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1 INTRODUCTION

This report provides a summary of a programme of work undertaken by Babcock (formerly UKAEA Ltd) under NDA's Direct Research Portfolio (DRP) - Lot 3 Work Package 5 Graphite Characterisation. It has been produced to bring together the findings from the different stages of the programme which have been reported separately.

The overall objective of this programme of work is to assist the NDA in its assessment of management options for Magnox reactor graphite. This is to be achieved by developing and delivering a chemical and radiological characterisation programme to provide improved characterisation data to support and underpin the NDA Reactor Decommissioning Waste Project.

There are over 99,000 tonnes (79,000 m^3) of graphite in the UK arising from operational and reactor decommissioning activities. This accounts for 33% of the total volume of ILW wastes destined for disposal in the Geological Disposal Facility (GDF). However, this volume is a less significant contribution to the overall GDF footprint because of the more compact repository systems designed for this type of waste.

At least 20% of the graphite inventory destined for the GDF is classified as Low Level Waste (LLW) but is not suitable for disposal at the Low Level Waste Repository (LLWR). Therefore, there is the potential for a significant reduction in the amount of graphite consigned to the GDF if an alternative management option for LLW graphite could be utilised. Based on current estimates of graphite radionuclide content graphite is also predicted to be a significant contributor to some of the long-lived mobile nuclides (e.g. Cl-36) that the GDF is required to manage.

Various management/treatment options exist that may enable alternative disposal routes, or reduction in volumes that would allow a reduction in the GDF footprint. The assessment of these options is dependent on the accuracy of the graphite inventory. For example, a better understanding of the graphite inventory may result in a greater portion of the inventory being able to be disposed of directly at the Low Level Waste Repository.

The NDA position on graphite management when the programme commenced was stated in its 2006 strategy document [1] "We will explore the management/treatment option for graphite waste, taking account of worldwide developments and best practice. Finding an innovative solution to graphite wastes would inform a business case for accelerated decommissioning at Magnox reactor sites". This strategy has been confirmed in the recent 2011 strategy document [2], "We have an on-going commitment to consider the best way to manage these wastes, as recognised by CoRWM's recommendation 8 and Government's response. We are undertaking a programme of work considering the options for the management of reactor graphite".

The programme of work summarised herein consisted of two stages – stage 1 involved an assessment of the requirements for a graphite characterisation campaign, completed in March 2010. Stage 2 involved acquisition of selected graphite samples and delivery of the characterisation programme.

2 SUMMARY OF STAGE 1 WORK

The assessment and enhancement of the reactor graphite inventory was split into two stages.

Stage 1 resulted in a characterisation programme which provided data relevant to future potential graphite management/treatment options. Definition of the characterisation was supported by: modelling of two representative Magnox reactors; assessment of potential samples from the graphite archive documented by Magnox; review of potential graphite management options to identify the important characterisation parameters; and optimisation of the analysis plan to obtain the most important information within project constraints. The work followed an adapted Data Quality Objective (DQO) approach to ensure that the characterisation programme would enable its objective to be met.

The approach to deliver Stage 1 covered:

- Review and summary of the available graphite management/treatment options;
- Specification of characterisation parameters for each option;
- Comparison of characterisation parameters to current inventory;
- Identification of the key risks and knowledge gaps in the current inventory data;
- Review of the usefulness of existing unirradiated/irradiated graphite samples in providing validation samples for subsequent modelling;
- Modelling the predicted inventory for Pile Grade A and B graphite in two reactors based on the availability of samples;
- Review of the usefulness of previous chemical and radiochemical characterisation work;
- Assessment of the impact of failed fuel on the derived inventory by assessment of available operational reactor histories;
- Production of a characterisation programme that will deliver improved chemical and radiological inventory data;
- Identification of reactor(s) with suitably large inventories of irradiated graphite samples held in archives.

Stage 2, which was to be reported once agreement to proceed was given by NDA, entailed the retrieval and analysis of specific samples from the national graphite archive. The results from this campaign were assessed against those produced by the model and the implications assessed for the interpolation/extrapolation of the inventory with time.

The modelling programme required a good knowledge of the impurities present in the graphite prior to irradiation, to allow for a full determination of the activation inventory. Additionally, to validate the programme, it was also necessary to identify a range of activated graphite samples to compare against the data generated by the model.

