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Industrial assessment of methods in WP4

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Document title

Industrial assessment of methods in WP4

Executive summary

The CARBOWASTE WP4 deals with treatment and purification issues for irradiated graphite (i-graphite). In the frame of task 4.3, the present document provides an industrial assessment of the techniques studied during the project in this Work-Package.

The techniques of graphite decontamination studied in the WP4 can be roughly separated into three groups:

- Physical Treatments
- Chemical Treatments
- Microbiological Treatments

None of those processes has succeeded on removing a large part of ^{14}C without mass loss. In an industrial point of view, decontamination techniques have to be improved to raise the ^{14}C decontamination factor.

As a conclusion of the WP4, it seems that a whole transformation of the i-graphite is necessary to remove ^{14}C from solid matrix.

Revisions

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1 Introduction

Graphite has been used as a moderator and reflector of neutrons in more than 100 nuclear reactors across Asia, Europe and North America. During irradiation in a nuclear reactor, graphite becomes radioactive due to the neutron activation of impurities.

Decommissioning of the reactors necessarily involves dismantling of irradiated graphite core components and management of this material as radioactive graphite waste. The worldwide inventory of irradiated graphite from these reactors is more than 230,000 metric tons [1].

The CARBOWASTE research project of the European Commission's Framework 7 aims to develop strategy and methods for irradiated graphite waste management for existing and future materials.

The CARBOWASTE WP4 deals with treatment and purification issues for irradiated graphite (i-graphite). In the frame of task 4.3, the present document provides an industrial assessment of the techniques studied during the project in this Work-Package.

The goal of theses techniques is to decrease the contents of radionuclides before the disposal of the waste. From these waste, the beta emitting ^{14}C ($t_{1/2}$ = 5,730 years), ^{3}H ($t_{1/2}$ = 12.32 years) and ^{36}Cl ($t_{1/2}$ = 301,000 years) isotopes are considered to represent the most likely contaminates to the food chain. This document deals exclusively with their treatment.

Tritium and ^{36}Cl can be removed from the waste in the same time than other isotopes of hydrogen or chlorine: the whole amounts of hydrogen or chlorine in i-graphite are low enough.

The ^{14}C case is different: ^{12}C is the main component of the i-graphite and a $^{12}C/^{14}C$ selective treatment is necessary to remove ^{14}C by keeping the mechanical cohesion of the waste. Selective treatments are possible due to the fact that most of the ^{14}C does not appear to be integrated into the graphite crystal structure but only bound on the surface of crystallites and pores.

The techniques of graphite decontamination studied in the WP4 can be roughly separated into three groups:

- Physical Treatments
- Chemical Treatments

- Microbiological Treatments

All of these processes have been analysed in an industrial point of view.

Treatment by graphite burning (incineration) was not involved in the CARBOWASTE project.

2 Technical results from WP4

2.1 Physical treatment

2.1.1 Thermal treatment

Thermal treatments of i-graphite consist in heating samples in a hot (up to 2000°C) inert atmosphere. Several tests performed before CARBOWASTE have shown that tritium and a part of the ^{14}C can be removed from the graphite.

CARBOWASTE tests were essentially performed by Forchungszentrum Jülich (FZJ) [2]. Different sources of i-graphite have been characterised:

- from the FZJ Merlin reactor (light-water-moderated reactor with a thermal column in graphite, Germany);
- from the Saint-Laurent A2 reactor (UNGG, France);
- from the Olbury 2 reactor (Magnox, UK).

The specific activities of the samples are different from one source to another.

The results of the tests are summarised in table 1.

The decontamination factor of ^{14}C is very low, whatever the test conditions were.

2.1.2 Laser ablation

The laser ablation of graphite was studied by Nesca, from South-Africa [3].

The tests consisted in burning graphite by a Nd:YAG laser system. All the tests were performed on non-irradiated graphite.

This method can be useful in case of a very local contamination of the graphite, at the surface of the components.

