in the waste will remain after treatment.
- It is highly unlikely for significant quantities of active uranium hydride to be formed from uncontainerised uranium metal in a vented grouted waste package.

---

<sup>§§</sup> The workshop attendees included industry experts from NNL, SL and Magnox Limited, academic experts from the UoB and RWM technical experts in specialisms of relevance to the disposability of waste packages containing uranium hydride to a GDF.

This is because there will be ready access of water and oxygen to any uranium hydride formed, which will result in it becoming surface oxidised.

- It is very highly unlikely for significant quantities of active uranium hydride to be formed from uncontainerised uranium metal in a vented raw waste package. This is because there will be ready access of water and oxygen to any uranium hydride formed, which will result in it becoming surface oxidised.
- Unless vigorous mechanical action or a significant external source of heat is present then surface oxidised uranium will not ignite, will remain relatively unreactive and be of little concern. This is because surface oxidised uranium hydride has already partially reacted and fresh unoxidised material needs to be exposed for a reaction to take place. The exception is in the case of large accumulations where conservative modelling of scenarios may predict the potential for a thermal excursion to develop. The precise conditions under which this can occur depend on the local environment and a general statement cannot be made, but as an indication, quantities in the order of more than 100 g may require detailed assessment.
- Burning of active uranium hydride in atmospheric oxygen is limited by the mass transport of oxygen gas. In a waste package, burning will be significantly hindered by the filters, etc. restricting oxygen ingress and the release of activity is similarly hindered due to restricted pathways. At various stages of the burning there will also be a net outflow of gas which will restrict oxygen ingress.
- Propagation of burning to other materials is generally limited by the power output of the burning material and poor heat transfer between materials. Also, Magnox and uranium metal are good conductors of heat, hence they will disperse the heat within large items, limiting the potential for propagation.

Generic technical gaps were also identified which are discussed in more detail in Section 7, where consideration is given to their importance to RWM;

- Understanding of the induction period before hydriding is initiated to understand whether or not uranium hydride can form during storage.
- Understanding the effects of in reactor irradiation to confirm (or not) the applicability of the inactive work carried out to real wastes recognising the physical / chemical changes in irradiated fuel.
- Understanding the effect of slow, long-term formation of uranium hydride to confirm (or not) whether similar behaviour is seen for real wastes which may be stored over many decades and where the reaction may take place more slowly than in the current experimental work.
- Understanding the hydriding reaction at the crystalline scale and the formation of  $\alpha$  and  $\beta$  uranium hydride. This will provide confidence in the applicability of the uranium hydride produced at elevated temperatures and used for the experimental work which contains more  $\beta$ -phase compared to uranium hydride formed at ambient temperatures which will contain more  $\alpha$ -phase.

- Better understanding of the reaction behaviour and particulate releases resulting from the addition of liquid water to active uranium hydride to provide better RF data.
- Better understanding of the degree of mechanical disturbance required to reactivate surface oxidised uranium hydride to better understand if surface oxidised uranium hydride can be reactivated in a given scenario.

Finally, when carrying out assessments it must be considered whether:

- 1) Uranium hydride formation is possible before or after conditioning a wasteform.
- 2) It is feasible that oxidation will have ensured that all the uranium hydride will have partially oxidised to the surface oxidised state or the final reaction phase prior to any possible initiating event.
- 3) A change in environment has resulted in a change in the availability of reactants, in particular an increase in oxygen availability.
- 4) Any events have taken place that may initiate further reaction, e.g. mechanical disturbance or increase in temperature.

This must be based on conservative, but reasonable, assumptions about the environments that the uranium hydride has experienced.



## 5 Impact on RWM Safety Cases

The potential presence of uranium hydride in waste packages sent to a GDF may impact the 2016 gDSSC. This section reviews the key principles and claims included within the 2016 gDSSC with respect to the potential impact and challenges of uranium hydride behaviour.

In this section, the approach adopted has been to first assess the expected impact of uranium hydride within a waste package if it were present and ignited, without detailed consideration of the precise form of uranium hydride or the type of waste package and the likelihood that this could occur for a particular waste and packaging arrangement. That is, its presence is assumed and ignition is assumed to occur.

Clearly, in all cases the potential for an event is dependent on the presence of uranium hydride in the waste package. Consequently, any assessment of a proposed waste package for disposal would first apply the principles outlined in Section 4.7 to determine if there was a credible risk of uranium hydride forming and persisting up to the time of the scenario being assessed. Generally, this will mainly involve identifying cases where containerised uranium metal could be present. The details of the waste package and wasteform properties will then determine whether potential initiating events pose a risk of igniting uranium hydride and how the burning would develop.

Where cases are identified that could have a significant adverse impact on the safety case the mitigating factors are identified that would influence either the frequency or severity of impact from an ignition event. These factors would be considered in a practical assessment of a proposed waste package but it is beyond the scope of the present study to address particular package designs and scenarios.

Knowledge gaps in the understanding of uranium hydride properties and behaviour are also identified below. These knowledge gaps are discussed in more detail and proposed routes to closure are identified in Section 7.

During the workshop, held to discuss the formation and behaviour of uranium hydride in waste packages potentially being consigned to a GDF, a number of scenarios intended to cover a range of uranium hydride challenges that might be expected if real packages were to be assessed through the RWM disposability assessment process were developed. These scenarios were then assessed against the appropriate areas of the disposability assessment process. The scenarios and the results of the assessment are presented in Appendix 1 and have informed the discussion in this section. It should be noted that these examples are not intended to be complete assessments of the scenarios considered. They only capture examples of how uranium hydride may be expected to behave and possible outcomes when real waste packages are assessed, and demonstrate that there is sufficient information available to carry out these assessments.

### 5.1 Transport Safety Case

The generic TSC aims to provide confidence in the radiological safety of the transport of radioactive waste to a GDF, without being specific to any potential GDF location.

Its aim is to provide confidence that the necessary transport operations will meet the regulatory requirements for radiological safety and can be achieved with radiation exposures below statutory limits, as well as RWM's own criteria. The TSC seeks to demonstrate that the procedures, assessments and approvals that are, or will be, in place to assure the safety of people and the environment through compliance with the IAEA Transport Regulations [35]. Through this compliance, the requirements for containment of activity, control of external radiation levels, prevention of criticality and prevention of damage caused by heat are met.

Two types of transport packages are considered in the TSC:

- Industrial Package Type 2 (IP-2).
- Type B.

The IAEA Transport Regulations consider the following conditions of transport:

- Routine Conditions of Transport (RCT).
- Normal Conditions of Transport (NCT).
- Accident Conditions of Transport (ACT).

RCT are incident free whilst under NCT a transport package is expected to endure minor mishaps. Under NCT, transport packages weighing greater than 15 t (as expected to be consigned to a GDF) are expected to survive the following situations, such that the transport package would restrict the loss of radioactive contents to not more than  $10^{-6} \text{ A}_2/\text{h}^{***}$ :

- Exposure to rainfall of approximately 5 cm/h for at least one hour, followed by
- A 0.3 m drop onto a flat, horizontal surface of such a character that any increase in its resistance to displacement or deformation upon impact by the transport package would not significantly increase damage to the transport package, so as to cause maximum damage to the transport package, followed by
- Penetration from a bar of 3.2 cm in diameter with a hemispherical end and a mass of 6 kg dropped and directed to fall, with its longitudinal axis vertical, onto the centre of the weakest part of the transport package from a height of 1 m above the transport package, followed by
  - A compressive load equal to the greater of the following:
    - The equivalent of five times the mass of the actual package.
    - The equivalent of 13 kPa multiplied by the vertically projected area of the package.

---

\*\*\*  $\text{A}_2$  values (in TBq) are defined for each isotope in the IAEA Transport Regulations [35], which also defines how to calculate  $\text{A}_2$  values for mixtures of isotopes, and are used to define activity limits for transport packages.

In accordance with the IAEA transport regulations IP packages are not assessed under ACT as IP-2 packages are not expected to survive ACT. The contents of IP-2 packages are therefore expected to be released during ACT.

Under ACT a Type B transport package is expected to survive the following situations, such that it would restrict the loss of radioactive contents to not more than 10 A<sub>2</sub> for krypton-85 and 1 A<sub>2</sub> per week for all other nuclides:

- A 9 m drop on to a flat, horizontal surface of such a character that any increase in its resistance to displacement or deformation upon impact by the transport package would not significantly increase damage to the transport package, so as to cause maximum damage to the transport package; followed by
- A 1 m drop on to a solid bar made of mild steel of circular section (15.0 cm ± 0.5 cm) in diameter and 20 cm long (unless a longer bar would cause greater damage) that is rigidly mounted perpendicularly on a flat, horizontal surface of such a character that any increase in its resistance to displacement or deformation upon impact by the transport package would not significantly increase damage to the transport package; followed by
- A solid mild steel plate measuring 1 m by 1 m and weighing 500 kg mass dropping in a horizontal attitude 9 m on to the transport package; followed by
- Exposure to a fire of at least 800 °C for 30 min; followed by
- Immersion in a head of water at least 15 m deep for a period of not less than eight hours in the attitude which will lead to maximum damage of the transport package.

The key principles enshrined in the IAEA Transport Regulations are to ensure safety (in both NCT and ACT) by:

- Containment of the radioactive contents.
- Control of external radiation levels.
- Prevention of criticality.
- Prevention of damage caused by heat.

How the presence of uranium hydride in a waste package may affect each key principle is discussed below.

Transport assessments undertaken as part of the disposability assessment process should consider whether uranium hydride is present and, if so, would there be enough oxygen present in the package to cause an issue and, if so, what kind of heating would ensue.

### 5.1.1 Containment of the radioactive contents

For the transport of a waste package containing unencapsulated uranium hydride and an amount of water under elevated temperatures, there is potential for hydrogen gas formation from corrosion to cause pressurisation of the waste package and transport package. An inert cover gas can be employed to prevent ignition of any hydrogen gas

generated. However, damage to the waste package may occur due to the pressurisation and the pressurisation limit of the transport package may be challenged.

Under ACT uranium hydride particulate may be released from both IP-2 and Type B transport packages. However, uranium oxide particulate will also be formed. An assessment will need to consider the total amount of particulate. This will depend on the total amount of uranium metal originally present, which is independent of whether it is uranium hydride or uranium oxide. Therefore, the presence or absence of uranium hydride should not affect the outcome of an assessment of disposability.

