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Treatment and Disposal of Irradiated Graphite and Other Carbonaceous Waste

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- Deliverable Report (D-WP.5.2.5)
- Use of Graphite Based Products for Decontamination Of Waste Streams -

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Use of Graphite Based Products for Decontamination of Waste Streams

Executive summary

This report covers the work undertaken by Necsa, in respects to the use of irradiated graphite for the decontamination of liquid and gaseous waste streams containing certain radionuclides, which include ^{14}C, ^{36}Cl, and ^{129}I.

This forms a part of Necsa's commitments to Work Package 5 under Task 5.2: Identification and Making of New Products. A more detailed summary of Necsa's work is included within the report deliverable for Task 5.2.2 – Interim report on potential new products within the nuclear industry.

This report is an updated version (April 2011) of the original deliverable completed in month 18 of the project.

The primary conclusions drawn from the work undertaken to date are:

- Irradiated graphite can be used to remove detergents used in South African nuclear installations.
- Absorption of ^{60}Co onto graphite is greatly improved with an increase in pH.
- The adsorption of ^{14}C onto graphite is minimal.
- The ^{14}C resulting from the neutron activation of nitrogen is highly mobile and therefore poses a huge contamination risk.
- i-graphite impregnated with Ag results in an increase in the absorption of ^{36}Cl.
- Fluidized bed design is the optimum design for adsorption compared to stationary columns.

Work by Necsa in this area is still ongoing, and any subsequent results to those provided within this report will be incorporated into the WP5 end of project summary report.

Revisions

Rev.	Date	Short description	Author	Internal Review	Task Leader	WP Leader
1	September 2009	Final Deliverable Report	J Goodwin	D Bradbury	W Meyer	D Bradbury
2	April 2011	Updated Report (April 11)	J Goodwin	D Bradbury	W Meyer	D Bradbury

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1 Introduction

There is very limited experience with recycling or reusing irradiated graphite to date. Conventional methods of graphite management include conversion to the gas phase and release as carbon dioxide, and direct burial in the form of packaged or encapsulated waste. Significant scientific work has been done to substantiate these alternatives, which are potentially viable methods of graphite management.

A requirement under Task 5.2, 'Identification and Making of New Products', is work to consider the use of i-graphite as an absorbent material to remove radionuclide's from both liquid and gaseous waste streams (thereby replacing expensive resins). The focus of this deliverable is to report on the work undertaken by Necsa in this area, and also to provide the results of this work. It should also be noted that the original deliverable report has been updated to encompass the most recent results of Necsa's work (upto April 2011).

2 As absorbent material to remove nuclides from liquid waste

2.1 Removal of Soap Detergents

At nuclear installations clothing decontamination is achieved with different detergents and the resulting effluent contains organic residues. In order to release this effluent to the environment, the organic contaminants must be removed. The result indicated in Figure 1 clearly demonstrates that irradiated graphite can be used to remove detergents used in South African nuclear institutions [1].

