Thermal Treatment of Plutonium Contaminated Material (PCM) wastes

Project Update – Distinctive meeting 17/11

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12/11/2015

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PCM waste – Background

Plutonium Contaminated Material – PCM Waste

- Stored in 200 litre drums
- PVC packaged: masonry, metal, glass, organic, polymer
- Unconditioned volume 30,000m^3
- 7% of UK ILW inventory by volume
- Baseline "conditioning": super-compaction and encapsulation

Opportunity: volume reduction by thermal treatment

- Enhanced passive safety
- Reduced interim storage costs
- Reduced waste disposal cost
- Treat all wastes without repackaging (inc. drum)
- Treat all wastes using common process and additive(s)

The heterogeneous nature of the waste material presents a considerable materials science and engineering challenge for PCM immobilisation.

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Aims of the project

To develop an understanding of waste / matrix interactions during thermal treatment of PCM wastes arising over four NDA sites. The specific objectives 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 /metal components
- Selection of glass forming additives to optimise waste digestion and waste form quality

"More broadly, the project will contribute to accelerating the acquisition of knowledge and experience required to support NDA in deploying thermal technologies as a national asset for ILW treatment."

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Work Packages (WP)

1. **Laboratory scale experiments using mock ups of PCM simulants and glass forming additives to understand the reactions / processes of waste digestion and incorporation**;

- Impact of waste composition on nature of wasteform (i.e. fraction of slag / metal component)
- Burn out of organics / PVC
- Surrogate partitioning and speciation, between glass, crystalline and metallic phases
- Overall and surrogate mass balance

2. **Evaluate wasteforms against product quality criteria**:

- Develop and implement plan for process and product optimisation.
- Using a fundamental understanding of waste / additive interactions and interaction with industry.

3. **Selection of optimised wasteforms:**

- Develop an understanding of product stability with respect to generic ILW disposal concepts.
- Accelerated dissolution experiments.

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WP1: laboratory scale experiments

1. **Laboratory scale experiments using mock ups of PCM simulants and glass forming additives to understand the reactions / processes of waste digestion and incorporation.**

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WP 1: Laboratory scale experiments

PVC waste simulant

Metallic waste simulant

Mixed waste simulant

Masonry waste simulant

Mock up drums in alumina crucibles and clay graphite crucible (metallic waste stream)

- 1:1 additive to waste ratio glass frit
- 1.43%wt CeO2 used as Pu surrogate
- 1%wt Boron used (tracer)

PCM simulants				
Weight (g)	PVC waste (g)	Metal waste (g)	Masonry waste (g)	Mixed waste (g)
Mild steel	41.1	41.4	41.3	41.1
Metal items	0	144	0	20.5
Masonry waste	0	0	82.6	54.7
Glass (PyrexÂ®)	0	0	0	6.8
PVC sheeting	51.5	20.7	13.8	13.7
CeO2	0.9482	2.143	1.4328	1.4159
Sub-total	91.6	208.05	138.53	137.28
Glass frit additive	91.87	208.05	138.76	137.3
Total weight	182.56	416.06	275.86	274.58
crucible	610.04	1035.6	574.68	499.48
Total weight including crucible	792.6	1451.66	850.54	774.06
1wt% boron addition	0.916	2.0805	1.3853	1.373

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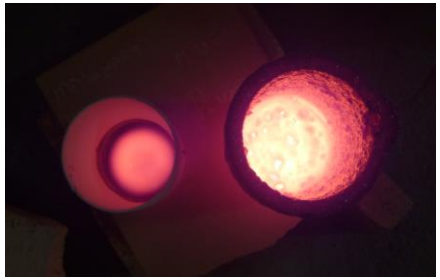
Vitrification of laboratory scale PCM drums

Addition of glass forming frit at a 1:1wt% ratio with waste simulants



1450˚C Melting temperature for 4 hours

Resultant Wasteforms: Melting behaviour shows no violent reactions between the waste simulant and glass additive.

metal waste feed incompatible with alumina crucibles, due to prohibitive corrosion, and "Salamander" Plumbago crucibles, formed from a clay/graphite composite, were preferred