### **5.1.2 Control of external radiation levels**

The presence of uranium hydride in IP-2 and Type B transport packages is not expected to affect the control of external radiation levels under RCT, NCT and ACT as the total amount of activity will remain the same whether the uranium has corroded to uranium hydride or uranium oxide.

### **5.1.3 Prevention of criticality**

Unlike uranium metal waste and other uranium corrosion products, for uranium hydride the hydrogen atoms can act as a built-in moderator. In most cases the amount of uranium hydride present will be small in terms of its effect on criticality. In addition, the protons in the hydride will arise from water already in the waste package therefore formation of uranium hydride represents only a minor redistribution of the protons (that dominate the thermalisation of neutrons) within the package rather than increasing the moderator content. However, it is recommended that RWM carry out an assessment into the effects of the presence of uranium hydride on criticality assessments.

### **5.1.4 Prevention of damage caused by heat**

With respect to damage caused by heat only, the additional effect of uranium hydride ignition on the temperature of a package needs to be considered; the effects from external heat sources should be similar to other packages (excepting the effect of temperature on reaction rates).

Clearly an initiating event would be required to trigger ignition, such as an impact event. The maximum heat that could be generated by a uranium hydride fire can be simply calculated for an assumed inventory. It is reasonable to assume that the transport package will be leak tight to rapid ingress, given the IAEA design requirements for a Type B package. Consequently, the rapid reaction phase will be limited by the amount of oxygen present within the transport package and is unlikely to cause significant heat generation that would compromise the integrity of the package. This can be readily calculated for specific transport package design and waste package types where necessary.

## **5.2 Operational Safety Case**

The generic OSC is a feasibility study to inform future design development and identify any challenges to feasibility that require resolution in order to give high confidence of

successful permissioning at the site selection stage. It is structured around key claims with supporting arguments and evidence. The key claims are:

- OSC.SC1: All reasonably practicable steps will have been taken to implement design provisions whose function is to prevent or minimise the risk of injury due to conventional hazards.
- OSC.SC2: All reasonably practicable steps will have been taken to implement design provisions whose function is to prevent or minimise routine exposures to radiation sources.
- OSC.SC3: All reasonably practicable steps will have been taken to implement design provisions whose function is to prevent or mitigate the consequences of radiation accidents.
- OSC.SC4: All reasonably practicable steps will have been taken to implement design provisions whose function is to prevent or mitigate the consequences of nuclear accidents (i.e. unplanned criticality).

How the presence of uranium hydride in a waste package may affect the key claims is discussed below.

### 5.2.1 Claim OSC.SC1

Claim OCS.SC1 states that “All reasonably practicable steps will have been taken to implement design provisions whose function is to prevent or minimise the risk of injury due to conventional hazards.”

Consideration may be given to the potential for uranium hydride to impact on conventional hazards by ignition and propagation to other wastes and hydrogen generation.

For the transport of a waste package containing uranium hydride and an amount of water in a transport package there is potential for hydrogen gas formation from corrosion to cause pressurisation of the waste package and transport package, which could result in the pressure driven release of particulate and volatile radionuclides. Measures will need to be in place should this be expected to occur. IP-2 packages are expected to fail under pressurisation. However, Type B packages will be designed to manage pressurisation up to 7 bar and processes to release that pressure upon receipt at a GDF will need to be implemented to mitigate the hazard of dispersion of radionuclides via pressure-driven release of particulate and volatile radionuclides upon the opening of such transport packages. The information required to calculate the potential hydrogen generation rate is available and at present no significant knowledge gaps are identified. On detailed assessment it may become apparent that credit may be taken for the incubation period before uranium hydride forms, i.e. it may be possible to show that the incubation period will always be greater than the duration of transport and hence uranium hydride cannot be formed during transport. If this is the case, then additional work may be required to provide underpinning for this argument.

If present in enough quantity, the hydrogen gas could ignite in an air-filled ullage. The generation of hydrogen gas is a conventional safety issue, covered by the Provision and

Use of Work Equipment Regulations 1998. The fault sequence of hydrogen gas generation pressurising a waste package is not considered in the OSC. As such, it is currently not anticipated in the GDF illustrative designs that purge lines will be required for opening containers. However, due to the potential presence of uranium hydride in waste packages transported in Type B transport packages, purge lines for releasing any hydrogen gas that has built up may need to be included in the design for the transport container receipt and opening facility. This would be a new requirement and would need change control.

For management of uranium hydride reaction after emplacement in the vault, early backfilling may be considered to reduce the rate of oxygen diffusion into vented waste containers potentially containing uranium hydride, so that vibrations or other disturbances do not result in rapid reactions, particularly as the container vents may become blocked once they are emplaced. Also, retrieval of such waste packages once they are emplaced would not be advisable due to the potential risk of initiating a thermal excursion. Therefore, early backfilling may need to be included in the GDF operational plans for wastes with potential to contain significant quantities of active uranium hydride. This would be a new requirement and would need change control.

## 5.2.2 Claim OCS.SC2

Claim OSC.SC2 states that “All reasonably practicable steps will have been taken to implement design provisions whose function is to prevent or minimise routine exposures to radiation sources”. This claim is not affected by the presence of uranium hydride.

## 5.2.3 Claim OCS.SC3

Claim OSC.SC3 states that “All reasonably practicable steps will have been taken to implement design provisions whose function is to prevent or mitigate the consequences of radiation accidents”. Radiation accidents are defined by the IAEA Fundamental Principles (SF-1), Principle 8: Prevention of accidents [36] as follows:

*“The most harmful consequences arising from facilities and activities have come from the loss of control over a nuclear reactor core, nuclear chain reaction, radioactive source or other source of radiation. Consequently, to ensure that the likelihood of an accident having harmful consequences is extremely low, measures have to be taken:*

- To prevent the occurrence of failures or abnormal conditions (including breaches of security) that could lead to such a loss of control;*
- To prevent the escalation of any such failures or abnormal conditions that do occur;*
- To prevent the loss of, or the loss of control over, a radioactive source or other source of radiation.”*

The presence of uranium hydride has the potential to affect the “*loss of, or the loss of control over, .....or other source of radiation*”. This can be either through its reactivity causing activity to be released in a thermal event or through the release of particulate in other events such as impact events leading to mechanical dispersal.

A thermal event could lead to the emission of particulate, driven by heating and gas generation from the uranium hydride ignition. Work to date has identified RFs for uranium hydride burning in air flow rates of up to 0.5 m/s. However, in the GDF there may be higher air flow rates; until a more design for the GDF is finalised the actual air flow rates that may be experienced cannot be defined. Therefore, there is a potential gap in the understanding of RF for uranium hydride burning in these higher air flow rates, in particular, understanding the air flow rates at which the RF becomes significant. However, for scenarios where uranium hydride remains contained in waste packages the air flow rates exposed to the uranium hydride may be lower than already investigated due to the container restricting oxygen ingress, despite potential higher flow rates around the waste package.

In practice, the rate of burning will be limited by the rate of atmospheric oxygen supply to the burning surface, as outlined in Section 4.7. Even following an initiating event, such as an impact, a waste package is likely to continue to provide a significant level of containment of the uranium hydride. This would inhibit both the ingress of oxygen needed to sustain burning, if indeed ignition occurs at all, and egress of particulate and volatile activity generated. Evidence provided by waste producers would, for example, evaluate the likely damage from credible impact events and indicate the types of scenarios and from this Decontamination Factors (DFs) may be applied and justified for application to recommended release fraction values.

With respect to general particulate release during an impact event, as identified earlier, uranium oxide particulate will also be present in waste packages that originally contained uranium metal that are consigned to a GDF. Assessments of disposability of these types of packages will also need to consider the total amount of particulate present and the containment provided by the wasteform and waste container. In many cases this will largely depend on the total amount of uranium metal originally present, i.e. the total amount of particulate is independent of whether the particulate is uranium hydride or uranium oxide. Therefore, the presence or absence of uranium hydride is unlikely to substantially affect the outcome of such an assessment and hence does not significantly affect the demands over other waste package types that will be consigned to a GDF.

#### **5.2.4 Claim OSC.SC4**

Claim OSC.SC4 states that “All reasonably practicable steps will have been taken to implement design provisions whose function is to prevent or mitigate the consequences of nuclear accidents (i.e. unplanned criticality)”.

Again, unlike uranium metal waste and other uranium corrosion products, in uranium hydride the hydrogen atoms can act as a built-in moderator. In addition, the protons in the hydride will arise from water already in the waste package. Therefore, formation of uranium hydride represents only a minor redistribution of the protons (that dominate the thermalisation of neutrons) within the package rather than increasing the moderator content. As noted previously, it is recommended that RWM carry out an assessment into the effects of the presence of uranium hydride on criticality assessments.

### 5.3 Backfilling

During backfilling there will be a temperature rise to a maximum of 80 °C due to the curing of the backfill [37]. This will have no significant effect on or be affected by the presence of uranium hydride because the temperatures are still relatively low, and backfilling will not cause sudden exposure of uranium hydride to any oxidants.

### 5.4 Environmental Safety Case

The ESC aims to show how radioactive waste can be disposed of in a GDF in a way that ensures environmental safety at the time of disposal and after GDF closure. The ESC does this by identifying and considering environmental safety functions and the Features, Events and Processes (FEPs) that may occur during the post-closure phase of a GDF.

The following environmental safety functions are considered in the ESC:

- Wasteform.
- Container.
- Local buffer/backfill.
- Mass backfill.
- Plugs and seals.
- Geological environment.

Uranium hydride could potentially influence these safety functions through either hydrogen generation or heat generation resulting from oxidation.

The amount of hydrogen released by uranium hydride hydrating will be very small in comparison to that released by the corrosion of other waste materials in the GDF (in the wasteform and of the waste containers). The information required to carry out assessments of hydrogen generation rates from uranium hydride is available.

Following backfilling, the time to resaturation will be variable. Water vapour will be present from the backfill that could react with any uranium hydride to generate hydrogen gas. However, excessive hydrogen gas pressure and damage to the structure is unlikely to be generated considering the likely inventory of uranium hydride and that the backfill grout formulation is designed to allow gas to be released. Even if an overpressure of hydrogen gas were to form in a waste package (e.g. due to a blocked vent), subsequent oxidant ingress will be slow, preventing rapid oxidation of any uranium hydride formed. If an ignition somehow occurred the consequences would be low because the mass of the package and backfill will provide a large heat sink and prevent any particulate escaping.

