LLW Repository Ltd

LLWR Environmental Safety Case

Cl-36 Mobility in Reactor Circuits and its Potential Significance for the ESC 2011 Inventory

A report prepared by Serco for and on behalf of the Low Level Waste Repository Site Licence Company.

SERCO/TAS/003756/008　　　　　　**Issue 3**　　　　　　**Date: January 2011**

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Prepared for   **LLWR**

Prepared by   **Serco**

Your Reference   **LLWRP1106**

Our Reference   **SERCO/E003756/008 Issue 3**

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Executive Summary

Chlorine is present in nuclear grade graphites as a result of the purification process. During the final phase of the manufacturing process chlorocarbons are introduced into the atmosphere of the graphitising furnace to remove any boron contamination as volatile boron trichloride. Some chlorine remains trapped within the graphite structure as a result of this process. The Cl-35 present in this trapped material can become activated to Cl-36, an isotope of importance to the long-term performance of LLWR.

This report describes a programme of work to develop further an understanding of the potential effects of Cl-36 mobility on the forward inventory of this radionuclide in UK LLW. The principal activities were to:
- Review the model for Cl-36 behaviour developed by Nirex in the mid-1990s particularly in the light of any further information which has become available on Cl-36 in Magnox and AGR circuits.
- Extend the model as appropriate to address the issue of transfer of Cl-36 to other waste streams.
- Confirm the understanding of the basis of the chlorine-36 estimates in the 2007 National Inventory [1] to establish whether Cl-36 mobility has been accounted for and, if so, how.
- Deploy the extended model to undertake preliminary scoping calculations to establish whether the release of chlorine from core graphites could have a material effect upon the Cl-36 inventories of LLW streams.

The assessment suggests that there are potentially significant effects, arising mainly from the redistribution of Cl-36 released from core graphites. The numerical data suggest an enhancement of Cl-36 levels in LLW of perhaps an order of magnitude for Hinkley Point B, and a factor of about two for Hinkley Point A. That the calculated effect is larger for Hinkley Point B than in Hinkley Point A probably reflects the higher flux experienced by AGR core graphites. The enhancements apply almost entirely to wastes arising after about 2070.

Although the assessment provides quantitative output, numerical values should be viewed with some caution. The methods and data used throughout this report are simple representations of complex processes, and would require significant further work before they could be used as the basis for a definitive modification of the forward inventory of Cl-36 in UK LLW.

The assessment consists of the following phases:
- The release of Cl-35 and Cl-36 from core graphites.
- The loss of chlorine from the circuit.
- The redistribution of released Cl-35 and Cl-36 between circuit materials.
- The activation of released Cl-35 to form Cl-36.

Each step has been examined using conceptually simple models. It is recognised that, in reality, each step is likely to mechanistically complex. However, the available information is too sparse to allow complex mechanistic models to be constructed and populated at the present time. It is, in any case, inappropriate to attempt complex assessments unless scoping calculations indicate a clear need.

Chlorine release
The assessment of the extent of release of chlorine from core graphites as a function of time depends on:
- The assumption that all the chlorine in the graphite is associated with the porous structure of the material.
- The assumption that chlorine is released immediately from initially open porosity, and immediately from closed porosity when it is accessed by radiolytic oxidation.

- A model for the rate of porosity opening with time.

The first two assumptions are conservative, in that they tend to maximise the extent of chlorine release. The form of the model for opening porosity with time is physically reasonable, but difficult to parameterise and bounding assumptions have been used. Further work would be required to improve the parameterisation of this part of the model.

Loss of chlorine, and the extent to which the 2007 National Inventory accounts for chlorine release
The limited data available suggest that only a small fraction of the chlorine released from core graphites is released to the environment.

Examination of National Inventory data suggests that the Inventory of Hinkley Point B does not take direct or indirect account of chlorine mobility. Examination of Hinkley Point A data suggests that at least some of the chlorine released from core graphites may be accounted for. The evidence is not, however, conclusive.

The redistribution of released chlorine between surface materials
A simple model based on relative exposed surface areas has been adopted for the redistribution of released chlorine between waste streams. This model is difficult to parameterise adequately on the basis of information available in the National Inventory. Significant work, based on engineering designs, would be required to parameterise this part of the model accurately. Redistribution of the chlorine based solely on relative surface areas remains a reasonable assumption, but is unsupported by data.

Activation of Cl-35
A simple model, which is in principle robust, has been used to model the activation of Cl-35 to Cl-36 after release. Parameterisation of the model, however, is not straightforward.

Contents

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1   Introduction

Cl-36 is primarily formed by the neutron activation of its precursor, Cl-35. The chlorine precursor is present at parts per million (ppm) quantities for most components that reside in regions of high neutron flux within a nuclear power reactor. There are other possible routes for Cl-36 production, the main ones being from potassium and sulphur; these generation routes are discussed further in Reference 2, but are unlikely to be important for low level waste (LLW) waste streams. Cl-36 is likely to be important in the safety case for the Low Level Waste Repository (LLWR).

Chlorine is present in nuclear grade graphites as a result of the purification process. During the final phase of the manufacturing process chlorocarbons are introduced into the atmosphere of the graphitising furnace to remove any boron contamination as volatile boron trichloride. Some chlorine remains trapped within the graphite structure as a result of this process.

An elicitation exercise to derive uncertainty distributions for the Cl-36 activity in LLW has recently been undertaken by a panel of experts [3]. The meeting noted the work reported by Nirex in 1997 [2] on the potential mobility of Cl-36 arising in the core graphites of AGR and Magnox stations. Release of Cl-36 to the coolant could lead to its being deposited on materials which will form part of waste streams destined for LLWR. If this is not accounted for, the Cl-36 inventory of LLWR might be underestimated. The workshop concluded [3] that the potential significance of this phenomenon for the inventory of Cl-36 in LLWR was not well understood.

This report describes a programme of work to develop further an understanding of the potential effects of Cl-36 mobility on the forward inventory of this radionuclide in UK LLW. The principal activities were to:

- Review the model for Cl-36 behaviour developed by Nirex in the mid 1990s particularly in the light of any further information which has become available on Cl-36 in Magnox and AGR circuits.
- Extend the model as appropriate to address the issue of transfer of Cl-36 to other waste streams.
- Confirm the basis of the Cl-36 estimates in the 2007 National Inventory [1] to establish whether Cl-36 mobility has been accounted for and, if so, how.
- Deploy the extended model to undertake preliminary scoping calculations to establish whether the release of chlorine from core graphites could have a material effect upon the Cl-36 inventories of LLW streams.

2   The Nirex 1997 graphite model

2.1   Introduction

UK Magnox and AGR power stations have graphite moderators, which contain trace quantities of chlorine at ppm levels. Prior to irradiation, the chlorine is present at natural isotopic abundance levels predominately as Cl-35. During irradiation some of this chlorine can be irradiated to form Cl-36, in proportion to the cumulative neutron flux generated in the core of the reactors.

A model was developed in the 1997 Nirex study (Reference 2) with the intention of calculating the maximum ILW inventory of Cl-36 that was likely to be present in the Nirex planning volumes taking into account the release of Cl-36 and its precursor Cl-35 from moderator graphite under irradiation. It was able to provide a prediction of the Cl-36 activity in the moderator and the total carryover of Cl-36 that would be released into the primary circuit and potentially plated out in other regions of the reactor. The basis of the model (the 'Nirex' model) is given in Reference 4. The experimental evidence underpinning the model is summarised in Reference 5. Evidence for the release and translocation of Cl-36 originating from the moderator is provided by the detection of Cl-36 on reactor components outside the neutron flux, where the presence of Cl-36 cannot be attributed to activation of Cl-35 *in-situ*. Specific examples are the presence of Cl-36 in desiccants and burst can detection (BCD) equipment.

2.2   Overview of the model

The Nirex model for release of Cl-36 from graphite is shown in Figure 1, and summarised below. The main point is that release of chlorine isotopes from graphite depends upon where they reside in the porous structure of the graphite.
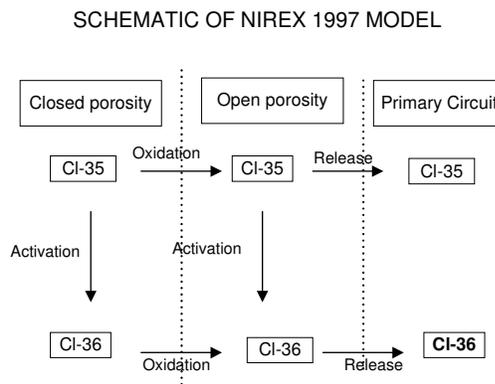
SCHEMATIC OF NIREX 1997 MODEL

Figure 1:   **Schematic of Nirex 1997 "Cl-36 carryover model" (Reference 5).**

Some chlorine will be associated with 'open porosity' – that part of the pore structure connected to the surface of the graphite. Experimental evidence suggests that Cl-35 in the open porosity is released relatively quickly at operating temperatures, before it can undergo significant activation [5].

Some chlorine will be associated with the 'closed porosity' – that part of the pore structure isolated from the graphite surface. Experimental evidence suggests that chlorine associated with this part of the graphite structure is not released at any significant rate, and significant activation of Cl-35 is possible. Although release of chlorine from closed porosity is extremely slow, closed porosity can

be converted to open porosity as the process of radiolytic oxidation removes carbon walls separating the closed pores from the open pore network. Once regions of porosity have been accessed in this way, the chlorine they contain is available for release.

Given that chlorine isotopes are assumed to be released very quickly from open porosity, only a very small fraction of the chlorine located in the initially open porosity will be activated. Cl-35 located in the initially closed porosity, however, can potentially reside in the flux for a considerable period, and thus undergo greater activation. The length of residence in the flux, and hence the quantity of Cl-36 released from the graphite, will therefore depend critically upon the rate at which closed porosity is opened up by graphite oxidation. The 1997 Nirex model assumed that closed porosity is converted to open porosity at a constant rate throughout the life of the plant. As discussed in Appendix B, however, this assumption is not supported by experimental data, which suggests that closed porosity is accessed faster in the earlier stages of radiolytic oxidation than in the later. This has implications for the generation and release of Cl-36.

2.3 Assessment of the model in the light of Cl-36 transfer to other waste streams

The features of this model were reviewed in the light of the requirement to assess the possible implications of Cl-36 carryover for the inventory of this radionuclide in low-level waste. The following issues emerged from the review;

- A key parameter for the quantity of Cl-36 released from core graphites is the rate at which closed porosity is converted to open porosity as a result of the effects of oxidation. The assumption used in the Nirex 1997 "carryover model" was that the rate was uniform since this is the assumption that will lead to maximum amount of Cl-36 released.