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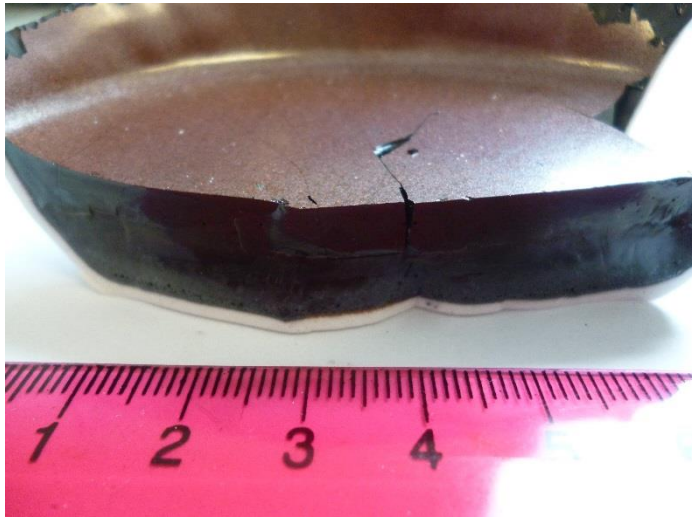
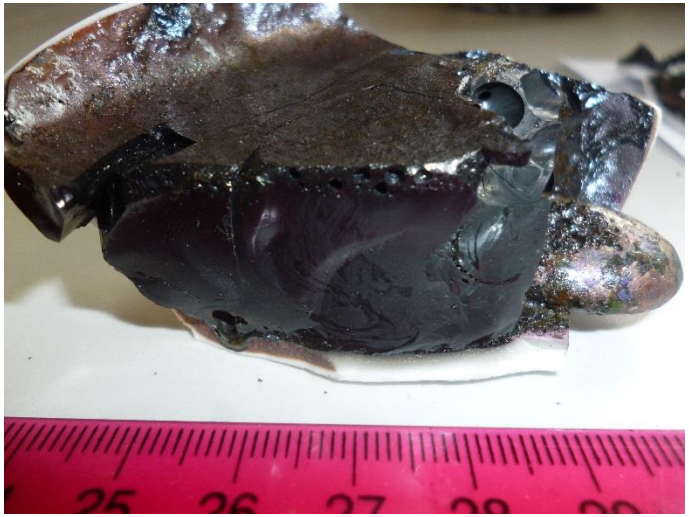
Resultant Wasteforms

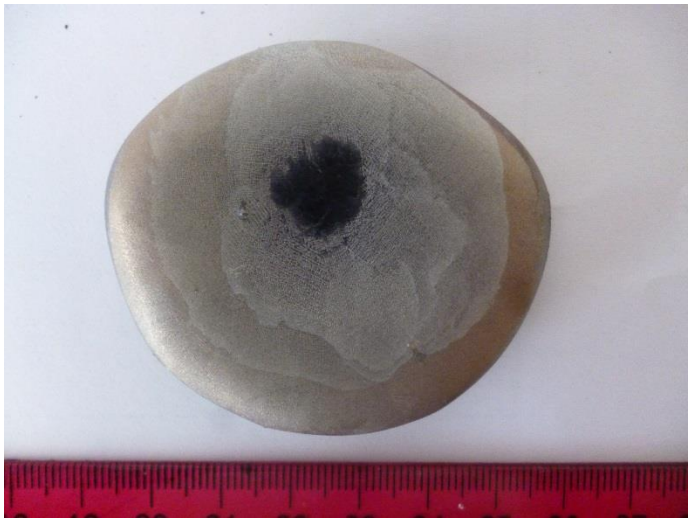


PVC waste



Mixed waste

Metallic waste



Resultant metallic waste fraction

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XRF results of vitrified waste forms

Component (Wt%)	PVC	Masonry	Metal	Mixed	Glass frit
SiO2	37.93	54.85	69.87	54.23	70.77
MgO	0.85	0.86	1.17	0.93	1.5
Al2O3	16.51	11.70	7.6	9.29	1.57
CaO	5.46	7.07	7.43	6.9	10.16
Na2O	6.02	6.81	7.72	6.53	13.27
Fe2O3	30.38	17.65	0.82	18.13	0.36
Other	2.2	1.25	3.98	3.08	1.26
Sum	99.31	99.53	98.59	99.09	98.89

High metal feeds necessitated the use of graphite-clay crucibles, imposing a reducing environment, leading to a combined slag / metal wasteform; the slag component was thus strongly depleted in FeO

Estimated volume reductions 90% for PVC and metal wastestreams and 80% for masonry and mixed wastestreams

