From Magnox to Chernobyl: A report on clearing-up problematic nuclear wastes

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About me…

2010-2013: Graduated from University of Salford - BSc Physics (Hons)
About me…

2013 - 2018: Started on Nuclear Fission Research Science and Technology (FiRST) at the University of Sheffield

Member of the Immobilisation Science Laboratory (ISL) group

• Wasteforms cement, glass & ceramic
• Characterisation of materials (Trinitite/Chernobylite)
• Corrosion science (steels)
Department Of Materials Science & Engineering

NUCLEAR FIRST
DOCTORAL TRAINING CENTRE

EPSRC
Engineering and Physical Sciences Research Council

The University of Manchester

The University Of Sheffield.
Fully funded project based PhD with possibility to go on secondment

• 3-4 month taught course at Manchester
• 2 mini-projects in Sheffield
• 3 years for PhD + 1 year write up

• Funding available for conferences and training

• Lots of outreach work

• Site visits to Sellafield reprocessing facility, Heysham nuclear power station & Atomic Weapons Authority
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Outreach
PhD projects…

4 main projects

1. Magnox waste immobilisation in glass
2. Magnox waste solidification
3. Chernobyl lava-like fuel containing materials
4. Americium space batteries

Overall title:

Thermal Treatment of Fuel Residues and Problematic Nuclear Wastes
Magnox waste immobilisation in glass

Sellafield
2014
Department of Materials Science & Engineering

**Magnox waste immobilisation in glass**

1956 – Calderhall
Worlds first civil nuclear power station
Magnox waste immobilisation in glass

1956 – Calderhall
Worlds first civil nuclear power station
Research impetus

Magnox waste immobilisation in glass

Wylfa 2014

- Almost 60 years of UK Magnox operations has created a significant quantity of radioactive wastes
- Magnox fleet of reactors used unenriched uranium metal clad in a Magnesium non-oxidising (Magnox) alloy (99% Mg, 1% Al)
Background

First Generation Magnox Storage Pond (FGMSP)
Background

First Generation Magnox Storage Pond (FGMSP)

Magnox waste immobilisation in glass
Magnox corosion

\[ Mg(s) + 2H_2O \rightarrow Mg(OH)_2(aq) + H_2 \]

- Conversion of solid material into hydrated material
- Uranium also incorporated into sludge
- Over 3148 m\(^3\) of consolidated sludge to treat at Sellafield
Current plan

Baseline treatment plan is encapsulation in cement matrix

- Interim storage in controlled warehouse facility in Sellafield
- Final storage in a geological disposal facility (yet to be built)
Geological Disposal

![Graph showing the radioactive content over time for different waste categories.](Image)
Magnox waste immobilisation in glass

Geological Disposal

- Geological Disposal Facility (GDF)
- ~1000 m below the surface
- Multi-barrier principle
Magnox waste immobilisation in glass

Geological Disposal

- Geological Disposal Facility (GDF)
- ~1000 m below the surface
- Multi-barrier principle

How much will it cost?

Excerpt from NDA doc…
Department of Energy & Climate Change, Waste Transfer Pricing Methodology for the disposal of higher activity waste from new nuclear power stations, 2011.

Step 3
For the nine scenarios considered here, the Parametric Cost Model estimates the Fixed Costs of a GDF to be in the range £4401-5015m.

Step 4
Combining the values for each scenario by Monte Carlo methods gives a distribution for GDF Fixed Costs with a minimum of £4401m, a P50 of £4408m and a maximum of £5015m.

This worked example assumes a single GDF.
Current plan

Cementation has two key drawbacks:

- Difficulty predicting long-term durability
- Significant increase in waste volume

Alternative wasteform needed to improve safety case & save on cost of geological disposal
Magnox waste immobilisation in glass

Vitrification

Proven technology for immobilisation of high level waste
Radiation resistant and potential for high waste loadings
Can incorporate wide spectrum of elements
Long-lived natural analogues (obsidian)
Waste simulants

Corroded Waste (wt%)

- Mg(OH)₂: 80%
- U: 10%
- U₃O₈: 5%
- Mg: 5%

Represents material that has significant corrosion and high in oxides and hydroxides

Metallic Waste (wt%)

- Mg(OH)₂: 20%
- Mg: 12%
- U: 68%

Represents fuel with little corrosion and high in metallic content (U & Mg)
Glass formulations

Magnesium aluminosilicate system (MAS)
\( \text{MgO-\text{Al}_2\text{O}_3-\text{SiO}_2} \) (1350 °C)

Magnesium borosilicate system (MBS)
\( \text{MgO-B}_2\text{O}_3-\text{SiO}_2 \) (1190 °C)
Glass samples

MAS Glasses: 1500 °C 5 hours, annealed at 560 °C, between 20-24 wt% waste loadings

