DERIVATION OF A RADIONUCLIDE INVENTORY FOR IRRADIATED GRAPHITE-CHLORINE-36 INVENTORY DETERMINATION

F.J. BROWN, J.D. PALMER, P. WOOD
United Kingdom Nirex Limited,
Harwell, Oxfordshire,
United Kingdom

Abstract. The irradiation of materials in nuclear reactors results in neutron activation of component elements. Irradiated graphite wastes arise from their use in UK gas-cooled research and commercial reactor cores, and in fuel element components, where the graphite has acted as the neutron moderator. During irradiation the residual chlorine, which was used to purify the graphite during manufacture, is activated to chlorine-36. This isotope is long-lived and poorly retarded by geological barriers, and may therefore be a key radionuclide with respect to post-closure disposal facilities performance.

United Kingdom Nirex Limited, currently responsible for the development of a disposal route for intermediate-level radioactive wastes in the UK, carried out a major research programme to support an overall assessment of the chlorine-36 activity of all wastes including graphite reactor components. The various UK gas cooled reactors reactors have used a range of graphite components made from diverse graphite types; this has necessitated a systematic programme to cover the wide range of graphite and production processes. The programme consisted of:
- precursor measurements - on the surface and/or bulk of representative samples of relevant materials, using specially developed methods;
- transfer studies - to quantify the potential for transfer of Cl-36 into and between waste streams during irradiation of graphite;
- theoretical assessments - to support the calculational methodology;
- actual measurements - to confirm the modelling.

For graphite, a total of 458 measurements on samples from 57 batches were performed, to provide a detailed understanding of the composition of nuclear graphite. The work has resulted in the generation of probability density functions (PDF) for the mean chlorine concentration of three classes of graphite:
- fuel element graphite;
- Magnox moderator and reflector graphite and AGR reflector graphite;
- AGR moderator graphite.

Transfer studies have shown that a significant fraction of the chlorine is released from the graphite during irradiation, both in natural precursor and activated form. The release rate of inactive chlorine and of chlorine-36 was modelled, to allow the calculation of a residual chlorine-36 inventory in operational and decommissioning wastes; actual measurements on operational wastes have confirmed this release. This has subsequently been used to assess the effect on disposal risks.

This paper provides a description of the work undertaken by Nirex to establish the residual inventory of chlorine-36 in irradiated nuclear graphite, and outline the implications for disposal of these wastes.

1. INTRODUCTION

Nirex was set up by the nuclear industry with the agreement of the Government to develop disposal facilities for intermediate level waste and some low level radioactive waste (ILW and LLW).

Chlorine-36 is potentially a key radionuclide in the disposal facilities post closure safety case because of its long half-life and chemical characteristics. Chlorine-36 arises from neutron activation of naturally occurring isotopes which are present as impurities in most reactor materials. Nirex therefore commissioned the work described here as part of an assessment of the chlorine-36 activity of wastes destined for the disposal facilities. The programme of work was carried out between 1993 and 1996.

Graphite is used for fuel element sleeves and reactor core components in gas cooled reactors, including Magnox and Advanced Gas-cooled Reactors (AGR). There is a large mass of graphite requiring disposal [1] which will be an important source of chlorine-36. The diversity of graphite types and components has necessitated a systematic programme to cover the wide range of production processes.

Chlorine in graphite can potentially be removed by radiation-induced and thermal processes. The initial concentrations may therefore be reduced in service, resulting in less chlorine-36 activity in the fuel element sleeves and core components. In addition, transfer of chlorine-36 to other reactor components as surface contamination is possible.