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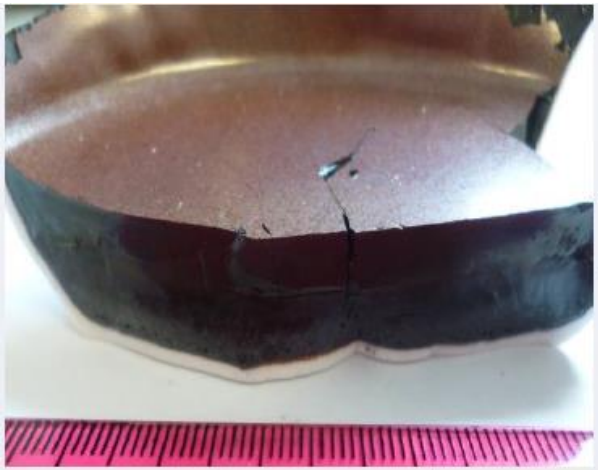
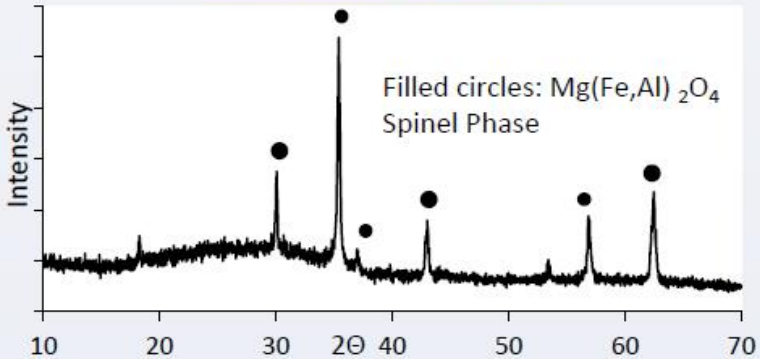
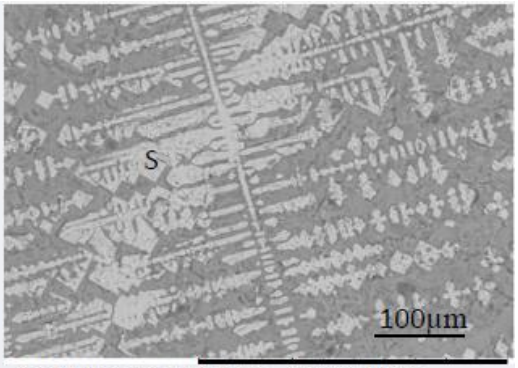
PVC Wasteform