- A significant fraction of the AGR coolant is released on a daily basis. This will lead to a release to the environment and will include a fraction of the Cl-36 that is mobile in the coolant. The model does not take account of any Cl-36 released with the CO_2 coolant, and the subsequent reduction of Cl-36 which will form part of the LLWR inventory. This has not been accounted for in the "carryover model. These comments also apply to Magnox reactors.

- The 'carryover model' does not attempt to predict how much of the chlorine that plates out on the reactor surfaces goes to material designated as ILW and how much goes to LLW. As a measure of conservatism, parts of the Nirex study assumed that the carryover went to ILW, but this does not necessarily reflect the actual position.

3 Developing the 1997 model

3.1 Introduction

In order to assess the potential significance of chlorine mobility for the inventory of LLWR, some quantitative estimate of the release of chlorine isotopes from irradiated graphite needs to be derived. This section of the report describes the derivation of a simple, semi-empirical mathematical representation of the relevant processes based on the model described in Section 2.

Following the assumption in the Nirex study that, under reactor conditions, all chlorine isotopes are released instantly from that part of the graphite porosity which is accessible to the coolant, Cl-36 generation can take place only in that porosity which is initially closed. As this porosity is opened up to the bulk coolant as a result of radiolytic oxidation, Cl-35, together with any Cl-36 which has been formed, is released instantaneously. The initial state for the activation/release process is that all the available Cl-35 is associated with the initially closed porosity. This can be assumed to be about half the total value measured analytically [5].

3.2 Loss of Cl-35 from the opening of closed porosity (CPV)

Consider first Cl-35 in the closed porosity. The rate of Cl-35 loss due to CPV opening will be given by:

$$\frac{dC}{dt} = \frac{dC}{d\varepsilon} \times \frac{d\varepsilon}{dt}$$

Where C = Concentration of Cl - 35 in closed porosity / Atoms $(m^3$ graphite$)^{-1}$

ε = Closed pore volume / $(m^3$ closed porosity$)$ $(m^3$ graphite$)^{-1}$

t = Time

Now,

$$\frac{dC}{d\varepsilon} = \frac{C}{\varepsilon}$$

Here we assume that closed porosity is lost exponentially as a function of reactor life (see the analysis of data from Reference 6 given in Appendix B), we have

$$\frac{d\varepsilon}{dt} = -\beta\varepsilon$$

Hence

$$\frac{dC}{dt} = -\beta C$$

Thus, if $C = C_0$ at $t = 0$

$$C = C_0 \exp[-\beta t] \qquad \qquad \ldots \ldots \ldots 1$$

3.3   Cl-36 in irradiated graphite as a function of time

Cl-36 is generated from the neutron activation of Cl-35 and lost from the graphite by the same processes by which Cl-35 is lost. Assuming that the loss of Cl-36 by radioactive decay is negligible, and that only a small fraction of the available Cl-35 undergoes activation (both of which assumptions are supported by data in the National Inventory) we have, if N is the number of Cl-36 atoms per m^3 of graphite

$$\frac{dN}{dt} = kC - \beta N$$
$$= kC_0 \exp[-\beta t] - \beta N$$

Where k = Atoms of Cl - 36 generated per atom of Cl - 35 per unit time

If $N = 0$ at $t = 0$, this has the solution

$$N = kC_0 t \exp[-\beta t] \qquad \qquad \dots \dots \dots 2$$

In the case where there is no opening of the closed porosity (ie $\beta = 0$) and no loss of chlorine from the open porosity, we have the calculation equivalent to that used in the National Inventory for the Cl-36 content of irradiated graphite, and Equation 2 becomes

$$N_T = 2k C_0 t \qquad \qquad \dots \dots \dots 3$$

The factor of 2 appears because the quantity of Cl-36 in this calculation includes the quantity in the closed and the open porosities – double that in the closed porosity alone.

3.4   Cl-36 lost from irradiated graphite as a function of time

If N_L is the number of Cl-36 atoms lost per m^3 of graphite, then

$$\frac{dN_L}{dt} = \beta N$$
$$= k \beta C_0 t \exp[-\beta t]$$

Thus, if $N_L = 0$ at $t = 0$

$$N_L = \frac{kC_0}{\beta} [1 - (\beta t + 1) \exp(-\beta t)] \qquad \qquad \dots \dots \dots 4$$

3.5   Sample calculation

As an example, Figure 2, Figure 3, and Figure 4 show the results of calculations based on activation rates calculated for Hinkley Point A. Data in the 2007 National Inventory [1] allow the average rate of generation of Cl-36 in core graphites to be estimated as 1.2×10^{20} atoms $(m^3$ of graphite$)^{-1}$ y^{-1}, assuming an initial chlorine concentration of 75 ppm [2]. This production rate is equivalent to the term $2kC_0$ in Equation 2. The initial production rate in the closed porosity, kC_0, is therefore estimated as 6×10^{19} atoms $(m^3$ of graphite$)^{-1}$ y^{-1}.
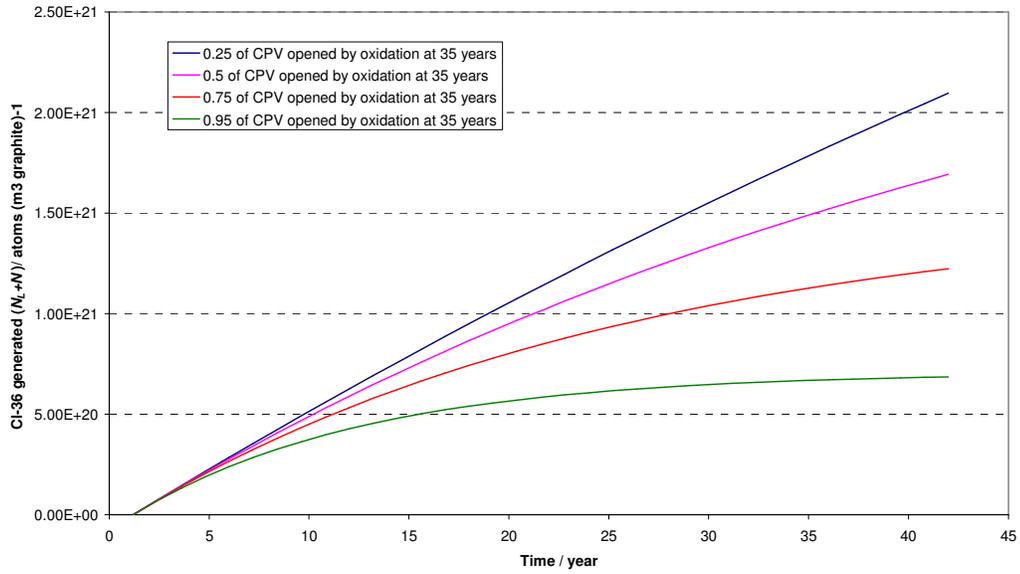
Figure 2: Predicted total Cl-36 generated in graphite per m^3 graphite for Hinkley Point A
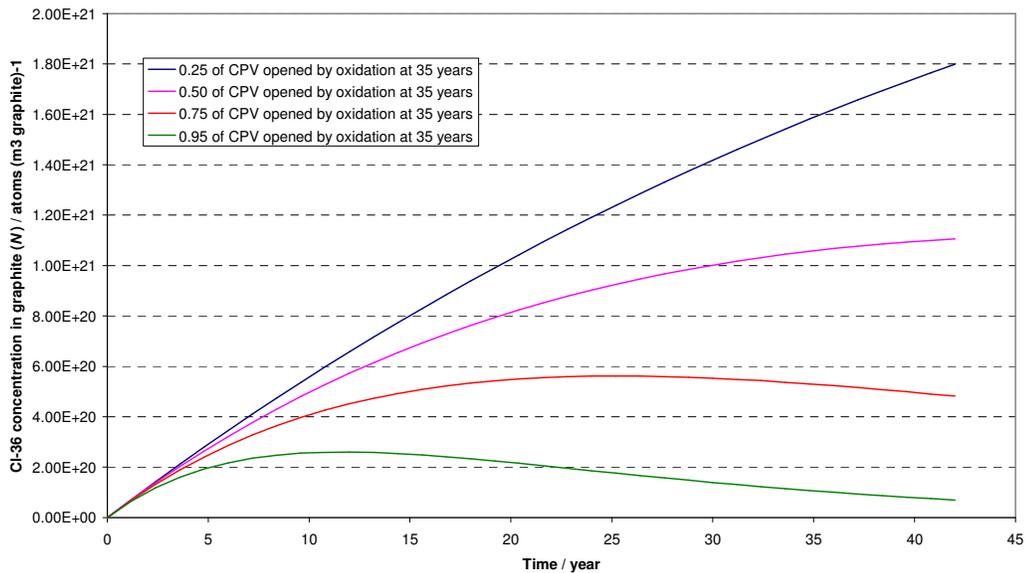

Figure 3: Predicted average Cl-36 concentration in graphite for Hinkley Point A
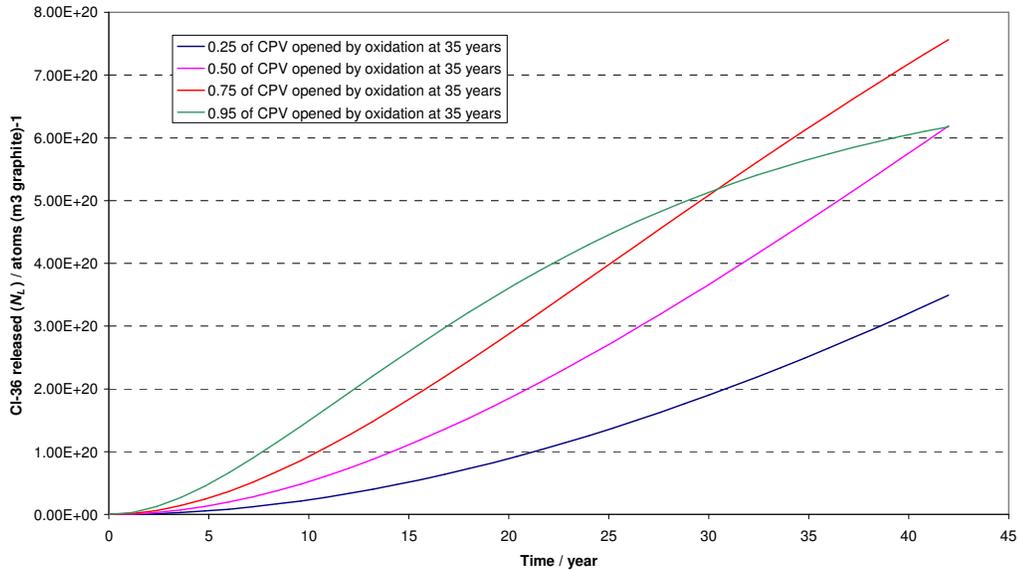
Figure 4: Predicted cumulative Cl-36 releases from Hinkley Point A graphite

Figure 2 shows the total predicted Cl-36 generated per m^3 of graphite (ie $N + N_L$). As the rate at which closed porosity opens increases, the amount of Cl-35 released unactivated increases and hence the total amount of Cl-36 generated decreases. Figure 3 shows the amount of Cl-36 retained in the graphite as a function of time. As expected, the amount decreases as closed porosity opens faster. Indeed, at the highest rates of opening the amount of retained Cl-36 actually falls with time at high irradiation, as the rate of Cl-36 release begins to exceed the rate at which it is generated. Figure 4 shows the cumulative quantity of Cl-36 release per m^3 of graphite, which increases with the increased rates of CPV opening.