This paper: outlines the Nirex chlorine-36 programme; describes work carried out to determine the chlorine concentrations in graphite to provide basic data for chlorine-36 inventory calculations; describes experimental work carried out to understand the loss of chlorine from graphite, in order to enable quantification of the levels of activated chlorine in graphite components. Such calculations are necessary in evaluating waste management options for graphite-containing wastes.
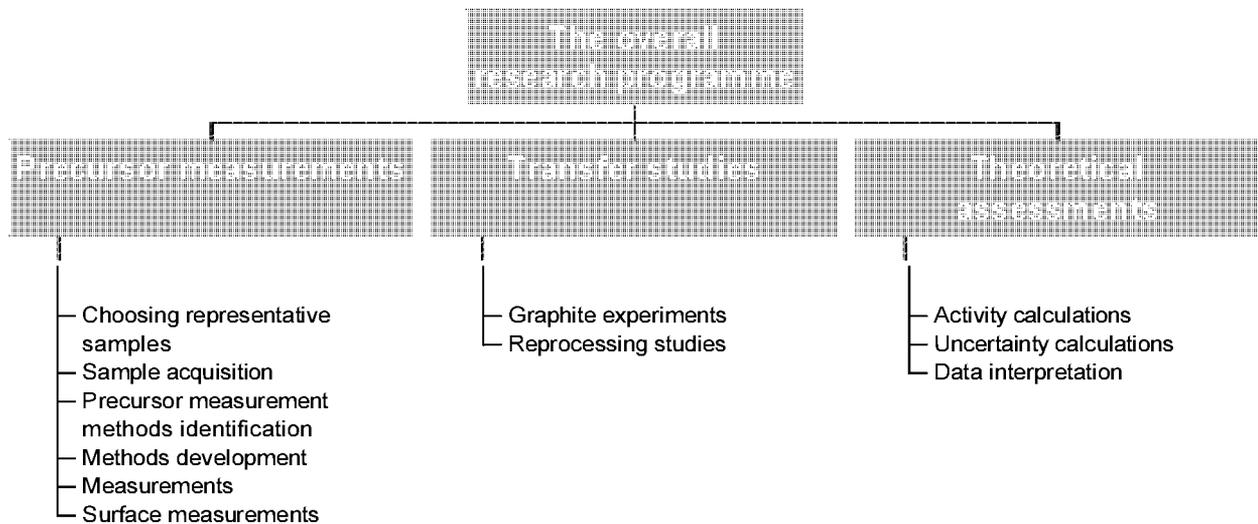
2. THE NIREX CHLORINE-36 PROGRAMME

Based on the limited information on the inventory of chlorine-36 available in 1993, the nuclide emerged as the dominant nuclide in preliminary disposal facilities post-closure assessments. This led to a reassessment of the inventory of chlorine-36 and led to the view that the chlorine-36 inventory data was not sufficiently robust to form a defensible basis for a future post-closure safety case. The uncertainty arose because of variable estimates of chlorine-36 in similar waste streams since there were few direct measurements of chlorine-36 in waste materials and few reliable measurements of chlorine precursor concentrations.

Nirex commissioned a major research programme to support an overall assessment of the chlorine-36 activity of wastes destined for the disposal facilities. The assessment was carried out between 1993 and 1996 with the support and assistance of all the major waste producers. This programme was aimed at providing the best defensible estimate of the chlorine-36 content of radioactive wastes arising in the UK.

There were two basic options for improving the inventory assessment: assessments based on precursors or direct measurement of chlorine-36 in waste streams. It was concluded that precursor measurements were the most appropriate and that direct measurements, which require chemical separation and measurement of soft β emissions, be used to complement an approach based on precursors.

The programme can be conveniently split into three parts. A large element of the work was concerned with making precursor measurements on a representative set of samples of all reactor materials (precursor measurements). Other studies concerned the transfer of chlorine-36 activity after it has been generated in order to assess its destination. Finally, chlorine-36 activity estimates for the materials that are irradiated in the reactors were based on data derived from the precursor measurements and the transfer studies (theoretical calculations), with confirmatory measurements to validate theoretical assumptions. The main elements of the programme are illustrated on the diagram below:

Technical
research programme

Precursor measurements | Transfer studies | Theoretical assessments

- Choosing representative
  samples
- Sample acquisition
- Precursor measurement
  methods identification
- Methods development
- Measurements
- Surface measurements

- Graphite experiments
- Reprocessing studies

- Activity calculations
- Uncertainty calculations
- Data interpretation

The waste producers played a major role in identifying and making available samples from their material archives.

