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SMALL-SCALE FIRE TESTING OF POLYMER AS AN ENCAPSULANT FOR MAGNOX WASTE

Gordon Turner
Nuclear Decommissioning Authority, Harwell, UK

Dave Willcox
Project Services, Gloucester, UK

Glen Baker
Project Services, Gloucester, UK

ABSTRACT

At Patram 04 in Berlin, a paper was presented on fire testing of polyurethane foam – a material that is used to mitigate the effect of fire on a transport package. A fire test using a five gallon steel pail was adopted by General Plastics Manufacturing Co. to understand the linear heat front and thermal degradation of transport containers. This paper confirms that the approach has wider applications as a cost-effective approach to demonstrating fire safety.

Magnox is a metallic alloy applied as fuel cladding in the first generation reactors in the UK. The high magnesium content (>95% magnesium) is a challenge to package safely. Two of the main encapsulants in the UK are Blast Furnace Slag / Ordinary Portland Cement (BFS/OPC) and Pulverised Fly Ash / Ordinary Portland Cement (PFA/OPC). As these contain water in the cement pores there is a concern that a fire accident could result in a steam reaction with the immobilised Magnox. These cement-based grouts are also not suitable for a specific number of Magnox-containing waste packages, as the material has been subjected to compaction which does not allow adequate infiltration of the grout to produce an acceptable wasteform. A polymer matrix has been proposed as an alternative encapsulant because of its improved flow and infiltration characteristics and lack of water content.

Instead of conducting a full-scale fire test using a 500 litre Drum waste package an approach was developed, similar to the technique discussed at Patram 04. This involved representing part of the side-wall of the 500 litre Drum waste container using a 'bucket' containing an encapsulated simulant.

Our main interest was the propagation of the heat front and its impact on the contents, especially the Magnox metal. The safe performance demonstrated in the test was due to a combination of several factors:

- A gap developing behind the steel wall of the bucket - due to loss of vaporised polymer;
- A distinct char layer of part degraded polymer;
- There was evidence of some metal loss but no sustained Magnox combustion – even though negligible sources of oxygen (air or water) were identified in the simulant.

INTRODUCTION

The mission of the Nuclear Decommissioning Authority (NDA) is to deliver safe, sustainable and publicly acceptable solutions to the challenge of nuclear clean-up and waste management. This means never compromising on safety, or security, taking full account of our social and environmental responsibilities, always seeking value for money for the tax payer, and actively engaging with stakeholders. The NDA Disposal System Safety Case is being developed for the long-term management of higher activity wastes. This includes safety assessments of transport to and operations at a deep geological disposal facility. One of the main faults and hazards to be considered is a fire accident.

The NDA publishes Waste Package Specification and Guidance Documentation [1] to ensure the safe packaging of the UK's radioactive waste. The NDA has formalised the process of checking designs of waste packages into the Letter of Compliance process to ensure that they are compatible with repository design and operation. One of the 16 technical areas includes fire accident performance.

Trawsfynydd Nuclear Power Station, a Magnox reactor design, ran from 1965 and ended its service life in 1991. First stage decommissioning (the removal of fuel) was completed in 1995. The second stage (care and maintenance of operational wastes) is due to be completed by 2012.

One of these wastes is Magnox metal arising from conditioning spent fuel in preparation to send to Sellafield for reprocessing. To reduce the number of fuel flask transports, the fins on the sides of the Magnox fuel were mechanically stripped to increase the packing fraction.

These wastes are still at Trawsfynydd Power Station and polymer has been proposed to encapsulate the Magnox metal into waste packages. This paper describes small-scale fire tests to demonstrate safety in fire accidents.

BACKGROUND

The Magnox fins were placed into a 500 litre Drum (a typical UK stainless steel waste container) [2]. The metal was compacted to improve the volume efficiency. To protect the sides of the drum, a cylinder former was added into which a compactor compressed the Magnox waste.