3.6   Comparison of prediction with National Inventory calculations

Inspection of Equations 2, 3 and 4 shows that ratios between any of the quantities N, N_T and N_L are all independent of the rate of Cl-35 activation (kC_0) and are a function of β and t only. This considerably facilitates comparison of data with model predictions.

Figure 5 shows the total quantity of Cl-36 generated within the moderator graphite as predicted by this model relative to the quantity predicted by the calculation route employed in the National Inventory, ie $(N+N_L)/N_T$. As half of the Cl-35 precursor is predicted to be associated with open porosity and is released before it can be activated *in situ* the ratio never exceeds 0.5. Opening of the closed porosity with time releases increasing amounts of Cl-35 from the graphite and prevents their activation *in situ*, thus reducing $(N+N_L)/N_T$. The greater the amount of closed porosity opened at a given time, the greater the effect.
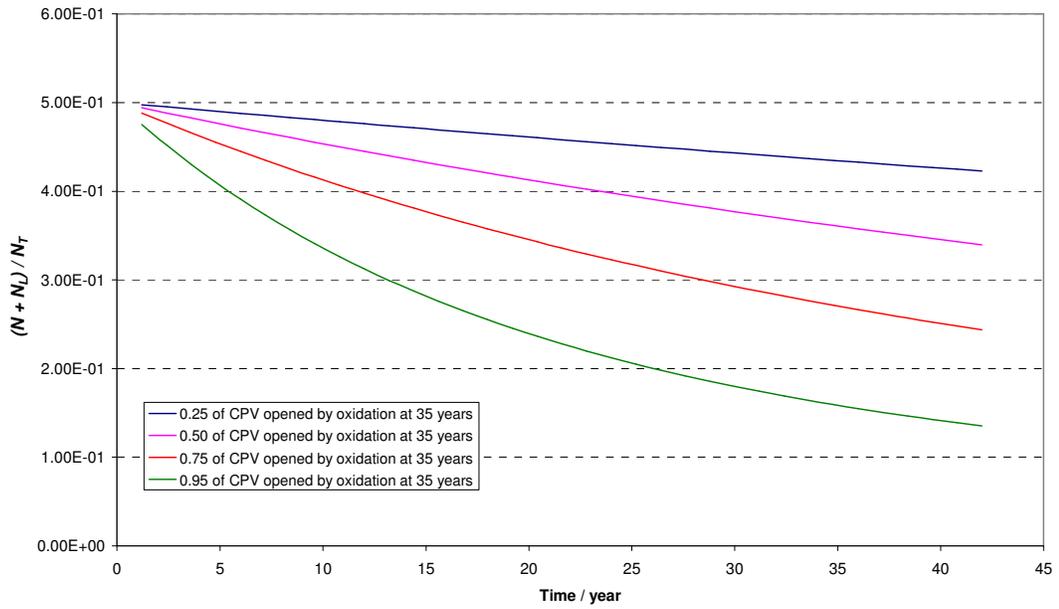
Figure 5: Quantity of Cl-36 generated in graphite relative to total inventory calculated for graphite in National Inventory
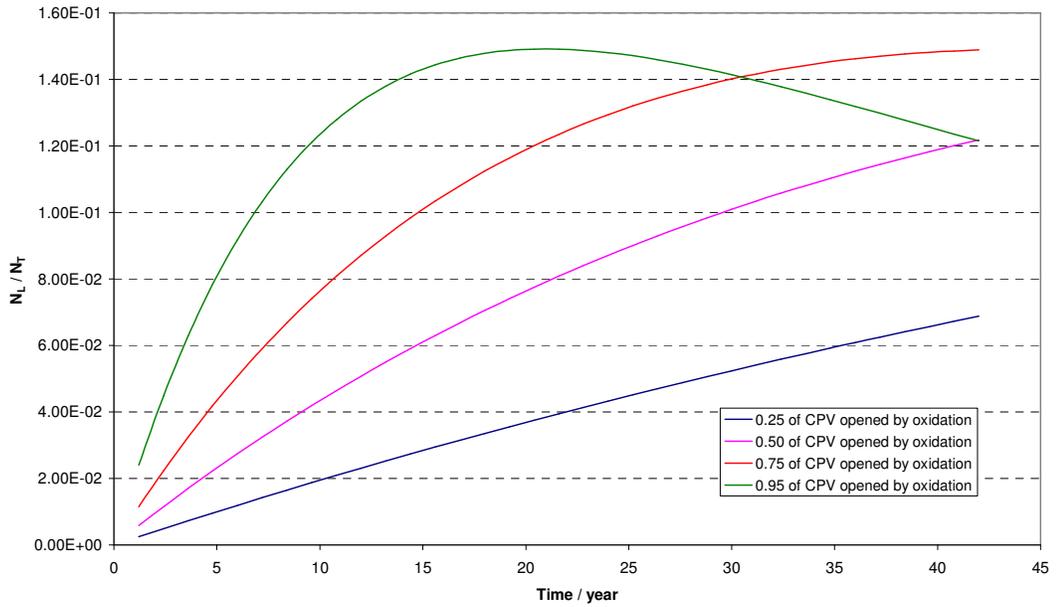
Figure 6: Quantity of Cl-36 released relative to total inventory in National Inventory
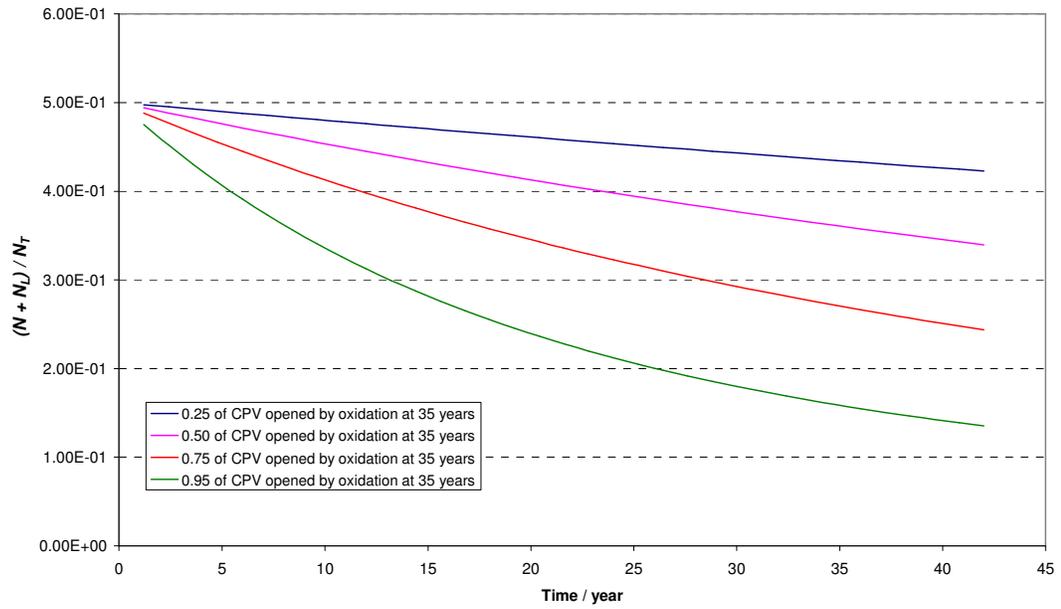
Figure 7: Quantity of Cl-36 in graphite relative to total inventory calculated for graphite in National Inventory

Figure 6 shows the quantity of Cl-36 released from irradiated graphite relative to the quantity predicted in National Inventory calculations (i.e. N_L/N_T) for different assumptions about the amount of closed porosity accessed by oxidation. Figure 7 shows similar information for the Cl-36 inventory of the graphite itself ($[N + N_L]/N_T$).

4 The basis for Cl-36 estimates in the 2007 National Inventory

Magnox have provided information on the route by which Cl-36 activities in decommissioning waste streams were estimated. This is reproduced as Appendix B. Similar information is not currently available from British Energy, but it seems probable that the same calculation route was followed. A summary of the approaches is given below.

The Cl-36 inventory of components in the flux is estimated on the basis of activation of Cl-35 *in situ* using calculated fluxes and assumed precursor concentrations. Cl-36 is found in a wide variety of waste streams because its principal precursor, Cl-35, is present in most reactor materials including steel, zircaloy, uranium, UO_2, graphite and concrete. No account is taken of any processes by which Cl-36, or its precursor Cl-35, might be released from in-core graphites.

The inventories of wastes originating in regions outside the neutron flux are based on fingerprint data obtained by the sampling and analysis of the same or of similar waste streams. As Cl-36 in these wastes can only have arisen as a result of Cl-36 transported in the primary coolant some allowance for transport has already been made, although, as discussed below, this allowance may not be adequate.