The possibility can be considered that resaturation occurs at such a rate that the reaction of water with uranium hydride generates significant heat that cannot be adequately dispersed. However, calculations for representative scenarios presented in Appendix 1 demonstrate that any heat generated in such a scenario could only result in an increase



in temperature in the region of the box of a few degrees at most. Again, the information required to carry out quantitative assessments of these scenarios is available. Once sufficient water is present, any reaction will be quenched.

The presence of uranium hydride in waste packages disposed of in a GDF is therefore not expected to affect environmental safety functions and FEPs considered in the ESC. No new FEPs were identified during the assessment of representative scenarios.

## 6 Disposability Assessments

The assessment in the Section 5 and the Appendices shows that in general, apart from the knowledge gaps identified below, the current knowledge of the behaviour of uranium hydride is considered sufficient to enable the assessments of the disposability of waste packages potentially containing uranium hydride to be performed. When performing disposability assessments, the assessors must consider whether:

- 1) Uranium hydride formation is possible before or after conditioning to a wasteform.
- 2) It is guaranteed that oxidation will have ensured that all the uranium hydride will have partially oxidised to the surface oxidised state or the final reaction phase.

This must be based on conservative but reasonable assumptions about the environment the uranium hydride has experienced.

### 6.1 Summary

The outcomes of the qualitative assessments made in this section are not inconsistent with work completed for SL. However, for the 2016 gDSSC there are additional challenges relating to the transport and operational phases of a GDF. In particular, performance under accident conditions, where there is the potential for the exposure of active uranium hydride, is the most onerous. Whether this occurs in practice depends on the detailed properties of the waste stream, the conditioning process and the package design.

## 7 Knowledge Gaps

The following knowledge gaps regarding the understanding of uranium hydride behaviour, and potential routes to closure, have been identified.

### **Duration of induction period**

The duration of the induction period before bulk hydriding starts is very dependent on the conditions experienced by the sample and is not currently well understood. Application of experimental studies to practical applications is unreliable because in most waste management situations the conditions under which the waste has been stored are not well understood and hence the induction period will be difficult to predict even if the factors affecting the induction period are better understood. In addition, given the decades of storage associated with legacy wastes it is difficult to justify induction periods that are sufficiently long to significantly affect any assessments of disposability, i.e. decades of storage should be much longer than any induction period. However, situations may arise for some wastes and changes in conditions, e.g. from air filled containers during storage to anoxic conditions in transport of waste to a GDF, where credit may be taken for a long induction period. At this stage it is not recommended that any work is carried out by RWM to better understand the induction period. If in the future a case arises for a waste where a long incubation period is beneficial to substantiate and, given the inherent uncertainties, can be taken credit for then experimental work may be required.

### **Slow long-term formation of uranium hydride**

By necessity, most trials are carried out on uranium hydride that has been formed at elevated temperatures and significant hydrogen overpressures so that sufficient material can be formed in a reasonable timescale. It is known that temperature can affect the proportion of the  $\alpha$  and  $\beta$  phases of uranium hydride and that these forms can react with atmospheric oxygen and water at different rates. Whilst these effects are not as significant as the difference in reactivity between active and surface oxidised uranium hydride, understanding how representative accelerated test conditions are of uranium hydride formation under more realistic conditions remains a knowledge gap.

For example, under typical waste storage or waste package conditions of room temperature and lower hydrogen pressures where the uranium hydride very slowly forms over months, years or decades, the relative proportion of the  $\alpha$  and  $\beta$  phases may change with time. It has been postulated that amorphous uranium hydride could form under some conditions, although it has not been positively identified in the literature and therefore no comment can be made on its reaction kinetics. This is more of academic interest as currently safety cases assume that the uranium hydride is either active, and hence ignites instantly, or is surface oxidised after exposure to water or oxygen and reacts much more slowly and the approach is unlikely to be changed by consideration of an additional uranium hydride phase. At this stage it is not recommended that RWM carry out any work in this area. The academic research should be monitored and the situation reassessed if information arises that changes this assessment.

**Understanding the hydriding reaction at the crystalline scale and the formation of  $\alpha$  and  $\beta$  uranium hydride**

The mechanistic details of the hydriding reaction, how the  $\alpha$  and  $\beta$  phases are formed and how the  $\alpha$  phase converts to the  $\beta$  phase are not fully understood. At present, safety cases assume that if a hydrogen partial pressure is present then uranium hydride will form. The uranium hydride will be either active or surface oxidised depending on the prevailing conditions. They also do not differentiate between the  $\alpha$  and  $\beta$  phases. Therefore, this is mostly of academic interest and it is not recommended that RWM carry out any work. However, there is the possibility that improved understanding may better define the conditions under which uranium hydride can form or persist for relatively short-term operations such as transportation, where the differing oxidation rates between the  $\alpha$  and  $\beta$  phases may be important. If in the future a case arises where a better understanding is beneficial and, given the inherent uncertainties, can be taken credit for, then experimental work may be beneficial.

**Mechanical disturbance required to reactivate surface oxidised uranium hydride**

Currently it is presumed that a significant mechanical disturbance, such as grinding, is required to reactivate surface oxidised uranium hydride. For current safety cases this has proved adequate because the processes under consideration have generally imparted little mechanical energy to the waste, compared with dry grinding with a pestle and mortar, under conditions where reactivation of surface oxidised uranium hydride would be of concern. However, situations may arise for some wastes where a better quantification of the mechanical disturbance required to reactivate surface oxidised uranium hydride is required if there is potential for more mechanical energy to be imparted to the waste. At this stage it is not recommended that any work is carried out by RWM to better understand the mechanical disturbance required to reactivate surface oxidised uranium hydride. If in the future a case arises where a better understanding would be beneficial and can be taken credit for then experimental work may be required which would need to adequately bound the mechanical disturbance that might occur.

**Behaviour of burning active uranium hydride in air flows from 0.5 m/s**

The required ventilation, air flows in a GDF could be much faster than have been tested to date (i.e.  $> 0.5$  m/s). Hence, a gap has been identified where determining the RF from active uranium hydride burning under increased air flow rates and the air flow rate at which this becomes significant may be required. To address this would require a review of current work to confirm the data requirements and the conditions to be used in any trials. Any trials will need a capability to manufacture uranium hydride under inert conditions and a uranium active rig to measure the RF when the uranium hydride is exposed to air.

**Addition of liquid water to active uranium hydride**

Depending on the relative amounts of liquid water and active uranium hydride and the rates of addition the reaction between the two may either be vigorous or be quenched. Current SL trials have investigated the case of relatively slow water addition rates for uranium hydride burning in air and for a large excess of water added to uranium hydride

under inert conditions. Research in this area is ongoing and a more structured programme may be beneficial in the long-term if additional scenarios requiring investigation are identified. RWM needs to identify in more detail situations where the addition of liquid water to active uranium hydride may be of concern and confirm that these cases are bounded by the work carried out by SL. If this is not the case then additional trials will be required using a capability which can manufacture uranium hydride under inert conditions and a uranium active rig to measure the RF when the uranium hydride is exposed to water.

### **Effects of irradiated uranium**

Irradiation may affect the hydriding of uranium and its subsequent behaviour. To date, nearly all experimental trials investigating uranium hydriding and uranium hydride properties have been on unirradiated uranium metal.

With respect to self-heating behaviour, in many cases uncertainty about the effect of irradiation will not affect the outcome of an assessment. For example, if there is a hydrogen overpressure then it will have to be assumed that uranium hydride may form, whether the uranium has been irradiated or not. Subsequently, the uranium hydride formed will be assumed to be either active, and hence reactive, or surface oxidised, and hence much less reactive, depending on the environmental conditions. Again, this will not be affected by whether the original uranium metal was irradiated or not and instead determined by information about the storage environment.

A gap in understanding has been identified with respect to the speciation of fission products within the corrosion products. Assessments by, for example, SL evaluate releases based on elemental volatility using data from studies of irradiated metal oxidation/burning. Volatile and semi-volatile releases from uranium hydride are likely to be reasonably represented (and conservative) by these data where the cause of the release is the elevated temperature. Non-volatile releases are not well represented by measurements for uranium metal oxidation because these depend on processes affecting entrainment of particulate into the surrounding atmosphere that are very different for uranium hydride. Consequently, experimental measurements of the particulate release from burning (unirradiated) uranium hydride have been made. The assumption in these studies is that the particulate properties are not substantially different from hydride formed on irradiated metal.

If, when RWM carry out assessments, perceived uncertainty in current RF values has a significant impact on predicted consequences, there may be a need to determine experimentally:

- 1) The uranium hydride powder properties (particle size distribution and morphology).
- 2) Volatile release during burning of irradiated-uranium hydride under representative environmental conditions.

### **Criticality safety assessments**

The hydrogen atoms in uranium hydride can act as a built-in moderator. Criticality safety assessments undertaken during the disposability assessments will need to consider the moderating properties of any uranium hydride present within a waste package.

### **Knowledge gaps not directly related to uranium hydride behaviour**

As well as the knowledge gaps identified above additional factors were identified that may provide mitigation or remove hazards. They are:

- Purge lines for releasing any hydrogen gas that has built up in the transport container may need to be included in the design for the transport container receipt and opening facility.
- Early backfilling for wastes that may contain, or form, active uranium hydride.

### **Summary of knowledge gaps, opportunities and routes to closure**

The following knowledge gaps were identified as areas of highest interest to RWM:

- The implications of increased air flows below ground ( $>1$  m/s) on uranium hydride burning behaviour, e.g. increased RF.
- Data are almost completely absent on hydriding of irradiated metal and the properties of the resulting uranium hydride. The biggest potential impact is on the activity RFs from burning uranium hydride; although current values used by SL are thought to be representative or conservative for irradiated uranium hydride. For other aspects of uranium hydride behaviour, the effects of irradiation are likely to be a lesser effect than uncertainty in the environmental conditions.
- Effect of the presence of uranium hydride on criticality safety assessments due to the potential for hydrogen atoms to act as a moderator.

The following gaps in understanding were identified as being largely of interest to the academic community. However, as waste treatment proposals become more developed and additional wastes are treated, there is the potential for the results to provide beneficial reductions in conservatism.

- Hydriding induction periods.
- Understanding the hydriding reaction at the crystalline scale and how the  $\alpha$  and  $\beta$  forms of uranium hydride are generated.
- Understanding how representative accelerated test conditions are of uranium hydride formation in more realistic conditions, e.g. slow hydriding rates, occurring in waste packages over a period of decades.
- Mechanical disturbance required to reactivate surface oxidised uranium hydride.

- The behaviour of uranium hydride on the addition of water and the ratio of uranium hydride to water and the rate of addition that results in quenching.

