LONG TERM BEHAVIOUR OF ^{14}C AND STABILITY ASSESSMENTS OF GRAPHITE UNDER REPOSITORY CONDITIONS

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ABSTRACT

The key objectives of the University of Manchester's nuclear graphite research within the CRP are to provide analysis on the long term behaviour and stability assessments of irradiated graphite waste. The research will concentrate on isotopic ^{14}C mobility under repository environments. This also requires an understanding the long-term behaviour of the final waste form under repository conditions.

Procedures to evaluate the long term leaching properties of radionuclides from irradiated graphite waste has been developed by combining ANSI 16.1 (USA) and NEN 7345 (Netherlands) standardised diffusion leaching techniques. The ANSI 16.1 standard has been followed to acquire the leachates and to determine the leach rate and diffusion coefficient. The NEN 7345 standard technique has been used to determine the diffusion mechanism of radionuclides. The investigation employs simulated Drigg groundwater as a leachant using semi-dynamic technique for the production of leachate specimens. Analysis of ^{3}H and ^{14}C activity release from Magnox graphite was measured using liquid scintillating counting. Preliminary results show that there is an initial high release of activity and decreases when the leaching period increases. This may be due to the depletion of contaminants that were initially bound by the internal pore networks and the free surface. During the leaching test approximately 275.33 ± 18.20 Bq of ^{3}H and 106.26 ± 7.01 Bq of ^{14}C was released into the leachant within 91 days. The work reported herein contributed several key findings to the international work on graphite leaching to offer guidance leading toward obtaining leaching data in the future: (a) the effective diffusion coefficient for ^{14}C from graphite waste has been determined.

The diffusion process for ^{14}C has two stages resulting two different values of diffusion coefficient, i.e., for the fast and slow components; (b) the controlling leaching mechanism for ^{3}H radionuclide from graphite is shown to be surface wash–off; and for that of ^{14}C radionuclide the initial controlling leaching mechanism is surface wash-off following by diffusion which is the major transport mechanism; and (c) The weight loss originates from the open pore structure which has been opened up by radiolytic oxidation; at the higher weight losses much of the closed porosity in the graphite has been opened. The investigation indicates that weigh loss has a major influence on the leaching of elements from the irradiated graphite.

1. INTRODUCTION

The largest source of irradiated graphite within the UK originates from reactor moderators and reflector material. The majority of this graphite has been exposed to very high levels of neutron irradiation resulting in activation of impurity radionuclides. There are also other sources of irradiated graphite components, in addition to the moderator and reflector, such as Material Test Reactor (MTR) thermal columns, fuel channel sleeves, graphite plugs, outer circumferential fuel sleeves, graphite boats and side locating struts. Once all the graphite moderated reactors have closed, the UK will have a graphite waste inventory amounting to approximately 100,000 tonnes. Therefore graphite waste treatment and behaviour in typical geological conditions is an increasingly important issue that the UK has to address and fully understand.

To ensure the safe disposal of graphite, the activity associated with the radionuclides and the possible release of these radionuclides during decommissioning and disposal requires fully assessing [1-3]. The radioactive radionuclides, which are considered of potential concern to the environment, include ^{3}H, ^{14}C, ^{36}Cl, ^{60}Co, ^{137}Cs and ^{155}Eu. Some of these radionuclides arise from the activation of impurities which were integral with the original graphite components, other radionuclides arise from other reactor materials, which has then been activated elsewhere in the core before being carried around the circuit in the coolant gas [4, 5]. The latter activated material may be associated with the graphite component internal porosity surfaces transported there via the complex porosity network.

There are twenty six Magnox reactors which were commissioned around the world between 1956 and 1972 at the sites of eleven power stations [6]. All Magnox reactors are cooled by CO_2 gas and moderated by graphite [6, 7]. The pressure vessels of the reactors were constructed from steel except the last four reactors that feature pre-stressed concrete vessels. In general these reactors have provided reliable electrical power generation over their operating lives [6]. The core of each reactor is an assembly of machined graphite blocks and the core graphite bricks comprised of fuel channels, control devices, samples and coolant flow routes. Small gaps were left between the moderator blocks during assembling procedure to allow for the expansion of the graphite blocks. The cores are attached together with keys to produce a strong structure [7]. To contain the effects of thermal transients and dimensional changes induced by irradiation in graphite bricks the keys are designed to tolerate comparative movement, radially and vertically, between neighbouring columns. Thermocouples are also inserted in each core to measure temperatures of the graphite material and channel outlet gas. The reactor core has typical inlet gas temperatures between 160 – 225 °C whilst outlet gas temperatures of between 345 – 370 °C [6].

Irradiated graphite samples from the Oldbury Magnox Reactor 1 core were used throughout this research and are shown in Table 1. A related pair of matching samples, in terms of irradiation history and properties was immersed in solution, representing typical repository conditions. The composition of the solution simulating ground water is shown in Table 2. The data collected was used to relate the leachability index to the graphite irradiation history.

TABLE 1: TEMPERATURES AND FAST NEUTRON DOSE FOR OLDBURY REACTOR 1 (2009) TREPANNED SAMPLES FROM FLATTENED REGION CHANNELS [28]

Sample ID	**Trepanned Sample Height (m)**	**Temperature (°C)**	**DIDO Equivalent Dose (10^{20} n.cm^{-2})**	**Displacement per atom* (dpa)**	**%wt loss***
1/2	2.66	294	45.56	6.0	33
2/2	3.01	302	48.15	6.3	38
5/2	4.26	329	51.49	6.8	33
6/2	4.70	338	50.95	6.7	33
9/2	5.86	356	45.55	6.0	25
10/2	6.22	361	42.86	5.6	27

* Calculated by the authors

TABLE 2: ORIGINAL SIMULATED GROUNDWATER COMPOSITION (WILKINS)

Compound	Deionised Water (g / l)
KCl	0.0066
$MgSO_4.7H_2O$	0.0976
$MgCl_2$	0.0810
$CaCO_3$	0.1672
Na_2SiO_3	0.0829
$NaNO_3$	0.0275
NaCl	0.0094
$NaHCO_3$	0.2424
pH	7.35

2. GROUND WATER LEACH TESTS

2.1. Sample Preparation for Leaching Tests on Active Graphite Samples

The six fuel channel PGA graphite sample discs, of nominal dimensions 6 mm x 12 mm diameter and mass of 1g, were immersed in leachant solution volumes of 50 ml for ten specified time periods. At periodic intervals, each leachant was renewed and the recovered leachates were analysed. The chemical composition of the simulant water has been described by Wilkins et al. [8] and is shown in TABLE 3.

TABLE 3: LEACHANT RENEWAL SCHEDULE

Leach Period	Leaching Interval Time (hours)	Total Time (hours)	Total Time (days)
1	2	2	0.1
2	5	7	0.3
3	17	24	1
4	24	48	2
5	24	72	3
6	24	96	4
7	72	168	7
8	336	504	21
9	672	1176	49
10	1008	2184	91

A modified version of the ANSI 16.1 standard [9] was used throughout the leaching trial. The ANSI 16.1 protocol determines the leachability of contaminants from encapsulated low-level radioactive waste samples. This standard provides a uniform procedure to measure and calculate the leachability factor of the

radionuclides released from waste forms as a result of leaching in demineralised water for 5 days or more. The demineralised water was tested out and found to be of pH 6. It is slightly acidic as it absorbs carbon dioxide until it reaches equilibrium with the CO_2 in the atmosphere.

The standard test procedure was modified for application on solid graphite samples instead of monolithic cement based waste samples, and requires the total quantity of leachate to be removed from the leach container at the end of each leach period and replaced with fresh leachant. According to the procedure the samples should have dimensions of 49 mm diameter and 58 mm height, hence, a geometric surface area of approximately 12700 mm^2. It also recommends using a leachant volume of 10 times that of the volume of the sample equating to 1270 ml.

During this study the sample size and the volume of the leachant were different from that of the encapsulant, however as the ANSI standard requires a volume/surface area ratio to be at least that of 10:1, the leachant volumes used throughout this study were calculated to meet this requirement. The external surface area of the samples was calculated from the physical measurements of the specimens. In order to represent typical UK repository conditions based at Sellafield, a simulated groundwater was used instead of demineralised water which is comparable to that of Drigg groundwater [8].

