EUROPEAN COMMISSION

Community Research

SEVENTH FRAMEWORK PROGRAMME

CARBOWASTE

Treatment and Disposal of Irradiated Graphite and Other Carbonaceous Waste

Grant Agreement Number: FP7-211333

Deliverable D-4.3.1

Basic investigation of graphite decontamination by TG-MS

Author(s):
Frank Druyts, Wim Verwimp, Steven Smets

SCK•CEN

Document Number: CARBOWASTE-D-1303-4.3.1
Date of issue of this report : 31/03/2013

Start date of project : **01/04/2008** Duration : **48 Months**

Project co-funded by the European Commission under the Seventh Framework Programme (2007 to 2011) of the European Atomic Energy Community (EURATOM) for nuclear research and training activities		
Dissemination Level		
PU	Public	
RE	Restricted to the partners of the CARBOWASTE project	
CO	Confidential, only for specific distribution list defined on this document	**X**

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Work package: 4 **Task: :** 4.2	**CARBOWASTE document no:** CARBOWASTE-1303-D-4.3.1 (e.g. May 2008 as date of issue: 0805)	**Document type:** D=Deliverable
Issued by: SCK•CEN (BE) **Internal no.:** CW1303-D-4-3-1		**Document status:** Final

Document title

Basic investigation of graphite decontamination by TG-MS
Final Report

Executive summary

This report describes the contribution of SCK•CEN to WP4 of CARBOWASTE. The main goal of our work is to investigate the efficiency of i-graphite decontamination by exposing the i-graphite to various gases and gas mixtures at elevated temperatures. In particular, we examine the removal of ^{14}C by thermogravimetric analysis. This final report gives an overview of our results obtained in nitrogen and argon. From our results it appears that it is extremely difficult to obtain a truly inert atmosphere, even with 99.9999% argon, in order to establish a baseline for experiments with an oxygen load. Therefore, it was concluded that extreme caution has to be taken when using TG-MS as a research tool for the decontamination of i-graphite. Additional testing was done on unirradiated graphite powder with three different TG systems in order to evaluate the sources of oxygen contamination in the systems. The report concludes with recommendations on how to perform future TG experiments.

Revisions

Rev.	Date	Short description	Author	Internal Review	Task Leader	WP Leader
00	dd/mm/yyyy	Issue	Name, Organisation	Name, Organisation *Signature*	Name, Organisation *Signature*	Name, Organisation *Signature*
01	05/04/2013	First issue	Druyts SCK	Van Hecke SCK	Vulpius FZJ	von Lensa FZJ
02	dd/mm/yyyy	2nd Issue				

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1. Introduction

This report describes the status of the contribution of SCK•CEN to WP4 of the CARBOWASTE project. CARBOWASTE was launched in April 2008 under the 7th EURATOM Framework Programme. Its objective is the development of best practices in the retrieval, treatment and disposal of irradiated graphite (i-graphite). It adresses both existing legacy waste as well as waste from graphite-base nuclear fuel resulting from a new generation of nuclear reactors (e.g. Very/High-Temperature Reactors (V/HTR). A major concern is the presence of ^{14}C in i-graphite. This radiocarbon has to be safely isolated from the biosphere due to its biocompatibility. It is specifically the purpose of WP4 of CARBOWASTE to identify suitable treatments for carbonaceous waste, aiming in particular at removal of ^{14}C. The contribution of SCK•CEN to WP4 consists in investigation whether heating i-graphite up to 1000°C in various gases and gas mixtures, including a.o. steam, can be effective in removing ^{14}C. This final report describes the steps we have taken to perform reliable experiments in high-purity argon to obtain a baseline for the measurements with argon/oxygen and argon/steam mixtures. Baselines were determined with three TGA systems in two different institutes.

2. Industrial Purification of Nuclear Graphite

The purpose of the tests is to investigate the decontamination efficiency of exposing irradiated graphite to various gas mixtures at elevated temperatures. The chosen technique for our experiments was coupled TGA-MS. It turned out however, during preliminary tests, that the ^{14}C threshold of the quadrupole mass spectrometer (QMS) was too high in comparison with the ^{14}C levels expected to be released by the irradiated graphite. Therefore, in the course of the project, it was decided to change ^{14}C detection from online QMS to a batch technique involving sampling of the off-gas and liquid scintillation counting.