Table 1 sets out the precursor measurements carried out for different materials and indicates both the measurement technique used and the number of measurements taken:

TABLE 1. PRECURSOR MEASUREMENT TECHNIQUES AND NUMBERS

Measurement techniques	Relevant materials	Number of measurements
NAA: Standard neutron activation analysis	Graphite	458
	Zircaloy	201
	Aluminium	10
RNAA: NAA enhanced using radiochemical separation	Ferrous materials	175
	Nickel alloys	10
	Magnox alloys	145
Chemical techniques	Uranium	124
	Uranium dioxide	104
Total		1,420

3. NUCLEAR GRAPHITES AND CHLORINE-36 PRECURSORS

Nuclear graphites come in a variety of types, the differentiating factors being the type of coke used, its ultimate use in a reactor and the manufacturer. Graphite is produced in batches termed heats. A summary of the types and usage of graphite used in Magnox and AGR reactors is given in Table 2

TABLE 2. TYPES OF GRAPHITE AND USAGE.

Graphite Type	Reactor	Component
Pile Grade A (PGA)	Magnox	Moderator
Pile Grade B (PGB)	Magnox	Reflector
Gilsocarbon	AGR	Moderator and Reflector
VFT	AGR	Fuel element sleeves and struts (pre 1990)
Nittetsu	AGR	Fuel element sleeves (post 1993)

It is important that graphite used in nuclear reactors contains a low level of impurities, particularly those which are effective neutron absorbers. The removal of boron from artificial graphites for nuclear purposes makes use of the high-temperature reaction between boron and chlorine to form volatile chlorine-containing compounds. Graphitised components are exposed to gaseous chlorine, or chlorine-containing compounds at temperatures of up to $2500^{\circ}C$. Under these conditions any boron within the graphite reacts with chlorine to form boron trichloride, a volatile material which escapes from the graphite as a gas. As a result of this treatment the graphite may contain residual chlorine, but because of the high temperatures the amount is likely to be small.

Chlorine-36 is produced in a nuclear reactor by three main routes: direct activation of the natural chlorine isotope chlorine-35 (the dominant route); direct activation of potassium-39; indirect production from sulphur-34 where an intermediate isotope, sulphur-35, is formed by neutron capture and then undergoes β decay to chlorine-35. The production of chlorine-36 from the latter two routes can only be of a similar order to that from the dominant route (chlorine-35) when the elemental precursor levels are 1200 times higher (for potassium) or 31,000 times higher (for sulphur) than that of chlorine.

4. PRECURSOR MEASUREMENTS

Prior to this programme of work there was only limited information on the chlorine concentration in fuel element and reactor core graphite and details of how the measurements were made are in the main unknown. Typical reported chlorine concentrations for fuel element graphite were in the range 2 ppm to 23 ppm which usually reflected the limit of detection. Ref. [2] tabulates chlorine concentrations in Gilsocarbon of 1.8-2.2 ppm; in general the chlorine concentration in PGA graphite was in the range 0.8 to 8.8 ppm and in Gilsocarbon graphite is in the range 1.4 to 7 ppm.

Neutron activation analysis (NAA) was selected to measure the chlorine concentrations in graphite. It was chosen because it gave a bulk measurement rather than a surface value and because it was sufficiently sensitive and accurate. In all cases the method was able to measure chlorine concentrations below 0.2 ppm. The porous nature of graphite prevents the use of surface etching to remove any possible superficial contamination of samples by chlorine. Therefore, particular care was taken during sample manufacture to minimise contamination and the samples were produced from material which was at least 2 mm away from an existing surface.

