Decontamination of Irradiated Nuclear Graphite Using High Temperature Molten Salt-17447

T. Grebennikova*, C.A. Sharrad*, A.N. Jones**
*School of Chemical Engineering and Analytical Science, University of Manchester, M13 9PL
**Nuclear Graphite Research Group, School of Mechanical, Aerospace and Civil Engineering, University of Manchester, M13 9PL

ABSTRACT

Irradiated graphite is one of the most significant, large volume waste streams in the UK. After shut down of gas cooled reactors there will be ~ 96,000 tonnes of nuclear graphite arising from pressure vessels, sealed or unsealed stacks, temporary surface storage and in silos, which may account for up to 30% by ILW volume of any future UK geological disposal facility. High temperature molten salt treatment (HMST) could be considered as a partitioning process of the activation and fission products from irradiated graphite. The main objective of the research is to optimize a specific graphite treatment technology compatible with older, current and future reactors to provide a safe and effective process to decontaminate graphite and reduce the waste inventory. In order to reach that purpose principal radionuclides contained in irradiated samples from Magnox reactors were investigated by germanium (Ge) gamma spectrometry. The next key tasks were to employ treatment at 450°C in LiCl-KCl eutectic which included the following procedures: electrochemical cleaning of the salt, initial cyclic voltammetry (CV) of graphite followed by several steps of chronopotentiometry (CP) with different current applied and CV was taken after each step. Once the treatment was established, experiments investigating the electrorefinement of the resultant salt mixtures were conducted as well as the comparison of gamma spectroscopy results of graphite before and after the treatment providing the result of total activity reduction of around 60%.

INTRODUCTION

Application of graphite in the nuclear industry began in the middle of last century and became the most significant, large-scale use of this material compared to other sectors [1]. The use of graphite started from the first experimental nuclear reactor built in Chicago in 1942 and was followed by a multitude of reactor designs, then later civil which were mostly for energy production Several research and material testing reactors (MTR), including a significant sub-group specifically built for the manufacture of plutonium, also use graphitic materials [2]. Most of these reactors have been already shut down, with others planned to be shut down in the next decade[3]. Due to the accumulation of approximately 96,000 tonnes of irradiated graphite[4] arising from the civil and military operation, the problem of graphite waste management is one of the most significant in the UK. The Nuclear Decommissioning Authority (NDA) proposed isolation in a future Geological Disposal Facility (GDF) as a baseline strategy [5]. However, it could take up to 30% of the volume of the proposed GDF. Novel methods could be to treat graphite before disposal in order to reduce the activity level of the majority of the bulk graphite

material [6].

The main factors why solutions have not been explored is that graphite is quite inert to any chemical reaction without a strong catalyst, so the realization of any treatment presents a considerable technical challenge [7]. Moreover, the use of proposed incineration or pyrolysis methods raises such issues as the difficulty of burning graphite, especially the very pure form used for nuclear purposes; release of radioactive gases, particularly C-14, Cl-36 and residual H-3; processing and disposal of the residual ash, in which other radioactive isotopes are concentrated; and the need to crush graphite into small pieces prior to processing [8]. An alternative new solution proposed for reducing activity levels in graphite is a high-temperature molten salt treatment (HMST). HMST is considered to be successful in spent fuel separation [9] but currently is not on the priority list for graphite treatment mostly due to the lack of research in this approach. There is a potential to separate actinide and fission products from the bulk of graphite material, allowing to reduce Higher Activity Waste (HAW) volume and to save considerable cost through reduced storage requirements.

The possibility to apply molten salts technology in the nuclear field has found some specific advantages. The main one is that molten salts as inorganic and non-aqueous media are less sensitive to radiolysis hazards than aqueous processes, and believed to be able to treat high burn-up, short-cooled nuclear fuels after irradiation with no significant penalty. One advantage that should be mentioned is a possibility to dissolve material with limited solubility in nitric acid (used commonly in hydrometallurgical processes), especially by electrochemical means [10]. There are different types of the molten salts technology investigated for nuclear application, and usually, the version applied depends highly on the material to be treated [11]. This programme of experimental research aims to investigate the thermal treatment of irradiated graphite in the molten salt environment, adapting the current technology used for actinide separation. A key challenge is the amount of these products in irradiated graphite is notably different from sample to sample and not evenly distributed, so investigations into whether this proposed treatment process can be successfully implemented need to take this into consideration. Investigation of the graphite purification by the removal of these elements in a molten salt medium may contribute significantly to reducing volumes of HAW requiring disposal thus reducing the liability of this material and possible enabling early site clearance of many UK legacy sites.