The six graphite samples underwent a 91 day leaching test as per ANSI 16.1. This solution had a starting pH of 7 - 8 and contained salts comparable to simulated repository Drigg groundwater (Table 2) [10]. The analysis of ^{14}C contained within the leachant solution was investigated using sample digestion and the investigation of ^{3}H was carried out by separation and analysis.

2.2. Scintillation Cocktail

Scintillation cocktail is a mixture of a solvent and a solute and when it interacts with the radiation emitted from the sample a count is recorded. For ^{3}H analysis Ultima Gold had been chosen because it has an excellent sample holding capacity and it is an ideal choice for aqueous samples due to its low surfactant content. Duplicate samples containing a known amount of Becquerel's of ^{3}H standard were processed in parallel to the samples and analysed in order to correct for any reduction in counting efficiency due to the effect of quenching substances. Quenching occurs when the energy emitted by the radionuclide is not collected completely by the photomultiplier tube of the counting instrument [11].

An Insta-Gel scintillation cocktail is used for counting ^{14}C beta emission using a Liquid Scintillation Counter. Insta-Gel Plus (1,2,4-Trimethylbenzene) is an almost water-insoluble hydrocarbon liquid based cocktail. It is excellent for the incorporation of water and aqueous soluble samples and organic samples due to its resistance to colour quenching and formation of a stable gel. It has very high sample holding capacity and ideal for counting large volumes of water and suspended solids.

2.3. Counting Efficiency Determination for ^{3}H and ^{14}C

In order to determine the effect of quenching on the counting efficiency of ^{3}H a set of six quenched standards is prepared by adding a quenching agent, *i.e.,* simulated groundwater, into an internal standard with a known amount of activity. In conjunction with the standard samples two blank samples were prepared by adding 4 ml of simulated groundwater into a vial containing 16 ml of UG scintillation cocktail. Then, the background count rates were determined by counting the blank samples. TABLE 4 shows determination of counting efficiency of tritium. The counting efficiency was found to be ~ 38 %.

TABLE 4: ^{3}H COUNTING EFFICIENCY DETERMINATION

Cocktail Vol. (ml)	Vol. H_2O (ml)	Vol. Std (ml)	Activity (Bq)	CPSB (Bq)	B:2S%	tSIE	Efficiency (%)
16.0	3.9	0.1	16.1	6.1	2.3	458.4	37.8
16.0	3.9	0.1	16.1	6.1	2.3	458.2	38.0
16.0	3.9	0.1	16.1	6.2	2.3	456.8	38.6
16.0	3.9	0.1	16.1	6.1	2.3	458.9	37.7
16.0	3.9	0.1	16.1	6.1	2.3	457.7	37.8
16.0	3.9	0.1	16.1	6.1	2.3	458.2	38.0
Average Efficiency							38.0

The counting efficiency of ^{14}C with a particular quench level was measured to determine the activity of ^{14}C. The determination of the counting efficiency was achieved by counting a series of quenched reference standards of ^{14}C. The ^{14}C in the leachate was recovered as a precipitate of $BaCO_3$. hence, any internal standard used was of a solid form. This method involves the counting of $BaCO_3$ suspended in a liquid scintillator adjusted for gel formation. Since the sample is solid and suspended in a gel the mixture of the cocktail, the standard and the simulated water will be affected by physical, colour and chemical quench. The effect of quenching due to the water (chemical quench) is expected but here there is an additional obstacle from the solid sample. Care was taken to ensure that the radioisotope was homogenously dissolved within the scintillator, the counting efficiency for ^{14}C is shown in Table 5.

TABLE 5: ^{14}C COUNTING EFFICIENCY DETERMINATION

Sample #	Mass $BaCO_3$ (g)	Vol. H_2O (ml)	C-14 Activity (Bq)	CPSB (Bq)	B:2S%	tSIE	Efficiency (%)
1	0.0303	4	85.143	48	1.22	324.17	57
2	0.0493	4	138.533	78	1.21	311.37	56
3	0.0714	4	200.634	112	1.22	319.06	56
4	0.0984	4	276.504	148	1.23	318.83	54
5	0.1253	4	352.093	179	1.24	319.93	51
6	0.1544	4	433.864	232	1.23	323.86	53

2.4. Graphite Leachate Preparation

The procedure of the sample preparation is described as follows; Six vials containing different amount of internal standard and equal amounts of a quenching agent, i.e., simulated groundwater was prepared. The internal standard, $BaCO_3$, was put into the counting vials containing 10 ml of Insta-Gel scintillation cocktail and, 4 ml of simulated groundwater was added. The ratio between the water and scintillator was 2:5. Homogenous mixing was obtained by warming the vial and shaking it thoroughly. A blank sample with a volume equivalent to the quenched standard solutions was also prepared to measure the background and used in the calculation to get the most possible accurate result.

The Disintegrations Per Minute (DPM) value in each standard is known. Each standard is counted and the CPM (Counts per Minute) is measured. From the standards in which the absolute radioactivity (DPM) per vial is different and the amount of activity of the vials the efficiency is calculated. Then, an efficiency curve is fitted to the calculated points. A correlation is made using the mass of the sample on one axis (X) and the % efficiency on the other axis (Y) and the resulting graph is shown in FIG. ***1***.

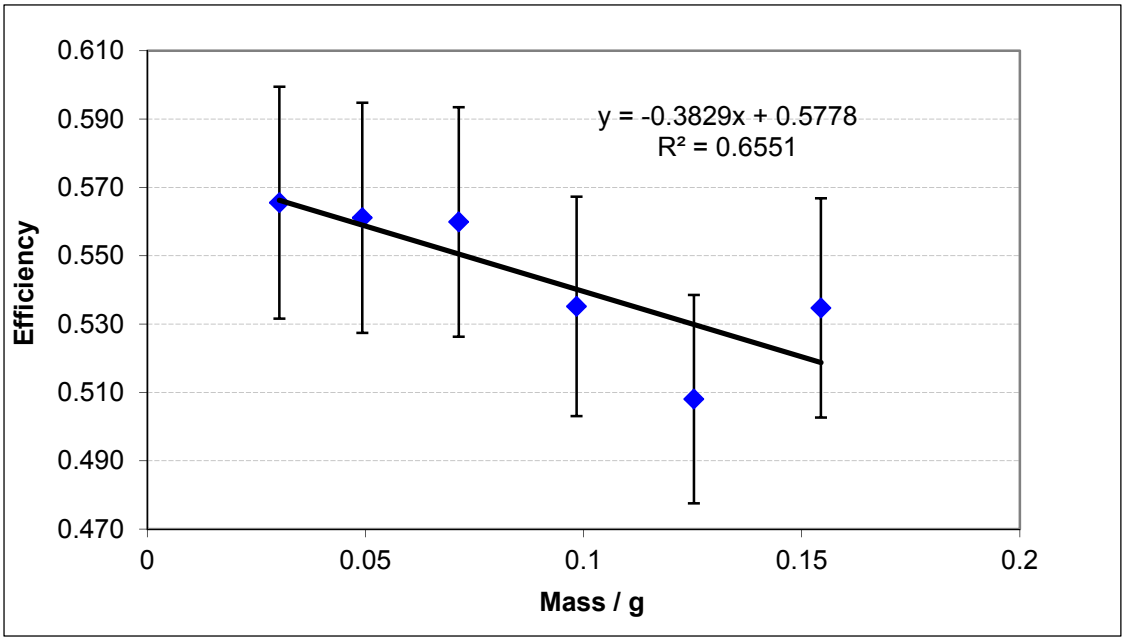

FIG. 1: The effect of quench on counting efficiency of ^{14}C

2.5. Measurement of ^{3}H by Digestion and Distillation of Leachant

The cumulative total release of ^{3}H from the irradiated graphite samples is shown in F 2. Over the 91 days of the experiment approximately 275.33 ± 18.20 Bq (from a 50 ml sample) of ^{3}H was measured using a Liquid Scintillation Counting. This value was derived from measurements taken on the most active sample. From F 2 it can be observed that the rate of leaching of ^{3}H increase as the time of leaching increases and starts to plateau after about 7 days. Samples with highest amount of leached radionuclides are the ones which were trepanned from the middle of the core. The initial rise may possibly indicate the leaching of the contaminant is from the surface of the graphite and it may be due

to its very high solubility. The background activity level of ^{3}H in the laboratory was found to be below the detection limits (minimum detectable activity is 0.2 Bq).

