Thermal Treatment of Plutonium Contaminated Materials (PCM) Waste

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Introduction – The UK PCM Waste Immobilisation Challenge

PCM waste storage at Sellafield

Plutonium Contaminated Material Waste:

- Stored in 200 litre drums: PVC packaged; masonry, metal, organic, glass.
- 30000 m³ UK waste by volume, 7% of UK ILW inventory.
- Baseline "conditioning": super-compaction and cementitious encapsulation
- The heterogeneous nature of the waste material presents a considerable materials science and engineering challenge for PCM immobilisation

Opportunity: Volume Reduction by Thermal Treatment

Advantages	Process conditions
• Enhanced passive safety • Reduced interim storage costs • Reduced waste disposal cost • Destroy all organic matter	• Treat all wastes without repackaging (Inc. drum) • Treats all wastes using common process

Although proof of concept studies have demonstrated PCM compatibility with thermal processes, a fundamental understanding of waste incorporation reactions and the impact of waste inventory on product quality remains to be established. This generic understanding of thermal processes is clearly critical for successful industrial application of thermal treatment of PCM waste.

Aims are to understand;

- The sequence of reactions leading to waste digestion in thermal treatment
- Control of Pu surrogate partitioning between off gas and waste form slag and metal components
- Selection of glass forming additives to optimise waste digestion and waste form quality

Experimental Methods

Using Ce as a Pu surrogate laboratory scale experiments using simulant PCM drum mock ups of PVC waste, metal waste, mixed waste and masonry waste have been performed in order to understand the reactions and processes of waste digestion and incorporation during thermal treatment.

Waste type	PVC	Metal	Masonry	Mixed
Mild steel (wt%)	44.0	20.0	30.0	30.0
PVC (wt%)	56.0	10.0	10.0	10.0
Metal items (wt%)	0	70.0	0	15.0
Masonry waste (wt%)	0	0	60.0	40.0
Glass (wt%)	0	0	0	5.0
Crucible	Alumina	Graphite / clay	Alumina	Alumina

Plutonium surrogate
Addition of 1.04 wt% CeO_2 Equivalent to twice upper PuO_2 inventory

Table above: Representative simulant PCM waste

Laboratory scale simulant waste, PCM drum mock ups

Addition of glass forming frit at a 1:1wt% ratio with waste simulants
↓
1560˚C Melting temperature for 4 hours
↓
Crucibles removed at 1560 ˚C and allowed to solidify at room temperature.

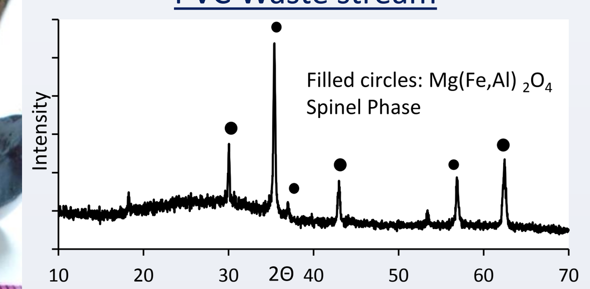
Waste form and process considerations

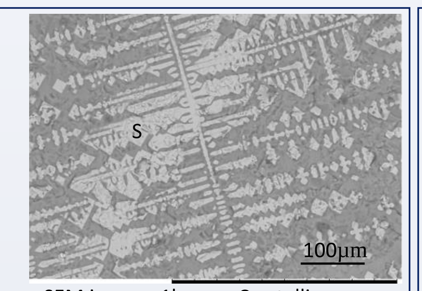
1. Requirement for high metallic feeds and for common process / additive. Unlikely that all metal can be oxidized therefore a wasteform consisting of slag and metal component will be targeted. If sufficient Partition Pu / Ce into slag phase this may allow metal to be recycled.
2. To achieve high partitioning ratio, metal component should be molten. For carbon and stainless steels require: 1425-1540 °C. Selected melting temperature of 1560 °C with 4 h melt time
3. Additive must be stable in equilibrium with molten steel. Use recycled glass cullet as additive (recycled soda lime silica glass) essentially Na_2O-CaO-SiO_2 glass with melting point in range 1100-1200 °C