4.1. Fuel Element Graphite

Samples from a wide range of components were measured to determine the general variability between different materials. There were 227 measurements on 22 different heats of graphite covering different years of manufacture, the two manufacturers and the two types of graphite (VFT or Nittetsu). The measured chlorine concentrations in the samples can be represented by a single probability distribution function (PDF).

4.2. Core Graphite in Magnox and AGR

There were 45 measurements on nine different Magnox moderator specimens; the measured chlorine concentrations were above the limits of detection. There were 58 measurements on twelve different Magnox reflector specimens; in one sample the chlorine concentration was below the limit of detection which was 0.41 ppm.

There were 118 measurements on twelve AGR moderator specimens. The measured chlorine concentrations were in the range 0.09 ppm to 3.63 ppm; in five samples the chlorine concentration was below the limits of detection. There were 10 measurements on two AGR reflector specimens; in one sample the chlorine concentration was below the limit of detection of 0.35 ppm.

4.3. Other precursors

Within the Nirex programme potassium concentrations were measured in a specimen of Nittetsu fuel element sleeve graphite as part of a laboratory comparison. Potassium concentrations were in the range 1.6-2.7 ppm. Unpublished measurements of sulphur concentrations in fuel element sleeve graphites are in the range 5 to 52 ppm and unpublished information on sulphur concentrations in Magnox core graphites shows 50 ppm. These levels are such that chlorine-36 production is dominated by activation of chlorine-35.

5. TRANSFER STUDIES

The precursor data allows a calculation of the chlorine-36 activity in fuel element sleeves provided it is assumed that there is no chlorine loss from the graphite. However, evidence relating to irradiated graphite from the Hanford reactors [3] has suggested that significant losses may be brought about by thermal or radiolytic effects. The impact of such losses could be to reduce the chlorine-36 inventory if the losses occurred prior to significant irradiation.

Evidence of potential losses was derived from simulated radiation and heating experiments, carried out to investigate chlorine loss early in the irradiation cycle, and measurements were made on actual irradiated materials to validate any hypothesis arising from the experiments. Irradiation effects were assessed using an electron beam as the radiation source, and purely thermal experiments were undertaken under conditions which allowed a direct comparison of thermal and irradiation-induced processes.

5.1. Fuel element graphite

Tests were performed on Nittetsu fuel element sleeve graphite samples with low and high initial concentrations of chlorine. Chlorine loss under irradiation to about 70% of the initial value was measured. Heating the specimens to a similar temperature and duration to the irradiation experiments gave some reduction in chlorine concentration in most of the tests.

In order to determine the loss of chlorine from fuel element sleeve graphite at much longer times than could be obtained from the irradiation tests, measurements were made directly of the chlorine-36 activity in a sleeve following irradiation in an AGR reactor, and the results assessed to infer the initial chlorine concentration which would produce this activity (Fig. 1). It seems probable that some process is operating by which chlorine, either as chlorine-36 or inactive precursor, is released from fuel element sleeves to the primary circuit.
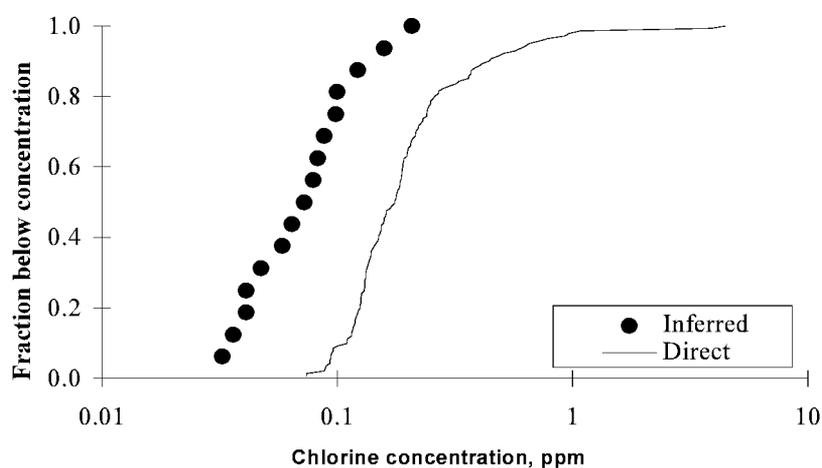

FIG. 1. Initial chlorine concentration in Nittetsu sleeves as measured by NAA and as inferred.