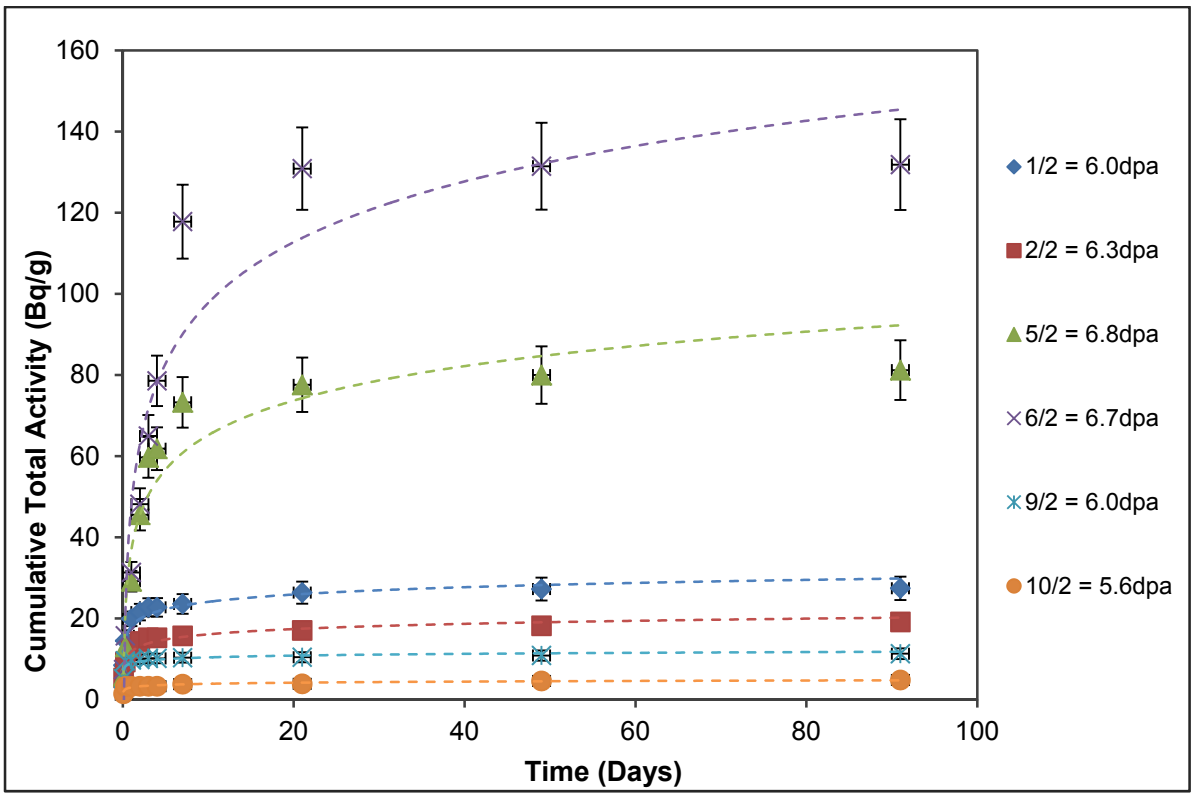

FIG. 2: Cumulative total ^{3}H activity release measured using liquid scintillation

2.6. Measurement of ^{14}C by Digestion (Wet Oxidation) of Leachant

The quantities of ^{14}C obtained in the experiments are shown in
F 3. The background level of the blank and the laboratory was below detection limits (Minimum detectable activity is 0.2 Bq). Over the 91 days of the experiment about 106.26 ± 7.01 Bq cumulative activity (in sample size of 50 ml) of ^{14}C containing carbon dioxide was captured using a dreschel bottle containing 0.1M sodium hydroxide from the most active sample. The highest amount of radionuclide leached is from the samples that were trepanned from the centre core bricks (i.e. 5/2 and 6/2) and exposed to highest radiation.

It can be seen from
F 3 that the rate of leaching of ^{14}C increase with increasing time and plateaus after about 21 days. The leaching period to equilibirum for ^{14}C (21 days) is longer than for ^{3}H (7 days). ^{14}C is mainly produced from carbonaceous deposits which are integral to the original graphite pores and surfaces, and from nitrogen impurity found in the form of gas which has accumulated on the surface of the graphite or nitrogen gas which is trapped within closed pores during calcination procedure during graphite manufacturing [12]. During leaching the leachant have to travel through the internal porosity via the complex porosity network which may result in a longer leaching time. As^{14}C can bond with the graphitic lattice structure [13, 14], this chemical formation may have a significant effect on the solubility of the nuclide and its chemical reaction rate with water. ^{3}H that was adsorbed at the pore

surfaces will be released when it makes contact with hydrogenous molecules in the leachant and leaches out more quickly than ^{14}C chemically bound radionuclide.

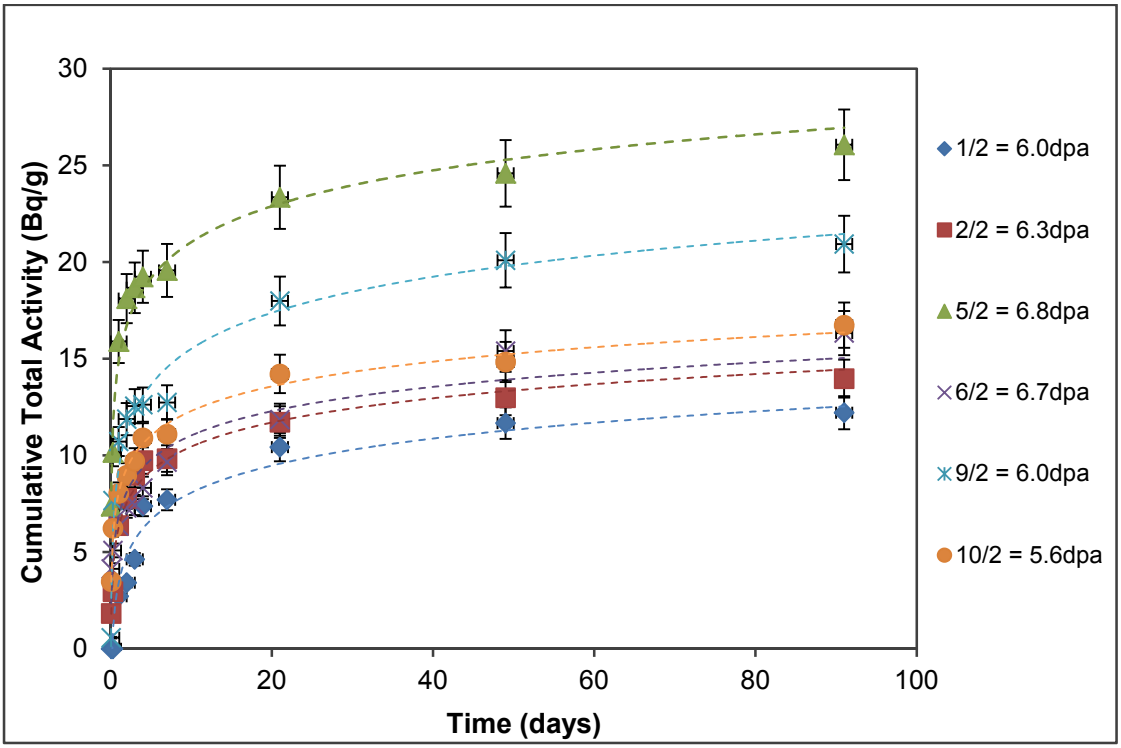

FIG. 3: Cumulative total ^{14}C activity release measured using Liquid Scintillation

2.7. Ground Water Leaching Rate of Graphite Specimens

The investigations carried out for mechanisms of leaching and measured rates have not produced extensive information in this area. The information on the chemistry of leaching in water is reported in literature around 25 years ago and due to this it is very scarce [15]. Therefore, the purpose of this investigation is to document the results of the leach tests conducted on the samples of graphite obtained from the Oldbury Reactor 1. The information produced will help (1) to obtain data and compare information with other studies that have been conducted and published by other scientists and organisations, (2) to understand better the processes determining leaching behaviour and (3) to determine critical leaching parameters for further encapsulation and modelling investigation. Short-term data may then be used to extrapolate to long times by utilising the data from different leachate experiments and modelling the effective leaching rate coefficient for leaching of radionuclides from a finite cylinder. The cumulative fractional leach radioactivity of ^{3}H and ^{14}C found in the leachates are shown in FIG. *4* and FIG. 5.