Resultant Waste form

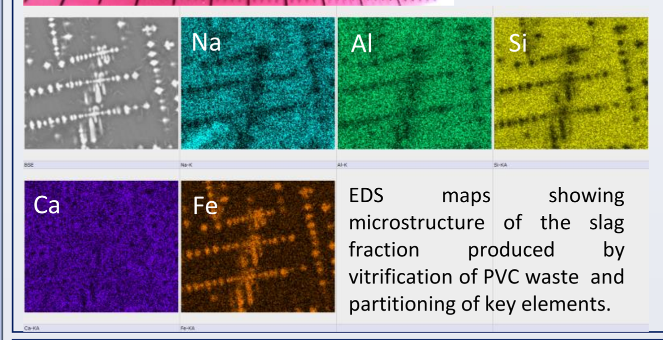
Melting behaviour shows no violent reactions between the waste simulant and glass additive. A metallic fraction resulted for the vitrified metal type. PVC and masonry waste types were composed of 100% glass waste form. Glass in masonry and metallic feed exhibited little crystallinity. Glass derived from PVC and Mixed were partially crystalline throughout. Cl presented in the PVC was volatilised at high temperature

PVC Waste stream





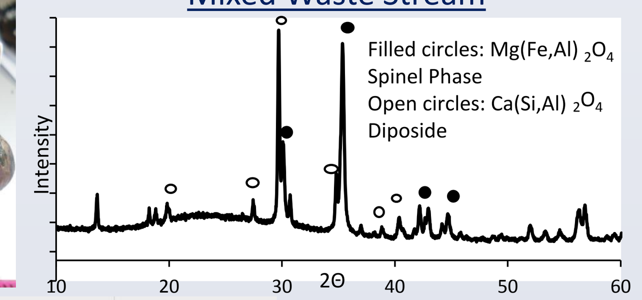
SEM image x1k mag. Crystalline phase labelled S corresponds to spinel phase.

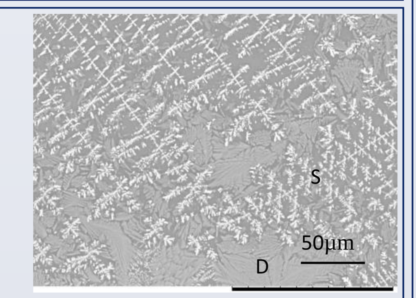


EDS maps showing microstructure of the slag fraction produced by vitrification of PVC waste and partitioning of key elements.

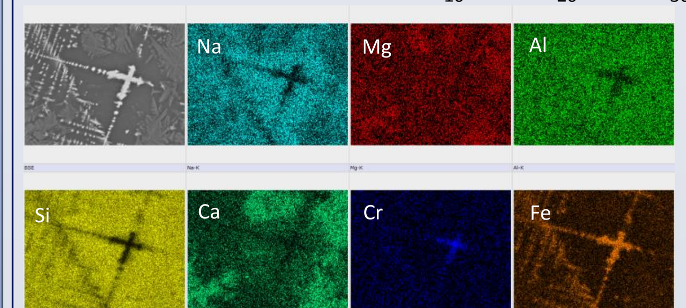
Phase Analysis
XRD pattern showing identified reflections corresponding to spinel phase $(Mg)(Fe,Al)_2O_4$ (Magnesioferrite). Diffuse scattering corresponding to the presence of an amorphous component in the form of $CaO-Al_2O_3-SiO_2-Fe_2O_3$ glass. The SEM image shows dendritic crystal structure corresponding to the identified spinel phase

Mixed Waste Stream



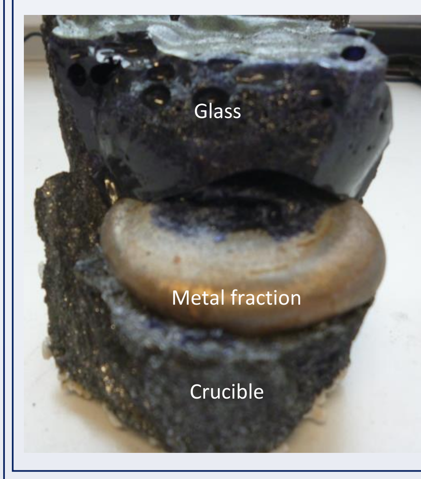


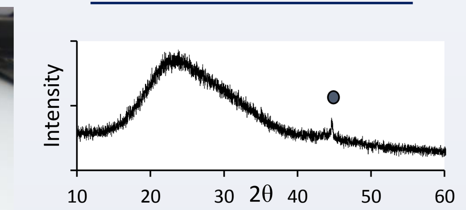
SEM image x1.5k mag . Spinel phase labelled (S) Diopside labelled (D).