In this section, we describe the technical details of the experiments. First, we describe the samples that were received from FZ Jülich. Then, we give a description of the experimental techniques that were used for the investigation of decontamination efficiency. Lastly, we put forward the experimental matrix.

2.1. Investigated graphite samples

A powder sample weighing approximately 10 g was received from Dr. Dirk Vulpius. The sample's origin is the thermal column of the MERLIN materials testing reactor at FZJ. The reported activity data are as follows:

Date		2008-08-01	2010-02-01	
			1,503	a
	half time / a	Bq/g	Bq/g	Bq
H-3	12,33	3,5E+03	3,2E+03	3,2E+04
C-14	5730	3,8E+02	3,8E+02	3,8E+03
Fe-55	2,73	1,1E+02	7,5E+01	7,5E+02
Co-60	5,271	4,2E+00	3,4E+00	3,4E+01
Ba-133	10,54	1,1E+01	1,0E+01	1,0E+02
Eu-152	13,3	5,0E+02	4,6E+02	4,6E+03
Eu-154	8,8	1,4E+01	1,2E+01	1,2E+02
Total				4,2E+04

For each test, we used a sample weight of approximately 200 mg.

2.2. Experimental techniques

The determination of the decontamination efficiency relies on heating the irradiated graphite samples in a furnace under a gas stream and measuring the C-14 content of the off gas. The furnace is equipped with a thermobalance, thus it is possible to follow the mass loss of the sample online. Our equipment comprises also a physisorption analyser, which allows to measure the specific surface area of the graphite samples.

2.2.1 Measurement of the specific surface area

We installed a Micromeritics Tristar II 3020 ga sorption analyser. This system allows to measure the specific surface area of nuclear materials, with the multipoint BET (Brunauer-Emmett-Teller) method. In this method, the weight of gas (in our case nitrogen) adsorbed by the investigated material as a function of relative pressure is plotted using the BET equation:

$$\frac{1}{W\left[\frac{P_0}{P}-1\right]} = \frac{1}{W_m C} + \frac{C-1}{W_m C}\left(\frac{P}{P_0}\right) \qquad (1)$$

Where W = weight of adsorbed gas [g]
W_m = weight of a monolayer of adsorbed gas covering the whole surface [g]
P/P_0 = relative pressure
C = the BET constant, related to the adsorption energy

From the slope and intercept of the BET plot, the weight W_m of a monolayer of adsorbed nitrogen gas can readily be determined. If the molecular cross-section of the adsorbate molecule is known, the total surface area of the sample can be calculated using:

$$S_t = \frac{W_m N A_{cs}}{M} \quad (2)$$

Where S_t = total surface area of the sample [m²]
N = Avogadro's number [6.023 10^{23} mol^{-1}]
A_{cs} = cross-sectional area of the adsorbate molecule [m²]
M = molecular weight of the adsorbate [$g.mol^{-1}$]

Finally, the specific surface area of the material can be calculated from the total surface area S_t and the sample weight w:

$$S = \frac{S_t}{W} \quad (3)$$

Where S = specific surface area [$m^2.g^{-1}$]

Figure 1 shows the experimental facility.