To measure the initial radionuclide inventory of the irradiated graphite before leaching tests two graphite samples from the same reactor was taken and combusted using Carbolite® furnace. The detailed procedure of combustion and analysis is detailed elsewhere [17]. The inventories of ^{3}H and ^{14}C in these specimens averaged 44 kBq/g and 64 kBq/g ±(8%) respectively. Moreover, the samples were separately characterised for density using immersion method and their weight was measured before immersion and **Error! Reference source not found.** shows the characterisation results for the six samples.

The cumulative fraction of inventory leached is calculated using eq. 1, i.e., by adding the leached fractions in each leach period. It is interesting to see that the highest leach rates for ^{14}C do not follow the neutron irradiation history of the samples. Samples which were exposed to a slightly lower dose have released much more contamination. As it can be seen that samples which have a higher density have released much more activity. However, it is difficult to speculate the exact reason for the cause of this difference between the release behaviour of these samples.

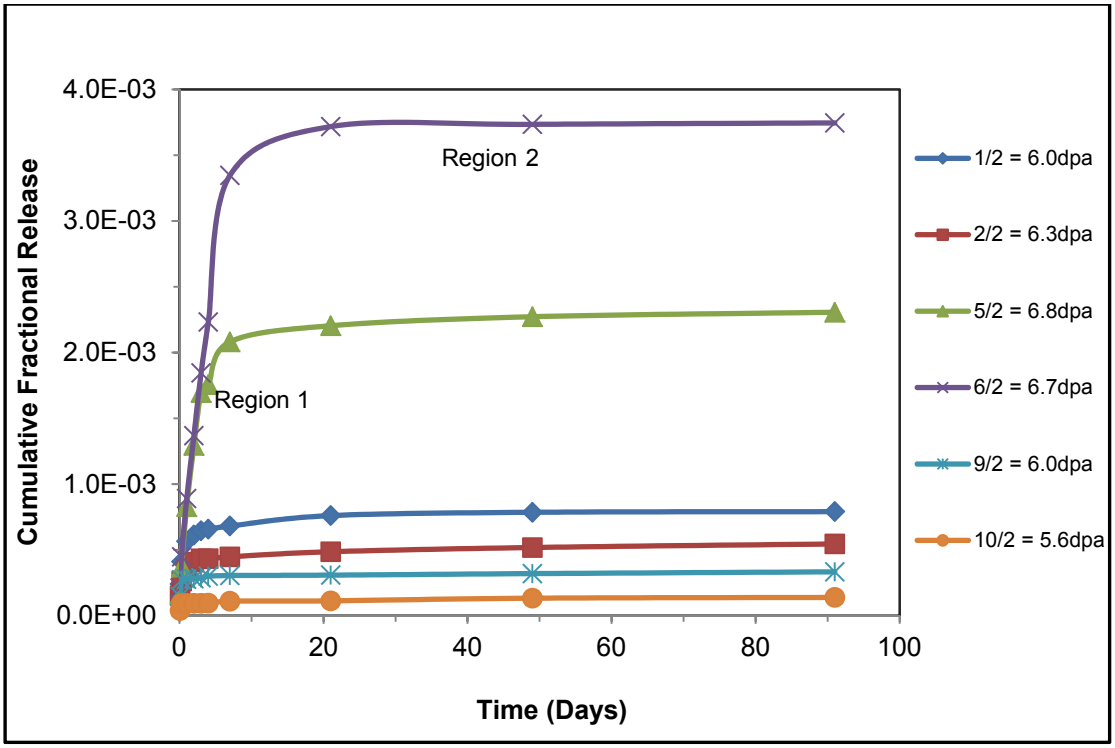

FIG. 4: Cumulative Fraction of ^{3}H Activity Leached in Simulated Groundwater at 20 ± 5°C

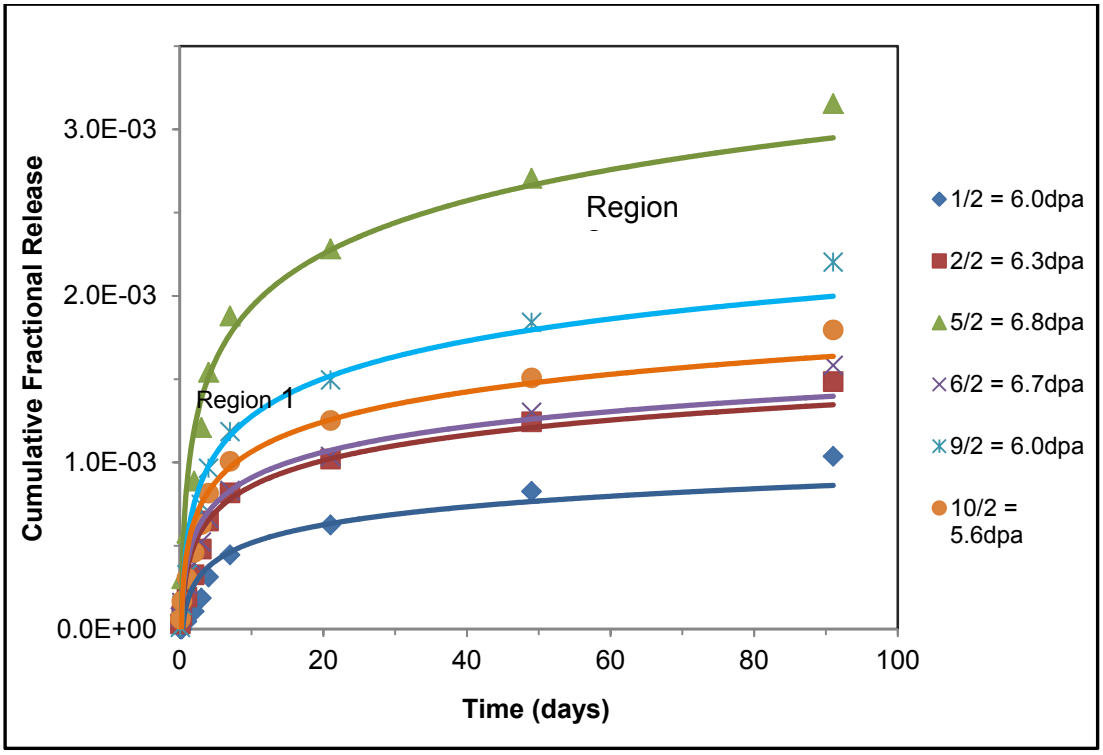

FIG. 5: Cumulative Fraction of ^{14}C Activity Leached in Simulated Groundwater at 20 ± 5°C

For ^{3}H the samples which have the highest leach rates are the one which were exposed to high neutron dose and are the one of which located at the centre of the reactor core channel (**Error! Reference source not found.** 1) On average about 0.13 % of ^{3}H and 0.19 % ^{14}C of the inventory have leached out from the irradiated graphite during the 91 day period.

The incremental leach rates (calculated using eq. 2) are reported in F 6 and Figure 7. Each best fit curve to the series of data points exhibits a characteristic initial sharp fall, possibly due to leaching of nuclides present on the surface of the graphite, followed by a more progressive decline towards apparent equilibrium.