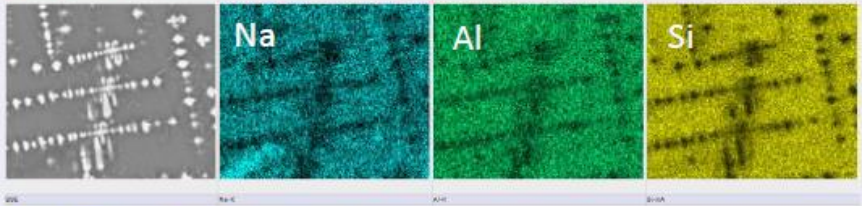


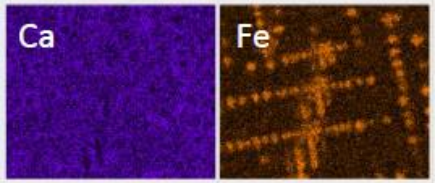
PVC Waste stream





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

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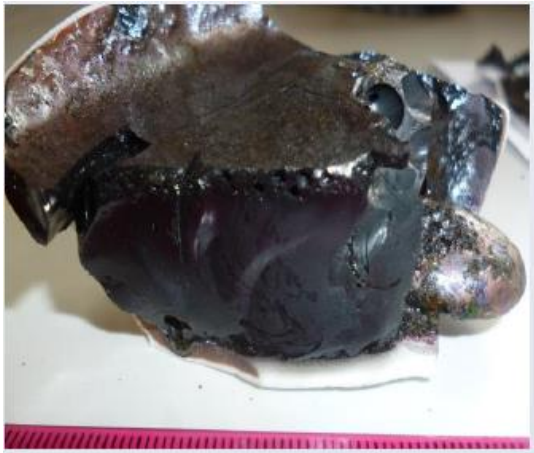
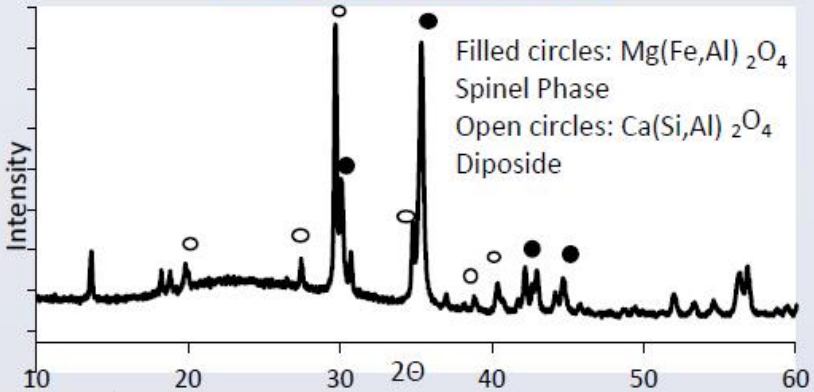
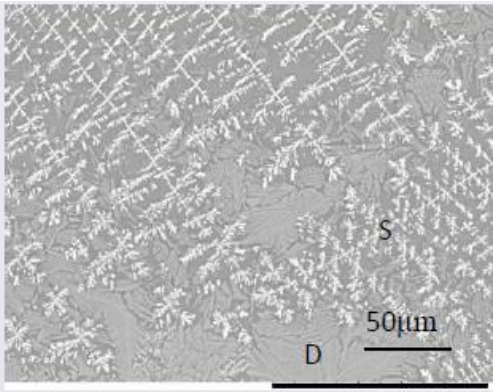
Mixed Wasteform

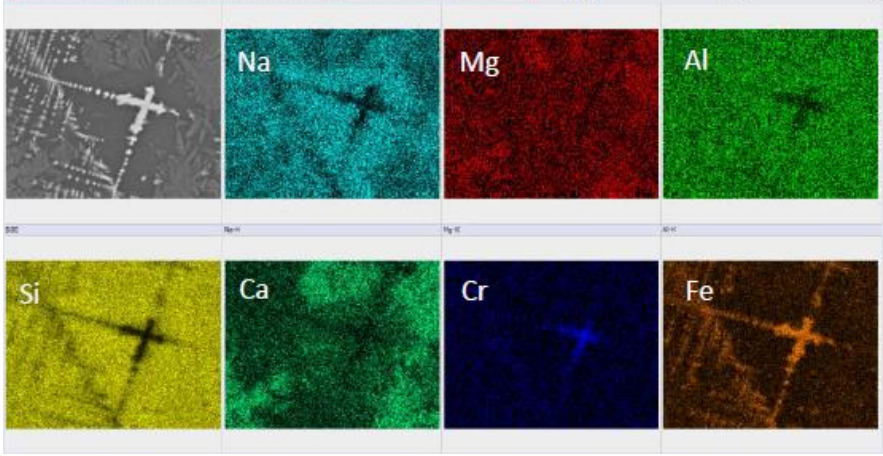


Mixed Waste Stream





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.

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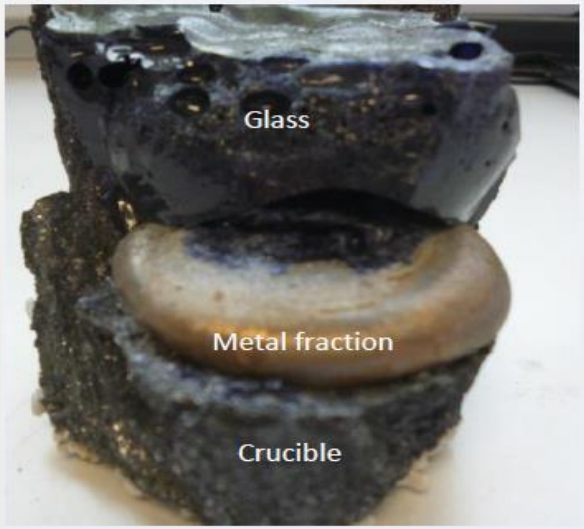
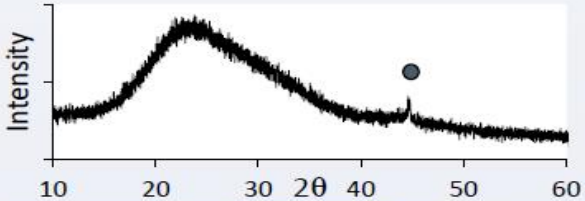
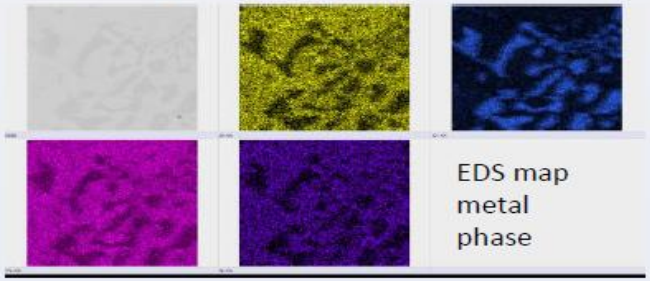
Metal and Masonry Wasteform