Wylfa and Sizewell A were identified as Magnox reactors with a suitably large inventory of irradiated graphite samples taken during the reactors' operational lifetimes [3]. The samples were stored at Berkeley and Sellafield, although the bulk of samples were held at Berkeley. The validity of these samples depended on their provenance i.e. knowledge of their location within the reactor cores prior to removal, in core residence time and treatment of samples after removal.

There appeared to be relatively good record systems that detailed the available inventories.

A range of inactive graphite samples representing the two grades (Piles Grade A and B, PGA and PGB) used in Magnox core construction were identified. These were located at the Downtons facility, and approvals for the retrieval and destructive analysis of these samples were gained in advance of the award of the Stage 2 work package.

Similarly, a range of irradiated graphite samples deriving from Wylfa (located at Berkeley and B170 Sellafield) and Sizewell A (located at Berkeley) were identified.

The range of analyses to be performed on both inactive and active samples were established and justified.

A high level model was produced to support assumptions about the neutron flux distribution and uniformity used to determine the specific samples to be analysed. The stage 2 work subsequently used a refined version of this model, using results from the inactive modelling campaign, to generate appropriate activation inventories. These results would then be compared to the results of the active analysis campaign to determine the accuracy of the model.

A draft report detailing the Stage 1 programme of work was delivered to NDA in July 2009 and the final version was issued in March 2010.

3 SUMMARY OF STAGE 2 WORK

The objectives of Stage 2 were to:

- Develop a model to predict the end-of-life inventories for the identified reactors;
- Compare the results of the model to the inventories in the RWI.
- Prepare, access and transport active graphite samples;
- Prepare, access and transport of inactive graphite samples;
- Analyse both active and inactive graphite samples;
- Develop the model to predict the inventories of the active samples
- Assess the modelling and experimental results and scalability of the model to other reactors;

Due to various delays in acquiring a suitable set of active samples (see Section 3.2), the inactive sample analysis proceeded significantly more quickly. The Stage 2 work package was therefore split into two (inactive and active) and reported separately. The first part of the Stage 2 work (inactive) was commissioned by the NDA in October 2009. The second part

(Active) was commissioned by the NDA in December 2009. Therefore, the two work packages overlapped.

Magnox/NDA additionally requested that analysis of a number of active Hunterston A graphite samples be carried out alongside those from Wylfa and Sizewell. These additional samples were accommodated in the programme and represent a significant cost saving to the NDA by co-analysis alongside Wylfa and Sizewell samples. These samples also allowed the testing of the theory that a reactor model could be simply extrapolated to provide suitably accurate inventory results for other stations in the Magnox fleet. Should this be the case, then this would be a valuable tool in developing a better and justified understanding of the graphite inventory, and could inform decisions regarding its management. The Hunterston samples included fuel sleeves as well as some poorly documented moderator samples, but no inactive moderator material. Information on aspects of reactor design was also not available.

3.1 Stage 2 – Inactive Analysis and Modelling

This focussed on the acquisition and analysis of the inactive graphite samples to allow the further development of the high level model produced during the Stage 1 work package. Development of the model would then allow the prediction of graphite activity at various points in the reactor core and enable whole core inventories to be predicted and comparison to the active samples.

Negotiations commenced with Magnox South and NNL in July 2009 for access to inactive samples located at the Downton archive. Some samples originally identified for analysis were not in their catalogued positions. Therefore alternative samples were identified. Additionally, some samples were found to consist of more material than originally anticipated. Therefore, in order to preserve as many potentially important samples at the archive as possible, some samples identified in the Stage 1 report were not retrieved.

The samples were delivered to the partner laboratory, National Physical Laboratory (NPL) for analysis of the precursor elements as identified in the Stage 1 work. This work was completed in December 2009.

Summary results of the inactive analyses are detailed in the Stage 2 Interim Report [4]. The precursor results were used in the model to calculate the predicted end-of-life graphite inventories for the Wylfa and Sizewell A reactors. These inventories were compared to those in the 2007 RWI and the inventory produced by the model using a generic suite of graphite precursor elements developed by NDA RWMD.

The conclusions were that where the precursor concentrations were similar, the graphite activation inventories were similar, which indicates that the two approaches to modelling align. The key radionuclide C-14 fell into this category. Where the precursor concentrations differ, then the final activation inventories also differ. For some radionuclides the variations were significant and these variations were assessed as probably caused by differences in precursors (number of precursors and concentrations) and activation pathways used in the model compared to that used in calculations used to predict RWI data. In general there was reasonable agreement between the model predictions and RWI and within the uncertainty bands declared in the RWI for the more important nuclides.