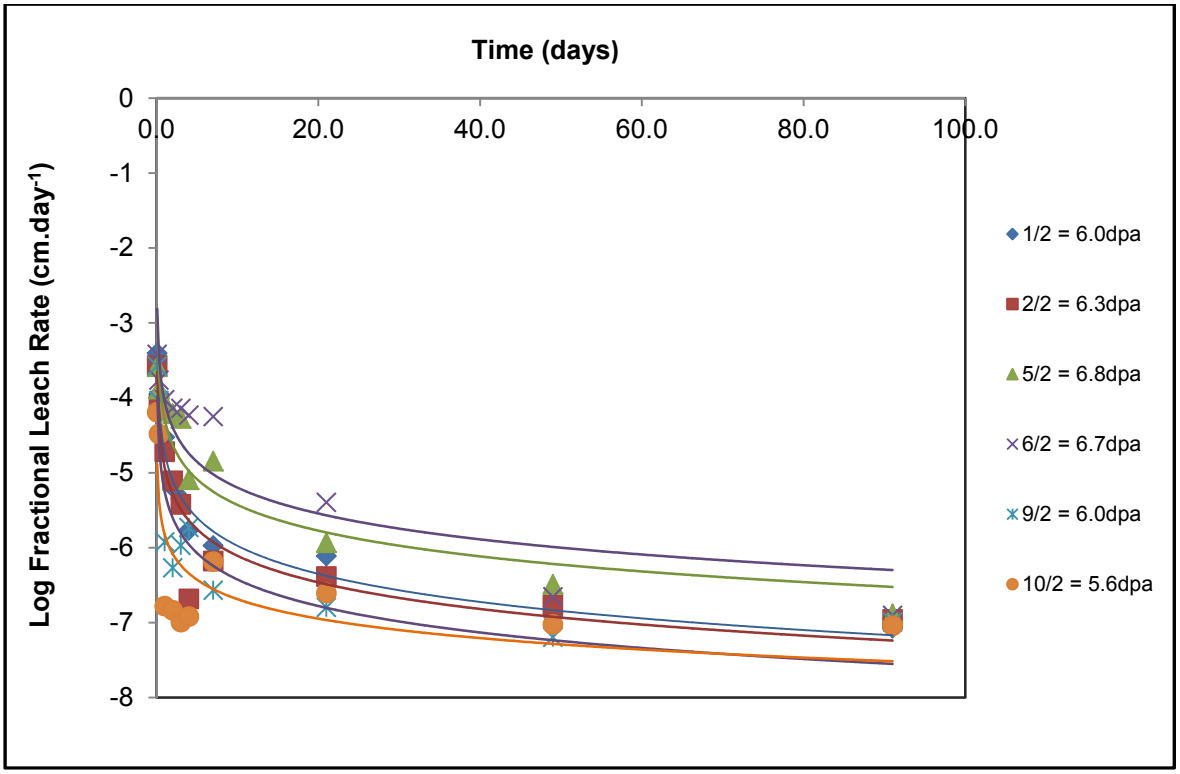

FIG. 6: Fractional Leach Rate of ^3H in Simulated Groundwater at 20 ± 5°C

Data presented for the graphs were derived from the following equations [14, 16]:

$$F = \frac{\sum A_n}{A_0} \quad \ldots\ldots\ldots\ldots\ldots \; eq.1$$

$$R = \frac{F}{t_n}$$

$$L = \frac{R.V}{S} \ldots\ldots\ldots\ldots\ldots\ldots..eq.2$$

Where:

F = Cumulative fraction of radionuclide released in a given leachant renewal period

A_n = Radioactivity in the leachate released during the leachant renewal period n, $Bq.g^{-1}$

V = Volume of specimen, cm^3

A_0 = Initial radioactivity inventory in the graphite specimen, $Bq.g^{-1}$

M = Mass of specimen, g

R = Cumulative fractional leach rate for the period, day^{-1}

S = Exposed surface area of specimen, cm^2

t = Duration of leachant renewal period, days

L = Cumulative leach rate of graphite per unit surface area of specimen, $cm.day^{-1}$

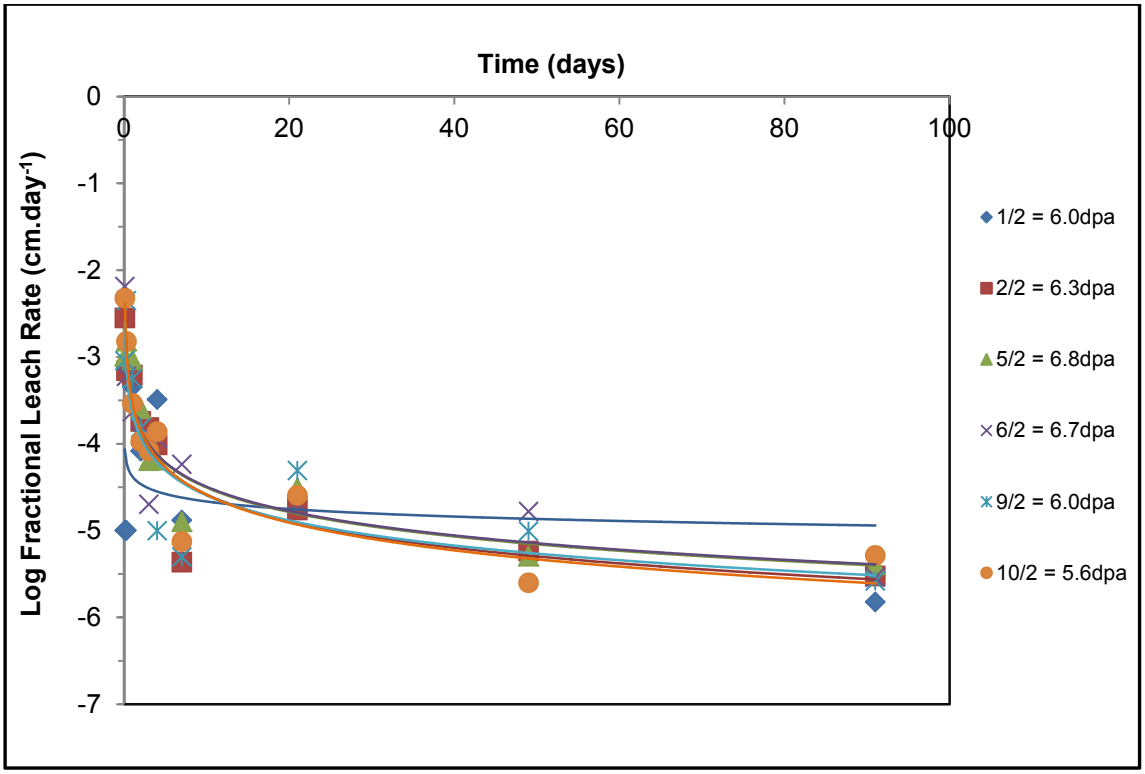

FIG. 7: Fractional Leach Rate of ^{14}C in Simulated Groundwater at 20 ± 5°C

The feasible mechanisms for the observed decline in leach rates with time could be due to the depletion of the ^{3}H and ^{14}C supply and the solubility of the radionuclide in water. The ^{14}C activity was not depleted during the leaching. Nevertheless, a significant fraction of ^{3}H was depleted from graphite samples. The reason for the depletion could be as mentioned above, the activity may have depleted due to the reactivity of ^{3}H, i.e., it may react with the leachant quickly or it is may be more readily available to react with the leachant.

The other interesting point is that the samples have almost the same dose (dpa), but the leach rate of the samples is different. This shows that weight loss and density change have played a major role on the release of radionuclide. Moreover, the order of the leaching rate of ^{14}C is lower than that of ^{3}H. This reveals that the amount of ^{14}C activity release is slower than the release of ^{3}H.

2.8. Determination of Leaching Mechanism

The determination of leaching mechanism methods used to evaluate diffusion-controlled release are frequently referred to as either "monolith leach tests" or "tank leaching tests." Two primary test methods are used for evaluation of monolithic materials. The first test method is the American Nuclear Society Method 16.1 (ANS 16.1, 1986) [9]. The second test method is a recent derivation of ANS 16.1 that has been adopted in The Netherlands as NEN 7345 (1994) [18].
The Dutch diffusion leaching test NEN 7345 was employed to assess the mechanism of release of radionuclides from waste that is monolithic in form. The test applies Fick's second law of diffusion (eq. 3) for evaluating leaching behaviour, calculation of effective diffusion coefficient, and long-term leaching predictions.

$$\frac{\partial A}{\partial t} = D_e \frac{\partial^2 A}{\partial x^2} \ldots\ldots\ldots eq.3$$

$where$:
D_e - effective diffusion coefficient [m^2/s]
A - Radionuclide concentration available in the solid phase
t - Leaching period [days] and
x - Distance from the surface [m]

In practice the NEN 7345 test is very similar with the American Nuclear Society Method 16.1 (ANS 16.1). In both test methods a molded and cured test specimen of defined geometry is immersed in deionised water (leachant). The leachant is then replaced by fresh leachant after specified period and the resulting leachant is sampled for chemical assay. The main difference between the tests is the basis for data reduction (the renewal periods are 0.25, 1, 2.25, 4, 9, 16, 36 and 64 days), and the calculation of effective diffusion coefficients and other parameters are provided. In addition, the diffusion models require that the cumulative fraction leached in any test is related to the ratio of the sample geometric surface area to geometric volume (S/V).