The original intention was to use a cementicious grout to infill and encapsulate the Magnox waste in the waste container. Concern was raised regarding the ability of the grout to in-fill all the voids and the potential in a fire for the waste to scavenge oxygen from the water in the grout to initiate a Magnox fire.

One option was to remove the Magnox and package in a safer manner. This would be expensive and require scrapping of a large number of stainless steel containers. Project Services were commissioned by Trawsfynydd Power Station to provide a submission to NDA's Letter of Compliance Process based on polymer as the encapsulant.

Polymer has very good flow properties so can in-fill all the spaces between the compacted Magnox. Polymer also has no associated water, so in any fire Magnox cannot scavenge oxygen from this encapsulant.

Thermogravametric analysis and mass spectrometer data has been produced for polymer [4]. Two distinct changes were detected. The polymer degraded first between 60 °C and 240 °C with a 10% loss in mass – possibly due to the release of unreacted monomer. Complete degradation of the polymer occurred between 350 °C and 450 °C (Figures 1 and 2).

These results indicate that loss of polymer could result in exposing the Magnox to high temperatures. To understand large-scale effects and (any) interactions with Magnox required a full-scale fire test.

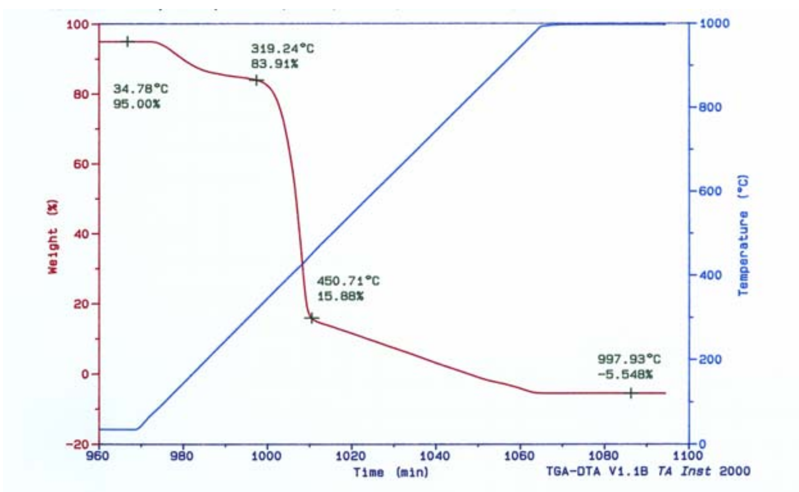

Figure 1: Thermogravametric analysis in argon

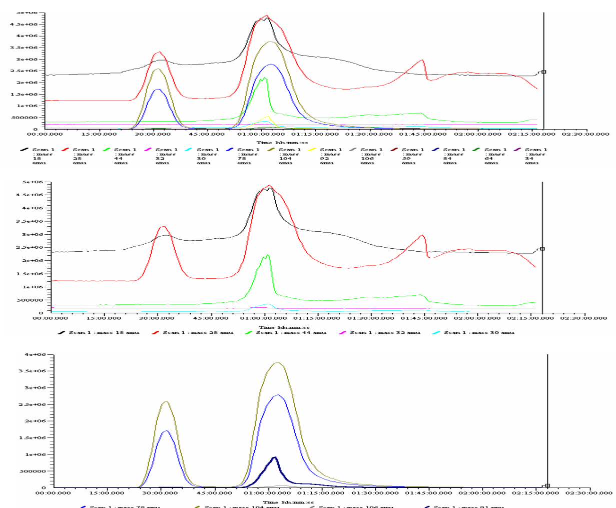

Figure 2: Mass Spectrometer results from the degradation of polymer

METHODOLGY

Because of its properties and use only in Magnox Power Stations, Magnox metal is a very difficult material to obtain and buy. Therefore, fire testing using a full-size 500 litre Drum waste package would be challenging. Small-scale testing is more attractive.