5 Implications of chlorine mobility for the inventory of LLWR

5.1 Introduction

The model described in Section 3 considered only the release of chlorine isotopes from core graphites. When considering the possible impact of the phenomenon on waste streams destined for LLWR, the model must be extended to take account of a number of other processes, as shown in Figure 8.
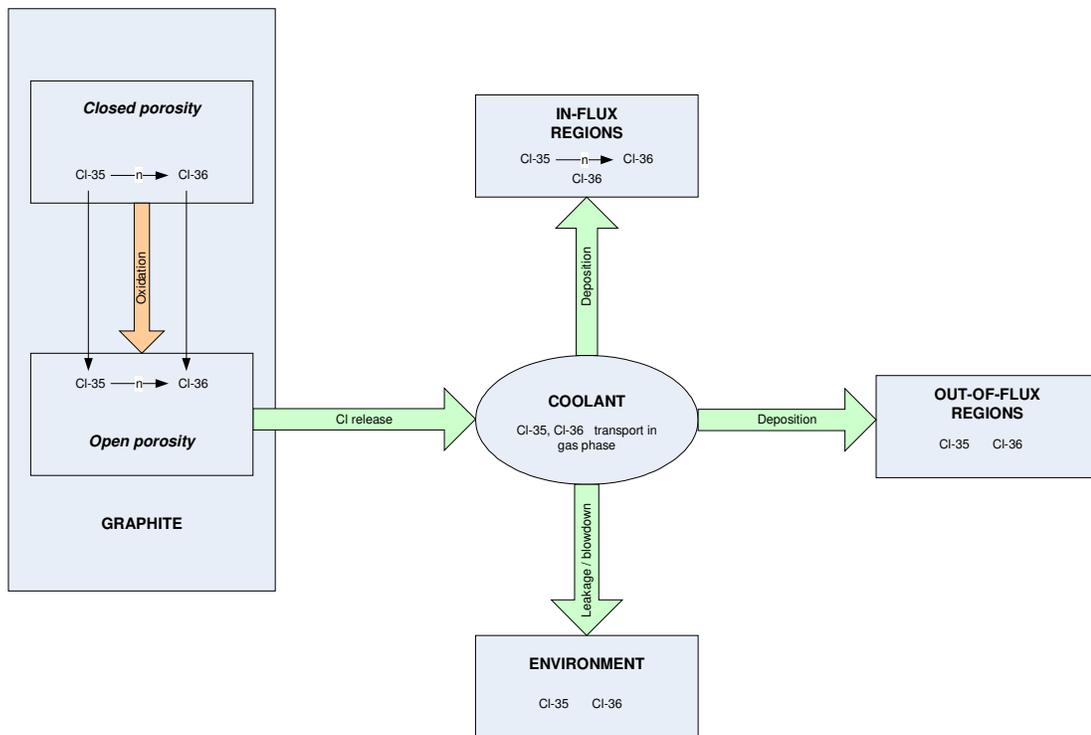
Figure 8: Chlorine transport processes in AGR and Magnox primary circuits

Release of chlorine isotopes from core graphites during irradiation will have a number of effects. It will, of course, reduce the Cl-36 inventory of these materials to a value significantly below that in the National Inventory. It may, however, adversely affect the Cl-36 inventories of other waste streams if the released chlorine isotopes plate out in other parts of the primary circuit.

Cl-36 may be deposited on regions of the primary circuit either in or outside the neutron flux, on waste streams currently designated as ILW or LLW. This will lead directly to an increase in the Cl-36 inventories of these materials. The deposition of released Cl-35 will also increase the Cl-36 inventory of circuit materials if it plates out in regions of the circuit within the neutron flux where activation can take place.

This leads to two mechanisms through which the inventory of Cl-36 in LLW streams might be increased:

- Deposition of Cl-36 on materials destined to become LLW, whether in or out of flux.
- Deposition and neutron activation of C-35 on materials situated in the flux which are destined to become LLW (primarily pressure vessel concretes).

5.2 Discharge to the environment

It is known that there is a regular loss of coolant from the reactors to the environment, through leakage of coolant and through deliberate blowdown which could lead to a discharge of Cl-36. Any loss of Cl-36 through this route would result in a reduction in the total inventory potentially destined for disposal within other waste streams.

Although the concentrations of Cl-36 in Magnox and AGR reactor coolants are not normally measured, discussion with Magnox staff has identified a study performed in 2003 by British Nuclear Fuels Limited (BNFL) into the formation and fate of Cl-36 at the Wylfa power station [7] in which attempts were made to determine a concentration. No Cl-36 was detected in the coolant, but an assessment of the Minimum Detectable Activity (MDA) in the samples indicated that Cl-36 concentration in the gas would be less than 1.7 $Bq.kg^{-1}$, corresponding to a maximum activity of 4×10^5 Bq in the 230 tonnes of coolant in each of Wylfa's two reactors. Assuming that about 3% of the coolant is lost per day through the ventilation system, this equates to the loss of about 4.3×10^6 $Bq\ y^{-1}$ from each reactor. Assuming deliberate blowdown three times per year adds a further 1.2×10^6 Bq to the annual discharge from each reactor, giving a total loss of about 2×10^8 Bq from each reactor over its 40-year lifespan.

The 2007 National Inventory [1] allows the Cl-36 inventory of Wylfa ILW graphite to be estimated at 5.5×10^{11} Bq per reactor on a best estimate basis, with potential uncertainties plus or minus an order of magnitude. These uncertainties arise primarily as a result of uncertainties in precursor concentration and neutron fluence. Calculations reported in Section 3.6 of this report suggest that somewhere between 5 and 15% of the quantity of Cl-36 reported in the National Inventory will be released to the gas phase, the exact quantity depending upon the amount of closed porosity accessed by oxidation. Figure 9 shows the range releases calculated if these release fractions are coupled with best estimate and lower bound National Inventory values for Cl-36 inventory. This is compared with the maximum quantity lost through discharge.
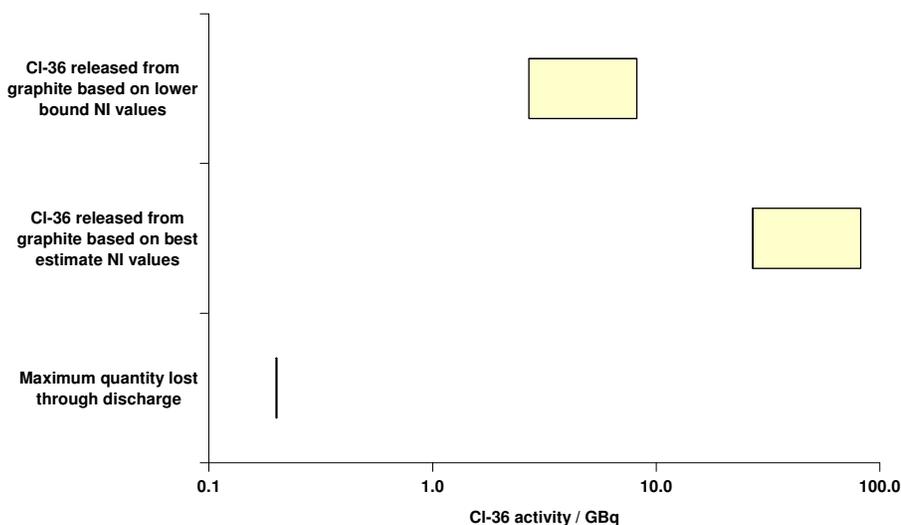

Figure 9: Comparison of total predicted Cl-36 release from Wylfa graphite with maximum amount discharged to atmosphere

It is clear that the maximum calculated discharge of Cl-36 to atmosphere is very much less than the quantity released to the gas phase from core graphites, even allowing for uncertainties in precursor concentration and neutron fluence. It therefore seems probable that only a relatively trivial amount of the Cl-36 released from core graphites is discharged to atmosphere

Although no data are available to supplement this conclusion with assessments made for other reactors, it seems reasonable, given the Wylfa data, to infer that loss to the environment through coolant leakage is not a significant factor when assessing the fate of Cl-36 released to the reactor circuit.

5.3   Accounting for mobile Cl-36 in the existing inventory

Having established that it is extremely unlikely that any significant quantity of Cl-36 is released to the environment, it is important to determine how much mobile Cl-36 might be accounted for in the existing inventory.

As discussed in Section 4 and Appendix A, the Cl-36 inventory of waste streams is determined either by activation calculations, or by through the use of fingerprint data. Fingerprint data have only been used for those materials experiencing no significant neutron flux in service. Clearly, Cl-36 concentrations estimated by activation calculations cannot account for the effects of Cl-36 mobility. Where Cl-36 inventories are estimated using fingerprint data, however, some or all of any Cl-36 mobilised in-circuit may be accounted for. The possibility that existing inventory data accounts for some or all of the Cl-36 released from core graphites is assessed in this section, through and analysis of Hinkley Point A (taken to be typical of the Magnox fleet) and Hinkley Point B (taken to be typical of the AGR fleet).

5.3.1   Hinkley Point A

The operational lifetime of Hinkley Point A was 35 years [8]. From Figure 6 the fraction of Cl-36 released to the circuit at 35 years relative to the value presented in the National Inventory probably lies in the range 0.06 to 0.15. The National Inventory gives the Cl-36 content of Hinkley Point A core graphite as about 1.1 TBq, leading to an estimated Cl-36 release of between 0.064 and 0.16 TBq.

These values should be compared with estimates of contaminant Cl-36 from Hinkley Point A. This comparison is subject to a number of difficulties:
- Not all contaminant Cl-36 will be due to Cl-36 released from core graphites. For example, leaching of Cl-36 generated by the irradiation of Cl-35 in steels and fuel cladding will be responsible for at least some of the Cl-36 in wastes from the fuel handling route. Distinguishing between sources of Cl-36 on the basis of National Inventory information is extremely difficult.
- Much of the contaminant Cl-36 is identified in wastes arising during operations. Whilst the inventory from operational ILW generated during station life should be accounted for, much of the operational LLW will have been dispatched to LLWR and will not appear in the National Inventory. The total Cl-36 inventory of operational LLW is therefore difficult to estimate.

Against this background, it seems most appropriate to estimate the contaminant Cl-36 at Hinkley Point A arising from core graphites already accounted for in the National Inventory in terms of bounding calculations.

One approach is to include all contaminant Cl-36 estimated from fingerprint data in the estimate of Cl-36 accounted for. This procedure almost certainly yields an overestimate of the amount of Cl-36 accounted for because it certainly includes Cl-36 arising from routes other than the irradiation of core graphites. This will be compensated for, to some extent, because the Cl-36 inventory of operational LLW will be underestimated, as the National Inventory does not account for LLW dispatched from Hinkley Point A before 2007. However the specific activities of these streams are

low, and the volumes seem unlikely to be large. The value of 0.30 TBq yielded by this process is almost certainly an upper bound

Alternatively one might include only those streams where the estimates are based on fingerprint data and the wastes arise from regions in direct contact with the primary coolant. It is probable that the majority of the Cl-36 found on these streams, which are primarily out-of-core metallic materials, desiccant and catalyst wastes, comes from material released from core graphites. However, they do not represent all the streams which might credibly contain Cl-36 deposited from the gas stream. The value of 5.5×10^{-3} TBq yielded by this process is almost certainly a lower bound.