METHODS

Salt preparation

LiCl and KCl salts (>99%, Sigma) were separately placed under a vacuum of 1 Pa at 170°C for 12 hours and mixed in the required proportion (LiCl/(KCl+LiCl) (mol/mol) = 0.6). The mixed salts were fused under vacuum, then the cell was filled with argon and heated up to 450°C with the ramp of 10°C/min and dwelled at that temperature for one hour. The initial CV was taken to record any impurities and if required the system was additionally purified by electrochemical cleaning. Finally, molten salt was syringed and kept in the dry box.

Graphite samples

The samples used for the research were irradiated to six dpa Pile Grade A (PGA) graphite samples retrieved from Oldbury and Wylfa Magnox reactors as trapped or installed sets, therefore the irradiation conditions of these graphite samples were typical of a reactor core at the sample position. They were machined and provided to the University of Manchester (UoM) by the National Nuclear Laboratory (NNL). The average diameter of the samples selected for this research programme is 12 mm; the height is variable from 4mm up to 6 mm.

Initially, a pre-treatment characterization of irradiated graphite samples was made by gamma spectrometry using Germanium Gamma Spectrometer. Then a graphite sample was placed under a vacuum of 1 Pa at 170 °C for 12 hours to reduce any moisture.

Experimental setup

The schematic drawing of the setup used for high-temperature molten salt experiments is shown in Fig.1 and can be divided into several areas. Starting with a blue area which includes gas and vacuum inlet and oil bubbler to control overpressure, followed by the main part colored in red responsible for the heating and treatment process, linking to the green area consisting of a gas outlet with H-3 and C-14 capture media and an orange area which collects data.
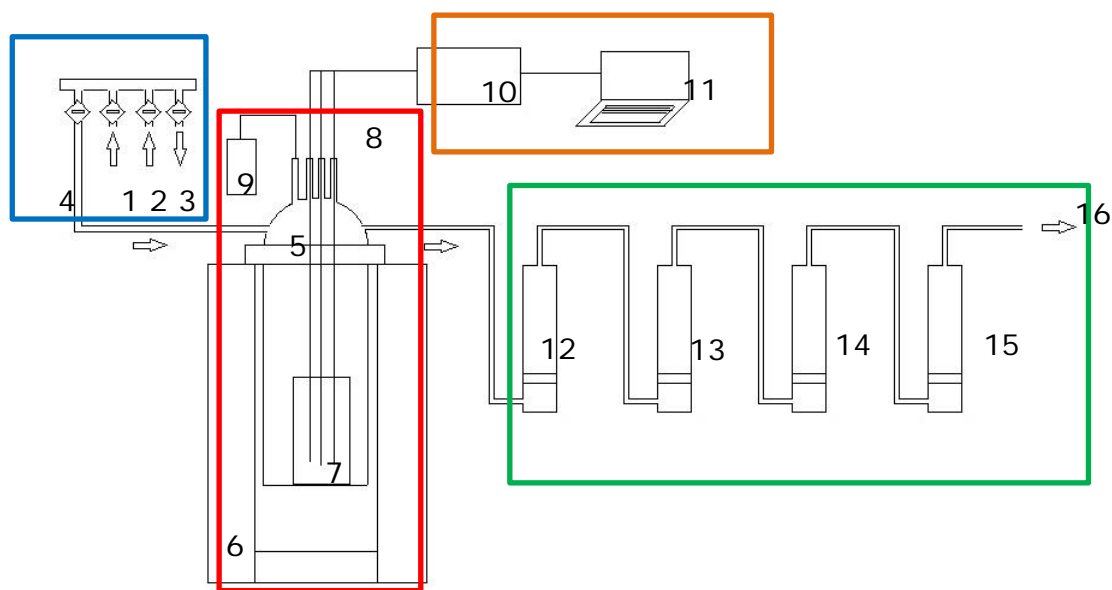

Fig.1 – Schematic drawing of the setup for the high-temperature molten salt experiment. 1 – vacuum inlet, 2 – argon inlet, 3 – connection with oil bubbler to control overpressure of the system, 4 – connection inlet to the cell, 5 – cell, 6 – furnace, 7 – crucible with salt, 8 – electrodes, 9 - digital thermometer, 10 – potentiostat, 11 – laptop, 12/13 – bubblers for trapping H-3 , 14/15 - bubblers for trapping C-14, 16 – gas outlet to fume cupboard.