To estimate the effective diffusion coefficient, D_e Crank (1989) [19] have used a one dimensional semi-infinite linear diffusion model based on data obtained from both monolithic specimens and compacted granular material. The model requires the following boundary conditions for leaching test to be fulfilled:

- the material is homogeneous in composition
- over the duration of the test no depletion has occurred
- leachant replacement cycles are frequent enough to make sure the leachate remains dilute relative to leachate saturation element of interest, and
- monolithic samples maintain physical integrity (e.g., no cracking or disintegration) during testing

Crank [19] has developed a solution of Fick's law of diffusion (eq. 4) for the above conditions from a product with semi-infinite dimensions, in which the initial concentration is uniformly distributed in the product and the concentration on the surface between the product and the leachate is constant with respect to time:

$$\frac{A - A_1}{A_1 - A_0} = erf\left\{\frac{x}{2\sqrt{D_e t}}\right\} \ldots\ldots\ldots\ldots\ldots eq.4$$

where:
$A = A(x,t)$ - concentration as a function of location within the solid test specimen and time
A_1 - constant concentration at x=0
A_o - initial concentration in the product which must be uniformly distributed
D_e - the effective diffusion coefficient
t - Time [s], and
x - Distance from the surface [m], positive values
The resulting diffusion equation derived from eq.4 for the boundary condition is:

$$D = \frac{\pi A_t^2}{4t(\rho A_0)^2} \ldots\ldots\ldots\ldots\ldots\ldots. eq.5$$

where:
D or D_e - diffusion coefficient for component x in the product [m^2/s]
A_t - cumulative release of the component [mg/m^2]

t - Leaching period time [s]
A_0 - maximum leachable quantity [mg/kg], and
ρ - Bulk density of the product [kg/m^3]

The NEN 7345 test uses specimens with a minimum diameter of 40 mm which is immersed in leachant in a closed vessel [18]. Serne, R.J, et al. [20] prepared various sizes of cylindrical grout samples to test the effect of sample size in diffusion of contaminants from monolithic samples. The authors have showed that there is no significant difference in the diffusion coefficient (leach rate) between the various sized samples when leached in groundwater or deionised water.

The analysis of the determination of the diffusion mechanism of contaminants was provided by Todorović and Ecke (2004).[21] They have used weakly bound chlorine to study the leaching of components from solid matrix and information on the physical properties of the matrix. They have analysed the leaching activities of the elements to determine whether the leaching of chlorine from the solid matrix is diffusion controlled or not. The investigation concluded that the diffusion controlled leaching behaviour is distinguished by the cumulative fractional release following a 0.5 slope on a log release vs. log time release plot. Rearranging eq. 5 yields:

$$A_t = \rho A_0 \left(\frac{4D_t t}{\pi}\right)^{\frac{1}{2}}$$

after logarithmic transformation:

$$log\left(\frac{A_t}{A_0}\right) = \frac{1}{2}\log(t) + \ log\left\{\rho\left(\frac{4D_t}{\pi}\right)^{\frac{1}{2}}\right\}$$

Regression analysis (NEN 7345, 1995) was used to determine how much the curve deviated from 0.5 slope. If slope of a leaching curve or its part is within 0.5±0.15 interval, then leaching during the test or its part is diffusion controlled. The detailed derivation of this diffusion criteria is reported by Soldatove, 1997.[22] Subsequently, the effective diffusion coefficient is calculated using the total availability of a contaminant as determined using the NEN 7341 (1994) [23] as the driving force for diffusion.

The mechanism of leaching is often documented as being a diffusion-controlled process. The permeability of a material determines how easy a leachant enters the specimen, and how fast radionuclides will be released over time. Water tends to flow around products with a low permeability rather than to enter it. Consequently, this is why products with a low permeability are more likely to show diffusion controlled release.[24]

Therefore, to determine whether the leaching is diffusion controlled or whether it depends on other mechanisms a graph was constructed using cumulative leach fraction data. The determination of the controlling leaching mechanism is based on the gradient of the linear regression of the logarithm of cumulative leach fraction versus the logarithm of time [18]. Next the criterion for diffusion was applied to determine the process, i.e., if the gradient of the graph is less than 0.35 the controlling leaching mechanism will be the surface wash–off, if the gradient values are between 0.35 and 0.65 the controlling mechanism will be the diffusion, and higher gradient values signifies the dissolution mechanism.[18]

The result of the linear regression for all samples for the analysis is shown FIG. 8 and F 9 for ^{3}H and ^{14}C, respectively. From FIG. it can be observed that the gradient values for all samples are less than 0.35 which indicate that the controlling leaching mechanism for leaching of ^{3}H from the graphite is surface wash–off. For ^{14}C it can be observed (F 9) that the gradients of the graphs are between 0.35 and 0.65. This reveals that the leaching of the radionuclide is due to surface wash-off and diffusion, and dissolution did not take place at all.

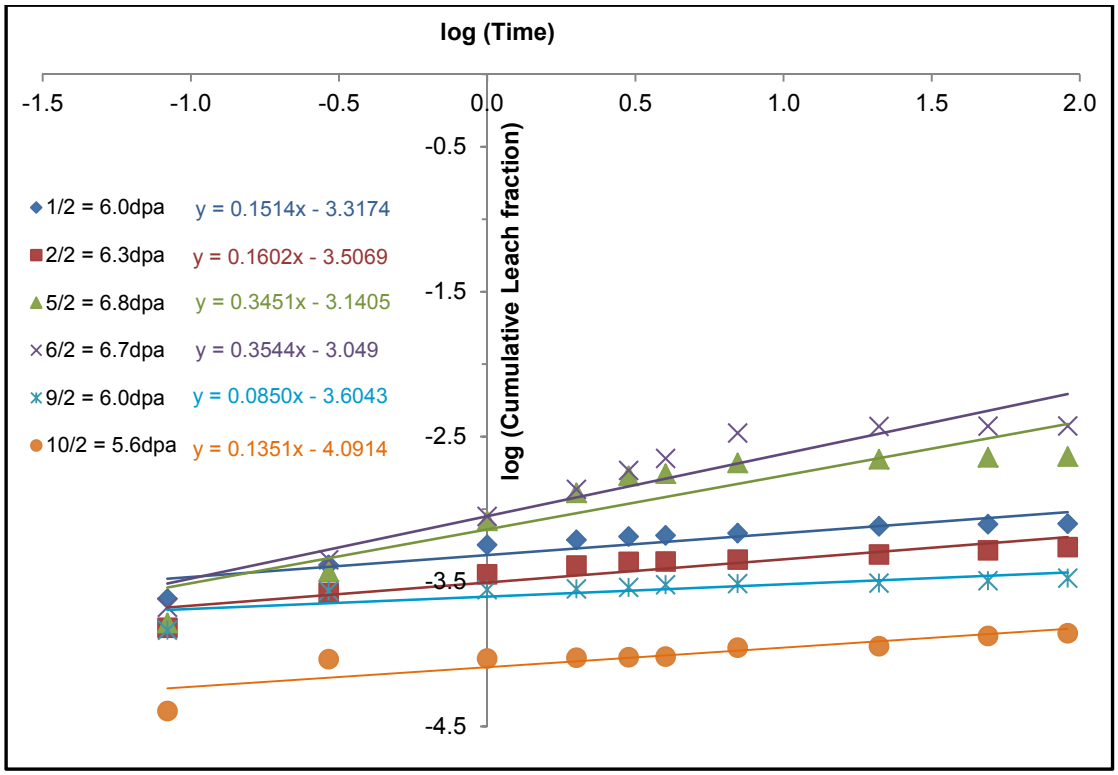

FIG. 8: Linear Regression Graph of the Logarithm of Cumulative Leach Fraction of ^{3}H versus the Logarithm of Time