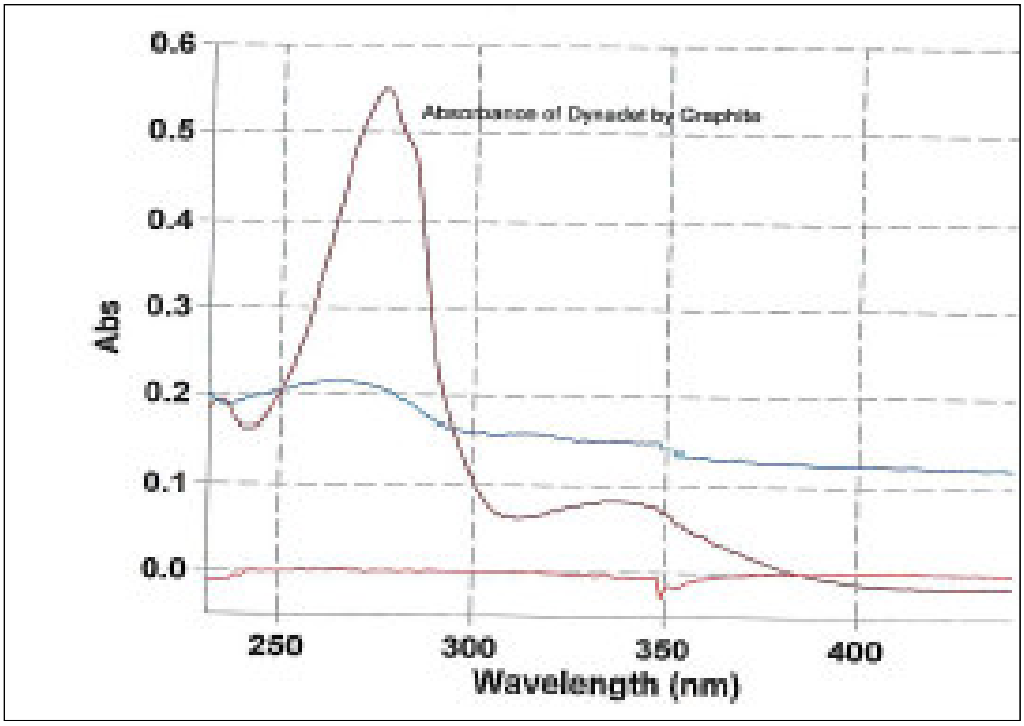

Figure 1: UV-spectra of the removal of organic detergents used in South African nuclear industries from effluent waste streams

-Brown: original waste stream with detergent

-Blue: waste stream after 1st absorption

-Red: waste stream after 2nd absorption

2.2 Removal of Radionuclides from Liquid Waste Streams

Research in the past has been focused on improving processes for the removal and recovery of radionuclide's from nuclear waste streams using ion exchange resins. Generally speaking, the expensive resin material is contaminated and has to be disposed of. By replacing the resin with irradiated graphite, contaminated material from the PBMR could be used to recover radionuclides from a PBMR waste stream. The absorption coefficient values for ^{89}Sr (50 000 ml/g), ^{110m}Ag (40 000 ml/g) and ^{131}I (8 000 ml/g) in Figures 2 and 3, illustrate that irradiated graphite can be used as an ion exchange medium [1].