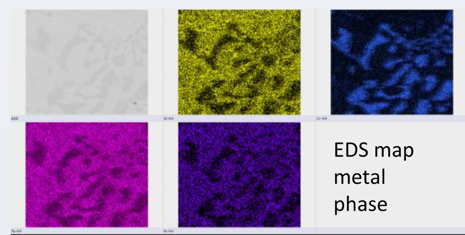


Phases analysis
XRD pattern showing identified reflections corresponding to crystalline $Ca(Si,Al)_2O_6$ (diopside), and $(Cr,Fe,Al)_2O_4$ (spinel) phases. Diffuse scattering corresponding to the presence of an amorphous component in the form of $CaO–Fe_2O_3–Al_2O_3–SiO_2$ glass. SEM image shows dendritic structure (spinel phase) and diopside crystal phase.

Metallic Waste stream



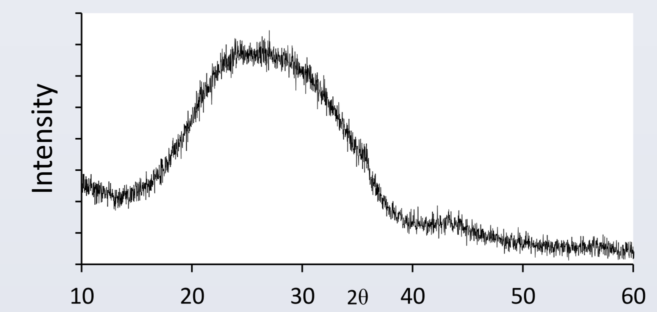




Analysis of slag phase
XRD patern showing diffuse scattering corresponding to an amorphous component in the form of $CaO-Al_2O_3-SiO_2-Fe_2O_3$ glass. Graphite inclusions present.

Analysis of metallic phase
EDS maps showing microstructure of metal fraction (Fe-Si-Ni alloy) produced and partitioning of key elements.

Masonry Waste Stream



$CaO-Al_2O_3-SiO_2-Fe_2O_3$ glass
No crystalline phases presents or undissolved material within glass matrix, as shown by XRD trace.

Discussion/Conclusion

PuO_2 (CeO_2 surrogate) from the PCM is physically and chemically immobilised in the resulting materials, i.e no residual PuO_2 (CeO_2) remains after processing.

All of the analysis indicated that Ce was incorporated into the oxide phase in all samples.

No residual waste remained following processing – Visual, XRD and SEM investigations lead to the conclusion that in all samples no unmelted waste or additives remained following processing.

No adverse waste / matrix reactions occurred during or following processing.

Further Opportunity for Vitrification of Legacy UK ILW – Silo Pond Scabblings Waste

The focus of this project is thermal treatment of PCM wastes relevant to four sites across the NDA estate. Since the aim is to develop a fundamental mechanistic understanding of waste incorporation reactions during thermal treatment, the research will be transferrable to treatment of wastes within the UK ILW envelope (which could also be co-treated with PCM). This project focuses on thermally treating conditioned cementitious waste streams and contaminated concrete scabblings; from silo fuel ponds at sites such as Bradwell and Sellafield.

decommissioning contaminated masonry from fuel ponds

Legacy and intermediate level wastes that may be considered for vitrification include many different materials, each presenting its own chemistry and physical makeup. Many types of ILW themselves possess the key oxides for glass making, chiefly SiO_2.
This affords an immediate potential benefit of high waste loading and volume minimisation
The objectives of this project is to evaluate whether masonry waste removed from the decommissioned silo ponds as scabblings contain sufficient amounts of glass forming oxides, mainly SiO_2, to aid vitrification of a passive glass waste form

Using masonry waste as the waste simulant, XRF results shows masonry waste contains 77% SiO_2. Using masonry waste as the SiO_2 component and boric acid and sodium carbonate, successfully formed borosilicate glass at 1100° C.