Figure 10 compares the range of Cl-36 concentrations derived from fingerprint data with estimates of potential release from core graphites. The data do not present a clear-cut picture. The amount of Cl-36 found on materials which have been in direct contact with the coolant is much less than the lower bound estimate for released Cl-36. On this basis little of the mobile Cl-36 is accounted for. Alternatively, on the basis of all the 'fingerprint' Cl-36 it might be argued that a significant proportion, possibly all, of the mobile Cl-36 has been captured in the estimates.
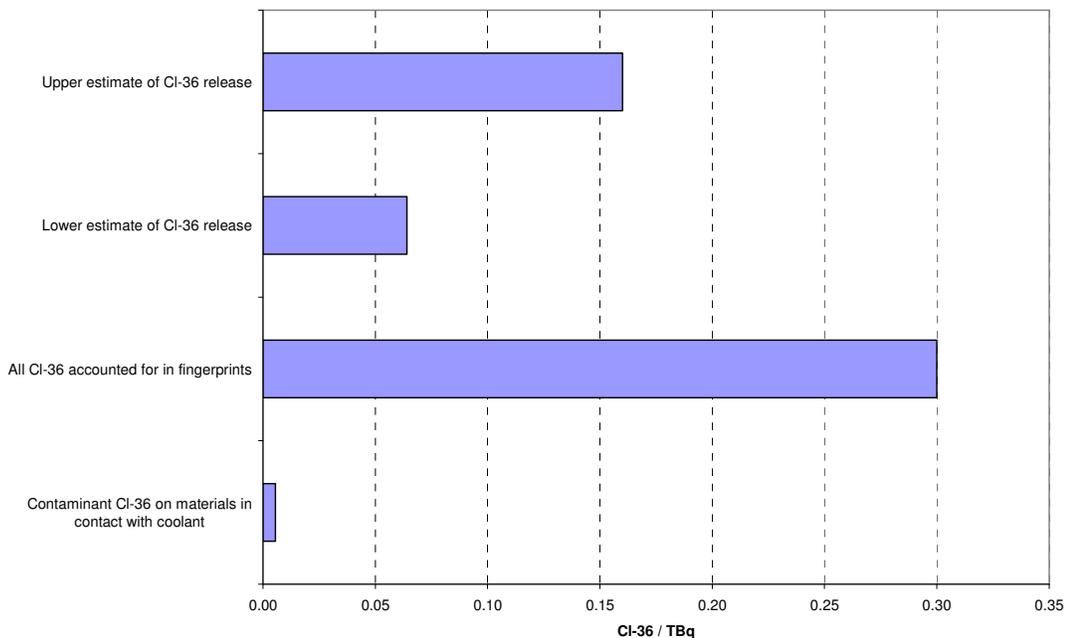

Figure 10: Hinkley Point A. Comparison of potential releases from core graphite with fingerprint measurements

5.3.2 Hinkley Point B

The expected operational life of Hinkley Point B is 30 years, with planned shutdown in 2016 [9]. From Figure 6 the fraction of Cl-36 released to the circuit at 30 years relative to the value presented in the National Inventory probably lies in the range 0.05 to 0.14. The National Inventory gives the Cl-36 content of Hinkley Point B core graphite as about 3.41 TBq, leading to an estimated Cl-36 release of between 0.17 and 0.48 TBq.

The only contaminant Cl-36 at Hinkley Point B estimated from fingerprints arises from operational LLW. The National Inventory gives a total Cl-36 arising for the last 8 years of life as 8.3×10^{-4} TBq. Scaling for the whole 30-year reactor life gives a Cl-36 inventory of 3.1×10^{-3} TBq. For reasons

discussed in Section 5.3.1, this must represent an upper limit to the amount of Cl-36 released from moderator graphite which is accounted for in the National Inventory.

It is clear that, for Hinkley Point B, the National Inventory does not account for any significant fraction of the predicted Cl-36 release from core graphites.

5.4   Summary

Calculations above clearly indicate that, for Hinkley Point B, the National Inventory values for Cl-36 are extremely unlikely to account a significant fraction of the Cl-36 predicted to be lost from core graphites. For Hinkley Point A the position is rather more complicated; here it is possible that some or all of the Cl-36 is accounted for, but the conclusion is highly dependent upon the assumptions made. In terms of LLWR inventory, therefore, these results would suggest that a upper limit to inventory enhancement would be given by the sum of any contributions from Magnox and AGR stations, whilst a lower limit could be taken as the contribution from AGR stations alone.

6 The distribution of released Cl-36

6.1 Approach

A detailed model for the redistribution of released Cl-36 around the primary circuit of an AGR or Magnox reactor, and thus for the impact of such a redistribution upon the Cl-36 inventory of materials to be disposed of to LLWR, is not practicable in the present state of knowledge. Such a mechanistic model would be extremely complex, and could not be sensibly parameterised. The approach taken here, therefore, is to examine two possible bounding cases, and an intermediate case based upon some simple assumptions.

In all cases redistribution of chlorine species can only take place to those surfaces in direct contact with the coolant. These will generally be associated with Stage 3 decommissioning wastes, and any enhancement of the inventory will be primarily associated only with these waste streams.

Case 1 – all released Cl-36 becomes associated with ILW streams
The bounding case which has the smallest effect upon the Cl-36 inventory of LLWR is clearly one in which all the released Cl-36 is deposited on surfaces in contact with the primary coolant destined to be part of an ILW stream. These are primarily materials which have been subjected to a significant neutron flux and therefore are assumed to come from the highest temperature parts of the circuit. If it is assumed that the deposition of Cl-36 is a chemically driven process, significantly favoured by the higher temperatures experienced by materials in the flux, then one might argue that deposition of Cl-36 on surfaces associated with ILW will be a favoured process.

Case 2 – all released Cl-36 becomes associated with LLW streams currently destined for LLWR
This is the bounding case with the largest effect upon the inventory of LLWR. Here all released Cl-36 becomes associated with surfaces associated with LLW streams. If it is assumed that the deposition of Cl-36 is a process driven by some mechanism such as vapour pressure, then released Cl-36 will deposit preferentially in the cooler parts of the circuit and thus become associated with LLW streams.

Case 3 – Cl-36 is apportioned between ILW and LLW streams on the basis of exposed surface area
An intermediate case which is, perhaps, more physically credible, assumes that Cl-36 does not deposit preferentially on either ILW or LLW streams, but is distributed simply upon the basis of exposed surface area.

In all three cases the wastes in question form part of the primary circuit, and are assumed to arise during final site clearance.

Case 1 and Case 2, although adequate for bounding calculations, suffer from fundamental physical flaws. Case 1 assumes that the temperature difference between ILW and LLW streams will be sufficient to favour deposition on ILW. However, chlorine is extremely chemically aggressive towards steel surfaces, even at temperatures well below those in any part of a reactor primary circuit. It therefore seems doubtful that association of released Cl-36 with ILW surfaces will be sufficiently favoured to drive the Case 1. Similarly, the chemically aggressive nature of chlorine, and the relatively high temperatures in reactor primary circuits make any sort of 'condensation' mechanism highly unlikely. In Case 3 the assumption is that over the range of temperatures in the primary circuits of AGR and Magnox reactors,. the effect of temperature on deposition rate is small. This is probably the most physically credible of the models, but requires a number of assumptions to be made to allow it to be implemented. These are discussed below.

In order to implement Case 3 it is necessary to know the relative surface areas exposed to the primary coolant associated with each waste stream. In practice this information is not available, and it is necessary to make some broad assumptions in order to proceed. The principal assumption

made here is that the relative bulk volumes of individual waste streams reflect the relative external surfaces areas associated with the wastes. For metallic streams this seems not unreasonable, but in the case of wastes streams which represent exceptionally thick components, for example concrete, this assumption becomes untenable. In the calculations described below for Case 3, this issue has been addressed by applying a factor to each waste stream to reflect the relative contribution to overall surface area made by unit bulk volume of the waste. The fraction of released Cl-36 associated with each waste stream, other than graphite, exposed to the bulk coolant is therefore given by the expression below.

$$D_i = X \left[\frac{f_i V_i}{\sum_{j=1}^{N} f_j V_j} \right] \qquad \qquad \dots \dots 5$$

Where D_i = The amount of released Cl - 36 associated with a given stream

f = The relative surface area per unit bulk volume

V = Stream volume

X = Total Cl - 36 released

In the calculations which follow, f has been taken to be 1 for all waste streams except concrete, and the effect of varying f upon the results has been assessed.

6.2   Hinkley Point A

The 2007 National Inventory gives the total Cl-36 associated with core graphites in Hinkley Point A as 1.07 TBq. Taking the release fractions for reactor life (35 years in this case) from Figure 6 yields a quantity released in the range 0.064 to 0.15 TBq.

In Case 1, of course, none of this Cl-36 forms part of the LLW inventory.

In Case 2 all released Cl-36 becomes associated with LLW generated during final site clearance. The Cl-36 inventory of all LLW associated with Hinkley Point A (6.9×10^{-2} TBq) therefore increases by a factor of between 1.9 and 3.3, depending upon assumptions about the rate of opening of closed porosity. The Cl-36 inventory of wastes arising after 2070 (6.4×10^{-2} TBq) increases by a factor of between 2.0 and 3.5.

Figure 11 shows the quantity of LLW released from core graphites which is distributed to LLW in Case 3 as a function of the relative surface area factor (f in Equation 5). From the figure it is clear that the quantity of material distributed to the LLW streams is effectively independent of f over a reasonable range. This arises effectively because of the very large bulk volume of LLW relative to ILW. Enhancements here are similar to those in Case 2, with enhancements between 1.9 and 3.3 for the total inventory and between 2.0 and 3.5 for post-2070 wastes.

6.3   Hinkley Point B

The 2007 National Inventory gives the total Cl-36 associated with core graphites in Hinkley Point B as 3.41 TBq. Taking the release fractions for reactor life (30 years in this case) from Figure 6 yields a quantity released in the range 0.18 to 0.48 TBq.

In Case 2 the Cl-36 inventory of all LLW streams associated with Hinkley Point B (2.8×10^{-2} TBq) is increased by a factor of between 7.1 and 19. For streams arising after 2070 the range is 7.6 to 19.