3.2 Stage 2 – Active

The delivery timescales for this work had been dominated by issues related to access to the identified irradiated graphite samples and contractual issues relating to duty of care.

As detailed in [5], the active graphite samples identified using the available archive records were based at Berkeley and the B170 facility at Sellafield. The Sizewell A samples were predominately stored at Berkeley. All the Wylfa samples were located at B170. The following details have been documented to emphasise the importance of sample management.

It was originally intended that the active analysis would commence at the end of 2009. However, there were lengthy delays in:

- Identifying the correct samples at B170 - NNL had problems identifying the required samples in the store to be delivered due to inaccuracies in the location entries of the archive records. This had not been resolved by March 2010. Due to additional lengthy delays, unresolved doubts about the accuracy of the inventory records and doubts over access to the B170 facility, a suitable set of Wylfa samples were identified at the Berkeley facility and (with NDA consent) the B170 source of active graphite samples was abandoned and replaced with the samples held at Berkeley.

- Identifying the correct samples at Berkeley – the archive records were not as comprehensive or as accurate as anticipated. Magnox delivered the initially identified Sizewell A samples from Berkeley but it was apparent that most of the physical samples were not always as described and most had been heat treated following removal from the reactor, making them unsuitable for the analyses required in this programme of work. The heat treatment of these samples was not detailed in the archive records. Only four active graphite samples were suitable for analysis, which were reported and discussed in [5]. This resulted in significant delays while correct Sizewell A and Wylfa samples were identified. Magnox were ready to deliver the new set of identified samples in September 2010. On receipt of these samples it was found that sub-samples (or slices) from the same channel sample were not packaged in separate containers. This made it impossible to examine the effect of sample depth between slices from the same location in the reactor core as it was impossible to identify from what part of the trepanned sample each slice had been taken (i.e. front, middle or back).

- Facilitating the sample transport – in order to get transport approval, accurate activities of the graphite samples were required which could only be undertaken once the samples had been retrieved. These activities were significantly different to those planned for (based on the archive records) and this required additional lengthy interactions to ensure that the samples could be safely transported and received by NPL.

Further queries were generated during sample assessment and receipt by NPL, and the need for the development of a prioritisation plan meant that analysis was finally started in mid-December 2010.

The additional set of Hunterston A samples (sleeves and moderator) were delivered to NPL with the Wylfa and Sizewell samples and were included in the analytical plan. A comparable set of inactive Hunterston A graphite sleeve samples had also been sourced and analysed. Inactive moderator samples from Wylfa and Sizewell were also reanalysed by Imperial College using neutron activation analysis to improve measurement data for some specific precursors.

3.3 Stage 2 – Outstanding Work (Active Stage)

The NPL measurement programme on all samples was prioritised to fit in with model development requirements and also Magnox's needs for Hunterston data for their own separate project on near surface disposal. This stage of the work is reported in [6].

The full set of measurement data from NPL was complete by June 2011. In parallel with the sample analysis, predicted inventories for each sample were calculated using the reactor model. The aim was to compare the predicted inventories with the laboratory results to test the validity of the model for each sample. The modelling calculations considered the location of the sample, along with the timing of its recovery from the reactor and its subsequent analysis at NPL had to be taken into account to compare it with analysis results. The results from NPL also included nuclides that would indicate if samples had been contaminated with fuel materials.

A study was also conducted to determine whether Sizewell and Wylfa data could be used to extrapolate treatments and predictions to Hunterston. These predictions were tested against the limited active samples available from Hunterston. The effect of changes in graphite density was also examined by modelling its impact on neutron properties and activation calculations.

The main conclusions from this stage and drawing from the results of substantive work on whole core modelling summarised in section 3.2 were as follows:

- The methodology used to derive the Magnox graphite data in the RWI follows a similar but much simpler scheme to that used in this study. It involves a predicted neutron flux and spectrum being applied to simplified core geometry, and the use of Lotus spread sheet activation calculations to predict nuclide inventories. The findings of this study have indicated that this approach is adequate for most nuclides provided that the input precursor concentrations are satisfactory in terms of completeness and accuracy, and that all important activation pathways are considered with reliable cross sections. The FISPACT code and databases used in this study are an industry standard that are regularly assessed and updated. The Lotus spread sheet calculations contain a very limited precursor list with generic concentrations for each element that are applied across the Magnox fleet; the neutron activation pathways and decay schemes are also not as complete as used in FISPACT although may be adequate for RWI purposes.