2.2 Chemical treatment

2.2.1 Steam reforming

The steam reforming treatment consists in reacting water steam on i-graphite in order to oxidising carbon by the following reactions:

$$C + H_2O \leftrightarrow CO + H_2 \text{ as the first step;}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2,\ C + 2\ H_2 \leftrightarrow CH_4 \text{ and } 2\ CO \leftrightarrow C + CO_2 \text{ as secondary reactions.}$$

The process has to be controlled in order to limit the oxidation to the surface. The total mass loss of the samples after the tests was lower than 10 %. Tritium is also released during the treatment.

In the CARBOWASTE project, the steam reforming tests have been performed by FZJ [4].

After several tests in virgin graphite, the experimental parameters have been fixed as follow:

- Temperature: 1000°C
- Atmosphere: Ar + H_2O
- Absolute humidity: 10 g/kg (corresponding of a partial pressure of 1,600 Pa)
- Gas flow: 1.5 L/h for samples of about 0.6-1 g
- Treatment time: 4-10 hours

Decontamination factors are presented in table 1, in comparison with thermal treatment results.

The decontamination factors for ^{14}C are very low, even if they are better than results obtained by thermal treatment (§ 2.1.1).

2.2.2 Treatment with oxygen

This treatment consists on adding a small amount of oxygen in the atmosphere during a thermal treatment as described in § 2.1.1. Oxygen oxidises the graphite matrix and allows improving the content of released ^{14}C and ^{3}H. First tries before CARBOWASTE had shown that the quantity of released radionuclides can be higher in proportion than total mass loss (due to oxidation).

In the CARBOWASTE project, the studies concerning treatment with oxygen have been performed by the University of Manchester and FZH [5].

Conclusions of those studies are:

- Thermal treatment experiments of i-graphite under gaseous conditions ranging from 0.1 to 1% oxygen have been performed on i-graphite.
- Decontamination factors of 1.15-1.20 for ^{14}C have been obtained from Merlin samples (14 - 20 % of the initial ^{14}C was released).
- Using test temperature of 1300°C, more than 90% tritium from Merlin graphite (decontamination factor: 30.4 and 15.4) and about 60% of tritium from Saint Laurent 2 graphite (decontamination factor: 2.85) was removed.

2.2.3 Leaching

The goal of leaching methods is to decontaminate graphite waste by removing the surface layer of the graphite (including pore walls) which may contain the majority of the bulk activity. This removal is performed by chemical dissolution.

In the CARBOWASTE project, the leaching studies have been mainly performed by the University of Manchester [6].

The leaching conditions were the following:

- Sample type: Solid and powder
- Volume: 10:1 leachant:sample ratio
- Temperature: 20-25°C, constant
- External environment: air condition
- Chemical agent
  - Water (H_2O)
  - Potassium Bromate (KBr): 0.1M, 0.2M, 0.3M, 0.4M, 0.5M
  - Hydrogen Peroxide (H_2O_2): 0.5M, 1M, 1.5M, 2M
  - Sulfuric acid (H_2SO_4): 0.1M
  - Hydrochloric acid (HCl): 1M
  - Phosphoric acid (H_3PO_4): 1M

Only the removals of ^{3}H and ^{14}C have been characterised. Conclusions of those studies are:

- The acidic environment yielded the highest release activities for both of ^{3}H and ^{14}C removal.
- The separate mechanisms for ^{3}H and ^{14}C have been proposed though several difference conditions and this difference in ^{3}H and ^{14}C interaction has been exploited.

- ^{14}C seems to be present in two separate forms i.e. leachable and non-leachable, the presence of two forms of ^{14}C provides insight in the mechanism of formation and the behaviour under continued irradiation.
- Hydrogen ion isotopic exchange is thought to be the mechanism behind ^{3}H release.
- Intercalation with penetration of interlayer spaces within the graphite structure is thought to be the mechanism behind ^{14}C removal.
- Throughout all leaching experiment no change in pH was observed.
- The weight loss of the samples after chemical leaching averaged 12% making the intercalation mechanism a preferred conclusion as a significant weight loss of the sample was not observed in material that had high acidic percentages of ^{14}C leached out.
- Steady state of release was achieved under all conditions by day 90, after this point very limited amounts of both ^{3}H and ^{14}C were released.

2.3 Bacteriological treatment

Some tests of contamination have been performed by microbiological treatment. In the CARBOWASTE project, those studies have been performed by PBMR and the University of Pretoria [7] [8].