At Patram 04, a paper [3] was presented by General Plastics Manufacturing Co. on a medium-scale fire test of foam materials that would yield engineering data relevant to full-size fires and packages. Based on this small-scale test approach, NDA and Project Services agreed a test programme to demonstrate the fire safety for this Magnox metal encapsulated in polymer.

A schematic of the proposed method is presented in Figure 3. Two simulant samples were prepared within a nominal 20 litre stainless steel container (nominal dimensions: 30 cm diameter, 30 cm deep). Once the volume of debris in the mould equated to approximately 35% of the container volume, the container was filled with VERI polymer and allowed to set (representative of the full-scale system in terms of voidage, compactness, size (scaled) and material). Two lifting points were added to enable easier handling of the container whilst heated.

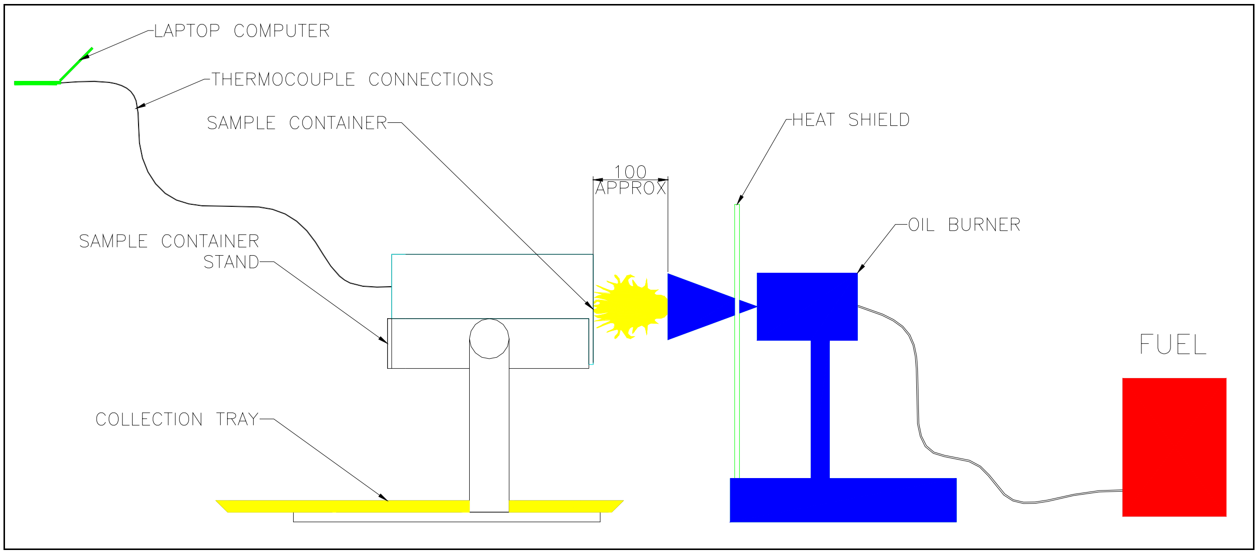

Figure 3. Fire test setup
(C) Project Services

VERI (Vinyl Ester Resin In-situ) polymer was formulated and supplied by Diversified Technologies Inc, and made up by NSG to the standard formulation.

Thermocouples were positioned at the base ("hotface") of the sample container and then at regular intervals (30 mm approx.) throughout the centreline of the container to monitor the temperature of the flame to provide a temperature profile throughout the sample.

A lid with a 25 mm diameter vent hole was placed onto the container. The hole served as a vent and allowed the thermocouples to be connected to the monitoring station. Each sample container was weighed and placed upon the holder approximately 100 mm from the burner exit cone. The thermocouples were connected to a laptop computer to monitor and record the temperatures. A collection tray was placed underneath the samples to collect any spillage.