- The more complex models utilised in this study have indicated that the errors introduced by the relatively simple geometry are within larger errors associated with other aspects of the model`s input data and treatment of these data. The more important errors are associated with precursor concentrations, the more complex behaviour of some nuclides, and the activation routes included in the model.

- The detailed modelling used in this study of the core flux and spectrum provides a higher resolution over the core, as compared to the scheme used to derive RWI estimates, and indicates the sensitivity of predicted concentration to location within the core and sample locations. Where nuclide concentrations are found to be sensitive to flux over the complete irradiation history of the core, there is predicted to be differences in nuclide concentrations between the flux flattened regions and the extremities of the core where flux is lower, as demonstrated by sample analysis results. However, as the core is designed to have a large flux flattened zone covering most of the core, the uniform flux approach taken to predict the RWI is adequate given that the most important uncertainties are associated with precursor concentration and code treatments of activation processes.

- The agreement between the RWI and MCNP-FISPACT predictions are generally within the uncertainty bands noted in the RWI for nuclides where easy comparisons can be made, as shown in previous whole core calculations and, for example, by comparison with sample results for C-14. A direct comparison between sample results and the RWI data is difficult as the samples were taken before the stations ceased generating and the RWI provides only an average specific activity for the whole of the graphite waste stream. However the location and timing of sample recovery and analysis is accommodated in the FISPACT calculations and good agreement is found within uncertainty levels declared in equivalent RWI predictions.

- The FISPACT calculations undertaken result in a greater number of predicted nuclides due to the increased number of precursors included and the larger number of activation pathways included in the code. The new precursor data reported in the Appendices in report TSG(11)0801, Issue 3, October 2012 entitled “Magnox Reactor Graphite Characterisation Stage 2 – Final Active Analysis Stage” has improved the quality of the data set for some specific elements. The impact of this new data is that earlier measurements for specific elements have been substantiated or improved for some important elements (e.g. Cl and Cs).

- Both FISPACT and RWI models are incapable of accurately describing nuclides that are affected by processes other than activation of bulk graphite. These include important nuclides such as Cl-36 and H-3 where both the concentration of the nuclide and its precursors can be changed by chemical and physical processes over the lifetime of the reactor. This is demonstrated by the poor agreement (greater than an order of magnitude) between the results obtained for these nuclides from samples from all the reactors, whereas reasonable to good agreement was found for less volatile nuclides. For Cl-36 and H-3, which are important nuclides in terms of disposability with respect to near surface (H-3 and Cl-36) and deep repositories (Cl-36), the RWI and FISPACT models significantly overpredict the results obtained from analysis of samples. However, for these relatively mobile nuclides this finding relies on the samples having maintained their inventories while they were in long term storage and there is a significant risk that this may not be the case.

- C-14 inventories are an important factor in disposability options for graphite and also for assessing the feasibility of decontamination procedures. The inventories predicted and measured in this study for C-14 are in reasonable agreement with the RWI and laboratory results. Previous pathway analysis undertaken in this project [6] has indicated that the predicted C-14 was generated by a combination of activation of N-14 and C-13. The route from C-13 was found to be minor to N-14 activation but nevertheless still a significant fraction of the predicted inventory (routes from gas-born precursors, e.g. N_2, were not considered in this study). Most of the decontamination strategies for graphite rely on the preferential removal of C-14 from bulk graphite, mainly based on the assumption that C-14 origination from N-14 or gas borne sources has a different chemistry to bulk graphite. However, the overall efficiency of a process will be constrained by C-14 origination from activation of the bulk graphite C-13 inventory, if present in significant amounts as predicted by pathway analysis in this study.

- Failed fuel cartridges have not had a significant effect on the activity of analysed samples as indicated by very low fission product and uranic/trans-uranic radionuclide concentrations measured. Extrapolation of this finding to all other Magnox reactors would require confirmatory sampling particularly at stations where significant fuel degradation has occurred.

- Graphite density loss was found to have a limited effect on predicted activation levels over a wide range of densities. Therefore scalability of results between reactors should not be significantly affected by this factor. Evidence for scalability between reactors was also found by comparison of scaled predictions with active analysis results of samples from Hunterston A. This assessment could have been improved by better knowledge of sample history and reactor design information.