The following knowledge gaps or opportunities were identified during the workshop (Appendix 1) and are related to assessing the consequences of the behaviour of uranium hydride and are not directly related to its behaviour:

- Consideration of whether uranium hydride behaviour is bounded by the behaviour of other materials that have previously been considered for transport or disposal at the GDF.
- Methodology development is needed to identify more realistic RFs/DFs for entombment of particulate material when compared to an intimately grouted wasteform.

Routes to closure for the knowledge gaps of significance to RWM have been identified in the detailed discussion in this section of the report, i.e. sections on:

- Behaviour of burning active uranium hydride in air flows faster than those previously investigated.
- Effects of the modified physical properties of irradiated uranium on the understanding of the hydriding reaction.
- Criticality safety assessments.

## 8 Conclusions

The understanding of the behaviour of uranium hydride in the context of RWM's safety cases has been assessed by a group including RWM, waste packagers and UK experts in uranium hydride behaviour.

A summary of the agreed understanding of the behaviour of uranium hydride is:

- For the formation of active uranium hydride there needs to be a suitable hydrogen partial pressure directly in contact with the metal.
- For significant quantities of active uranium hydride to persist, oxidant access must be limited, i.e. a sealed system is required.
- It would be possible for active uranium hydride to be transferred into, and to persist within, a waste product.
- It is highly unlikely for significant quantities of active uranium hydride to be formed from uncontainerised uranium metal in a vented grouted waste package.
- It is very highly unlikely for significant quantities of active uranium hydride to be formed from uncontainerised uranium metal in a vented raw waste package.
- Unless vigorous mechanical action or a significant external source of heat is present, then surface oxidised uranium will not ignite, will remain relatively unreactive, and will therefore be of little concern. The exception is in the case of large accumulations of surface oxidised uranium hydride where conservative modelling of some scenarios may predict the potential for a thermal excursion to develop.
- Burning of active uranium hydride in atmospheric oxygen is limited by the mass transport of oxygen gas. In a waste/transport package, burning would be significantly hindered by the filters, restricting oxygen ingress, and the release of activity would be similarly hindered due to restricted pathways.
- Propagation of burning to other materials would generally be limited by the power output of the burning material and poor heat transfer between materials.
- During the burning of uranium hydride, the particulate release fraction reported for uranium hydride should be applied to the total mass of corrosion products assumed to be co-located.
- For particulate release resulting from mechanical dispersion of corrosion product during, for example, a drop scenario of a waste container, the uranium hydride will disperse in a similar way to uranium oxide corrosion product and therefore the two materials do not need to be treated differently.

In general, apart from the gaps identified below, the current knowledge of the behaviour of uranium hydride is considered sufficient to enable assessments of the disposability of waste packages containing uranium hydride to be performed.



When carrying out assessments it must be considered whether:

- 1) Uranium hydride formation is possible before or after conditioning a wasteform.
- 2) It is feasible that oxidation will have ensured that all the uranium hydride will have partially oxidised to the surface oxidised state or the final reaction phase prior to any possible initiating event.
- 3) A change in environment has resulted in a change in the availability of reactants, in particular an increase in oxygen availability.
- 4) Any events have taken place that may initiate further reaction, e.g. mechanical disturbance or increase in temperature.

This must be based on conservative, but reasonable, assumptions about the environments that the uranium hydride has experienced.

The assessment should be based on conservative but reasonable assumptions about the storage environment.

The following knowledge gaps are of most relevance to considerations of disposability:

- The implications of increased air flows below ground ( $>1$  m/s) on uranium hydride burning behaviour, e.g. increased RF.
- Data are almost completely absent on hydriding of irradiated metal and the properties of the resulting uranium hydride. The biggest potential impact is on the activity RFs from burning uranium hydride, although current values used by SL are thought to be representative or conservative for irradiated uranium hydride.
- Effect of uranium hydride on criticality safety assessments due to the potential for hydrogen atoms to act as a moderator.

Routes to closure of the knowledge gaps of significance to RWM have been proposed in Section 7 of the report, i.e. sections on:

- Behaviour of burning active uranium hydride in increased air flows.
- Effects of the modified physical properties of irradiated uranium on the understanding of the hydriding reaction.
- Criticality safety assessments.

The other knowledge gaps, which are captured in Section 7, are of lesser relevance to RWM.

## References

- [1] A. C. Adeogun, “Carbon - 14 Project phase 2: inventory,” AMEC/200047/003 Issue 1, 2016.
- [2] N. Bensen, R. P. Straetz and J. E. Draley, “Autoclave tests of tuballoy uranium slugs and alloys,” CT-3043, 1945.
- [3] D. F. Hayes, “A summary of accidents and incidents involving radiation in Atomic Energy activities, June 1945 thru December 1955,” ID-5360, 1956.
- [4] G. E. Zima, “Pyrophoricity of uranium in reactor environments,” HW-62442, 1960.
- [5] T. C. Totemeier, “Characterization of uranium corrosion products,” *J. Nucl. Mater.*, vol. 278, no. 2-3, p. 301–311, 2000.
- [6] RWM, “Geological Disposal: Overview of the generic Disposal System Safety Case,” NDA Report no. DSSC/101/01, 2016.
- [7] RWM, “Geological Disposal: Generic Transport Safety Case – Main Report,” DSSC/201/01, 2016.
- [8] RWM, “Geological Disposal: Generic Operational Safety Case – Main Report,” DSSC/202/01, 2016.
- [9] RWM, “Geological Disposal: Generic Environmental Safety Case – Main Report,” DSSC/203/01, 2016.
- [10] RWM, “Geological Disposal: An overview of the RWM Disposability Assessment Process,” WPS/650/03, 2014.
- [11] J. M. Haschke, “Actinide hydrides,” in *Synthesis of lanthanide and actinide compounds*, Kluwer Academic Press, 1991.
- [12] J. Bloch and M. H. Mintz, “Kinetics and mechanisms of metal hydrides formation – a review,” *Journal of Alloys and Compounds*, vol. 253, pp. 529-541, 1997.
- [13] J. W. Ward and J. M. Haschke, “Comparison of 4f and 5f element hydride properties,” in *Handbook on the physics and chemistry of rare earths vol 18 - lanthanides / actinides: chemistry chapter 123*, Elsevier Science B.V., 1994.

- [14] R. M. Harker, "The influence of oxide thickness on the early stages of the massive uranium-hydrogen reactions," *Journal of Alloys and Compounds*, vol. 426, pp. 106-115, 2006.
- [15] B. Kasemo and E. Törnqvist, "The kinetics of hydrogen interaction with  $\text{TiH}_x$  films,  $0 \leq x \leq 2$ ," *Applied Surface Science*, vol. 3, pp. 307-328, 1979.
- [16] L. Owen and R. Scudamore, "A microscope study of the initiation of the hydrogen," *Corrosion Science*, vol. 6, pp. 461-468, 1966.
- [17] P. Shi, L. Shen, B. Bai, D. Lang, I. Lu, G. Li, X. Lai, P. Zhang and X. Whang, "Preferred hydride growth orientation of U – 0.79 wt.% Ti alloy with  $\beta + \text{U}_2\text{Ti}$  micro," *Journal of Nuclear Materials*, vol. 441, pp. 1-5, 2013.
- [18] M. Hill, R. Schulze, J. Bingert, R. Field, R. McCabe and P. Papin, "Filiform-mode hydride corrosion of uranium surfaces," *Journal of Nuclear Materials*, vol. 442, pp. 106-115, 2013.
- [19] J. Bloch and D. Bami, "Effect of gas phase impurities on the topochemical-kinetic behaviour of uranium hydride development, J. Less Common," *Journal of the Less Common Metals*, vol. 139, pp. 371-383, 1988.
- [20] J. Bloch and M. H. Mintz, "Types of hydride phase development in bulk uranium and homium," *Journal of Nuclear Materials*, vol. 110, pp. 251-255, 1982.
- [21] J. Bloch, F. Simca, M. Kroup, A. Stern, D. Shmariahu, M. Mintz and Z. Hadari, "The initial kinetics of uranium hydride formation studied by a hot-stage microscope," *Journal of the Less Common Metals*, vol. 103, pp. 163-171, 1984.
- [22] A. Banos, N. J. Harker and T. B. Scott, "A review of uranium corrosion by hydrogen and the formation of uranium hydride," *Corrosion Science*, p. <https://doi.org/10.1016/j.corsci.2018.03.002>, 2018.
- [23] T. Majchrowski, "Uranium technical guide," NNL(16)13736 Issue 1, 2016.
- [24] A. Thorburn, M. Brogden and N. Hodge, "Encapsulation of Magnox fuel - small scale uranium corrosion trials - third report," NS(06)7219, 2006.
- [25] R. J. P. Cribb and T. Davis, "Uranium-Magnox fuel elements: post-irradiation examination and assessment progress report no. 161," TRG Memorandum 7399, 1976.
- [26] G. Storey, "Pond corrosion of Hunterston A fuel elements," Fuel Examination Division Note 519, 1976.

- [27] N. Hodge and C. Broan, "Uranium corrosion in cementitious systems - recovery and analysis of corroded uranium samples from tophat trials D and R," NNL(16)13739 Issue 1 RP/BEP\_B873/TECH/00343/A, 2017.
- [28] C. J. Broan, "Activity release from uranium hydride ignition: Experimental measurement of Release Fraction in horizontal airflow," NNL(15)13391, RP/BEP\_B873/TECH/00221/A, 2015.
- [29] C. J. Broan and R. Orr, "Activity release from uranium hydride: Uranium hydride burning in air with water addition," NNL(16)14040, 2016.
- [30] R. Caillat, H. Coriou and P. Perio, "A new form of uranium hydride," *Compt. Rend. Hebd. Seances Acad. Sci.*, vol. 237, pp. 812-813, 1953.
- [31] R. N. R. Mulford, F. H. Ellingbr and W. H. Zachari, "A new form of uranium hydride," *Journal of the American Chemical Society*, vol. 76, pp. 297-298, 1954.
- [32] R. E. Rundle, "The structure of uranium hydride and deuteride," *Journal of the American Chemical Society*, vol. 69, pp. 1719-1723, 1947.
- [33] H. E. Flotow, H. R. Lohr, B. M. Abraham and D. W. Osbourne, "The heat capacity and thermodynamic functions of beta-uranium hydride from 5 to 450 K," *Journal of American Chemical Society*, vol. 81, pp. 3529-3533, 1959.
- [34] W. Bartscher, A. Boeuf, R. Cadiuffo, J. M. Fournier, W. F. Kuhs, J. Rebizant and F. Rustichelli, "Neutron diffraction study of beta-UD<sub>3</sub> and beta-UH<sub>3</sub>," *Solid State Communications*, vol. 53, pp. 423-426, 1985.
- [35] International Atomic Energy Agency, "Regulations for the Safe Transport of Radioactive Material," Safety Requirements Number SSR-6, 2002.
- [36] International Atomic Energy Agency, "IAEA Safety Standards Series - Safety Fundamentals," No. SF-1, 2006.
- [37] D. P. Prentice, B. Walkley, S. A. Bernal, M. Bankhead, M. Hayes and J. L. Provis, "Thermodynamic modelling of BFS-PC cements under temperature conditions relevant to the geological disposal of nuclear wastes," *Cement and Concrete Research*, vol. 119, pp. 21-35, 2019.
- [38] D. R. Linde, Ed., *Handbook of Chemistry and Physics*, 88th ed., CRC Press, 2007 – 2008.