For the test, the waste container was positioned 100 mm away from the oil burner with a flame shield in contact with its base. The burner exposed the hotface of the container to a flame temperature of approximately 1050 °C. The test period began when the hotface temperature (recorded by an additional thermocouple) exceeded 800 °C and lasted for 60 minutes. After the burner was turned off, the test container was allowed to continue burning and temperature recording was not stopped until all measured temperatures passed through their individual maximums.

The following data was collected as part of the two tests:

1. Initial weight of test container
2. Final weight of test container
3. Extinguish time
4. Recession distance - the distance from the hotface to the non-degraded polymer matrix.

It was expected that the polymer, a thermoset, would char and the Magnox would not support self-contained combustion as first there is no available oxygen and second a sufficiently large volume of Magnox has to be heated to the ignition temperature (~0.01 m^3).

FIRE TEST

Two buckets were prepared at NSG on 15 March 2006, containing about 13 kg of Magnox strip and loaded with 17 kg of polymer and transported to WarringtonFire for testing. Both were estimated to contain 35% mass Magnox which was quite difficult to achieve (even with flat strip).

At WarringtonFire a kerosene burner (cone dimensions: 280 mm wide x 152 mm high) provided the flame of up to about 1060 ^{o}C. The radial heat flux was in the order of 20 W/cm^2. The test rig is shown in Figures 4 and 5. The gap between the holder and bucket was filled with insulation.

After careful monitoring of the first fire test, several changes were made to the second sample. To obtain better direct flame contact over the whole base surface, the burner was aimed at the lower quarter of the circular base of the sample and the lid was removed to assist with venting of off gases and preventing flame impingement onto thermocouple wiring loom.

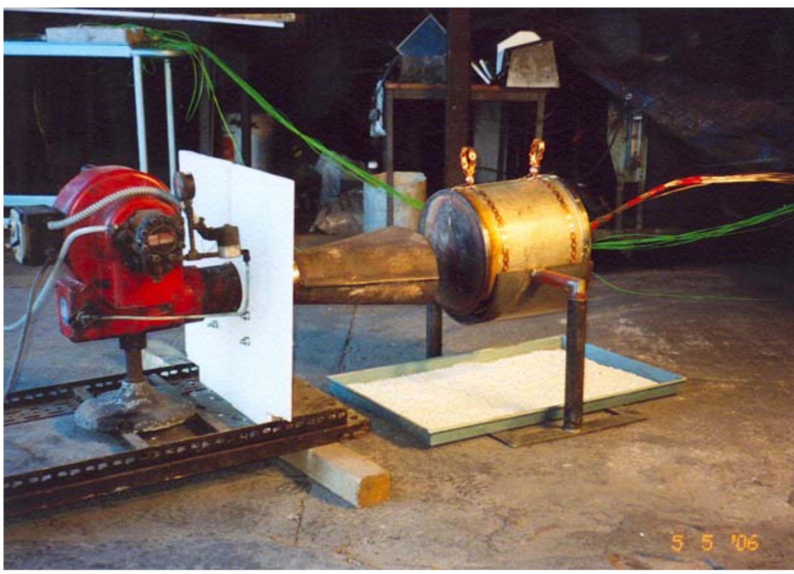

Figure 4: Fire test rig with Sample 1 in position
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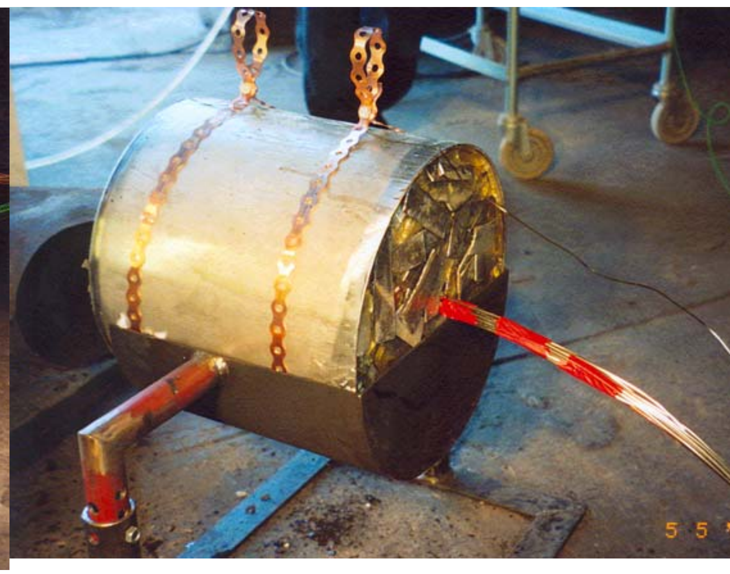