4 RECOMMENDATIONS

The main conclusions from this study are summarised in the following Table and recommendations discussed in more detail in the subsequent paragraphs [6].

	Conclusions	Lessons Learned
RWI	Activation methodology is adequate to describe reactor geometry and neutron flux distribution and was successfully tested against model derived in this project. RWI methodology is scalable between reactors in fleet.	Improvements to precursor data set and concentrations and use of improved activation code (pathways and cross sections) would increase reliability. Mobility of precursors or nuclides is not addressed in the estimate of inventories.
FISPACT-MCNP	Detailed flux distribution was found to be uniform over main part of core. State-of-the-art activation code produced a wider range of nuclides than RWI but general agreement was found within declared uncertainties of the RWI. Model is able to predict the inventory of samples retrieved and analysed at different dates i.e. before station closure. Graphite density changes are unlikely to prevent an adequate scaling of predictions to other reactors with different densities. Methodology is scalable between stations.	Simple flattened flux distribution over main core volume is adequate to predict a reliable inventory. A separate lower neutron dose zone could be used to describe the reflector. Locations of samples at channel surfaces are adequate to be representative of bulk moderator activation rates. Mobility of precursors or nuclides is not taken into account in the code treatments.
Precursor Data	Inventory predictions are very sensitive to precursors used in calculations, together	Pathway analysis is an important step in defining the most important precursors.

	with their concentration. Various pathways to nuclides are possible from different precursors.	Some large variation in precursor data was observed and variations were observed between graphite of the same grade from different reactors. This indicates reactor specific precursor data may be required to scale between stations.
Active Samples	Historic samples could be modelled with reasonable agreement using the FISPACT-MCNP model. Extrapolation to RWI data was difficult due to the nature of the data presented in the RWI and its comparison with active samples recovered and analysed at a different time to station closure. No significant contamination with fuel materials was found.	Historic samples held in the archive are adequate to validate activation code predictions for the less mobile nuclides but are unable to validate predictions for the more mobile nuclides (e.g. Cl-36 and H-3). This maybe because of losses of these nuclides during storage. Suitably removed and treated samples should be recovered from reactor cores to enable a more reliable measurement of these nuclides if necessary.

TABLE COMPARISON OF TOPIC AREAS WITH CONCLUSIONS AND LESSONS LEARNED FROM THE PROGRAMME

- As demonstrated from the findings in this report, accurate precursor concentrations are key to the success of activation calculations and inventory estimates. This study recovered a relatively limited number of unirradiated graphite samples for analysis from a restricted number of reactors and during this exercise a significant amount of knowledge was gained in terms of sample analysis strategies and techniques. Consideration should be given to a full reactor fleet sampling plan which covers a fuller set of samples from all reactors (including AGRs) and a statistically larger set of analyses. This would reduce the risk of unexpected or uncertain inventories.

- Consideration should be given to improving the schemes used to predict the RWI for Magnox core graphite. This could include widening the precursor list and improving the calculation methodology to predict inventories generated by neutron activation. A first step could be to use the precursor data derived in this study within the existing or enhanced Magnox schemes (more cross sections to be included) and then compare with results from FISPACT or equivalent state-of-the-art codes for verification.

- For some important nuclides (e.g. Cl-36 and H-3 in relation to disposal), the uncertainty introduced by analysis of historic samples is difficult to address. Consideration should be given to retrieval of end-of-life samples for quantification

of the more mobile nuclides, mainly Cl-36 and H-3. This would require specialised recovery strategies to obtain larger and deeper samples to avoid deterioration of the sample between station and sub-sampling for analysis at the laboratory and to ensure the sample is representative of the bulk graphite (i.e. not the surface). Care also needs to be taken in recovery, handling and storage. Where new samples are taken from operational stations -potentially Wylfa and AGRs - consideration should be given to retrieval for radiochemical analysis in addition to standard physical/mechanical tests. The number of samples required would not be significant due to the uniform geometry of the core but would need to account for the different thermal and hydraulic condition that different locations have been exposed to.

- Consideration should be given to determining the split between C-14 generated by various activation routes. This split is an important factor in the success of decontamination strategies. This could be assessed by more detailed activation pathway analysis using FISPACT or a similar code, but it is likely that this is best understood via laboratory trials such as thermal desorption techniques.

- No significant contamination was observed in this study but consideration should be given to quantifying fuel contamination of graphite in any reactors where significant fuel problems have occurred.

REFERENCES

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