5.2. Core graphite

PGA specimens irradiated at 515°C exhibited chlorine concentrations after exposure substantially below the values measured before irradiation. PGA specimens subjected only to thermal exposure at 515°C also showed a marked decrease in chlorine concentration. The data indicate a rapid decrease in concentration to about half the initial value. There is little evidence for a subsequent decrease in concentration over the timescales involved in these experiments. Given the similarity between the behaviour observed in the two experiments, it seems reasonable to conclude that the loss of chlorine from PGA graphite in the irradiation experiments was primarily the result of thermal processes.

Data obtained on AGR moderator graphite exposed at 515°C showed that irradiated specimens lost significant amounts of chlorine. The data show the thermally exposed specimens also lost chlorine. The data are, however, significantly more scattered than those for PGA graphite, possibly as a result of lower initial chlorine concentrations. The mean ratio, of chlorine concentration after irradiation or thermal exposure to the initial value, is calculated to be 0.7.

A number of samples of core graphite irradiated in reactors were obtained and the chlorine-36 inventory of 30 specimens was determined by an acid dissolution method. For Oldbury samples, the values obtained for inferred precursor concentration are in general significantly below the mean value derived for Magnox moderator graphite (FIG. 2); the cumulative distribution function (CDF) for inferred concentrations is broadly similar in form to that of the directly measured values, but displaced along the concentration axis to concentration values lower by more than a factor of two. This observation provides evidence that chlorine has been lost from the graphite on irradiation as the concentrations are below those after the initial chlorine loss. For AGR moderator graphites the CDF of the inferred concentrations lies at much lower values than those associated with the virgin material and below that following the initial chlorine loss; this strongly implies the loss of chlorine during irradiation. This is confirmed by chlorine-36 being found in reactor desiccants, used to dry the coolant in a clean-up circuit.
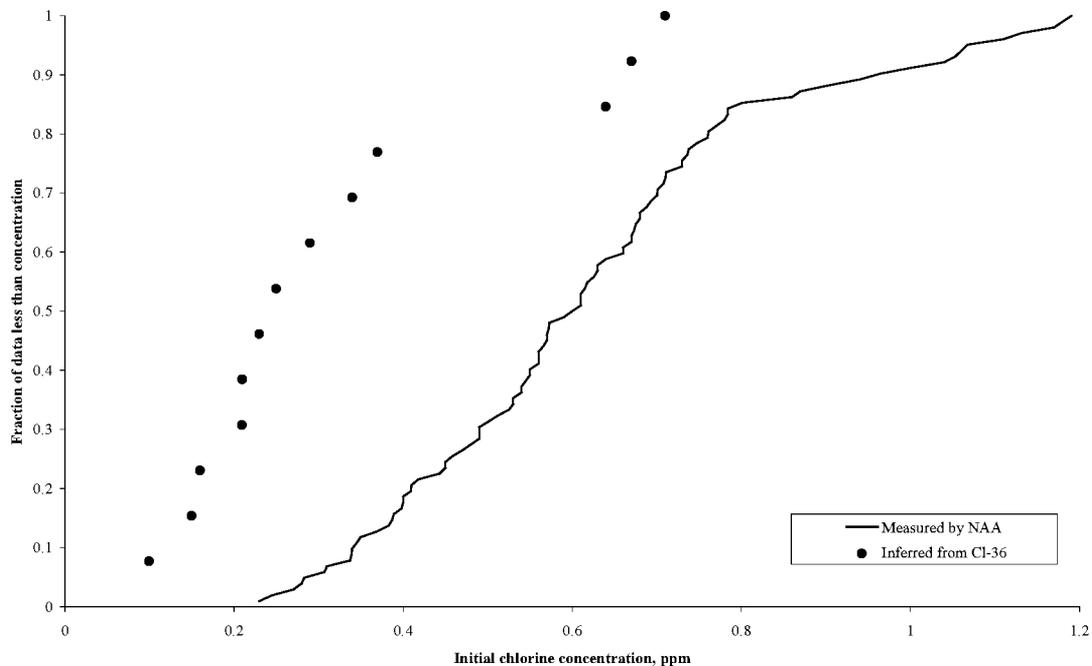