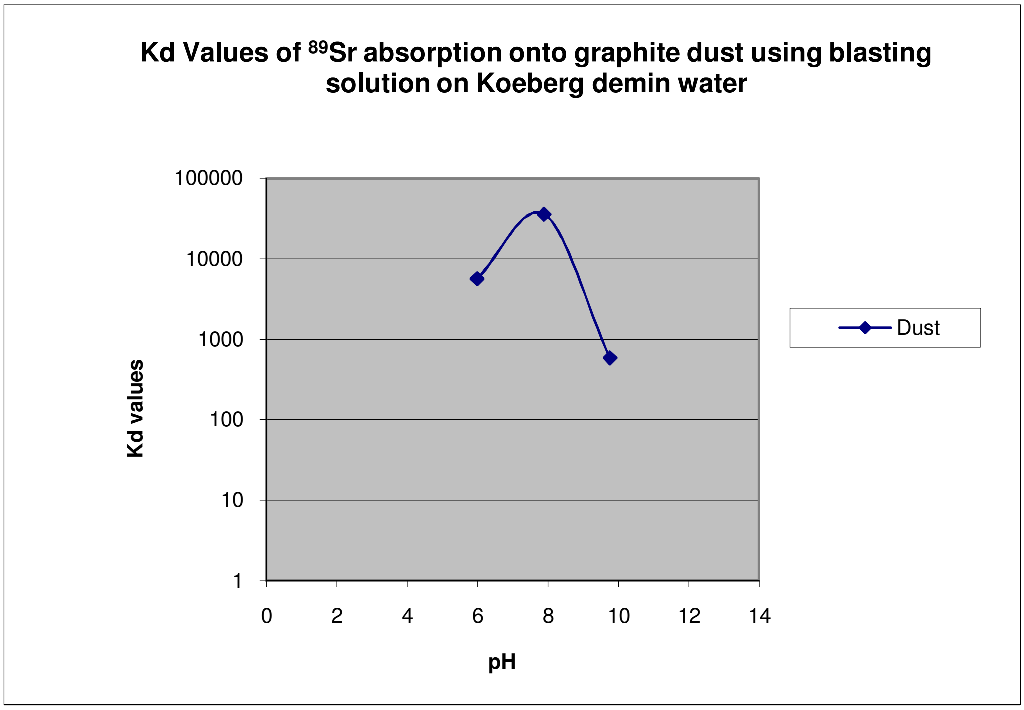

Figure 2: Removal of ^{89}Sr from a PBMR waste stream using irradiated graphite as ion exchanger material.

The absorbed ^{110m}Ag was recovered from the graphite by using an eluting solution of 1M HNO_3 and 2% H_2O_2. The results (Figure 4) indicate that more than 95% of the ^{110m}Ag was recovered after one bed volume.

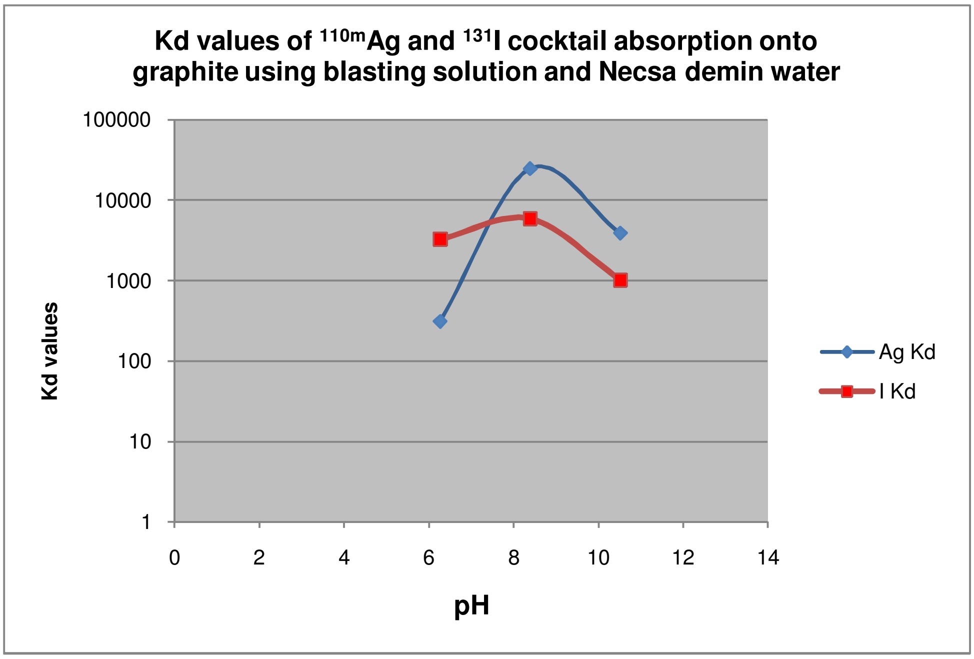

Figure 3: Removal of ^{110m}Ag and ^{131}I from a PBMR waste stream using irradiated graphite as ion exchanger material