Figure 5: Close-up view of Sample 2 in the fire test rig
(C) Project Services

The thermocouples confirmed a significant heat front moved into the encapsulated Magnox. Once the temperature of the burner was established, fumes (polymer degradation products) were seen to exit the far end of the bucket. Tar like substance dripped from the far end of the holder as well as gases and vapours. These ignited and remained flaming for the duration of the fire test as shown in Figures 6 and 7.

Figure 6: Sample 1 after 8 minutes into the fire test
(C) Project Services

Figure 7: Sample 2 after 21 minutes into the fire test
(C) Project Services

During the cooling phase, the high temperatures dissipate out through the base of the container as well as further in towards the centre. Within 2 hours the temperatures in the wasteform are around 200 ^{o}C and reducing. The recession distance is shown in Figure 8 for Sample 2.

POST-TEST ANALYSIS

Initial analysis involved weighing the two samples and comparing against the original mass. See Table 1:

Table 1. Weight loss

Sample No.	Sample before test (inc. Container)	Sample after test (inc. Container)	Mass loss (kg)	Mass loss (%)
1	36.85 kg	35.75 kg	1.10 kg	2.99%
2	36.95 kg	34.59 kg	2.36 kg	6.39%
Sample No.	**Sample before test (exc. Container)**	**Sample after test (exc. Container)**	**Mass loss (kg)**	**Mass loss (%)**
1	27.51 kg	26.41 kg	1.10 kg	4.00%
2	27.61 kg	25.25 kg	2.36 kg	8.55%