FIG. 2. Initial chlorine concentration in Oldbury moderator graphite as measured by NAA and as inferred from chlorine-36 activation.

6. THE CHLORINE-36 INVENTORY IN GRAPHITE

Calculation of the chlorine-36 inventory of graphite must account for the experimental data on release of chlorine described above. The graphite structure is highly porous and two types of porosity have been identified: open porosity, where there are paths available to the surface and closed porosity where no such paths exist. Some of the closed porosity is converted to open porosity by oxidation during irradiation.
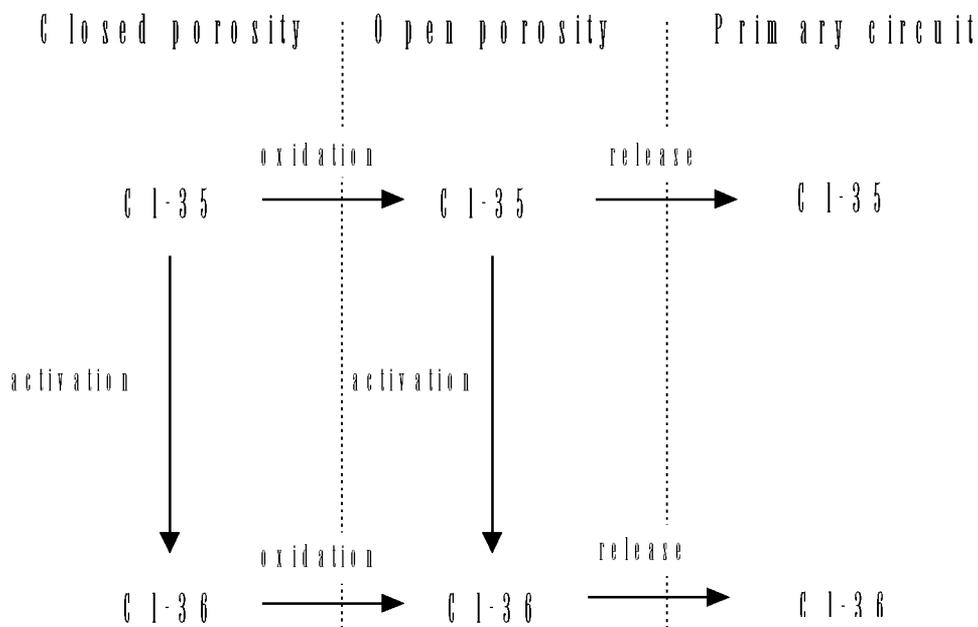
Closed porosity   Open porosity   Primary circuit

oxidation   release
Cl-35   ———►   Cl-35   ———►   Cl-35

activation   activation

oxidation   release
Cl-36   ———►   Cl-36   ———►   Cl-36

FIG. 3. Schematic of activation and release of chlorine in graphite.

A possible explanation of the chlorine release behaviour has been used to develop a model to allow estimation of the activation and release of chlorine and chlorine-36. It is based on the hypothesis that chlorine is present in both the open and closed porosity after the purification stages of nuclear graphite manufacture (FIG. 3). The chlorine in the closed pores would be contained but the chlorine in the open pores would be released. Some of the chlorine in the open pores escapes prior to operation, and so the concentration in the open pores is lower than in the closed pores. During the early stages of reactor operation, thermal action releases the remaining chlorine in the open pores before it has been significantly activated. Because none of the chlorine in the closed pores is released, this chlorine would be available for activation to chlorine-36.