Metallic Waste stream





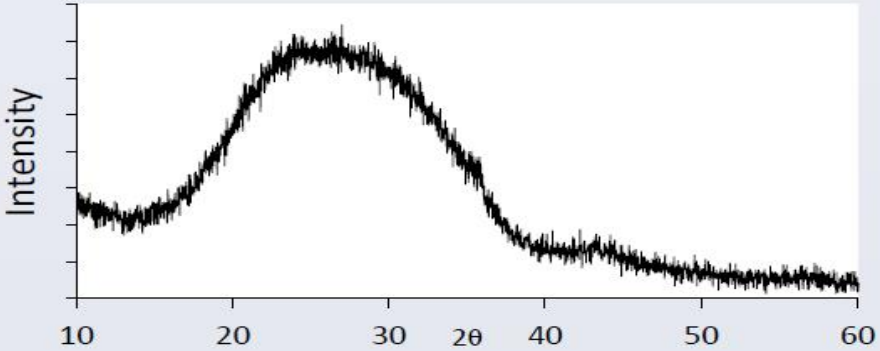
Analysis of slag phase

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.

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Discussion/ main findings

- 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.

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WP2 – Product optimisation

2. **Evaluate wasteforms against product quality criteria**.

- Develop and implement plan for process and product optimisation.
- Using a fundamental understanding of waste / additive interactions and interaction with industry.

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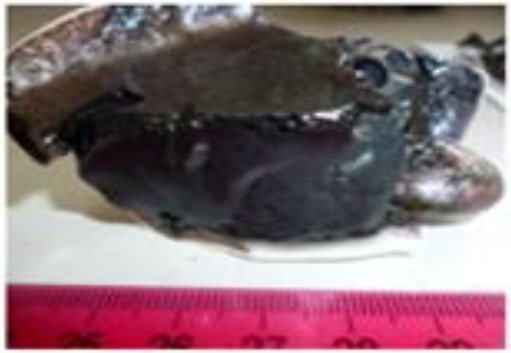
Optimisation: How to treat the metallic fraction?

Option 1: Separate the glass and metallic fraction

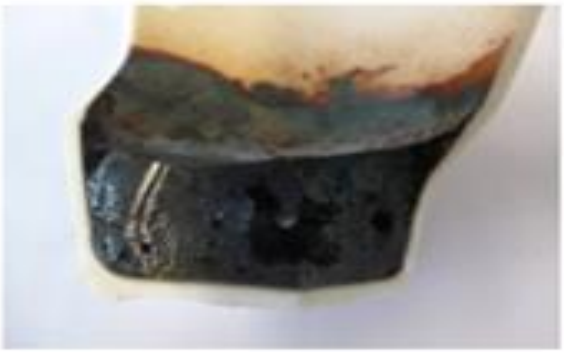
- It may be possible to treat the resulting metal phase as LLW
- Require slag and metal phase to be tapped separately from the melter this would require post processing separation (undesirable) or the slag and metal phases to be tapped separately from the melter in- situ (not demonstrated).

Option 2: Oxidise all of the metallic content to give a 100% glass wasteform

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.



Addition of Fe_2O_3 at a 1:1 molar ratio with expected metallic fraction



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Small Scale PCM melts 200 ml crucibles

waste component	weight (g)
PVC	5.91
Stainless steel (drum)	11.74
Stainless steel (waste fraction)	39.91
Copper	0.2
Al	0.35
Lead	0.83
CeO2 (1.043wt%)	0.67
B2O3 (1wt%)	0.64
total	60.25

weight of metallic fraction: 31.83g

Moles Fe: 56g/mol
Moles: 0.56

Moles of Fe_2O_3: 156.69
1:1 molar ratio: 0.56

Fe_2O_3: 89.06g + (10wt%)