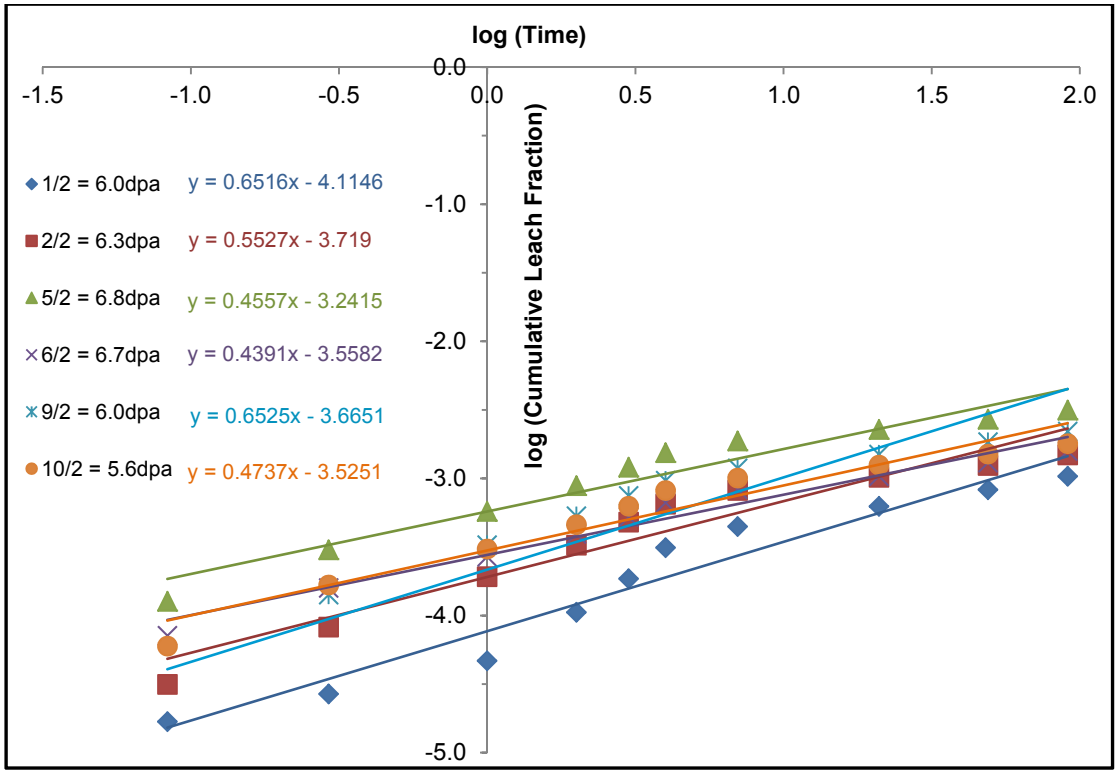

FIG. 9: Linear Regression Graph of the Logarithm of Cumulative Leach Fraction of ^{14}C versus the Logarithm of Time

This can be explained more clearly using incremental leach fractions graph of ^{3}H and ^{14}C which is expressed as cm.day^{-1} on log scale versus time graph as shown in FIG. *10* and Figure 11, respectively. From both radionuclides incremental leach rates; it can be observed that the leaching pattern can be divided into two regions. Region 1 demonstrates initial release of radionuclides and then a reduction in the release take place over a longer period of time (Region 2). ^{3}H shows an initial rapid release of radionuclides within the first 7 days and a drastic reduction in the release observed over a longer period of time. In contrast, ^{14}C showed an initial rapid release of radionuclides and there is more release when measured at day 21. Then, a reduced rate of release observed over a longer period of time.

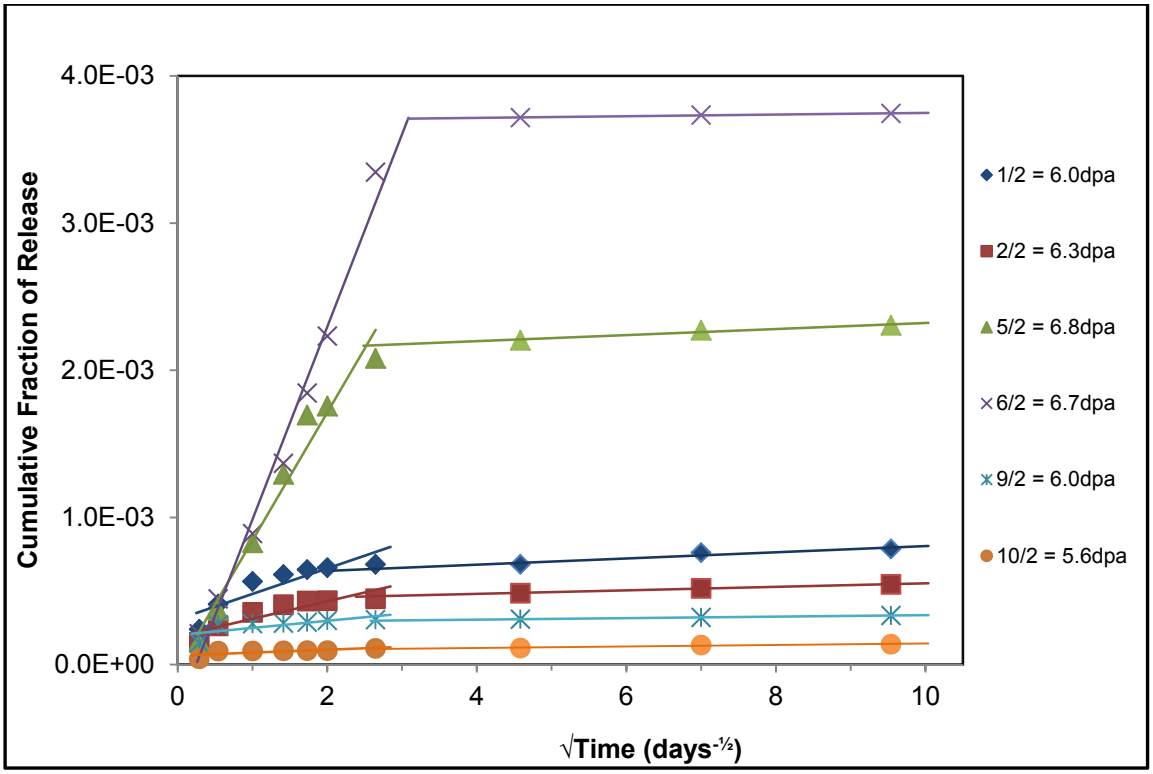

FIG. 10: Cumulative Fraction of ^{3}H Activity Leached in Simulated Groundwater at 20 ± 5°C

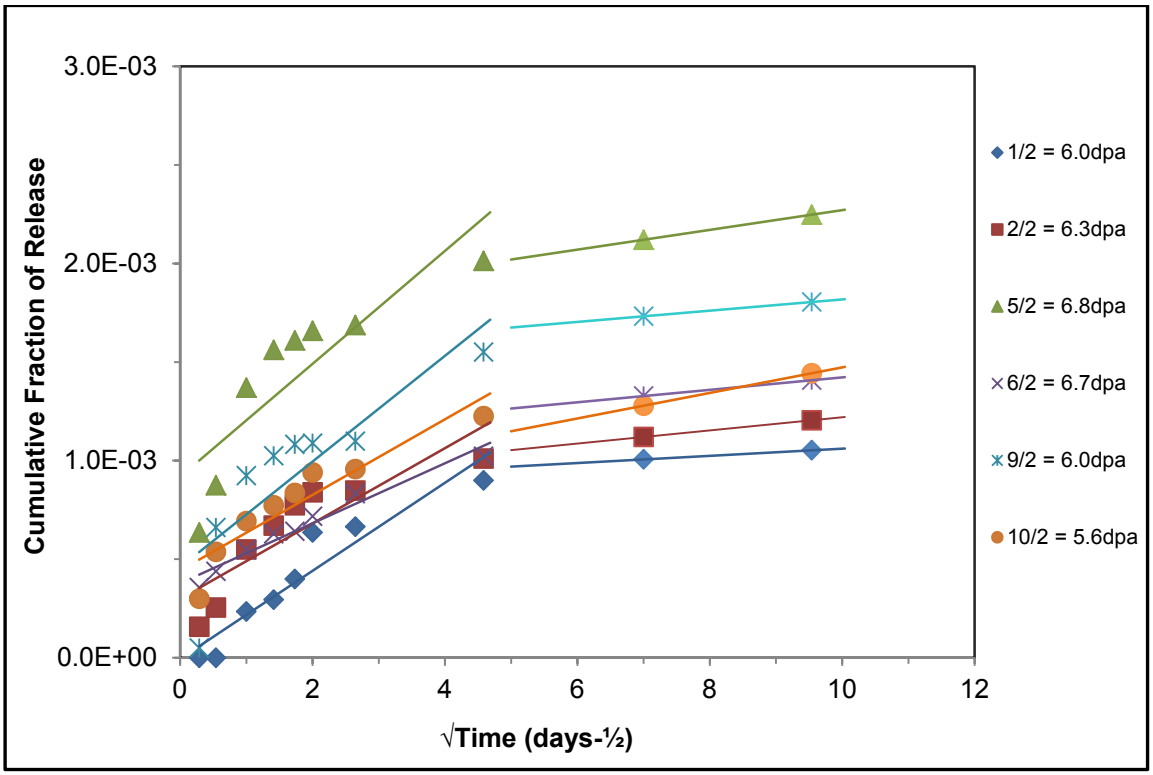

FIG. 11: Cumulative Fraction of ^{14}C Activity Leached in Simulated Groundwater at 20 ± 5°C

2.9. Leaching Factor/ Effective Diffusion Coefficient

The mechanism of diffusion is very complex due to the microstructure of the graphite and the presence of impurities / contaminants that may affect the rate of leaching. In addition the diffusion can also be influenced by the variation in temperature in the laboratory, the chemical composition of the leachant solution, the change in chemistry of the leachant due to the radionuclides diffused out and the effect of radiation.