During reactor operation radiolytic oxidation of the open pores enlarges them so that they break into some of the closed pores [Refs 4, 5, 6] and would allow the chlorine-36 to escape out of the graphite. In both Magnox and AGR reactors about 40% of the initial closed pore volume is opened up during operation, and the model assumes that this occurs linearly with power output over the reactor life.

The model can be fitted to be consistent with all of the experimental data, assuming a chlorine concentration in the closed pores of three times that in the open pores. The total chlorine release due to oxidation is consistent with the final measured chlorine concentrations in irradiated PGA graphite. A similar case can be made for Gilsocarbon used in AGR reactors. The chlorine-36 loss through life is supported by the measurement of chlorine in desiccants and drier liquors and the total release is consistent with the measured losses in irradiated AGR graphite.

It is therefore concluded that the model forms an adequate basis for estimating the chlorine losses in Magnox reactor and AGR cores. The model is also broadly consistent with the data for sleeve material.

7. DISCUSSION

The information gained in the Nirex chlorine-36 programme can be used to estimate inventories of graphite-bearing wastes. This has been performed as part of the inventory estimate for wastes destined for the disposal facilities. The total inventory estimate is given in Table 3; 29% of the inventory is from graphite wastes -23% from "carry-over" and 6% still associated with graphite.

TABLE 3. CHLORINE-36 INVENTORY OF DISPOSAL
FACILITIES REFERENCE VOLUME

Chlorine-36 Inventory (TBq)			
Waste Volume, m^3	Lower Bound	Mean	Upper Bound
275,000	9	12	15

TABLE 4. BREAKDOWN BY SOURCE MATERIAL
OF UK CHLORINE-36 INVENTORY

Material Source	Inventory
Graphite	51%
Fuel	30%
Clad	8%
Research/Isotopes	6%
Other	5%

It has been necessary to carry out a systematic programme covering all materials that have been irradiated in the UK nuclear programme. Table 4 gives a breakdown by major sources of the total chlorine-36 production in all waste materials. These calculations estimated that 51% of the total chlorine-36 inventory was as a result of irradiation of graphite.

The detailed probabilistic calculation of chlorine-36 inventories has enabled production of a robust, defensible estimate of the chlorine-36 requiring disposal. Disposal assessments such as that carried out for a repository at Sellafield in Nirex 97 [7] showed chlorine-36 to be a significant contributor to peak risk.

The Nirex chlorine-36 programme has shown that graphite is a significant source of chlorine-36 and will have a significant impact on the radionuclide burden to disposal facilities. It is important to properly characterise the sources of graphite.

REFERENCES

[1]   *1998 UK Radioactive Waste Inventory*, Nirex Report N3/99/01, ISBN 184029 283 4.

[2]   Regan, J D, Cripps, S J, Kelly, B R, Hambleton, B and Nicholson, J R, *Design Features Facilitating the Decommissioning of Advanced Gas-Cooled Reactors*, Commission of the European Communities, EUR 9207 en, 1984.

[3]   Miller, R L and Steffes, J M (editors), *Radionuclide Inventory and Source Terms for the Surplus Production Reactors at Hanford*, Union Carbide, UNI-3714 Revision 1 Appendix 3, 1987.

[4]   Blanchard A, Ketchen J, Schofield P and Campion P, *'A graphite oxidation experiment to high weight-loss under CAGR conditions'*, in Gas Chemistry in Nuclear Reactors and Large Industrial Plant, ed A Dyer, Heyden London (1980)

[5[Campion A, Lind R, Blanchard R, and Koch C, *Proc 4th Int Conf on Carbon and Graphite*, 459, (1976)

[6]   Standring J and Ashton A, *Carbon*, **3**(2), 159 (1964)

[7]   *Nirex 97: An Assessment of the Post-Closure Performance of a Deep Waste Repository at Sellafield*, Nirex Report S/97/012 December 1997.