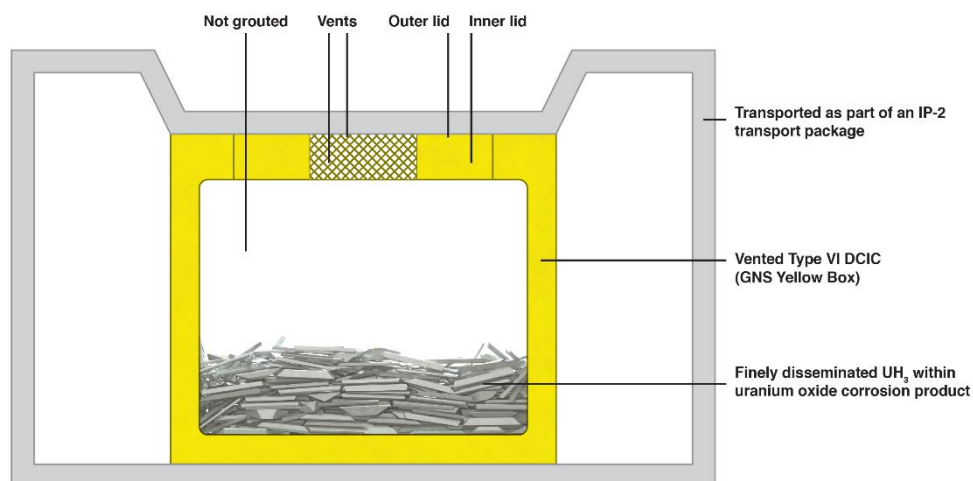
## Appendix 1 - Assessment of Representative Scenarios

The following scenarios for the presence of uranium hydride in waste packages consigned to a GDF were assessed against the appropriate areas of the disposability assessment process, using the agreed summary of uranium hydride behaviour, in a workshop with RWM technical and safety experts. The scenarios are not intended to be exhaustive. They do, however, cover a range of the forms of uranium hydride and types of waste packages that might be expected if real packages were to be assessed through the RWM disposability assessment process. Therefore, these scenarios provide an insight into the issues that may arise when RWM carry out any assessments related to the potential presence of uranium hydride. The scenarios are:

- **Magnox FED with associated uranium in a Type VI DCIC.** In this scenario Magnox FED containing finely disseminated uranium hydride within uranium oxide corrosion product is packaged in a vented Type VI DCIC (GNS Yellow Box). The waste is unencapsulated and is dried by heating under vacuum to remove all free water. The waste package is transported as part of an IP-2 package.
- **Sealed robust container containing one fuel element packaged in a 3 m<sup>3</sup> Box.** This example consists of a fuel element comprising 12 kg of uranium in a sealed container with exactly the right amount of water in the container to have reacted to form the maximum possible amount of uranium hydride (58 % or ~ 7 kg). There is no residual water in the container and it may have undergone extended storage so that the container has become degraded. The container containing the fuel element is packaged in a vented stainless steel 3 m<sup>3</sup> box with other waste that does not contain uranium hydride. The sealed container is not grouted internally. However, the waste within the 3 m<sup>3</sup> box is grouted. The 3 m<sup>3</sup> box may or may not have a grout annulus. The 3 m<sup>3</sup> box will be transported in a sealed Type B SWTC under inert cover gas.
- **FGMSP bulk metallic uranium fuel packaged in a vented SSB.** The waste is not grouted and is transported in a sealed Type B SWTC under inert cover gas.

## Magnox FED with Associated Uranium in a Type VI DCIC

In this scenario Magnox FED with associated uranium metal, containing finely disseminated uranium hydride within uranium oxide corrosion product, is packaged in a vented Type VI DCIC. The waste is unencapsulated and is dried by heating under vacuum to remove all free water. The waste package is transported as part of an IP-2 transport package. See Figure 7.



**Figure 7:** Diagram of Magnox FED with associated uranium scenario.

During storage and transport, no hydrogen gas will result from the corrosion of the DCIC as this is occurring in an atmosphere where oxygen will be present and under these conditions hydrogen gas is not formed. However, hydrogen can be formed from the reaction of Magnox metal with any water vapour, noting that no liquid water should be present in the waste. The vent will allow passage of hydrogen gas out of the waste package as it is formed, meaning that no significant hydrogen gas overpressure will develop. This means that bulk hydriding cannot occur. In addition, as the waste package is vented then there will always be access to a supply of oxidant; mainly atmospheric oxygen, but also water vapour. Therefore, uranium hydride could only be present in small amounts and will be surface oxidised. Any uranium hydride that does remain will be surface oxidised and disseminated throughout the uranium corrosion products and hence will have little potential for further oxidation and heat generation.

The small amount of uranium hydride that could be present will be found as a layer of surface oxidised uranium hydride located at the uranium oxide-metal interface and will be at the later stages of reaction extent (shown in Figure 4). Any ongoing oxidation will be very slow and unlikely to result in any significant thermal events. Due to the decrease in surface area of this interface over time, the total amount of uranium hydride present will reduce.

As fission products will be contained within the irradiated uranium, they may be made available for release by the hydriding process.

The key discussion points and conclusions raised for each RWM disposability assessment area are given below.

### **Wasteform**

In this scenario the robust nature of the waste container provides the greatest contribution to the waste package performance. In effect the wasteform is the waste itself with no additional conditioning media and this is a challenge associated with the non-encapsulation of the waste. Wastes that are considered suitable for packaging for disposal in this manner are generally dry, resistant to atmospheric corrosion, relatively free of non-fixed contamination and chemically inert, i.e. not exhibiting reactive or exothermic behaviour. As described earlier, the environmental conditions in this scenario are such that bulk hydriding cannot occur and any surface oxidised uranium hydride formed as part of the reaction with water will not be present in significant quantities. Therefore, it may be expected that the wasteform would behave in a benign and predictable manner in normal operating conditions with any particulate being retained by the DCIC vent filters.

No credit is taken for the contribution of the wasteform to immobilisation as the waste is unencapsulated and under accident conditions the wasteform will not prevent release of particulate material. However, it was acknowledged that the presence or absence of uranium hydride does not significantly affect the total amount of immobilised waste present in the waste container.

### **Container integrity and durability**

No liquid water should be present within the waste package during interim storage, so the DCIC corrosion rate is expected to be very slow. Any uranium hydride present will be surface oxidised and at the later stages of its reaction extent so the rate of heat generation from the reaction with oxygen (or water vapour) would be low. Hot-spots of reacting active uranium hydride are therefore not expected, so localised self-heating that may create accelerated corrosion of the container will not be an issue.

As the waste is unencapsulated, there is potential for mechanical agitation to move uranic material which is denser than the Magnox component of the waste to the bottom of the package; this is judged to be nowhere near enough to cause ignition. However, these fragments are attached to Magnox and only small amounts of fuel are allowed to be included within the FED; larger pieces of fuel are removed. The presence or absence of uranium hydride does not significantly affect the amount of uranium that could move to the bottom of the waste package.

### **Impact accident performance**

As the container is normally vented, the creation of a small gap between the lid and container body following a drop will not significantly change the atmospheric oxygen ingress rate. The ongoing oxidation of any small amounts of uranium hydride that may form will therefore be able to continue.

On impact, particulate material, potentially including particles of surface oxidised uranium hydride and associated fission products, will be released as the wasteform is unencapsulated and friable. A proportion of the uranium hydride and uranium oxide particulate is expected to be within the respirable <10 µm fraction. As the majority of the particulate is likely to arise from the uranium oxide, the presence or absence of additional uranium hydride derived particulate is likely to have little effect. This is because the uncertainty associated with the amount of uranium oxide likely to be present and released is likely to be greater than the amount of uranium hydride potentially present.

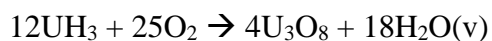
As well as the limited inventory of surface oxidised uranium hydride, and because the waste is dry, it is not credible that a rapid reaction of uranium hydride with liquid water can take place to produce significant quantities of hydrogen gas that could pressurise the container.

No specific complications are anticipated to be caused by the presence of uranium hydride, i.e. any pressure driven release of material will not be affected by the presence of uranium hydride as it is a small proportion of the total particulate inventory.

### Fire accident performance

As the waste is unencapsulated, fire accident conditions are more onerous because no insulation is provided. Magnox ignites at temperatures over 600 °C. However, burning will be limited by the rate of oxygen diffusion into the waste package and Magnox fires tend to be extinguished quite quickly if starved of oxygen. Any surface oxidised uranium hydride present will be rapidly oxidised and this will release some energy. As there is little surface oxidised uranium hydride present the total amount of energy release will be minimal and hence, as illustrated in the following calculation, will be trivial and not generate significant additional heat when compared to the burning of a small amount of the Magnox present or any remaining uncorroded uranium metal.