Hespe, E. D. [14, 25] from IAEA suggested that leach factor or diffusion coefficients may be used to compare leaching data. Assuming the diffusion is the primary mechanism a straight-line relationship should exist between the terms:

$$\frac{\sum A_n}{A_0} \Big/ \frac{S}{V} \; and \; \sqrt{t_n} \qquad (a)$$

the quantity of radionuclide leached out from a unit surface area during time, t_n is given by (Crank, 1975 [19]):

$$A_n = 2A_0 \frac{\sqrt{Dt_n}}{\sqrt{\pi}} \qquad (b)$$

Thus, from (a) and (b):

$$m = 2\frac{\sqrt{D}}{\sqrt{\pi}} \; x \; \frac{S}{V}$$

where:
m = Gradient/ slope of the straight line
D = Leaching factor/ Effective Diffusion Coefficient

Therefore,

$$D = \frac{\pi m^2 V^2}{4S^2}$$

FIG. *10* shows the fractional leach activity of ^{3}H radionuclides from all six samples studied versus square root of leaching time. As it can be observed from this figure, for all leaching test samples, there is an initial fast release during the first period and then has reached approximately to its equilibrium. This behaviour reveals the presence of one value of diffusion coefficient for the fast component and for the very slow component the value of the diffusion coefficient is close to zero or very low. But for ^{3}H, as can be observed from Figure 10, there is an initial fast release. The diffusion coefficient for ^{3}H nuclide reported in is only for the initial fast release and the average diffusion coefficients of each sample.

TABLE 6: DIFFUSION COEFFICIENT VALUE ^{14}C RADIONUCLIDE LEACHED FROM IRRADIATED GRAPHITE WASTE

Radionuclide	Average Diffusion ($m^2.s^{-1}$)	Diffusion ($cm^2.s^{-1}$)
^{3}H	5.83×10^{-9}	5.83×10^{-5}
^{14}C	1.75×10^{-13}	1.75×10^{-9}

The fractional leach activity of ^{14}C radionuclide from all six samples studied versus square root of leaching time is shown in FIG. *11*. It can be observed from the figures for all leaching tests there is an initial fast release during the first period followed by slow leaching in the subsequent periods. This behaviour reveals the presence of two different values of diffusion coefficients for the fast and slow components or the region where the leaching is approaching equilibrium. So, the calculated diffusion coefficient for ^{14}C nuclide reported in Table 6 is the average values of these two components diffusion coefficients and the average diffusion coefficients of each sample. From the data (TABLE) it can be deduced that ^{3}H have larger value of diffusion coefficients than ^{14}C radionuclide and can diffuse out more readily than ^{14}C.

2.10. Comparison with Previous Studies

It is of importance to compare the ^{3}H and ^{14}C leaching data of our studies with those obtained by White et al. (1984) [26] and Gray and Morgan (1988 &1989) [15, 16]. It is a special of interest to compare our investigation with White et al. since both tests were carried out on Magnox reactor graphite. White et al. used Hanford simulated groundwater while Gray and Morgan used demineralised water as a leachate within these experiments.

To enable comparison, both White et al. and Gray and Morgan have used samples cut from the inner-most bar retrieved from a reactor. However the authors note moderator bars are exposed to the maximum neutron Fluence in the reactor and received different dose under reactor operation. Therefore, the graphite is not homogeneous, thus, a small sample from one bar may not be representative of the average of the material surrounding it. Hence, to minimise this uncertainty we have used six samples retrieved from one channel wall but from different brick and reactor position.

The ^{14}C data obtained in our investigation is scattered showing similar characteristics with the result observed by White et al. performed on CEGB Magnox reactor graphite at 25 °C and pressure of 1 bar. The temperature and pressure in the laboratory was controlled at 20 ± 5 °C throughout the entire work and the cause for scattering of the data can only be attributed to the slow rate of release of ^{14}C from the graphite matrix.

The average cumulative leach fraction results of ^{3}H and ^{14}C reported her are similar to the results obtained by White et al. (Table 7) The value of ^{14}C attained by the author is slightly higher; this implies that the irradiated graphite samples used for this investigation, in general, are much more reactive. The mean initial radionuclide inventory for ^{14}C obtained by White et al. was 21 kBq/g and as mentioned above the samples used in this experiment have a mean activity of 64 kBq/g, which lends support to the argument. From the results it was observed that the leach rates are decreased by factors

of 15 to 140 after 91 days. This is very similar to the reduction observed by White et al. who have found a reduction by factors of 50 to 100 after 100 days.

TABLE 7: CUMULATIVE FRACTION AND INCREMENTAL LEACH RATE OF ACTIVITY LEACHED AT DAY 100 OBTAINED BY WHITE ET AL.

Radionuclide	**Simulated Groundwater at Day 100**	
	Cumulative Fraction of Activity Leached	**Incremental Leach Rate (cm.day^{-1})**
^{3}H	4.8×10^{-3}	2.7×10^{-6}
^{14}C	1.4×10^{-3}	6.0×10^{-7}

In contrast, the cumulative fractional ^{3}H activity obtained is less than from the value discovered by White et al., but the result is relatively good given the initial inventory difference; 220 kBq/g which is 5 times more active than the initial radionuclide inventory obtained by the author. The difference on the initial inventory and cumulative leach fraction may be influenced by weight loss which may have been produced by of radiolytic oxidation. As Shown in Table 3 the graphite involved in the leaching experiment have suffered a weight loss of up to 38 % during operating time. The weight loss is originate from the open pore structure opening up by oxidation and at the higher weight losses by opening up of much of the closed porosity in the graphite [27]. For instance, it was reported that (Morgan, W.C, 1988 [15]) the graphite samples which were used by Gray and Morgan may have been suffered 2 % weight loss. Therefore, weight loss is a significant factor that should be taken account of in inventory estimations and leaching investigation.

The cumulative leach fraction data obtained by Gray and Morgan (1988) [16] from an investigation performed on Hanford graphite (3.6×10^{-5} to 9.2×10^{-5} of inventory) at 20°C are far more less than from the amount found in our experiment (1.04×10^{-3} to 3.16×10^{-3} of inventory). But it is in good concurrence with their investigation result they have performed and obtained on graphite from French G-2 reactor (1989) [15] (2.6×10^{-3} to 8.5×10^{-3} of inventory). The reasons for these similarities and difference in the results obtained can be due to the experimental methodologies followed, differences in test duration, temperature, sample size, sampling frequency and/ or the leachant used.

3. CONCLUSIONS

A procedure for the evaluation of the leaching properties of radionuclides from irradiated graphite waste has been developed based on a standardised diffusion leaching tests. The procedure employs simulated Drigg groundwater as a leachant using semi-dynamic technique for the production of leachate specimens. During the leaching test approximately 275.33 ± 18.20 Bq of ^{3}H and 106.26 ± 7.01 Bq of ^{14}C was released into the leachant within 91 days from Magnox graphite measured using liquid scintillating counting. The results show that there is an initial high release of activity and decreases when the leaching period increases. This may be due to the depletion of contaminants that

may be absorbed by the pore networks and the surface. The diffusion process for ^{14}C has two stages resulting two different values of diffusion coefficient, i.e., for the fast and slow components. The controlling leaching mechanism for ^{3}H radionuclide from graphite is shown to be surface wash–off; and for that of ^{14}C radionuclide the initial controlling leaching mechanism is surface wash-off following by diffusion which is the major transport mechanism.

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