97.69g of Fe_2O_3 added to metallic waste stream

Diameter of crucible 8cm

1450˚C 4 Hours. No metallic waste fraction

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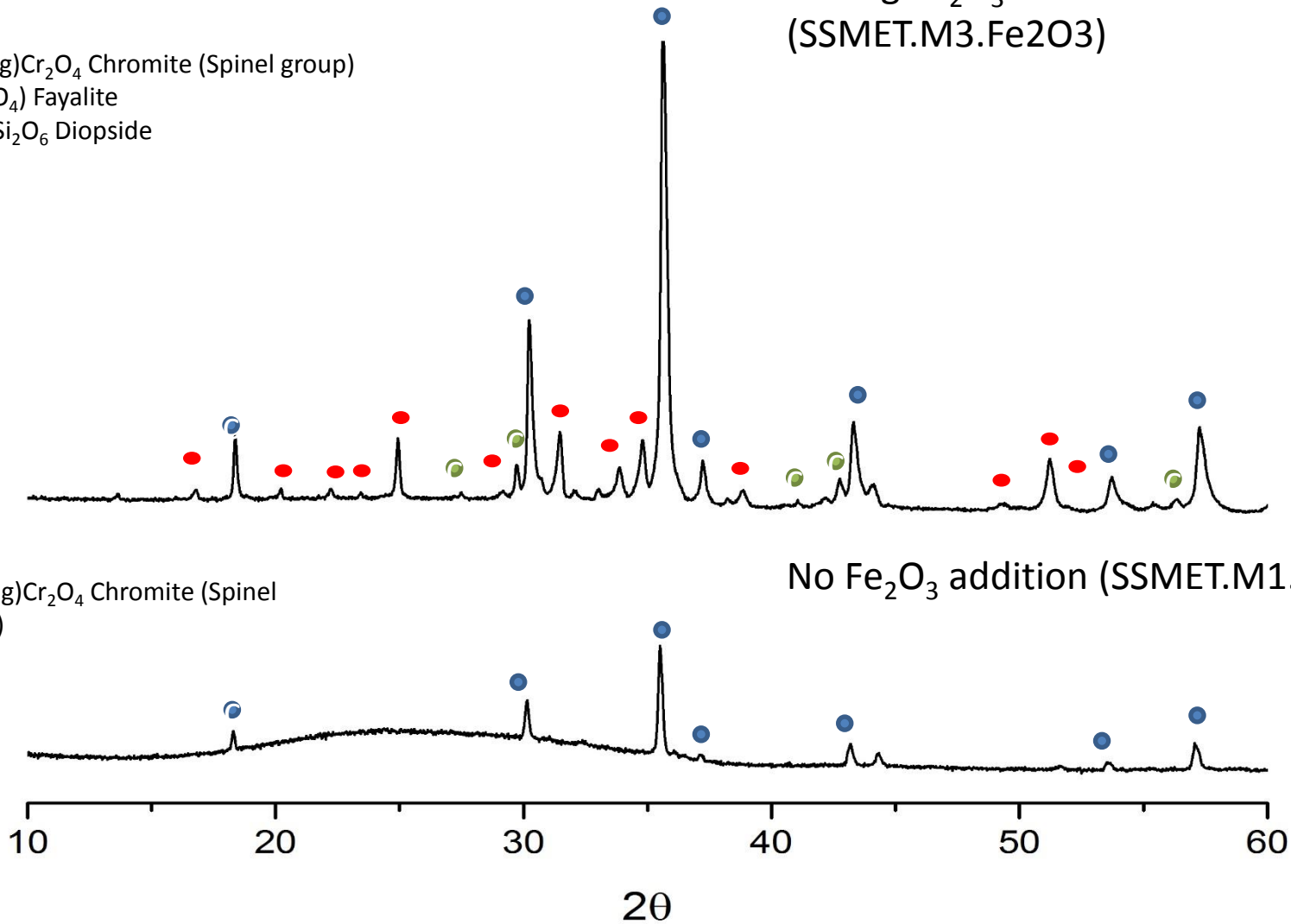
XRD – characterisation

98.96g Fe_2O_3 addition (SSMET.M3.Fe2O3)

- (Fe, Mg)Cr_2O_4 Chromite (Spinel group)
- (Fe_2SiO_4) Fayalite
- $MgCaSi_2O_6$ Diopside

No Fe_2O_3 addition (SSMET.M1.GF)

- (Fe, Mg)Cr_2O_4 Chromite (Spinel group)