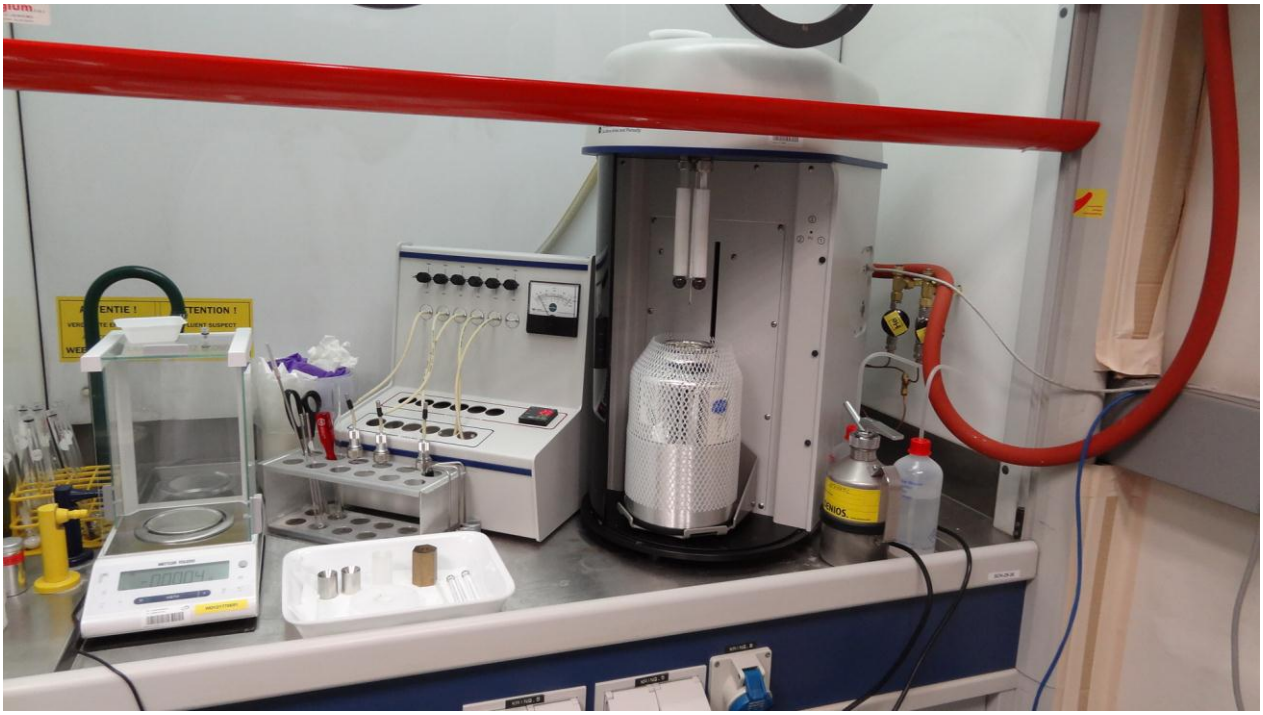

Figure 1. BET equipment for the measurement of the specific surface area of irradiated graphite.

2.2.2 Coupled TGA-MS

The coupled TG-MS equipment consists of three parts: (i) steam generator, (ii) TG/DTA, (iii) QMS. The experimental facility is incorporated in two coupled airtight glove boxes, in order to allow working with radioactive and toxic samples.

(i) Steam generator

The steam generating equipment is designed to deliver up to 2 g/h of water and 200 ml/min of argon to the TG/DTA furnace. The system consists of:

- A liquid mass flow meter capable of delivering water mass flow rates between 0.1 and 2 g/h H_2O
- A gas mass flow meter capable of delivering argon mass flow rates between 4 and 200 ml/min Ar
- A mixing chamber where water and argon are mixed at 200°C, resulting in total evaporation of the water

(ii) TG/DTA

The center part of the equipment is formed by the TG/DTA system. For the tests, the graphite samples, consisting of a powder, were placed in a cylindrical alumina crucible. We used sample weights of approximately 200 mg. The samples were heated in a tubular furnace with an internal diameter of 20 mm and a height of 300 mm, heated by metallic resistors. The furnace temperature was measured with a Pt/Pt 10% Rh type S thermocouple. The temperature programme of the TG/DTA system allows to heat, cool, or work isothermally in the temperature range of ambient up to 1200°C. After introducing the sample, the furnace was heated at a rate of 50°C/min from 20°C tot 110°C. The furnace temperature was held at 110°C for three hours in order to determine the amount of water vapour present in the sample. Then, the temperature was raised again at a rate of 50°C/min from 110°C to 900°C. The furnace remains at this temperature for seven hours. After this isotherm, the furnace is cooled to 110°C at a rate of 50°C/min and held at 110°C for three hours in order to check the total weight loss of the sample.

The accuracy of the furnace temperature is periodically checked by measuring the melting point of pure certified reference material with DTA and comparing the measured value with the real melting point. From these checks we can conclude that the uncertainty on the furnace temperature (in K) is less than one percent. During the isothermal part of the experiments, deviations from the setpoint temperature are typically less than 1°C peak-to-peak. Zero line tests with an empty crucible under reference conditions (500°C, air flow) yielded a peak-to-peak noise of approximately 2-5 µg for the microbalance.