Assuming that 1 kg of uranium is present and has reacted so that there is now 10 % surface oxidised uranium hydride, 80 % uranium dioxide and 10 % unreacted uranium and this is oxidised by oxygen to  $\text{U}_3\text{O}_8^{\dagger\dagger\dagger}$  and water vapour:



$$\Delta_f H^\circ \text{UH}_3 = -127.2 \text{ kJ/mol [23]}$$

$$\Delta_f H^\circ \text{O}_2 = 0 \text{ kJ/mol [23]}$$

$$\Delta_f H^\circ \text{U}_3\text{O}_8 = -3574.8 \text{ kJ/mol [23]}$$

$$\Delta_f H^\circ \text{H}_2\text{O}(\text{v}) = -241.8 \text{ kJ/mol [23]}$$

Heat of reaction for one mole of uranium hydride

---

<sup>†††</sup>  $\text{U}_3\text{O}_8$  is the most likely phase formed at ~ 600 °C.



$$= ((4 \times -3574.8 + 18 \times -241.8) - (12 \times -127.2 + 21 \times 0)) / 12 \text{ kJ/mol}$$

$$= -1427 \text{ kJ/mol}$$

For the uranium hydride present in 1 kg of uranic material

Molar mass of uranium hydride =  $238 + (3 \times 1) = 241 \text{ g/mol}$

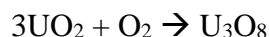
Moles of uranium hydride per kg =  $1000/241 = 4.15 \text{ mol}$

Amount of uranium hydride per kg =  $10 \% = 0.1$

Heat of reaction =  $-1427 \times 4.15 \times 0.1$

$$= -592 \text{ kJ}$$

#### **Oxidation of the remaining 80 % $\text{UO}_2$ to $\text{U}_3\text{O}_8$**



$$\Delta_f H^\circ \text{UO}_2 = -1085 \text{ kJ/mol [23]}$$

$$\Delta_f H^\circ \text{O}_2 = 0 \text{ kJ/mol [23]}$$

$$\Delta_f H^\circ \text{U}_3\text{O}_8 = -3574.8 \text{ kJ/mol [23]}$$

Heat of reaction per mole of uranium dioxide

$$= ((-3574.8) - (3 \times -1085 + 0)) / 3 \text{ kJ/mol}$$

$$= -106.6 \text{ kJ/mol}$$

For the uranium dioxide present in 1 kg of uranic material =

Molar mass of uranium dioxide =  $238 + (2 \times 16) = 270 \text{ g/mol}$

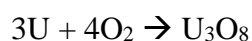
Moles of uranium dioxide per kg =  $1000 / 270 = 3.70 \text{ mol}$

Amount of uranium dioxide per kg =  $80 \% = 0.8$

Heat of reaction =  $-106.6 \times 3.70 \times 0.8$

$$= -316 \text{ kJ}$$

#### **Oxidation of the remaining 10 % U to $\text{U}_3\text{O}_8$**



$$\Delta_f H^\circ \text{U} = 0 \text{ kJ/mol [23]}$$

$$\Delta_f H^\circ \text{O}_2 = 0 \text{ kJ/mol [23]}$$

$$\Delta_f H^\circ \text{U}_3\text{O}_8 = -3574.8 \text{ kJ/mol [23]}$$

Heat of reaction per mole of uranium =

$$\begin{aligned} & (-3574.8 - (3 \times 0 + 4 \times 0)) / 3 \text{ kJ/mol} \\ & = -1191.6 \text{ kJ/mol} \end{aligned}$$

For the uranium present in 1 kg of uranic material =

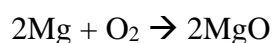
$$\text{Molar mass of uranium} = 238 \text{ g/mol}$$

$$\text{Moles of uranium per kg} = 1000 / 238 = 4.20 \text{ mol}$$

$$\text{Amount of uranium per kg} = 10 \% = 0.1$$

$$\begin{aligned} \text{Heat of reaction} &= -1191.6 \times 4.2 \times 0.1 \\ &= -500 \text{ kJ} \end{aligned}$$

### **Oxidation of Magnox**



$$\Delta_f H^\circ \text{Mg} = 0 \text{ kJ/mol [23]}$$

$$\Delta_f H^\circ \text{O}_2 = 0 \text{ kJ/mol [23]}$$

$$\Delta_f H^\circ \text{MgO} = -601 \text{ kJ/mol [38]}$$

Heat of reaction per mole of magnesium

$$\begin{aligned} &= ((2 \times -601) - (0 \times 2 + 0)) / 2 \text{ kJ/mol} \\ &= -601 \text{ kJ/mol} \end{aligned}$$

For 60 g of Magnox

$$\text{Molar mass of magnesium} = 24.3 \text{ g/mol}$$

$$\text{Moles of magnesium per 60 g} = 60 / 24.3 = 2.47 \text{ mol}$$

$$\begin{aligned} \text{Heat of reaction} &= -601 \times 2.47 \\ &= -1484 \text{ kJ} \end{aligned}$$

Total energy release by oxidation of uranium hydride, uranium dioxide and uranium metal:

$$= -592 - 316 - 500 \text{ kJ}$$

$$= -1408 \text{ kJ}$$

The energy released by the reaction of 1 kg of the uranic material defined above is less than that released by the oxidation of only 60 g of Magnox. Therefore, the presence of surface oxidised uranium hydride will not have a significant effect on the heat generated by the burning of the waste. Note that in practice the uranic content must be much less than this to meet the IP-2 specification and ignition would require an external heat source.

### **Transport safety**

Under routine and normal transport conditions, i.e. considering a 0.3 m drop and transport vibrations, no significant issues are identified.

The waste is dry, so uranium corrosion rates are limited by water vapour diffusion rates through the vent. Even though the waste has a large surface area, hydrogen gas and heat generation rates are both expected to be low, so will be managed by release through the vent. It should be noted that IP-2 transport containers do not need to be purged and may be vented. If the IP-2 transport container is not vented during transport, then this will promote hydrogen build-up and hence provide the conditions required for uranium hydride to form. This will require assessment which should be able to be carried out using the current understanding of the behaviour of uranium hydride in the first instance. If credit needs, and can, be taken for the incubation period before bulk hydriding is initiated, then additional work may be required to provide support.

Under accident conditions during transport, for an IP-2 transport package, no credit can be taken for the container and the performance of the wasteform alone is assessed. The wasteform contains particulate material, so will have a high RF if containment is breached, but due to the limits on activity content there is unlikely to be enough uranic material present to cause a significant activity release. Additionally, the majority of the particulate will be uranium dioxide and hence the presence of any uranium hydride will not have a significant effect on the amount of particulate that could be released.

### **Operational safety**

During normal operations, IP-2 transport packages are considered to be contact-handleable during receipt and opening within the underground reception area, so this area could be manned. If there were to be a significant reaction of uranium hydride when the waste package is removed from the transport container, then this could lead to the release of volatile radionuclides through the vent and subsequent dose to operators. However, significant quantities of uranium hydride will not be present, and this scenario cannot occur.

The waste may generate some hydrogen gas from radiolysis and reaction with water. However, it is considered that not enough hydrogen gas will be generated to produce a significant overpressure, and the vent will also allow any hydrogen gas formed to escape.

No additional fault sequences have been identified, over and above those that would be already present due to the uranium oxide corrosion product, which is present in large excess.

Following emplacement within a vault, the temperature and humidity may increase, resulting in the potential for the hydrogen generation rate to be increased, and an increased potential for the formation of uranium hydride. However, these areas are not manned and the ventilation system extracts air via a filtered stack, so that even if uranium hydride were to form it would be of little consequence.

### **Post-closure safety**

The uranium hydride within the waste, if present, will be surface-oxidised as there has been plenty of time for oxidation by water vapour to occur. Prior to resaturation, and once the waste package is fully saturated, there will not be significant uranium hydride generation because either the conditions of formation are not met or any uranium hydride formed will be quickly oxidised by the water present. There will also be sufficient water present to remove any heat generated from any reactions of uranium hydride.

The maximum potential vulnerability may be at the time of resaturation. In this case rapid hydrogen generation could result, if for some unexpected reason a significant quantity of active uranium hydride were able to form in a waste package, and just the right amount of water was to enter the waste package to react with the uranium hydride, but no more water is available to provide a heat sink to quench the reaction. Even under these conditions, it is considered that a hydrogen overpressure would not be generated as the vault backfill will be designed to be gas-permeable. However, this scenario is not credible for the waste package considered in this section owing to the limited uranium content and its lack of containment that does not lead to conditions for bulk uranium hydride formation.

If there were to be a criticality, the heat generated could drive water flow. The presence or absence of uranium hydride in this situation will make no difference to the outcome.

As shown in the earlier calculation, the source term is so small and the heat sink so large that any temperature rise due to uranium hydride oxidation is expected to be insignificant.

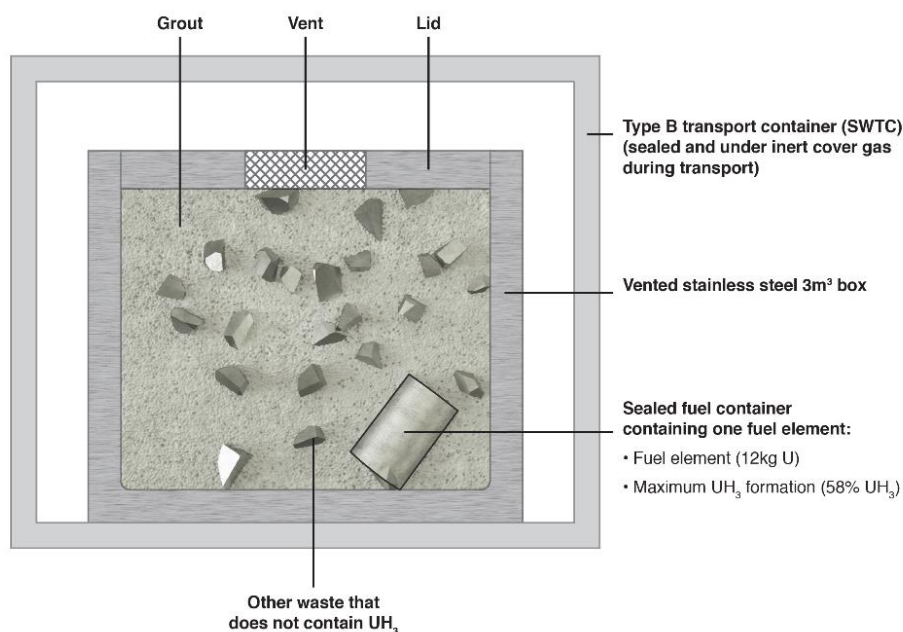
### **Summary**

No issues were identified for this waste package; this is a result of a small amount of surface oxidised uranium hydride being present within the waste and no mechanisms being identified which could change this.