The cell used for the molten salt experiment is presented in Fig.2 and includes such parts as a quartz body with an alumina crucible, a borosilicate lid of the cell with gas inlet fitting and gas outlet fitting. Other fittings on the top of the cell are for a

carbon glass counter electrode, tungsten working electrode and tungsten working electrode with graphite basket and Ag/AgCl reference electrode.
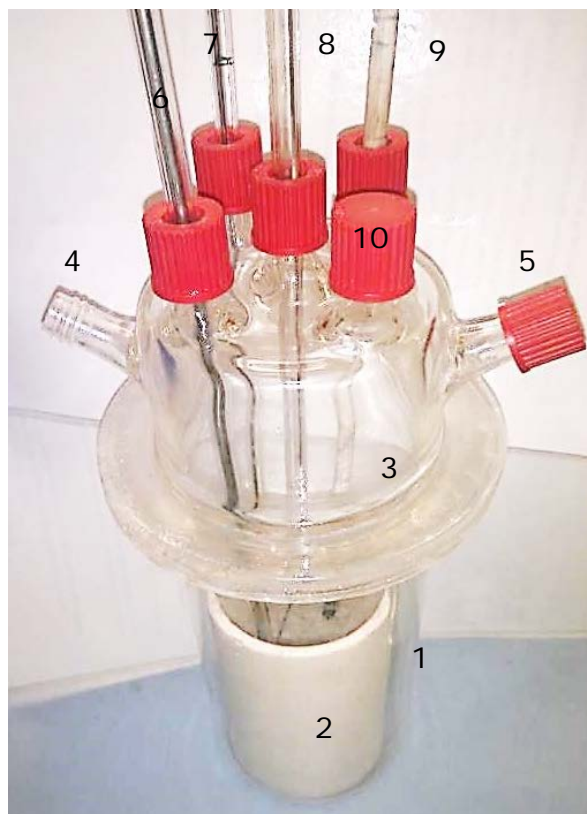

Fig. 2– The cell used for molten salt experiments: 1 - quartz body of the cell, 2 – alumina crucible, 3 – borosilicate lid of the cell, 4 - gas inlet fitting, 5 - gas outlet fitting, 6 – carbon glass counter electrode, 7 – tungsten working electrode for salt cleaning, 8 – tungsten working electrode with graphite basket, 9 – Ag/AgCl reference electrode

For each experiment 50g of prepared LiCl-KCl salt was used. Once the tungsten mesh basket with the graphite sample was fixed above the alumina crucible with salts, the cell was evacuated and filled with argon. Then the cell was heated up to 500°C with the ramp of 10°C/min and dwelled at that temperature for one hour. After measuring a reference CV of the pure salt mixture, the mesh basket connected to the tungsten wire was inserted into the melt. All electrochemical procedures were performed using Autolab PGSTAT101 potentiostat. Chronopotentiometry with the current of 70mA was applied to the system. Afterwards, the graphite sample was pulled out of the melted salt and the CV of melted salt was recorded. The final characterization of the graphite samples was obtained using Germanium Gamma Spectrometer.

DISCUSSION

Pre-treatment characterization

Two samples of each reactor were selected and analyzed using similar conditions to identify type and extent of radionuclide contamination and select the range of elements for further comparison after treatment methods.

The presence of radioisotope contaminants in nuclear graphite is typically due to the activation of the initial impurities or subsequent contamination arising within the reactor circuit. However, for items such as fuel sleeves which may have been pond stored, further fission contamination is likely due to immersion in these aqueous solutions [12].

Fig.3 shows the levels of average activity measured in kBq/g for each identified isotope and its distribution across selected samples. Co-60 isotopes provide the main level of activity.It was noted the level of Co-60 present is slightly lower in Oldbury samples compared to all other samples investigated. To understand the distribution of activity level for other isotopes, Co-60 was excluded from the data, and the results are presented in Fig.4. It is essential to consider that H-3 and C- 14 sources are pure beta emitters and therefore cannot be identified using gamma spectrometry due to the absence of gamma for these isotopes.