Tests have been performed with non-irradiated graphite and with graphite with implemented ^{14}C. This last graphite was not a real i-graphite from reactor.

It has been found bacteria and conditions on which a part of the initial carbon is consumed on bacteria and gas. Tries with implemented ^{14}C have shown the resistance of the bacteria in such an environment.

However, new tries have to be performed in order to determine the capability of the process in contamination of real i-graphite.

3 Industrial issues

3.1 Different kinds of i-graphite

The origin of the i-graphite is a first importance parameter on the efficiency of the decontamination treatment. It was well shown with the physical treatments for example where results with Merlin samples are different from results with Magnox samples.

So there is no panacea in the processes performed and characterised in the CARBOWASTE WP4.

So that, a very good characterisation of the structure of the i-graphite, associated with a good knowledge of the history of the graphite (location in reactor, fluency, temperature, cycles…) are necessary to choose and develop the best process for decontamination.

For example, in case of a localisation of the radionuclides in the near surface, process as thermal treatment (with a small amount of oxygen) or by laser ablation could be efficient.

For i-graphite with a deeper presence of radioisotopes, with a stronger bounding on the graphite, these processes will not be efficient.

3.2 National legislation

On top of theses differences on i-graphites, legislations on storage of irradiated waste are not the same from one country to another.

For example the case of ^{36}Cl is not treated by the same way in the different countries.

The rules concerning radioactive rejects (^{14}C and ^{3}H in the atmosphere for example) are not the same.

So that, one process can be more compatible with one national legislation than another one.

3.3 Effluents and rejects

A majority of the processes tested during CARBOWASTE leads to a production of a large quantity of liquid effluent, which can be very difficult and expensive to manage.

Thermal treatment and steam reforming processes do not produce liquid effluent, but their capability on decontamination of i-graphite on ^{14}C are quite low; a large part of the initial radioelement remains on i-graphite after treatment.

In order to remove the remaining ^{14}C, it seems that a whole transformation of the i-graphite (such as incineration) is necessary.

4 Conclusions

The CARBOWASTE WP4 deals with treatment and purification issues for irradiated graphite (i-graphite). The goal of theses techniques is to decrease the contents of radionuclides before the disposal of the waste.

During CARBOWASTE, different techniques have been studied in the WP4:

- Thermal Treatments
- Laser Ablation
- Steam Reforming
- Treatment with oxygen
- Leaching
- Microbiological Treatments

None of those processes has succeeded on removing a large part of ^{14}C without mass loss. In an industrial point of view, decontamination techniques have to be improved to raise the ^{14}C decontamination factor.

As a conclusion of the WP4, it seems that a whole transformation of the i-graphite (such as incineration) is necessary to remove a large part of ^{14}C from solid state.