MBS Glasses: 1250 °C 3 hours, annealed at 610 °C, between 33-37 wt% waste loadings
Magnox waste immobilisation in glass

MgO-Al₂O₃-SiO₂ (MAS) system – Phase analysis

Fingerprint peaks - Uraninite

Diffuse scattering - we have formed X-ray amorphous glass

Dendritic crystals

Crystallite size: ~2 µm
**MgO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} (MAS) system – Phase analysis**

- **Fingerprint peaks - Uraninite**
  - Diffuse scattering - we have formed X-ray amorphous glass
  - Dendritic crystals
  - Crystallite size: ~2 µm

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**Magnox waste immobilisation in glass**
MgO-B$_2$O$_3$-SiO$_2$ (MBS) system – Phase analysis

Diffuse scattering - we have formed X-ray amorphous glass

Crystallite size: ~5 µm

Metallic waste glass crystallises - Uraninite and triuranium octoxide

Oxygen

Magnesium

Silicon

Uranium
Thermal analysis - DTA

MBS glasses:
- Glass transition ~670 °C
- Liquid from 1151-1200 °C

MAS glasses:
- Glass transition ~630 °C
- Liquid above 1375 °C

Heated sample from RT to 1500 °C – MAS unsuitable due to high melting temperature
Chemical durability – 90 °C, SA/V: 1200 m⁻¹

Accelerated dissolution to test durability

MAS corroded waste sample released more uranium due to higher oxidation state.

Release rates comparable to UK HLW, but several orders of magnitude lower activity.
Chemical durability – Alteration layers

Suggests alteration layer is not a passivating region
Potential volume reduction

Total untreated waste volume 3148 m³
- Increased to 11,584 m³ with cementation
- Reduced to 2365 m³ with vitrification

Cost of ILW disposal = £8990 / m³

Therefore vitrification can save up to £82 million ($100 million)
Conclusions

• A single glass formulation (MBS) can be used to treat both extremes of the waste expected in Sellafield’s Magnox sludge.

• Vitrified products can be produced at industry friendly temperatures with suitably high waste loading

• Significant cost savings compared with cementation and MBS samples show comparable dissolution rates to UK HLW glass
PhD projects...

4 main projects

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3. Chernobyl lava-like fuel containing materials
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Thermal Treatment of Fuel Residues and Problematic Nuclear Wastes
Background

April 26 1986 reactor 4 of Chernobyl NPP exploded spreading radioactive particles across Europe.

Level 7 International Nuclear Event Scale and the worst nuclear power plant accident in history – 31 direct deaths.
Background

Chernobyl lava-like fuel containing materials

New safe confinement

Reactors 1, 2, 3, 4
RBMK-1000 Reactor

Pressurised LWGM reactors

UO₂ fuel slightly enriched clad in zircaloy tube

Positive void coefficient – reactivity increases as amount of steam increases.
Components that became part of lava:

- 90 tons uranium oxide fuel
- 45 tons zirconium cladding
- 20 tons steel
- 770 tons concrete
- 280 tons material dropped into reactor

Lava temperature $<1700 \, ^\circ C$

Chernobyl lava-like fuel containing materials

Formations

Fuel (UO$_2$) → Explosion → Fuel fragments

- UO$_x$
- U glass
- UO$_2$
- (Zr,U)SiO$_4$ - Chernobylite
- ZrO$_2$+U
- UO$_x$+Zr
- Zr-U-O
Two main compositions of lava:

**Brown lava** – Iron contamination & high uranium content (~10wt%)

*Example: Steam discharge rooms*

**Black lava** – Lower uranium content (~5wt%)

*Example: Elephant’s foot*
‘Lava-like’ Fuel Containing Materials (LFCM)

Two main compositions of lava:

Brown lava – Iron contamination & high uranium content (~10wt%)
Example: Steam discharge rooms

Black lava – Lower uranium content (~5wt%)
Example: Elephant’s foot

Chernobyl lava-like fuel containing materials
Key motivations

Chemical durability of the lavas is under question due to ingress of water from leaks and ground water flow – humidity and temperature expected to accelerate the rate of weathering.

Secondary uranium phases observed may also provide a significant pathway for release of radioactivity from the site.

Formation of soluble uranium phases is undesirable from the safety case point of view.