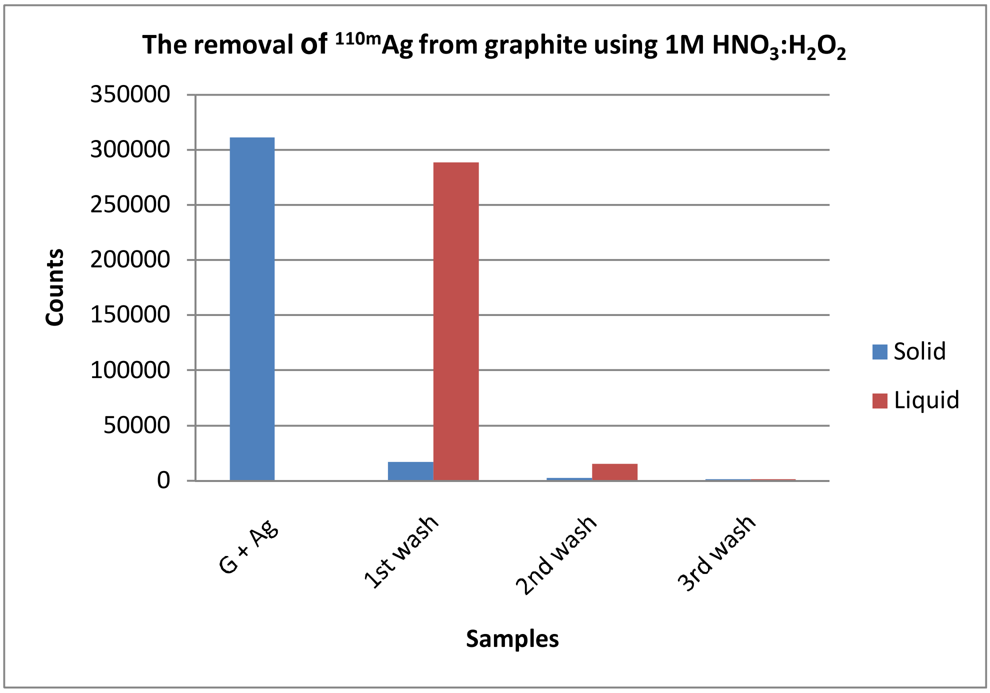

Figure 4: The removal of ^{110m}Ag from graphite using 1M HNO_3 and 2% H_2O_2

In addition, the treatment of graphite with silver nitrate was undertaken to enhance the removal of radioactive iodine from waste streams. Preliminary results of experiments to determine the absorption of ^{131}I on the carbon nanotubes were most promising. The K_d value for ^{131}I on carbon nanotubes was about 50 000 units. As the nanotubes were conditioned in an acidic $AgNO_3$ solution for 24 hours, the K_d value for ^{110m}Ag was very low, but it had a substantial effect on the K_d value for ^{131}I.

Preliminary results of experiments to determine the absorption of ^{137}Cs and ^{60}Co on graphite are promising. Results of experiments are summarised in Table 1:

Table 1: Kd values for ^{137}Cs and ^{60}Co on graphite.

Sample	**K_d**
Cs-graphite (pH<5) treated with $AgNO_3$	5.46
Cs-graphite (pH8-9) treated with $AgNO_3$	3.99
Cs-graphite (pH>12) treated with $AgNO_3$	1.17
Cs-graphite (pH<5)	0.24
Cs-graphite (pH8-9)	0.54
Cs-graphite (pH>12)	10.19
Co-graphite (pH<5) treated with $AgNO_3$	4.2
Co-graphite (pH8-9) treated with $AgNO_3$	153.0
Co-graphite (pH>12) treated with $AgNO_3$	631.2

The results showed that ^{137}Cs could not be absorbed onto graphite, but ^{60}Co is absorbed at higher pH [1].

More recent work by Necsa [3] has provided additional results; this deliverable report has been updated to accommodate this work which is reported below.

The considerable amount and number of long-life radioisotopes (e.g. radiocarbon (^{14}C), chlorine (^{36}Cl), iodine (^{129}I), technetium (^{99}Tc), selenium (^{79}Se), caesium (^{135}Cs) etc.) are present in irradiated graphite, due to neutron activation. In order to determine the physical adsorption properties of radiocarbon (^{14}C) onto graphite (important in order to develop a mechanistic model for impurity removal), experiments were performed to study the adsorption of ^{14}C from a liquid waste stream onto irradiated graphite.