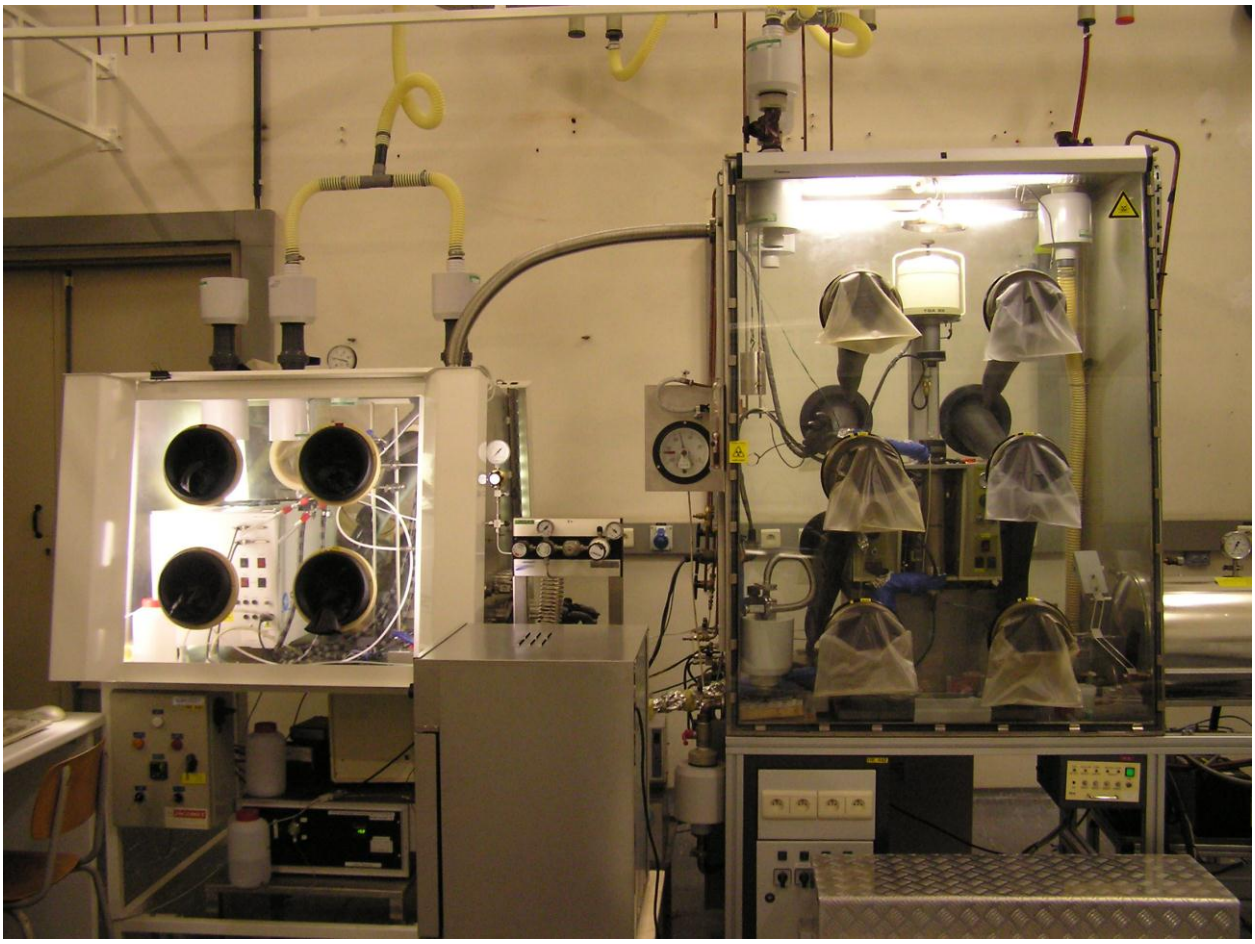

Figure 2. Overview of the airtight glove boxes with the TG/DTA furnace (right glove box) and quadrupole mass spectrometer (left glove box).

(iii) Mass spectrometry

The initial purpose of the experimental setup was to measure the ^{14}C production online during heating of the samples. For this, a quadrupole mass spectrometer coupled to the exit of the TG/DTA was available. But there are some problems that hamper the application of mass spectrometry to online detection of ^{14}C:

- The natural isotope contribution of ^{14}C is 10^{-13}
- The detection limit of the QMS is approximately 1 ppm
- The ^{14}C mass spectrometry peak would see interference by ^{13}C and ^{14}N
- The graphite we dispose of is in powder form. Therefore, it will be difficult to guarantee a plug flow which is needed to obtain correct time-dependent information with the QMS.

Therefore, we decided to abandon on-line ^{14}C measurements and to apply off-gas capturing and total ^{14}C measurements.