Calculations for Case 3 (Figure 12) show the same pattern as those for Hinkley Point A, with little variation over a reasonable range for f. Enhancements here are similar to those in Case 2, with enhancements between 6.2 and 6.8 for the total inventory and between 16 and 17 for post 2070 wastes.
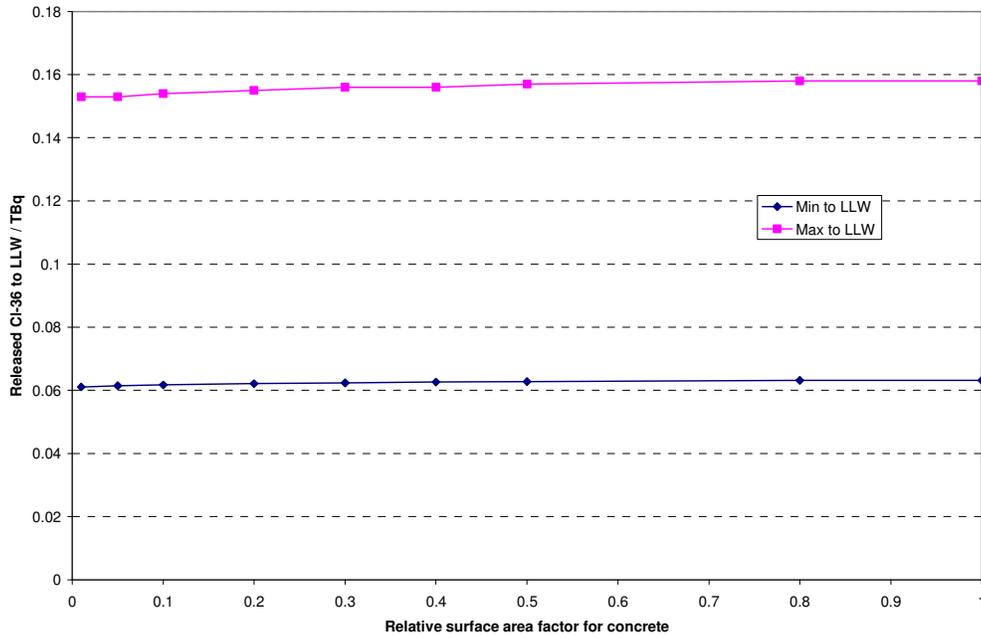

Figure 11:   Cl-36 to Hinkley Point A LLW streams
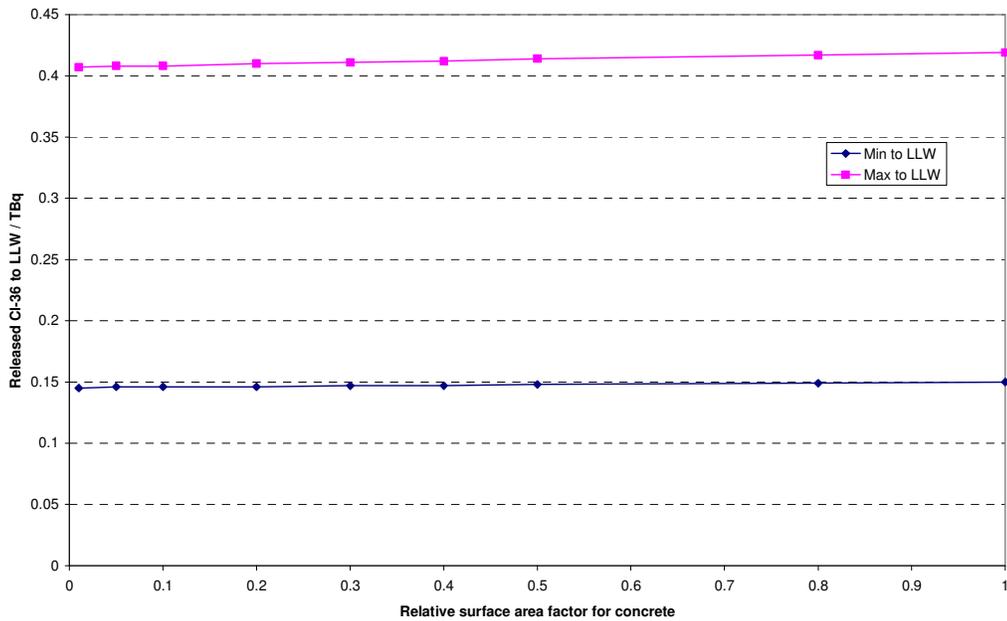
Figure 12:   Cl-36 to Hinkley Point B LLW streams

6.4 Summary

The calculations described above indicate the potential for a significant enhancement of the Cl-36 inventory of LLW streams under physically reasonable scenarios. For Hinkley Point A the enhancement is modest – an overall increase in Cl-36 inventory of a factor of 2 or 3 – whereas for Hinkley Point B the factorial increase could be as high as 17 in the worst case.

7 The distribution and activation of released Cl-35

7.1 Approach

In addition to the release of Cl-36 from core graphites, Cl-35 is also released. This Cl-35, if it is deposited in regions of the circuit within the neutron flux, can be activated to form Cl-36 and thus, potentially, contribute to the Cl-36 inventory of wastes for disposal at LLWR. The approach taken here to assessing the potential significance of this mechanism is to assume that released Cl-35 plates out around the circuit and thus increases the amount of precursor material available for activation. Hence, if the original and final precursor concentrations of any activated component are known, the new inventory can be determined straightforwardly by scaling.

The model described in Section 3 is based on the instantaneous release of Cl-35 from the initially open porosity of the graphite, followed by the slower release of Cl-35 from the closed porosity of the graphite as it is accessed by radiolytic oxidation. The cumulative quantity of Cl-35 released from the closed porosity of core graphite at time t, I_L, is, by analogy with Equation 1, where I_0 is the quantity in the closed porosity of the graphite at time zero:

$$I_L = I_0 \left[1 - \exp(-\beta t) \right] \qquad \qquad \dots \dots \dots 6$$

Cl-35 released from initially open porosity and deposited upon a substrate will be exposed to the flux for the same period of time as Cl-35 in the substrate. Cl-35 released from the closed porosity, on the other hand, will be exposed for a rather shorter period of time, on average, because of its gradual release from the graphite. This can be accounted for by taking the time averaged release from the closed porosity of the graphite $\bar{I}_L$ as the enhancement of precursor from this source. Assuming that the quantity of Cl-35 associated with the open and closed porosities are initially equal, it follows from Equation 6 that:

$$\bar{I}_L = I_0 \left\{ 1 + \frac{1}{\beta t} \left[\exp(-\beta t) - 1 \right] \right\} \qquad \qquad \dots \dots 7$$

Deposited Cl-35 is assumed to be at the surface of the material and therefore subjected to the surface flux. Where there is a substantial flux profile through a component, only a fraction of the precursor in the substrate will undergo significant activation. This can be accounted for by defining a quantity I_{eff}, as follows, where I_{subs} is the quantity of precursor in the substrate:

$$I_{eff} = I_{subs} \left[\frac{\textit{mean flux in substrate}}{\textit{flux at surface}} \right] \qquad \qquad \dots \dots 8$$

Assuming that the quantity of precursor associated with the open and closed porosity of core graphites are equal, the Cl-36 inventory of a component exposed to the flux is therefore enhanced by the factor given in Equation 9, where α is the fraction of the total released Cl-35 released which deposits on the component:

$$\textit{enhancement factor} = \frac{I_{eff} + \alpha \left(I_0 + \bar{I}_L \right)}{I_{eff}} \qquad \qquad \dots \dots 9$$

In determining the distribution of Cl-35 around the circuit it is assumed that it is distributed between ILW and LLW streams on the basis of exposed surface area (Section 6 Case 3).

7.2   Data

Cl-35 release rate

The quantity of Cl-35 released from closed porosity (effectively the closed porosity opening rate) is that used for the bounding cases adopted in Section 6.

Mean flux in components relative to surface flux

One metre thickness of concrete reduces the thermal neutron flux by between three and six orders of magnitude, depending on the exact composition of the concrete [10]. Assuming exponential decay, this is equivalent, for a 4.5m wall thickness – typical of a Magnox pressure vessel – of an average flux in the concrete of between 1% and 3% of that at the surface. A value of 2% has been adopted in these calculations

The attenuation of thermal neutrons by steel is about a factor of 1.75 cm^{-1} [10]. Taking the thickness of steel components in Hinkley Point A to lie in the range of about 2 to 11 cm, implying mean neutron fluxes between about 16 and 60% of that at the surface. A value of 30% has been adopted for the calculations reported here for both AGR and Magnox reactors.

Cl concentrations in structural materials

Values adopted for precursor concentrations were taken from Table 1 of Reference 11, and are reproduced in Table 1 below.

Material	Assumed Cl concentration / ppm	Comments
Concrete	50	Bounds given as 11-130ppm
Core graphite	4	Value varies between reactors. Value chosen midway between Hinkley Point A and Hinkley Point B values
Stainless steel	74	Bounds given as 40 and 120 ppm
Mild steel	52	Bounds 3.5 to 180 ppm

Table 1:   Cl concentrations in reactor structural materials [11]

7.3   Results

The calculated enhancements to the Cl-36 inventories of the Stage 3 LLW streams from Hinkley Point A and Hinkley Point B are shown in Figure 13 and Figure 14 respectively. The enhancement for Hinkley Point A is estimated as being up a factor of 1.25 in the worst case, whilst for Hinkley Point B the worst-case enhancement approaches a factor of 2. These values, however, rely on high rates of CPV opening combined with high relative surface areas for concrete. Best estimates would probably be significantly lower, perhaps half these values.

The results also indicate that the redistribution of Cl-35 from core graphites to circuit materials is likely to have a much smaller impact on overall Cl-36 levels in Stage 3 LLW streams than the redistribution of released Cl-36.
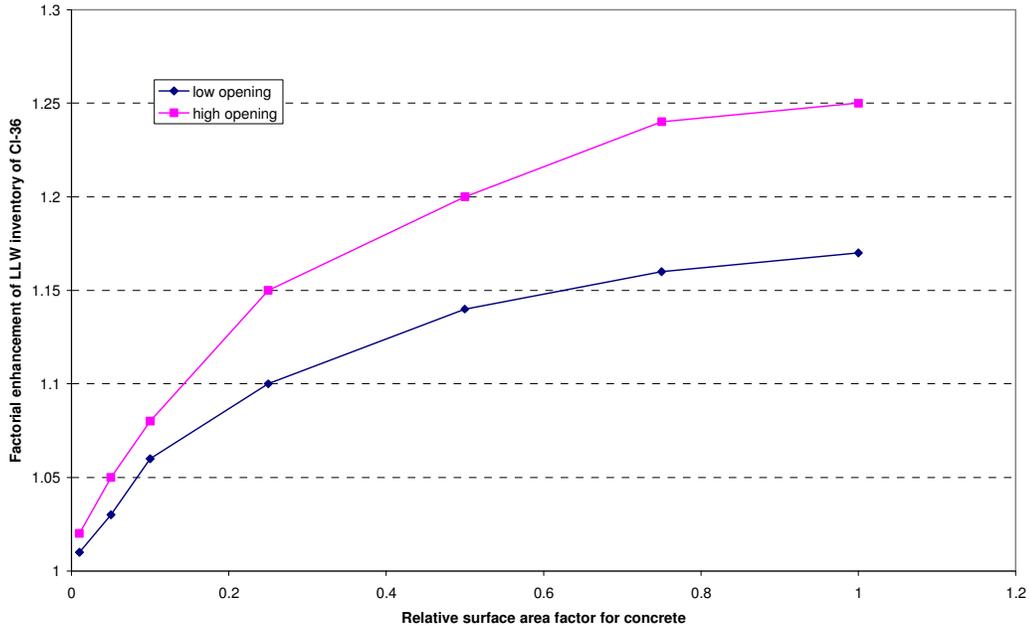
Figure 13: Enhancement to Cl-36 inventory of Stage 3 LLW from Hinkley Point A due to Cl-35 redistribution
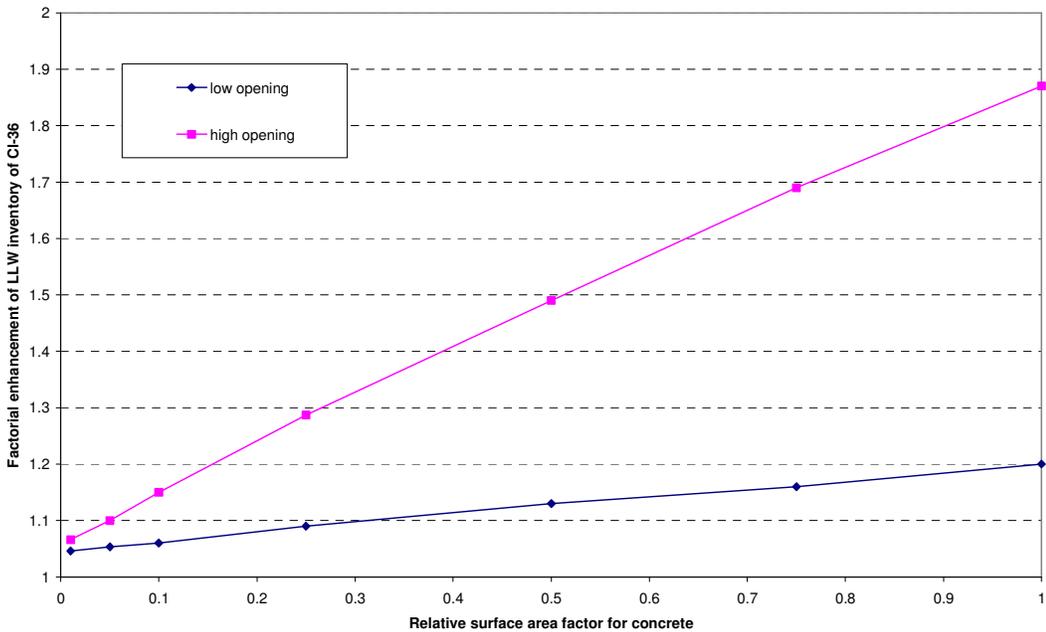