The maximum mean activity recorded in a single sample from those investigated in this study was from the Wylfa reactor and was equal to 40kBq/g, contributed predominantly by Co-60. The next level of activity was provided by Ba-133 isotope presented in Oldbury sample and was equal to 0.43kBq/g. The level of activity presented by other isotopes was relatively small and did not exceed 0.15kBq/g.
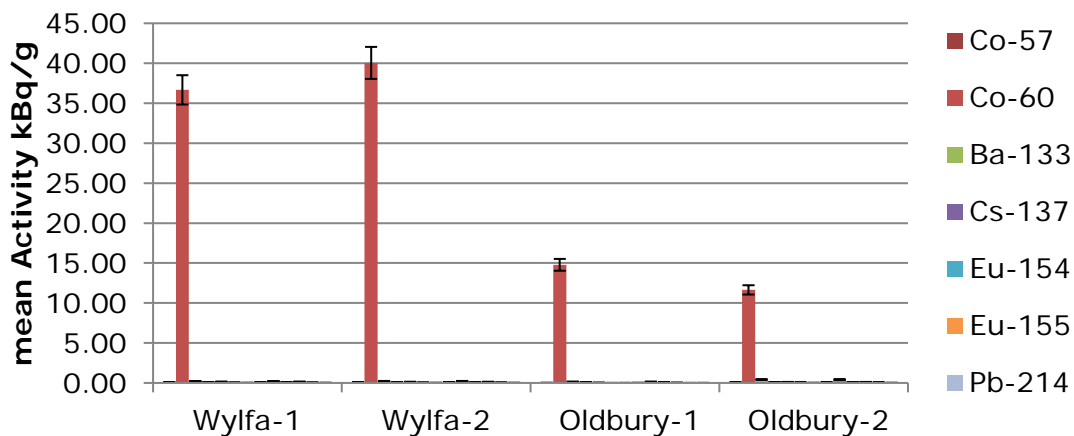

Fig. 3 – The comparison of the mean activity level for the range of isotopes identified in the samples from Wylfa and Oldbury reactors.
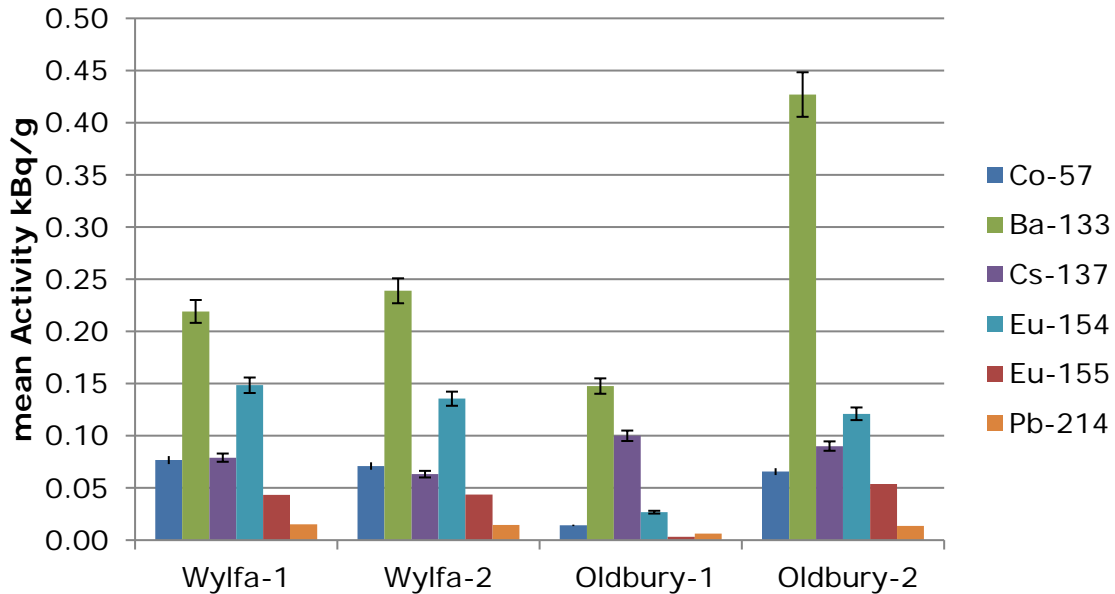
Fig. 4 – The comparison of the mean activity level for the range of isotopes excluding Co-60 established in the samples from Wylfa and Oldbury reactors.