2.2.3 ^{14}C measurements

For the ^{14}C measurements two possible pathways were considered:

(i) Absorption of CO_2 in CarboSorb, followed by liquid scintillation counting
(ii) Capturing of CO_2 in a liquid sorbent, followed by mass spectrometry

Either technique offers the advantage of combining the versatility of the steam generator and thermal analysis equipment with high precision ^{14}C measurements.

2.3 Experimental matrix and planning

It was decided, in agreement with the WP4 leader, to apply four different gases or gas mixtures to the i-graphite powder:

1. Argon as inert gas
2. Argon with 2 % oxygen
3. Argon with water steam
4. 100 % carbon dioxide (to study the Boudouard equilibrium)

The investigated temperature range is 600-1000°C.

3. Experimental results

3.1. BET measurements

BET measurements were used to determine the specific surface area of Merlin powder. To this purpose two different batches of powder were used (CW1 and CW2) with weights of 0.3957 g and 0.4793 g respectively. On each batch, three separate measurements were performed. The results are shown in Table 1. This yields an average specific surface area of 4.9 m²/g.

Table 1. Specific surface area for two different batches of Merlin i-graphite powder.

Batch number	Measurement number	Specific surface area (m²/g)
CW1	1	5.1617
CW1	2	4.6596
CW1	3	4.6744
CW2	1	5.3049
CW2	2	5.1067
CW2	3	4.6744

3.2 TGA measurements

Tests were performed in 99.9999% pure argon. An overview of all the obtained results is given in Annex 1. In this section, we will limit ourselves to a description of typical results.
Prior to each test, a blank test was performed to obtain a baseline to subtract from the actual measurement. Figure 4 shows the results of a blank test in Ar. A slight increase in weight is observed during the test at 900°C. After this test, the crucible was removed from the furnace and filled with approximately 100 mg of Merlin powder according to the procedure described in Annex 1. This sample was then submitted to a temperature programme including heating up to 110°C and holding the sample at 110°C for three hours (in order to remove remaining moisture in the sample), heating up to 900°C (at a slope of 20°C/min) and holding the furnace temperature at 900°C for one hour. The resulting TGA curve is shown in Figure 5. A linear weight decrease, corresponding to oxidation of the sample, is noted from the start to the end of the section at 900°C and there is no indication of a decrease in oxidation rate during this one hour time period, indicating that after enough time at 900°C, the graphite powder would be completely consumated by oxidation.