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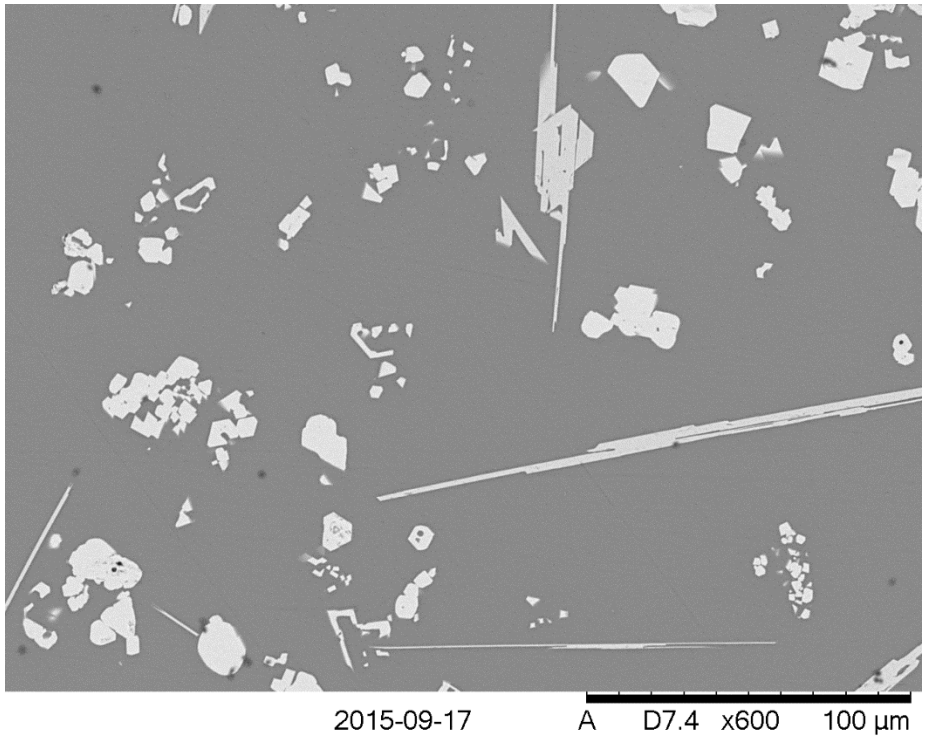
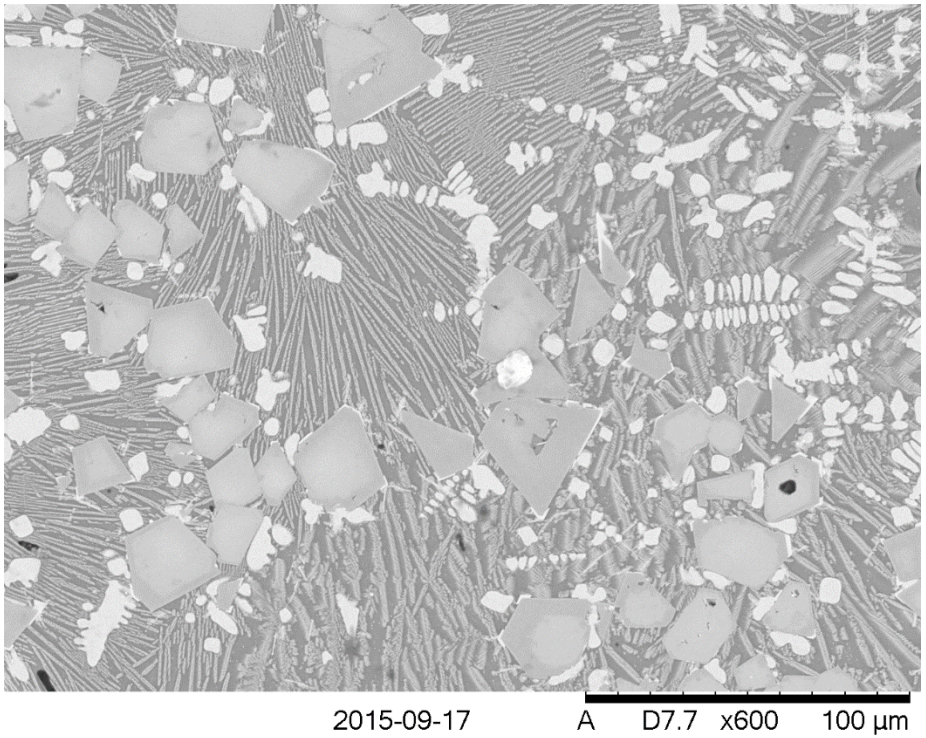
Microstructure differences with the addition of iron (III) oxide



Metallic waste stream No Fe_2O_3 addition



Metallic waste stream Fe_2O_3 addition

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Problems with larger scale

Alumina crucibles were heavily corroded from the high metallic content

Large metallic fraction

Issues with kinetics

Still work to be done but work does show the potential for different waste treatment and glass formulations for PCM waste

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WP3 – Product Stability

3. Selection of optimised wasteforms:

- Develop an understanding of product stability with respect to generic ILW disposal concepts.
- Accelerated dissolution experiments.