Figure 14: Enhancement to Cl-36 inventory of Stage 3 LLW from Hinkley Point A due to Cl-35 redistribution

8   Discussion

The results of this study are intended only to be indicative of the potential effects of redistributing Cl-35 and Cl-36 to other parts of the primary circuit of AGRs and Magnox stations. Whilst the data reported in Reference 5 very strongly suggest that chlorine species are released from core graphites, there exists considerable uncertainty over the exact mechanism by which release takes place and the rate of any release. Furthermore the factors driving the distribution of released chlorine between other waste streams are not well understood. Nevertheless, the calculations reported here, which are based on physically reasonable assumptions and data, indicate that chlorine redistribution has a potentially significant effect upon the Cl-36 inventories of LLW streams arising from Stage 3 decommissioning. This section discusses aspects of the calculation and evaluates the potential significance of the results for LLWR.

8.1   Release of chlorine from irradiated graphite

As already noted, there is strong evidence that chlorine is released from core graphites [5]. The mechanism, however, is somewhat more speculative, and its refinement is inhibited by the paucity of data and the difficulty inherent in its interpretation. However, the basic mechanism considered in Reference [2] has the merit of being conceptually straightforward and consistent with such data as are available. In particular:

- The assumption that chlorine concentrations in open and closed porosity are the same seems physically reasonable given that the chlorine is introduced as a chlorocarbon during the final stages of graphite production when the bulk of the porosity is formed.

- The assumption that chlorine associated with open porosity is released instantaneously at startup is in accordance with experimental data [5], and is broadly consistent with analytical data from graphite specimens trepanned from reactor cores.

- The assumption that chlorine is released from closed porosity instantly when it is accessed through the process of radiolytic oxidation is reasonable by analogy, but is less well supported by the data.

- The assumption that the quantity of closed porosity decays exponentially with dose (effectively with time) is physically reasonable and mathematically convenient, but may not be an entirely accurate description of the development of porosity of graphite undergoing radiolytic oxidation in CO_2-based coolants.

It is not straightforward to parameterise the model for the release of Cl-35 or Cl-36 from core graphites based upon the physical principles described in Section 3. In particular, the extent to which closed porosity is opened at end of life will depend upon the exact irradiation history of the material. Thus there is considerable uncertainty about the rate at which closed porosity is accessed and the consequently the extent of chlorine release at any point in time. Under these circumstances, bounding assumptions, which represent opening 25% and 95% of the closed porosity initially present, have been adopted. Calculations of Cl-35 and Cl-36 release undertaken using the upper limit should therefore be clearly recognised as upper bound values and should not be taken as representing any sort of best estimate.

Improved modelling of the opening of initially closed porosity will require access to a better source of raw data than that currently available to the author.

It is concluded that the empirical model for chlorine release adopted here is adequate for scoping calculations. It does not, however, represent a detailed mechanistic description of the processes occurring in irradiated graphite, and this limitation should be borne in mind.

8.2   Redistribution of released chlorine in AGR and Magnox circuits

A detailed description of the redistribution of released chlorine between different parts of the reactor circuit is well beyond the scope of a simple model, and is not justified, given the simple nature of the models for chlorine release and Cl-35 activation adopted here. In any case, it is far from clear that a complex model for chlorine deposition could be sensibly parameterised.

Against this background, the most physically reasonable approach is one in which chlorine is deposited on LLW and ILW, with the extent of deposition being controlled entirely by surface area. However, an absence of reliable surface area data has meant that waste volume has been used as a proxy, with the need to define a factor which reflects the much lower ratio of exposed surface area to waste volume ratio to be expected of components of substantial thickness – in the case of Hinkley Point A and Hinkley Point B the relevant components are the concrete structures associated with the primary circuit. This parameter is difficult to assess with any accuracy, and results are calculated for a range of values between 0.01, which is almost certainly too small, and 1.0, which is certainly too large.

The effects of this parameter on the amount of additional Cl-36 in the LLW streams of Hinkley Point A and B are shown in Figure 11 and Figure 12. It is clear that the choice of value is of little significance, primarily because whatever value is chosen the total available surface area is dominated by LLW streams.

In the case of Cl-35, which is subsequently activated to form Cl-36, the situation is somewhat different. The enhancement of Cl-36 in LLW streams as a result of this mechanism is markedly dependent upon the assumption made about concrete surface area (Figure 13 and Figure 14). This reflects the fact that increasing the assumed available surface area of the concrete increases the proportion of Cl-35 deposited on concrete, which has the highest rate of Cl activation of any of the LLW streams and thus increases the average rate at which Cl-35 is activated.

8.3   Activation of released Cl-35

In undertaking this assessment the Cl-35 was assumed to be distributed using the model discussed in Section 8.2. All the issues considered there with respect to the distribution of released Cl-36 apply also to the distribution of released Cl-35.

The model for Cl-35 activation, which is simply based on factoring the result of the activation calculation reported in the National Inventory by the increase in Cl-35 concentration brought about by release of material from core graphites, is simple in concept. As discussed below its implementation is subject to significant uncertainties and approximations in the underlying data, which are necessary to keep a scoping assessment tractable. These are discussed below. Nevertheless, given the uncertainties in methods and data elsewhere in the calculation, any elaboration of the calculation route seems unjustified.

Implementation of the model for Cl-35 activation depends crucially upon two parameters: the concentration of Cl-35 precursor assumed for the activation calculations underlying the National Inventory data and the calculated mean neutron flux in the component.

Precursor concentrations are subject to substantial uncertainty. In addition, the values used in the National Inventory calculations were not available to the author. The procedure adopted here was therefore to adopt generic values reported in a study by Nirex [2]. Whilst these are probably fairly representative of the values used in the activation calculations, there remains some uncertainty over their detailed applicability.

The mean neutron flux in individual components relative to that at the surface depends not only on the nature of the material from which the component is fabricated, but also its geometry and its thickness. In order to maintain the complexity of the present assessment within reasonable bounds, some fairly broad assumptions have been made on these issues, and a simple exponential decay

of flux with depth into the specimen assumed. These approaches represent significant approximations.

8.4   Accounting for mobile chlorine in the National Inventory

It seems clear from the discussion in Section 4 of this report that no explicit attempt is made to account for any Cl release processes when developing data for the National Inventory. Some account might be taken of Cl release indirectly where Cl-36 is reported as part of the radionuclide inventory of reactor components outside the neutron flux, or as surface contamination on other components. The analysis of National Inventory data in Section 5 of this report suggests that for AGRs it is highly unlikely that a significant quantity of any released Cl-36 is currently accounted for in the National Inventory. In the case of Magnox stations, the possibility exists that some or all of the released Cl-36 is accounted for, but the uncertainties are large, and a definitive conclusion is not possible. The most useful conclusion which can be drawn from this assessment is that a minimum enhancement of the Cl-36 inventory of LLW resulting from Cl redistribution would be based upon calculated enhancements to AGR LLW streams alone, whilst a maximum estimate would be based on calculated enhancements to Magnox and AGR LLW streams.

The reasons for the differing conclusions reached for AGR and Magnox stations is far from clear. One might speculate that, given that decommissioning of Magnox stations is under way, better quality data on decommissioning streams are available for Magnox and that this goes at least some way to rationalising the discrepancy. Such a conclusion, however, is highly speculative.

8.5   Potential significance for LLWR

Figure 15 shows the factorial enhancement for Stage 3 wastes (ie those arising post 2070) for Hinkley Point A and Hinkley Point B calculated using the models and data outlined in this report. The calculations suggest that the enhancement at Hinkley Point B due to the release of Cl-36 could be about a factor of 10, whereas the corresponding value from Hinkley Point A is significantly less than a factor of two.

Whilst these results can be taken to suggest a large impact on the post-2070 Cl-36 inventory of UK LLW, it is important to view the numerical values obtained with some caution. As discussed at length above, the methods and data used throughout this report are intended only to be simple representations of potentially complex processes, and were devised to allow tractable scoping calculations to evaluate whether significant effects were possible. The actual values generated are inevitably suspect, and would require substantial refinement and validation before they could be used as a basis for the definitive modification of LLW inventories. Whilst, therefore, the results indicate that significant effects are possible they should not be taken as a reliable quantification of those effects.

Examination of Figure 15 leads to two qualitative conclusions on which more reliance can be placed. First it is apparent that, for both the reactors considered, the enhancement due to direct release of Cl-36 is much greater than that due to the activation of released Cl-35. This can be ascribed to the much greater flux (and hence rate of activation per unit precursor) experienced by core graphites than that experienced by LLW streams. The results suggest that any further investigation of these effects should prioritise improvements to the estimates of the effects of direct Cl-36 release.