Post-treatment characterization

Fig.5 shows the change (by %) in mean activity of each isotope from all samples studied after the different duration of the electrochemical method was applied. As it can be seen the results presented shows the efficient decontamination of Ba-133 and Bi-214. The suggestion of surface trace contaminations of these elements could explain the received results. However, for the main contaminant of the analysed samples, which is isotope Co-60, the maximum average reduction in activity level was only around 60%. That could be due to the number of reasons. Due to the nature of impurities in the virgin graphite [12], the trace amount of cobalt can be found in the closed pore structures. That makes it difficult for the molten salt to reach it. At the same time, the current used in the experiment might be not efficient enough to break some parts of the closed pore structure of the selected graphite. The further investigation using tomography will be used to confirm this statement, as well as the trend in other elements.
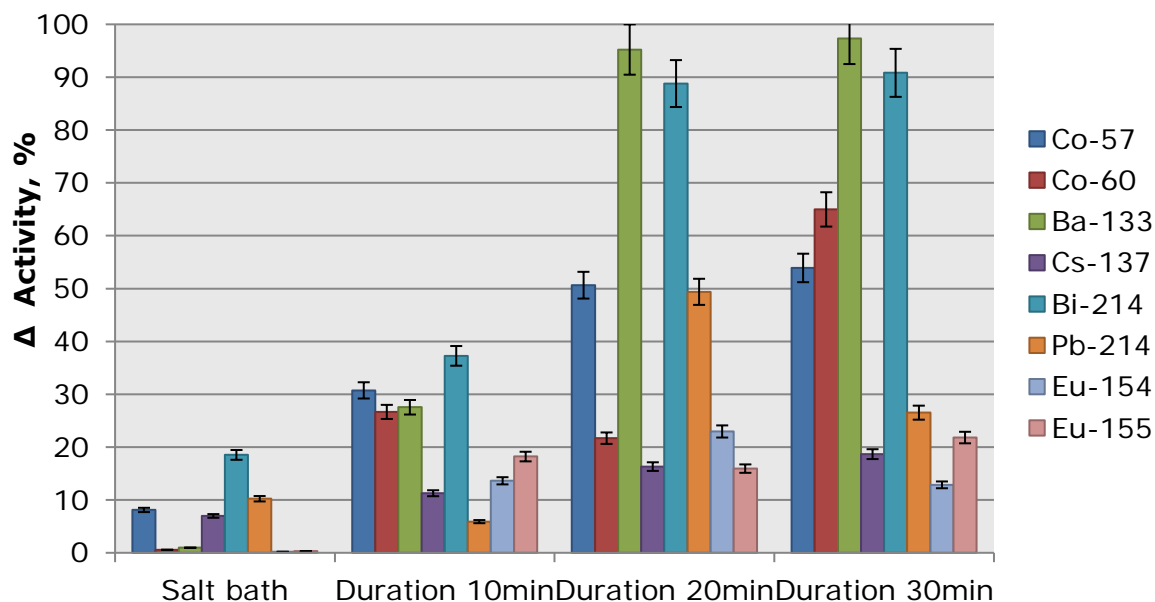
Fig.5 - The change (by %) in mean activity levels of contaminated graphite samples by isotopes during chronopotentiometry at 70mA in LiCl-KCl eutectic at 500°C.

CONCLUSIONS

To conclude, the molten salt method has been shown to decontaminate graphite of all common contaminating isotopes with the reduction of total activity levels to around 60%. The most efficient separation was achieved for isotopes Ba-133 and Bi-214. The main reduction in activity levels was due to the removal of Co-60 from graphite from Co-60 which was the main contaminant in the selected samples. It may be possible to improve the described treatment method by using higher current settings, using different electrode designs or processing the graphite samples to provide a   larger surface area/volume ratio, and work is ongoing in these areas. The studies conducted thus far show that HMST shows considerable promise for the treatment of irradiated graphite in order to reduce HAW volumes. Further work will also investigate the nature of the loaded salt including conversion to an appropriate waste form and the potential re-use of the decontaminated graphite obtained from this treatment method.

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