Simulated masonry waste

SiO2	77.05%
CaO	8.54 %
Al2O3	3.46%
Fe2O3	1.22%

XRF results, masonry waste

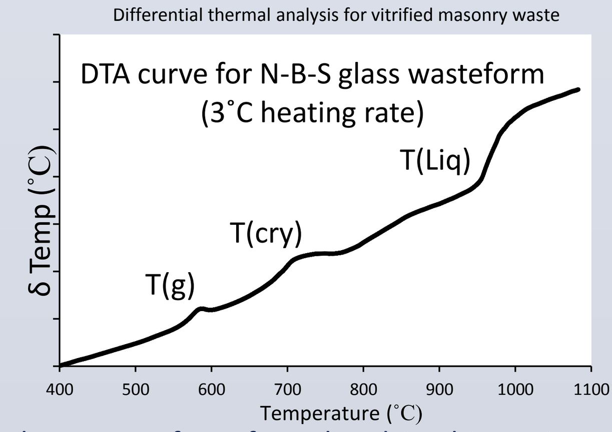
TEMA milled masonry waste

vitrified masonry waste, 68 wt% SiO_2 (masonry waste), 18 wt% B_2O_3, 14 wt% Na_2O

XRD patterns shows amorphous borosilicate structure with no undissolved material in the matrix of the glass. Borosilicate glass is used for HLW vitrification. Glass is an excellent medium for waste immobilisation due to the small volume of resultant waste-form, the large number of elements which can be incorporated in the open glass structure and glasses potentially high durability

In order to avoid unwanted crystallisation during processing the molten glass must be maintained at temperatures sufficiently in excess of T(liq) until it has passed the nozzle during pouring.

Differential thermal analysis for vitrified masonry waste



Strong evidence that the glass waste form formulated in this project would be compatible for currently available thermal treatment technology platforms

Future Work

Fundamental glass properties that need to be established	Quantification method
Viscosity- temperature relationship	Viscometer
Homogeneity waste solubility	SEM, EDX, Phase analysis
Waste solubility	XRD to determine amorphous structure
Chemical durability	Durability testing such a PCT
Volatilisation/ off gas considerations	Wet chemistry

Industrial Impact of Research Project

The project will address a key knowledge gap in developing new knowledge and fundamental understanding of PCM waste incorporation reactions in thermal treatment processes. This will lead to a scientifically underpinned product and process, with cost savings of >£360 M for disposal and several £100M for waste treatment.
The project, funded by the UK Nuclear Decommissioning Authority, contributed to the ISL research group being awarded "University of Sheffield Enterprise Innovation and Impact Award" in recognition of the research that has been taken and used to create positive social impact in the wider community.

Mike James (left) Neil Hyatt (right) at the awards evening (Sept 2014).

"It has been a very fruitful partnership, where we understand one another. We understand the need to harness science and engineering to address real world challenges, and the team at Sellafield Ltd understands the need to harness fundamental science in order to solve technical problems. This gives us very similar outlooks from different ends of the science spectrum"
Professor Neil Hyatt, Director Immobilisation Science Laboratory

"This work has provided us with important evidence to support our baseline strategy towards a major investment in thermal treatment of plutonium contaminated materials."
Mike James, Head of technology for Sellafield Ltd

The Research has also gained widespread media coverage

Articles featured from left to right: 1.Process Engineer 2.IFL Science 3.Science Newsline 4.Nature World News 5. Clean Technica

Further Work – The challenge of treating of high metallic waste streams

It may be possible to treat the resulting metal phase as LLW or VLLW, if efficient and reproducible Pu partitioning into the slag phase can be achieved to the required threshold. This would require the slag and metal phases to be tapped separately from the melter in *operando* or separated from the slag post processing (which is not desirable).
The project has shown that by adding Iron (III) oxide, it is possible to oxidise all of the metallic content producing a complete glass wasteform

Vitrified mixed waste showing metallic waste fraction

Addition of Fe2O3 at a 1:1 molar ratio with expected metallic fraction →

Vitrified mixed waste with Fe_2O_3 addition showing resultant glass formation. No metallic waste fraction.

Poster Summary

Considering the high overall costs of waste disposal and the growing requirements for improved quality of the final waste form, the benefits offered by thermal processing become very significant. Key drivers for the application of thermal treatment processes include the reduced volume, improved passive safety, and superior long term stability, of the vitrified wasteform products. The project has demonstrated these benefits are derived from the oxidation of the metallic waste fraction, destruction of organic components, and evaporation of entrained water, combined with simultaneous immobilisation of radioactive and chemotoxic elements within a glass or slag (i.e. a partially crystallised glass) material.

Currently a fundamental lack of scientific knowledge and understanding significantly hinders the uptake of thermal treatment processes for the immobilisation and disposal of plutonium contaminated material waste.
The project will contribute to accelerating the acquisition of knowledge and experience required to support the NDA in deploying thermal technologies as a national asset for ILW treatment

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