It is also apparent that the effects are greater for Hinkley Point B than for Hinkley Point A. This is due to the higher fluxes, and thus rates of activation, experienced in AGRs. In this context it should also be noted that the values reported are based on the assumption that none of the released Cl-36 is presently accounted for in the National Inventory. As discussed in Section 5.3 this seems to be the case for Hinkley Point B, but it is not clear that this is the case for Hinkley Point A. This

would suppress any predicted enhancement for the Magnox station. This suggests that any refinement of this assessment should be focussed on the effects on AGR inventories.
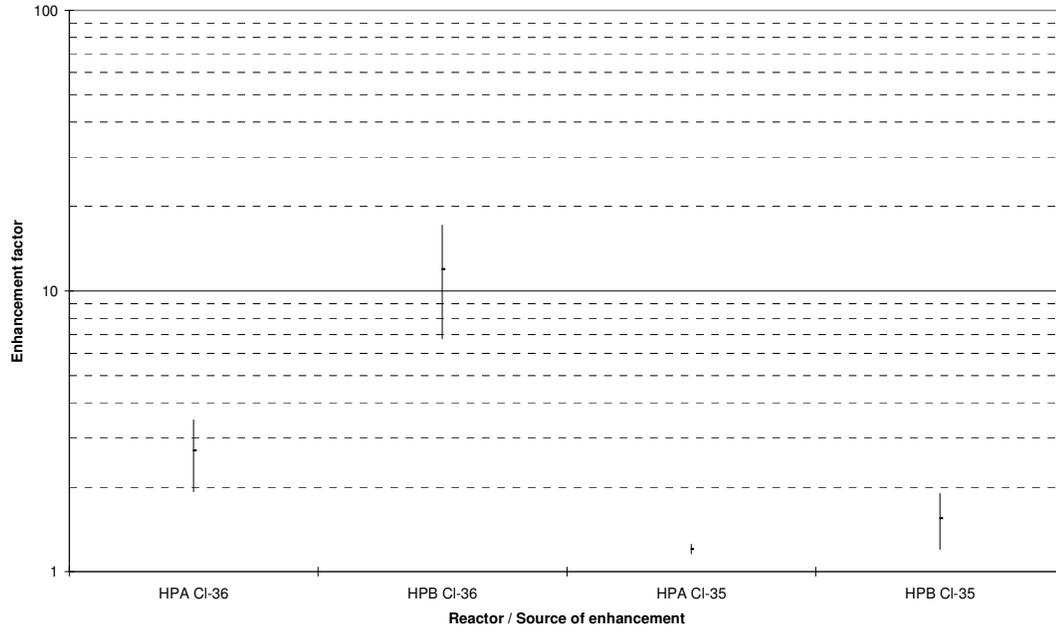

Figure 15: Calculated enhancement factors for Cl-36 inventories in post 2070 LLW

9   Conclusions

The model proposed by Nirex [2] to describe the release of chlorine from core graphites in Magnox and AGR stations has been further developed and used to undertake a preliminary scoping assessment of the likely effect of this phenomenon on the Cl-36 inventory of future UK LLW streams.

The assessment suggests that there are potentially significant effects, arising mainly from the redistribution of Cl-36 released from core graphites. The numerical data suggest an enhancement of Cl-36 levels in LLW of perhaps an order of magnitude for Hinkley Point B, and a factor of about two for Hinkley Point A. That the calculated effect is larger for Hinkley Point B than in Hinkley Point A probably reflects the higher flux experienced by AGR core graphites. The enhancements apply almost entirely to wastes arising after about 2070.

Although the assessment provides quantitative output, numerical values should be viewed with some caution. The methods and data used throughout this report are simple representations of complex processes, and would require significant further work before they could be used as the basis for a definitive modification of the forward inventory of Cl-36 in UK LLW.

The assessment consists of the following phases:
- The release of Cl-35 and Cl-36 from core graphites.
- The loss of chlorine from the circuit.
- The redistribution of released Cl-35 and Cl-36 between circuit materials.
- The activation of released Cl-35 to form Cl-36.

Each step has been examined using conceptually simple models. It is recognised that, in reality, each step is likely to mechanistically complex. However, the available information is too sparse to allow complex mechanistic models to be constructed and populated at the present time. It is, in any case, inappropriate to attempt complex assessments unless scoping calculations indicate a clear need.

Chlorine release
The assessment of the extent of release of chlorine from core graphites as a function of time depends on:
- The assumption that all the chlorine in the graphite is associated with the porous structure of the material.
- The assumption that chlorine is released immediately from initially open porosity, and immediately from closed porosity when it is accessed by radiolytic oxidation.
- A model for the rate of porosity opening with time.

The first two assumptions are conservative, in that they tend to maximise the extent of chlorine release. The from of the model for opening porosity with time is physically reasonable, but difficult to parameterise and bounding assumptions have been used. Further work would be required to improve the parameterisation of this part of the model.

Loss of chlorine, and the extent to which the National Inventory accounts for chlorine release
The limited data available suggest that only a small fraction of the chlorine released from core graphites is released to the environment.

Examination of National Inventory data suggests that the Inventory of Hinkley Point B does not take direct or indirect account of chlorine mobility. Examination of Hinkley Point A data suggests that at least some of the chlorine released from core graphites may be accounted for. The evidence is not, however, conclusive.

The redistribution of released chlorine between surface materials

A simple model based on relative exposed surface areas has been adopted for the redistribution of released chlorine between waste streams. This model is difficult to parameterise adequately on the basis of information available in the National Inventory. Significant work, based on engineering designs, would be required to parameterise this part of the model accurately. In any case, redistribution of the chlorine based solely on relative surface areas, although a reasonable assumption, is unsupported by data.

Activation of Cl-35

A simple model, which is in principle robust, has been used to model the activation of Cl-35 to Cl-36 after release. Parameterisation of the model, however, is not straightforward.

10 Acknowledgements

11 References

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Appendix A Magnox North and South waste stream compilation

Discussion with the radioactive waste inventory compilers for Magnox North and South (Ashok Ghandi and Wilf Hudd, Magnox South and Nicky Westall, Magnox North) confirmed the following points .

A separate modelling exercise with subsequent assessment of activation products was performed for each site. This was carried out by a central support team to ensure the techniques and standards were applied consistently.

The same approach was taken for all of the reactor structure assessments using MCBEND to estimate fluxes and subsequent activation calculations using assumed precursor concentrations in the components concerned to calculate the Cl-36 component.

The best available precursor data was used and the Nirex work from the 1990's was available for use.

Miscellaneous activated components removed from the reactors during operations and held in accumulation facilities (usually in the bioshield) are assumed to have a Cl-36 activity due to activation of precursors in the material.

Estimates of Cl-36 for LLW routinely sent to LLWR, and estimates for LLW expected during Care and Maintenance Preparations, are based upon available fingerprint information derived by measurement of contamination for the areas from which the waste originates.

Estimates for accumulated ILW Miscellaneous Contaminated Items are generally based on (amended) fingerprints for LLW arising from the same area. Cl-36 estimates for other accumulated wastes (e.g. sludges and ion exchange materials) are based upon sampling and analysis.

The Cl-36 was assumed to be static in the components concerned, so no loss during station operation or subsequent care and maintenance is assumed.

Desiccant and catalyst Cl-36 estimates are based upon sampling and analysis measurements of waste; if no measurements were available then the estimate was based upon measurements of similar wastes at other sites.

Reactor modelling assessments for the reactor structures include the bioshield but not the gas circuit. Cl-36 in boilers and the gas circuit external to the bioshield (Final Site Clearance Non-reactor Mild Steel LLW) at the steel pressure vessel stations has been determined by contamination measurements at some sites. These measurements have been used to deduce values for equipment at sites where measurements have not been made. No loss of Cl-36 from the reactor is assumed during these assessments.

In summary, mobile Cl-36 has not been accounted for in the Magnox waste streams, with the exceptions of waste streams in which it has previously been directly measured, for example, the desiccants, catalysts and parts of the gas circuit.

Appendix B Modelling the opening of closed porosity by radiolytic oxidation

The original Nirex modelling of chlorine release from graphite [5] assumed that initially closed porosity opened at a constant rate with dose until it had all been accessed. This is one potential representation of the behaviour, but is not the only possibility. A model in which the amount of closed porosity decays exponentially with dose would have the advantage that the amount of closed porosity would always be greater than or equal to zero without the need for a discontinuity in the representation.

The applicability of exponential and linear models was tested using data from Reference 6, which provides graphs of closed porosity and weight-loss as a function of dose. These graphs were used to construct Figure B1, which shows closed porosity as a function of total dose – which can be used as a substitute for time as dose rate in the experiment was effectively constant. Superimposed on the derived data are the best fit decaying exponentials and the best fit straight line determined by least squares. It is clear that, over the range of data available, either representation of the data is adequate, although the decaying exponential is, perhaps, marginally superior.

On these grounds it is entirely reasonable to select a decaying exponential as representing the evolution of closed pore volume with time, and it is this approach which is adopted in the present work.
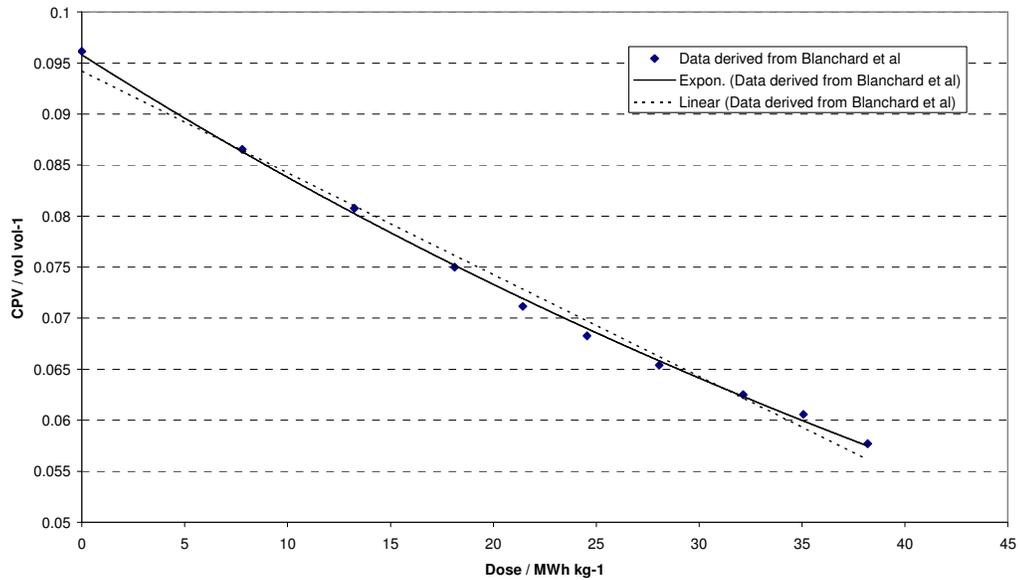

Figure B1: The evolution of closed porosity with dose: experimental data and alternative representations.