The result in Table 2 indicates that the adsorption of ^{14}C onto graphite is minimal and leaching, therefore, poses a huge contamination risk.

Table 2: Results of ^{14}C adsorption (on i-graphite)

	Sample	K_d
1.	^{14}C in demin water	3.7
2.	^{14}C in demin water	0
3.	^{14}C in HNO_3	-20
4.	^{14}C in NaOH	0

The negative value in experiment 3 indicates that the final concentration of ^{14}C in the effluent was substantially higher than the starting concentration of ^{14}C in the effluent after the experiment, indicating the additional release of ^{14}C from the irradiated graphite specimen. To confirm this hypothesis, another experiment was conducted with 1M HNO3 without any ^{14}C and, after 24 hours of contact time, the solution contained ^{14}C, indicating that ^{14}C leached from the i-graphite.

The results indicate that the ^{14}C resulting from the neutron activation of nitrogen is highly mobile and poses a contamination risk.

Experiments were performed to study the adsorption of different radionuclides (^{60}Co, ^{36}Cl, ^{131}I and ^{22}Na) from a liquid waste stream (acid and alkaline) onto irradiated graphite. The result in Table 3 indicated that only ^{60}Co in an alkaline medium will be absorbed onto i-graphite. When the i-graphite is impregnated with Ag, the absorption of ^{36}Cl in acid solution increased.

Table 3: Adsorption of different radionuclides onto irradiated graphite

Sample	**K_d**
i-graphite + ^{60}Co in 0.25M NaOH	3079.3
i-graphite + ^{60}Co in 4M HNO_3	58
i-graphite + ^{36}Cl in 1M NaOH	0.53
i-graphite + ^{36}Cl in 4M HNO_3	3.6
Ag impregnated i-graphite + ^{36}Cl in 1M NaOH	1.3
Ag impregnated i-graphite + ^{36}Cl in 1M HNO_3	469.6
i-graphite + ^{131}I pH 3	4.455
i-graphite + ^{131}I pH 3	4.942
i-graphite + ^{131}I pH 10	0.666
i-graphite + ^{131}I pH 10	0.371
i-graphite + ^{22}Na 1M NaOH	4.0
i-graphite + ^{22}Na 1M NaOH	0.1
i-graphite + ^{22}Na 4M HNO_3	0
i-graphite + ^{22}Na 4M HNO_3	0

3 As absorbent to remove nuclides from gaseous waste streams

3.1 Experimental Set-up

In order to determine the possibility of using irradiated graphite to remove radionuclides from gaseous waste streams, an experimental setup was designed. The requirements of the research equipment required included [2]:

- High vacuum generation + measurement
- Mobile
- Sub-system for desorbing (gaseous) adsorbed species on PTFE filter pieces; max temperature 500^{O}C; desorbed species detected by FTIR.
- Sub-system for determining the absorptive capacity of graphite's towards a number of gases (I_2, CO_2, CO, NO_x, etc) at ambient temperature.

The system used for this work consisted of the following:

- Vacuum system: fore-vac pump, turbo molecular pump + backing pump, liquid nitrogen trap, trolley.
- Vacuum manifold + vacuum and pressure gauges.
- Liquid nitrogen freeze-out container + liquid nitrogen dewar.
- PTFE filter desorption vessel + heating mantle and temp control. An inert gas flush probe is included to facilitate transfer of the desorbed species to the FTIR gas cell. The vessel is connected to a standard 10cm FTIR gas cell. Only IR active species can be detected. The gas cell is connected to the freeze-out vessel.
- Gas supply, flow control and mixing manifold. At least four supply lines, each with mass flow controller, power supply and readout unit, and isolation valves. This system allows accurate mixing and flow control of a test gas with a carrier gas.
- Test vessel for determining the absorptive capacity of graphite towards specified gases. Graphite is contained in a removable canister with screw thread for fixing it vacuum tight to the test vessel. The outlet of the vessel is connected to the FTIR gas cell. The test gas mixture, with known concentration and flow rate, flows through the graphite

canister. The test gas is absorbed by the graphite until it reached saturation. The test gas is then detected by the FTIR. The test gas concentration, flow rate, and flow time to saturation allows the calculation of the test gas absorptivity per mass unit graphite.