Simulant LFCM needed to recreate the microstructure and morphology of the Chernobyl lavas.
Experimental technique

**Synthesis:**

Compositions selected from surveying available literature

Several trial melts and temperatures to tweak

**Multi-scale Characterisation:**

XRD – Microstructure

SEM/EDX – Crystal morphology

DTA – Thermal properties

PCT-B & ICP-OES – Durability
Chernobyl lava-like fuel containing materials

**XRD**

**Black LFCM**

- $\text{(U}_{0.93}\text{Zr}_{0.07})_2\text{O}_2$ PDF 01-078-0666
- $\text{ZrO}_2$ PDF 01-072-1669
- $\text{Zr(SiO)}_2$ PDF 01-071-0991
- $\text{Fe(Fe}_{1.96}\text{Cr}_{0.03}\text{Ni}_{0.02})_4\text{O}_4$ PDF 01-080-0389

**Brown LFCM**

- $\text{(U}_{0.93}\text{Zr}_{0.07})_2\text{O}_2$ PDF 01-078-0666
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SEM-EDX

Brown LFCM

Chernobylite

Actual LFCM by Boris Burakov – Radium Institute
SEM-EDX

Black LFCM

Chernobyl lava-like fuel containing materials

Actual LFCM by Boris Burakov – Radium Institute
Future work

Investigate the secondary uranium minerals forming on ‘aged’ LFCM samples.

Secondary phases include studtite and rutherfordite.
Chernobyl lava-like fuel containing materials
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Thermal Treatment of Fuel Residues and Problematic Nuclear Wastes
Worlds largest stockpile of plutonium ~114 tonnes

\[ ^{239}_{94} Pu \xrightarrow{n} ^{240}_{94} Pu \xrightarrow{n} ^{241}_{94} Pu \xrightarrow{\beta^-} ^{241}_{95} Am \quad (\sim 14 \text{ years}) \]
Amercium space batteries

**Worlds largest stockpile of plutonium ~114 tonnes**

\[
\begin{align*}
^{239}\text{Pu} \xrightarrow{n} &\quad ^{240}\text{Pu} \\
\quad &\quad ^{241}\text{Pu} \xrightarrow{\beta^-} ^{241}\text{Am} \\
&\quad (~14\text{ years})
\end{align*}
\]
Worlds largest stockpile of plutonium ~114 tonnes

Radioisotope Thermoelectric Generators (RTGs) (a.k.a Space Batteries)

\[ ^{239}_{94} Pu \xrightarrow{n} ^{240}_{94} Pu \xrightarrow{n} ^{241}_{94} Pu \xrightarrow{\beta-} ^{241}_{95} Am \quad (\sim 14 \text{ years}) \]
Americium space batteries

Voyager 1 & 2 (1977)

New Horizons (2006)

Mars Science Laboratory, Curiosity

Cassini (1997)
Voyager 1 & 2 (1977)

New Horizons (2006)

Mars Science Laboratory, Curiosity

Cassini (1997)

Americium space batteries
How does a RTG work?

Pu-238

Americium space batteries
How does a RTG work?

Pu-238

General Purpose Heat Source (GPHS) Module (expanded view)

- Fuel clads in fueled position
- Aeroshell
- Carbon fiber sleeve
- Graphite impact shell
- Irridium metal cladding
- Plutonium-238 dioxide fuel pellet (heat source)

Amercium space batteries
How does a RTG work?

Pu-238 Americium space batteries
Pu-238 is becoming scarce (several kg) – product of developing nuclear weapons

European Space Agency (ESA) identified Am-241 as isotope of choice:

- Utilisation of waste from nuclear industry – abundance
- Can be separated from economically
- High melting point
- Alpha decay only (minor gamma)
Immobilisation of Americium in durable ceramic phase…

\[ \text{Am}_3\text{NbO}_7 \]

Cannot use Americium in lab…

\[ \text{Ce}_3\text{NbO}_7 \]

Use Cerium as Surrogate for Americium

Difficult synthesis process
- New material – not in ICSD database
- Structure simulated from $\text{Nd}_3\text{NbO}_7$
- XRD shows good agreement, slight difference between observed data and refined crystal – needs more high resolution data
Neutron Diffraction

- 800 MeV Synchrotron into tungsten target @ 84% light speed

- HRPD instrument – highest resolution in the world

Americium space batteries
Neutron Diffraction

- ND shows good agreement, slight difference between observed data and refined crystal
- Due to space group of material – current work
Overall Conclusions

From Magnox Project:

- Large quantities of waste – larger still with current plan
- Vitrification possible with a single durable wasteform
- Significant cost savings from vitrification over cementation

From Chernobyl Project:

- Hazardous material – durability in question
- Simulant LFCM can be created in the lab
- Represents real material – structure & morphology

From Space Battery Project:

- Potential to use Am in RTG
- Novel material created $\text{Ce}_3\text{NbO}_7$
- Difficult synthesis method
Special thanks to:

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Prof Russel J. Hand
Dr Martin C. Stennett
Dr Claire L. Corkhill
Mr Adam J. Fisher
Mr Daniel J. Bailey
& the ISL team!

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Thank you for listening!

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