## Sealed Fuel Container Containing One Fuel Element from PIE Packaged in a 3 m<sup>3</sup> Box

This example consists of a fuel element comprising 12 kg of uranium in a sealed fuel container, with exactly the right amount of water in the fuel container to have reacted to form the maximum possible amount of uranium hydride (58 % or ~ 7 kg). There is no residual water in the sealed fuel container and it may have undergone extended storage so that fuel container has become degraded. The sealed fuel container containing the fuel element is packaged in a vented stainless steel 3 m<sup>3</sup> box with other waste that does not contain uranium hydride. The sealed fuel container is not grouted internally. However, the waste within the 3 m<sup>3</sup> box is grouted. The 3 m<sup>3</sup> box may or may not have a grout annulus and this does not affect the following assessment unless specified. The 3 m<sup>3</sup> box will be transported in a sealed Type B SWTC under inert cover gas. See Figure 8.

While active uranium hydride is assumed to exist and persist within the sealed fuel container, as there is no supply of oxidants, no additional uranium hydride can form as all the uranium metal has been converted to uranium hydride or uranium dioxide. The uranic corrosion products are expected to spall off from the uranium metal as they formed, resulting in friable particulate within the sealed fuel container.



**Figure 8:** Diagram of sealed fuel container containing one fuel element in a 3 m<sup>3</sup> box.

The key discussion points and conclusions raised for each RWM disposability assessment area are given below.

### Wasteform

In this scenario there is a greater contribution from the wasteform to the waste package performance than in the previous case. Although the waste is infilled with grout, the

uranic material within the sealed fuel container is not immobilised, and no credit can be taken for the integrity of the sealed fuel container. The cementitious infill grout will provide a large heat sink, simply through its thermal mass, should an exothermic reaction progress. A grout annulus, if present, will provide an even larger heat-sink.

The infill grout is a key feature that limits water and oxygen diffusion in and prevents the release of particulate from the sealed fuel container. The infill grout will also provide chemical containment of radionuclides.

If the fuel container is not disrupted, the potential presence of active uranium hydride will not pose an issue. If the sealed fuel container corrodes and is penetrated without disturbing the rest of the wasteform, even though water vapour is present within the grout matrix, the reaction rate of any active uranium hydride will be limited by the rate of diffusion of atmospheric oxygen through the box vent or water vapour from the infill grout, which is expected to be very slow. A sudden exposure to oxygen or water vapour will be required for there to be a rapid reaction of the active uranium hydride that could result in ignition.

If the sealed fuel container were to fail at some point and water allowed to access the waste, it was identified that work would be required to calculate the amount of gas that would be generated by the rapid reaction of the active uranium hydride, and whether or not the box vent is sized to accommodate this in addition to any gas generated by corrosion, etc. As the rate of reaction will be limited by the rate of diffusion of the water into the sealed fuel container from the infill grout, then it is expected that the calculation will show that the reaction, and hence the rate of gas generation, will be slow.

### **Container integrity and durability**

Due to the high pH environment associated with the infill grout and annulus grout, if present, the stainless steel 3 m<sup>3</sup> box is unlikely to corrode. Therefore, there are no anticipated issues resulting from container evolution.

### **Impact accident performance**

The sealed fuel container containing the fuel element cannot be assumed to be robust to an impact. If the sealed fuel container was near the bottom or edge of the waste package and this region of the waste package was damaged during an impact accident, there is the possibility that the sealed fuel container containing the fuel element could be pierced and the uranium hydride exposed to air. This uranium hydride is assumed to be active and hence will still be very reactive and will ignite if exposed to a ready supply of atmospheric oxygen. It is difficult to argue that the supply of atmospheric oxygen during an impact accident will be sufficiently limited to prevent ignition. However, the rate of burning will be limited by the rate of atmospheric oxygen supply to the burning surface. As the air flow rate in a repository is currently expected to be greater than that tested in the SL uranium hydride burning RF trials then additional testing at higher air flow rates may be required unless credit is taken for residual partial containment of the uranium hydride that shields it from the full impact of the air flow.

There will be less protection from impacts without a grout annulus. A grout annulus could potentially be used to maintain some level of containment, particularly if current assumptions about drop height or movement were made less challenging during GDF emplacement.

### **Fire accident performance**

A grout annulus, if present, will protect the waste to some extent from the highest temperatures.

There is also the potential for an impact accident to expose active uranium hydride which ignites, resulting in activity releases from the ignition as well as the impact.

Methodology development is needed to identify more realistic RFs for entombment of particulate material, when compared to an intimately grouted wasteform, and also for the scenario of an impact followed by ignition of active uranium hydride. Currently RWM assume an RF of 1 for BEP and an RF of 0.7 was assumed for particulate in isolated areas within the MEP bulging drums. In particular the RF where an impact is followed by the release and burning of uranium hydride will need to be developed.

A final consideration is to understand whether or not uranium hydride behaviour in these accidents is bounded by any other materials that have previously been considered for transport or disposal at the GDF.

### **Transport safety**

Under routine and normal conditions of transport, considering a 0.3 m drop and transport vibrations, the container is expected to maintain integrity and no rapid reaction of uranium hydride or excess heat generation is expected. Even if the can was breached by the impact, the reaction rate would be slow as it is limited by the rate of oxygen diffusion through grout and no releases would be expected.

The SWTC is required to survive an impact accident intact, although it is possible that some of the contents of the waste package would be released into the cavity, and a limited amount of material may be released through the lid seal following impact (1 A<sub>2</sub>/week). Whether the uranium hydride is exposed to atmospheric oxygen (and, potentially, water if the transport container is submerged) and undergoes a thermal excursion depends on the performance of the transport package seal, the wasteform, and particularly any grout annulus, under these accident conditions. Due to limited atmospheric oxygen or water ingress through the lid seal, a thermal excursion would not be expected, but particulate release may still occur. However, this issue is not specific to uranium hydride and would also apply to the uranium dioxide present. There is a risk that, if the container containing the fuel element is breached, the retained volatile radionuclide inventory could be released, which if it then escaped through the lid seal may breach the 1 A<sub>2</sub>/week limit. Further calculations would be required to confirm this and define whether or not any further information is required. It was noted that canned fuel from PIE tends to have a higher burn-up and therefore may have a higher volatile inventory than average Magnox fuel.

In a combined accident scenario, fire temperatures then reach 800 °C for 30 min. As the SWTC is a large heat sink, the key question is whether the uranium hydride is exposed to the atmosphere by the impact. To answer this, the combined performance of the SWTC and waste package (including any grout annulus) would need to be demonstrated. Credit cannot be taken for the waste package performance unless this is tested.

### Operational safety

During normal operations, the waste container and any grout annulus are expected to maintain containment and limit atmospheric oxygen ingress, so no activity releases are anticipated.

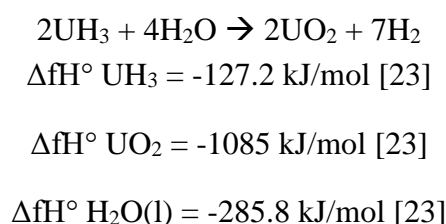
Under GDF impact accident conditions, all barriers (waste container, grout annulus (if present), encapsulant grout and sealed container) would need to fail in order to enable ignition of the active uranium hydride. It was considered that the consequences of such ignition (release of volatile radionuclides and particulate) would be similar to those of uranium dioxide particulate in an unencapsulated wasteform being exposed during an impact accident. However, significant energy would be required to break the waste package and the only potential accidents that would result in such impacts are a shaft drop scenario or vault roof collapse occurrence.

Fire is not expected to occur within the GDF. However, fire risk is inherent to the active uranium hydride material, so confidence is needed that the containment provided by the waste package is sufficient to limit atmospheric oxygen ingress and prevent a significant thermal event that could have an impact. If a release was triggered, the consequences would be significant in terms of GDF contamination and would not be considered to be tolerable (it should be noted that the High Efficiency Particulate in Air filtration employed in a GDF will prevent releases of contamination outside of the GDF). Such an event is not within the current design basis of the ventilation system.

### Post-closure safety

The active uranium hydride within the sealed container will remain chemically reactive and it is assumed that the sealed container will corrode slowly (as it is in a high pH environment) and be penetrated, allowing slow ingress of oxygen and / or water. The reaction and oxidation of active uranium hydride to uranium dioxide will be slow as there is no rapid influx of oxidant, and the wasteform (and any grout annulus) provides a large heat sink. If resaturation was at such a rate that the subsequent reaction generated significant heat, it is possible that this heat could not be adequately dispersed. This scenario is explored in the following calculation.

Reaction with water gives:





$$\begin{aligned}\text{Heat of reaction} &= ((2 \times -1085) - ((4 \times -285.8) + (2 \times -127.2)))/2 \text{ kJ/mol} \\ &= -386 \text{ kJ/mol}\end{aligned}$$

$$\begin{aligned}\text{For 100 g of uranium hydride} &= -386 \times 100 / (238 + 3 \times 1) \\ &= -160 \text{ kJ}\end{aligned}$$

For the 7 kg of uranium hydride assumed to be present in this case this results in 11 MJ of energy being released. This is enough to heat 1 m<sup>3</sup> of water by 3 °C.

Therefore, even for rapid resaturation of a 3 m<sup>3</sup> box, resulting in the reaction of the active uranium hydride fast enough that the heat generated could not escape from the system, this could only result in an increase in temperature in the region of the box of a few degrees at most. Once the waste package is fully saturated, water will quench the reaction.