3.2 Objectives & Results of the Work

The objective of this work was to investigate the rate of mass transfer of CO_2 with respect to interior design and the quality of activated carbon. If the process is successful, it will used to investigate mass transfer of Iodine and Tritium (radioactive).

Results in Figure 5 indicated that a fluidized bed design is the optimum design for adsorption compared to stationary columns. During fluidization the activated carbon particles mix with each other (laminar layer that is formed around the particle is always disturb and mixing disturbs the concentration gradient, thus enhancing the rate of mass transfer). In the stationary column the air flow will channel through the path with less resistance (less force per area) and therefore some of the air flow will was not exposed to the activated carbon particles resulting in a decrease in absorption rate.

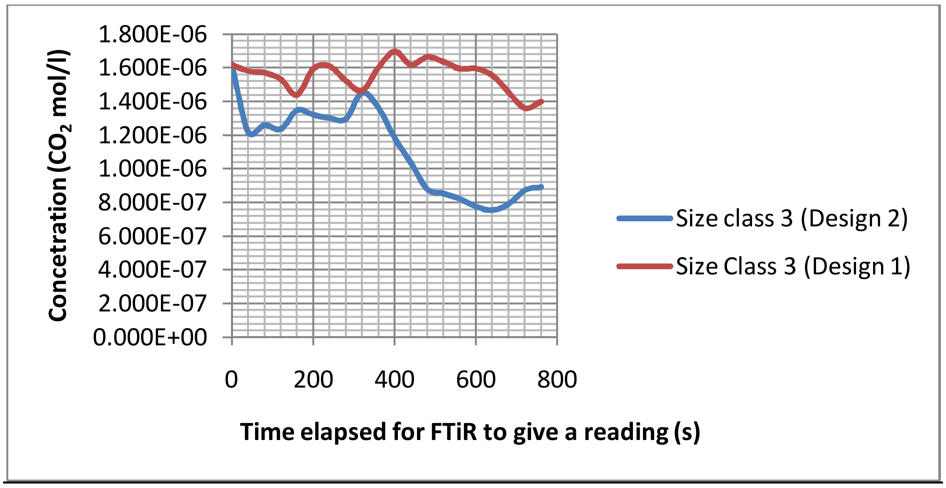

Figure 5: **Relationship of Carbon dioxide absorption on different designs**
-Design 1: Stationary columns
-Design 2: Fluidized bed

4 Conclusions

The primary conclusions drawn from the work undertaken to date are:

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- Fluidized bed design is the optimum design for adsorption compared to stationary columns.

Necsa are continuing with their work in this area, and it is hoped that additional results will be available for the end of project deliverable due in week 45 of the Carbowaste project.

5 References

[1] Meyer. W.C.M.H. Necsa report "Progress report on the Carbowaste Programme for 2008/2009

[2] Meyer. W.C.M.H. Necsa ¼ Carbowaste Project Report, Doc No: NWR-CAWGEN-REP-09001. Dated June 2009.

[3] Meyer. W.C.M.H. Necsa Work Package 5 Progress Report for 2010/2011. Issued 01 April 2011.

9 Glossary

FTIR	Fourier transform infrared spectroscopy
Kd	Adsorption
PBMR	Pebble Bed Modular Reactor (Pty) Limited
PTFE	Polytetrafluoroethylene
UV	Ultraviolet