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Dissolution experiments

AIM: Understanding of product stability with respect to generic ILW disposal concepts, through accelerated dissolution experiments.

The Product Consistency Test (PCT)

"Evaluate the chemical durability glass waste forms by measuring the concentrations of the chemical species released to a test solution."

- Controlled atmosphere in nitrogen to avoid carbonation.
- Test solution – Calcium hydroxide
- Simulate environment in a GDF repository
- Using boron as a tracer

Experimental setup

- 4 PCM wasteforms (PVC, Metal, Masonry and Mix) and vitrified contaminated pond scabbling waste.
- Run in triplicate (3 samples and blank solution)
- Sample in anaerobic chamber
- Sampling points 1,3,7,14,28 days + 1 month for the next 12 months

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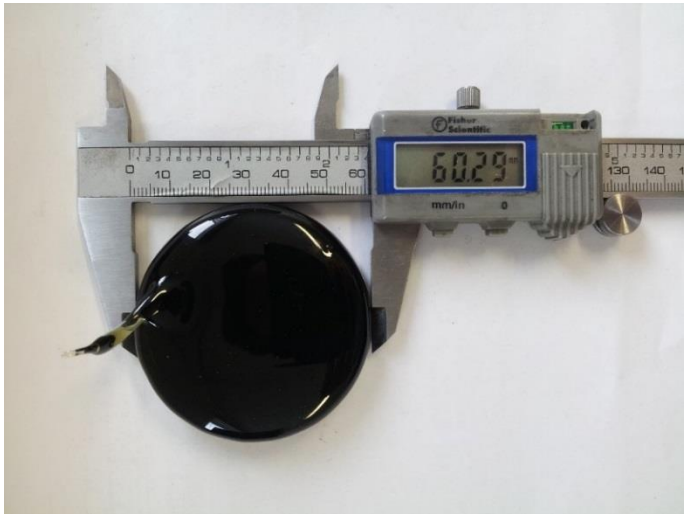
Glass formulations for contaminated masonry waste

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



component	Wt%
SiO2	77.05%
CaO	8.54 %
Al2O3	3.46%
Fe2O3	1.22%
K2O	1.08%
MgO	0.42%

- Many types of ILW themselves possess the key oxides for glass making, chiefly SiO_2. XRF results (table left) shows masonry waste contains 77wt% SiO_2. Using masonry waste as the SiO_2 component and boric acid and sodium carbonate, successfully formed borosilicate glass at 1100° C.
- Strong evidence that the glass waste form formulated in this project would be compatible for currently available thermal treatment technology platforms.

Characterisation/structure of glass: XRD, SEM, XANES, Raman

Processability: DTA, Viscosity reading

Wasteform Performance: Anaerobic long term dissolution studies.

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Future work – Placement

- Approach developed here would be compatible with commercially available in container thermal treatment technologies.

New GeoMelt Vitrification Plant at Sellafield Site to Serve as Test Facility and Partnership Platform for Nuclear Waste Disposal across Europe

KURION

Isolating Waste from the Environment

Warrington, UK and Irvine, California, USA - The UK's National Nuclear Laboratory (NNL) has just announced a joint project with U.S. waste treatment company Kurion, to deploy a full-scale, active, In-Container Vitrification (ICV) plant based on Kurion's GeoMelt® technology, at NNL's flagship Central Laboratory on the Sellafield site.

Planned placement with Kurion for Feb/March to assist with glass formulation for immobilisation of various ILW streams; including PCM waste and contaminated soils/concrete.

http://www.nnl.co.uk/news-media-centre/news-archive/nnl-and-kurion-announce-joint-project/http://www.nnl.co.uk/news-media-centre/news-archive/nnl-and-kurion-announce-joint-project/http://www.nnl.co.uk/news-media-centre/news-archive/nnl-and-kurion-announce-joint-project/

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A busy 18 months left

But by the end….

Complete understanding of thermal treatment of PCM waste will be achieved, from waste processing to characterisation right through to long term behaviour of vitrified waste form within a GDF repository.

Thanks for listening

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