### Summary

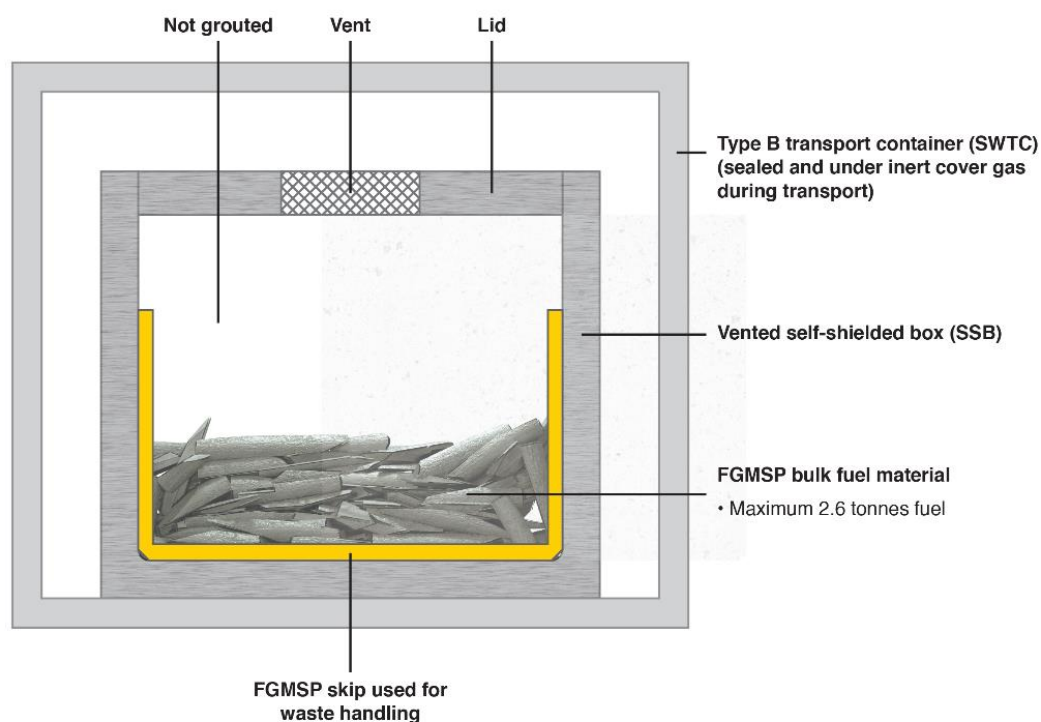
No issues were identified for this waste package under normal conditions. Under accident conditions, making the transport and operational safety cases may be more challenging; further consideration may be needed and potentially a new methodology may need to be developed to demonstrate the case. It was also noted that both uranium hydride and uranium dioxide will both require similar assessments in accident scenarios as both provide a supply of particulate for release.

The following additional gaps were identified, above those already identified in this scenario:

- RF data may be needed to support the assessment of accident scenarios. In particular, the RF where an impact is followed by the release and burning of uranium hydride.
- Methodology development is needed to identify more realistic RFs and DFs for entombment of particulate material when compared to an intimately grouted wasteform.
- Consideration of whether uranium hydride behaviour is bounded by any other materials that have previously been considered for transport or disposal at the GDF.
- Demonstration of the combined performance of the SWTC and waste package including the grout annulus is required.
- Calculation of the retained volatile radionuclide inventory within the sealed can and information on the performance of the can, grout annulus and waste package during an impact accident at the GDF is required.

## FGMSP Bulk Metallic Uranium Fuel Packaged in a Vented SSB

This scenario comprises a maximum 2.6 t of FGMSP bulk fuel material consisting of a mixture of uranium bars and clad fuel elements with pinhole corrosion. The waste is in a skip (that was used to store the material underwater) that is placed directly into a SSB. The waste is not grouted and the SSB is transported in a sealed Type B SWTC under inert cover gas, see Figure 9. It is assumed that some water will be present during transport, and that the SWTC will be sealed, creating the potential for a hydrogen overpressure to form. Therefore, there is the potential for bulk hydriding of the uranium metal to take place during the transport periods allowed for Type-B transport packages. The volume and pressure of hydrogen generated needs to be assessed to determine the total amount of uranium hydride produced. It may have to be assumed, as a worst case, that there is the optimum ratio of water to uranium metal present that maximises the amount of uranium hydride formed. This will also have to be assumed to include some active uranium hydride.



**Figure 9:** FGMSP bulk metallic uranium fuel packaged in a vented SSB.

The key discussion points and conclusions raised for each RWM disposability assessment area are summarised in the following sections.

### Wasteform

Similar to the first scenario (Magnox FED with associated uranium in a Type VI DCIC), a greater contribution to the waste package performance is provided by the waste container than the wasteform in this case. No credit can be taken for immobilisation of radionuclides or hazardous materials as the waste is unencapsulated and the wasteform does not provide chemical containment. Similarly, no credit can be taken for the

wasteform behaving in a benign and predictable manner. The environmental conditions within the packaging arrangement are such that the presence of active uranium hydride cannot be ruled out. The waste package performance is reliant entirely on the container. The skip does not provide any containment.

SL has carried out some calculations that consider a scenario where the vents are blocked, bulk hydriding occurs, and then a vent unblocks again, in which case the rate of atmospheric oxygen ingress through the vent is limited so that a thermal excursion cannot be sustained and the uranium hydride becomes surface oxidised. Additional calculations are required for the SWTC sealing and opening scenario.

Should a thermal excursion occur if active uranium hydride is formed and reacts with oxygen, then there is no cementitious grout present that could dissipate the thermal energy produced.

### **Container integrity and durability**

The presence of uranium hydride would not worsen the potential for container corrosion as metals, water and potentially organics are available so most mechanisms of internal corrosion are already viable.

### **Impact accident performance**

If uranium hydride has formed during transport then, on opening the transport container, atmospheric oxygen will return to the waste package (via the vent) and may surface oxidise the top layer of potentially active uranium hydride formed. However, this will take some time and so for an accident occurring during unloading of the transport package, little oxidation may have taken place. Any uranium hydride formed during pond storage will be surface oxidised.

An impact accident may create a gap in the lid of the waste package and also disturb the layer of corrosion products, allowing faster atmospheric oxygen ingress and ignition of any active uranium hydride present.

Although, following transport, the SWTC and the waste package therein would be handled in a remote access area, if the material ignited this would result in loss of particulate and volatile radionuclides through the vent and/or any gaps in the waste package resulting from an impact accident.

In terms of the potential for particulate release, as there is likely to be considerably more uranium oxide particulate present than uranium hydride, the presence of uranium hydride in itself is probably not significant.

### **Fire accident performance**

There is no wasteform to provide insulation, so the fuel elements and any uranium hydride formed during transport could be exposed to temperatures in the order of 900 °C. Even if it does not ignite, if the temperature exceeds ~300 °C the uranium hydride may decompose, forming hydrogen gas that may result in over-pressurisation

and pressure-driven release of particulate and volatile radionuclides. This raises the questions of whether or not the:

- Hydrogen gas generation rate at these high temperatures is significant enough to pressurise the waste package. This will need to also consider the volumes of hydrogen potentially being generated by the corrosion of other waste materials which would be expected to be larger.
- Lower flammable limit for hydrogen is reached and does it matter?

### **Transport safety**

Transport assessments of Type B transport packages requires the duration of transport to be assumed to be 28 day in the case of a Type B(M) transport package and a year in the case of a Type B(U) transport package<sup>+++</sup>. Under elevated temperatures (up to 100 °C), there is potential for hydrogen gas formation from corrosion to cause pressurisation of the transport container. As the transport package will be sealed, an assessment of the hydrogen gas generation rates and the potential for pressurisation will be required, as described in the waste package accident performance assessment section, above. An inert cover gas is usually added to the container to prevent ignition of any hydrogen gas generated.

Although the corrosion rate of Magnox and uranium metal is accelerated at higher temperatures, the temperatures expected to be attained during transport are not high enough to ignite bulk uranium or Magnox metal, or to decompose uranium hydride.

As noted above, on opening the transport package the potential rate of ingress of atmospheric oxygen and its reaction with any active uranium hydride that could be present will need to be considered.

### **Operational safety**

In addition to the hazards noted in the waste package accident performance assessment, the generation of hydrogen gas is a conventional safety issue, covered by the Provision and Use of Work Equipment Regulations 1998. As this waste/transport package has the potential to generate hydrogen through corrosion, and hence to pressurise, this leads to a different fault sequence to those considered previously in the GDF OSC. Currently, it is not anticipated in the GDF illustrative designs that purge lines will be required for opening containers. However, this scenario demonstrates that purge lines for releasing any hydrogen gas that has built up may need to be included in the design for the transport container receipt and opening facility.

If the inlet cell is contaminated by particulate and volatile radionuclides as a result of the ignition of active uranium hydride, it would become a C4/C5 area and clean-up and maintenance of SWTCs would be more difficult. However, the GDF design will need

---

<sup>+++</sup> Type B packages are designated as Multilateral (M) or Unilateral (U) if they require approval by Competent Authority of each country the package passes through or just by the competent authority of the country of origin respectively.

to be robust to such an incident occurring. If such an incident occurred within the transfer tunnels or disposal vault, this would also cause maintenance and access issues.

Early backfilling may be advisable to reduce the rate of oxygen diffusion into the waste containers within a stack, so that vibrations or other disturbances do not result in rapid reactions; particularly as the container vents may become blocked once they are emplaced. Also, retrieval of such waste packages once they are emplaced would not be advisable; due to the potential risk of a thermal excursion occurring. Therefore, early backfilling may need to be included in the GDF operational plans for wastes with potential to contain significant quantities of active uranium hydride.

### **Post-closure safety**

Any uranium hydride generated prior to post-closure is expected to have oxidised to uranium dioxide as there has been plenty of time for oxidation by water vapour, or oxygen in the air, to occur. There is potential for bulk hydriding to occur if vents block (due to corrosion), if any uranium metal in the package has not already corroded and some water is present to react and generate a hydrogen overpressure. However, this is not considered to be an issue during post-closure.

Following backfilling, the time to resaturation will be variable. Water vapour will be present from the backfill, but there is unlikely to be a hydrogen overpressure as the backfill is designed to allow gas to be released. Even if a hydrogen overpressure forms, due to a blocked vent as discussed above, subsequent oxidant ingress will be slow. If an ignition somehow occurred the consequences would be low because the backfill will provide a large heat sink and prevent any particulate escaping. Once sufficient water is present, any reaction will be quenched.

### **Summary**

Many issues were identified and discussed for this scenario. Where these issues relate to the presence and potential reactivity of uranium hydride it was felt that the current understanding of the behaviour of uranium hydride, along with the understanding generated by addressing the gaps in uranium hydride behaviour already identified, would be sufficient to be able to adequately assess these issues.

The scenario challenges the GDF OSC, but several potential mitigations were also identified. It was also noted that uranium hydride and uranium dioxide will require similar assessments in accident scenarios as both provide a source of particulate for release.

The following knowledge gaps were identified:

- Calculations that consider a scenario where the SWTC is sealed, bulk hydriding occurs, and then the SWTC is opened.
- Understanding whether or not the hydrogen gas generation rate during a fire is sufficient to pressurise the waste package.
- During a fire, is the lower flammable limit for hydrogen reached and what are the consequences if it is reached?

- The potential rate of ingress of atmospheric oxygen and its reaction with any active uranium hydride that could be present on opening the transport package.





## **Radioactive Waste Management Limited**

Building 329  
Thomson Avenue  
Harwell Oxford  
Didcot  
OX11 0GD

**t** +44 (0)1925 802820

**w** [www.gov.uk/rwm](http://www.gov.uk/rwm)

© Nuclear Decommissioning Authority 2022