5 Table

Table 1: Results of thermal treatment and Steam reforming tests

Exp. No.	Sample	Irradiation conditions		Experimental conditions				Mass loss [%]	Release [%]						Decontamination factor[4]	
		Cool. gas	T [°C]	Treat. gas	T [°C]	Treatment time [h] Heating	Treatment time [h] Isothermal		HTO	HT	^{3}H total	$^{14}CO_2$	^{14}CO	^{14}C total	^{3}H	^{14}C
V4	Merlin	Air	RT	N_2 + 0.14% O_2[1]	1300	0	10	0.89	85.9	7.7	93.6	3.4	2.5	5.9	15.4	1.05
V5	Merlin	Air	RT	N_2 + 1% O_2	900	3	2.5	6.64	10.1	0.2	10.3	8.6	3.3	11.9	1.04	1.06
V6	Merlin	Air	RT	N_2 + 1% O_2	700	2.5	7.75	7.22	26.5	0.2	26.7	14.5	7.3	21.8	1.26	1.19
V7	SLA2 9260	CO_2	258.5	N_2 + 0.14% O_2[1]	1300	0	10.5	0.91	65.0	0.2	65.2	1.4	0.6	2.0	2.85	1.01
V8	Merlin	Air	RT	N_2 + x% O_2[2]	1300	0	21	5.12	65.6	31.3	96.9	2.5	8.2	10.7	30.4	1.06
V9	Merlin	Air	RT	Pure N_2	1100	3.75	20	0.20	4.6	56.3	60.9	0.12	2.0	2.1	2.55	1.02
V10	Merlin	Air	RT	Pure N_2	1100	3.75	25.5	0.01	1.2	0.09	1.3	1.5	1.3	2.8	1.01	1.03
V11	Merlin	Air	RT	Pure N_2	1100	3.75	20.5	0.16	15.2	21.1	36.3	0.6	1.4	2.1	1.57	1.02
V12	SLA2 9260	CO_2	258.5	Pure N_2	1100	3.75	20.5	0.45	13.3	7.3	20.6	0.4	2.0	2.4	1.25	1.02
V13	Magnox	CO_2	270	Pure N_2	1100	3.75	11	0.14	1.8	0.8	2.6	0.5	1.9	2.4	1.02	1.02
V14	Merlin	Air	RT	N_2 + 0.1% O_2[3]	750	2.5	5	0.22	1.1	0.1	1.2	0.8	0.4	1.2	1.01	1.01
V15	Magnox	CO_2	270	N_2 + 0.1% O_2[3]	900	3	5	0.70	2.9	0.3	3.2	61.7	38.3	100,0		
V16	Magnox	CO_2	270	N_2 + 0.3% O_2[3]	900	3	5	3.90	4.8	0.05	4.9	3.1	1.5	4.6		
V17	Merlin	Air	RT	N_2 + 0.3% O_2[3]	900	3	5	1.62	30.0	0.07	30.1	9.9	4.1	14.0	1.41	1.14
V18	Merlin	Air	RT	N_2 + 0.3% O_2[3]	900	3	5	2.72	33.0	0.4	33.4	4.7	0.9	5.6	1.46	1.03
V19	SLA2 9260	CO_2	258.5	N_2 + 0.3% O_2[3]	900	3	5	2.43	2.8	0.02	2.8	2.1	0.5	2.6		
Merlin-1	Merlin	Air	RT	Ar + steam (1.6 kPa)	1000	3.25	4	1.58	58.0	15.4	73.4	12.1	8.0	20.1	3.69	1.23
Merlin-2	Merlin	Air	RT	Ar + steam (1.6 kPa)	1000	3.25	10	3.64	74.7	18.2	92.9	16.3	12.7	29.0	13.4	1.36
FH1	SLA2 5120	CO_2	391.5	Ar	1000		40	0.70			29.4			2.4		

RT = Room temperature
Red values: Determined by assuming an averaged initial radionuclide content

[1] Ceramic tube with measured ingress of O_2
[2] New ceramic tube, unknown ingress of O_2
[3] Quartz tube with defined amount of O_2 in the treatment gas
[4] The ratio of initial specific radioactivity to final specific radioactivity resulting from a separation process [McGraw-Hill: Dictionary of Scientific and Technical Terms]. 1000 and above is excellent; 10 and below is poor [Hutchinson encyclopaedia].

6 References

[1] IAEA TECDOC 1521 "Characterization, Treatment and Conditioning of Radioactive Graphite from Decommissioning of Nuclear Reactors" – September 2006

[2] CARBOWASTE – Technical Report T-4.4.1 "Preliminary Report on 14C Reduction in Graphite and Spent Fuel Matrix (Bench Scale)" – T. Podruzhina, K. Baginski, D. Vulpius, W. von Lensa – June 2010

[3] CARBOWASTE - Deliverable D-4.3.10 "Decontamination by Means of LASER Ablation" – M. Lombaard – March 2012

[4] CARBOWASTE – Deliverable D-4.3.4 "Decontamination Factors by Steam Reforming" – B. Kraus – January 2013

[5] CARBOWASTE - Deliverable D-4.3.6 "Decontamination Factors by treatment with oxygen" – L. McDermott, G. Black, R. Worth, W. Bodel, K. Baginski, D. Vulpius – February 2013

[6] CARBOWASTE - Deliverable T-4.3.3-b "Characterisation and Chemical Treatment of Irradiated UK Graphite Waste" – L. McDermott – December 2011

[7] CARBOWASTE - Deliverable D-4.4.2 "Radiocarbon Reduction in Graphite by Microbiological Treatment" – M.L. Dunzik-Gougar, P. Williams, I. Mafishane and G. Ashy Pete – March 2012