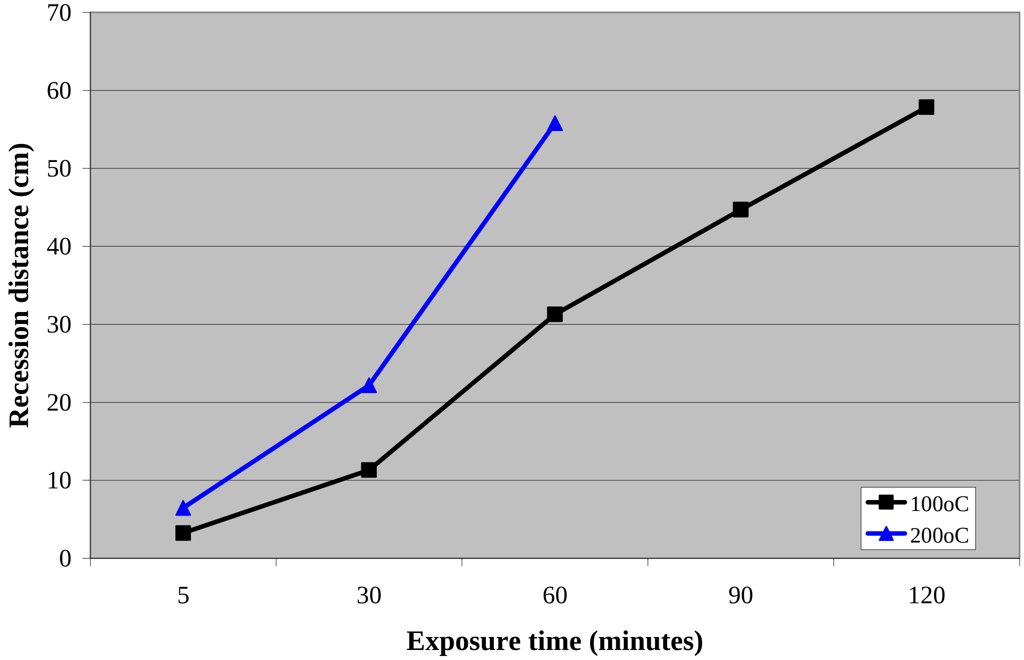

Figure 8: Recession distance for Sample 2
(C) Project Services

The buckets were sectioned and viewed 18 May 2006 at NSG. Careful examination of the sample containers made it possible to determine the depth of heat penetration and its effect on the polymer.

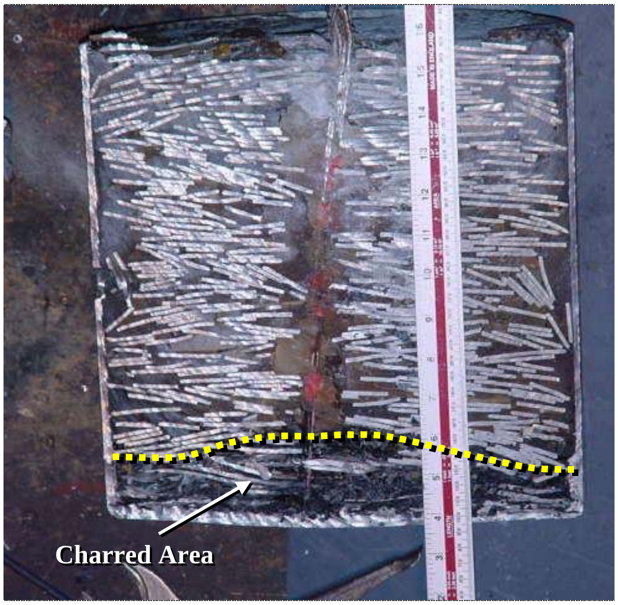

Figure 9: Sample 1 sectioned
(C) Project Services

Figure 10: Sample 2 sectioned
(C) Project Services

There is a distinct char layer into the wasteform of 50 mm for Sample 1 and 85 mm for the Sample 2 (Figures 9 and 10). Most of the damage is in the centre of the samples, tapering out to the outer extremities with only minor damage at the outer edge. This appears to be parabolic in shape. Close to the heat source, the initial part of the char layer is ash and a ‘gooey mess’ close to the intact wasteform.

This examination also revealed damage to the Magnox metal at the point closest to the base of the container to a depth of approximately 5 mm.

CONCLUSIONS

Two small-scale samples were tested under fire accident conditions to better understand the performance of polymer encapsulated Magnox metal in a UK 500 litre Drum waste container. Project Services successfully applied the “oil burner” method, presented at Patram 04 by General Plastics Manufacturing Co. on fire testing foams, to polymer which has similar challenges for fire testing.

Initial TGA/MS tests on polymer indicate two stages in the degradation: 10% loss (free monomer) between 60 ^{o}C and 240 ^{o}C followed by full loss with no discernable residue between 350 ^{o}C and 450 ^{o}C. In contrast, large-scale effects observed in these tests indicated that there is significant retention of material (char) above 450 ^{o}C. This char layer would assist in maintaining thermal insulation against the propagation of heat further into the polymer-encapsulated Magnox metal, and a partial barrier to the movement of particulates and volatiles.

The loss of mass was dominated by the polymer. Also observed was a small amount of thinning of Magnox in the 3-5 mm closest to the heating source. The Magnox strip in this region was discernibly thinned and looked ‘eroded’. Hence there must have been some loss or interaction of the polymer with the Magnox metal.

The small-scale Magnox metal in polymer test programme was successfully applied to the fire performance safety case.

ACKNOWLEDGMENTS

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