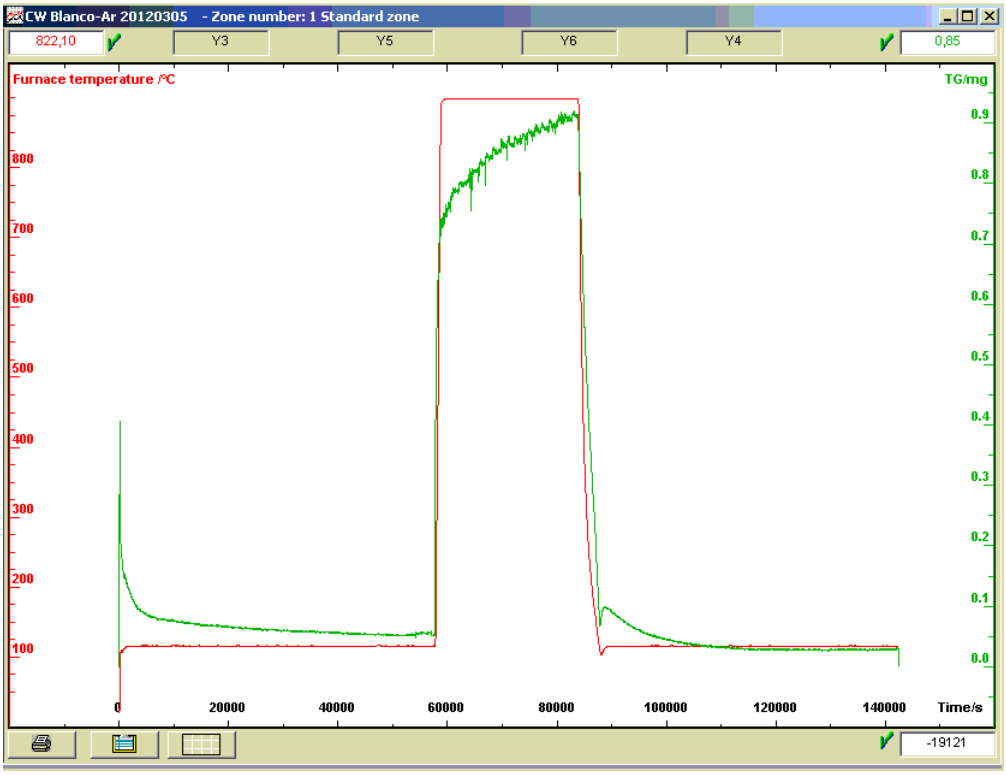

Figure 4. Blank test (with an empty alumina crucible) in the SETARAM TGA at 900°C in pure argon.

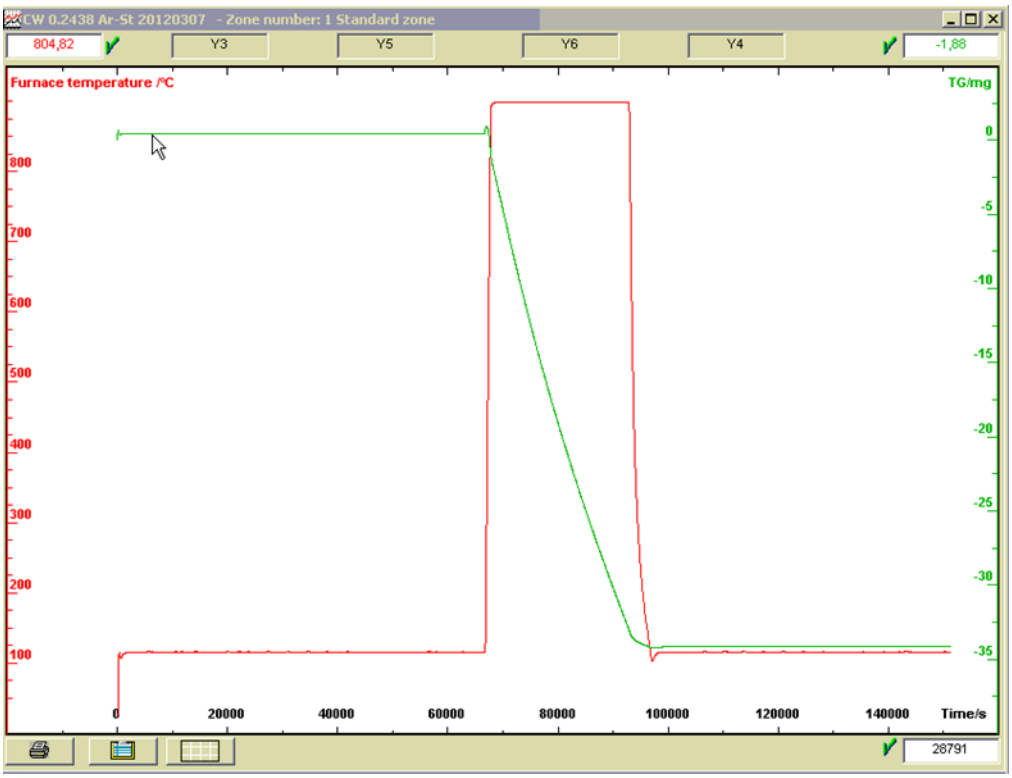

Figure 5. TGA result for Merlin powder in 99.9999% Ar at 900°C.

Additional tests confirmed this behaviour: for long enough exposures to 99.9999% Ar at 900°C, the Merlin power was completely consumated. Changing the Ar bottle (assuming a production fault of the Ar) did not remediate this. This indicated that somehow the gas circuit to the TGA system was not completely free of oxygen at the beginning of the test. A new, shorter gas tubing circuit was installed, with the gas bottle close to the glove box and Ar purging of the circuit and TGA system overnight before the start of the test. A typical result for the tests with this new gas tubing is shown in Figure 6. It can be seen that the decrease in weight is no longer linear and is less pronounced than for the earlier setup. This indicates that there is indeed an importance influence of the gas circuit and the test (preparation procedure). Therefore it was decided to adapt the procedure in order to minimize the presence of oxygen during the test, and to perform tests, on the same type of graphite, with three different TGA systems: our SETARAM TG 92-12, a newly acquired STA 449F1 coupled to a mass spectrometer, and a SETARAM system at FZJ. The results of these tests are described in the following section.

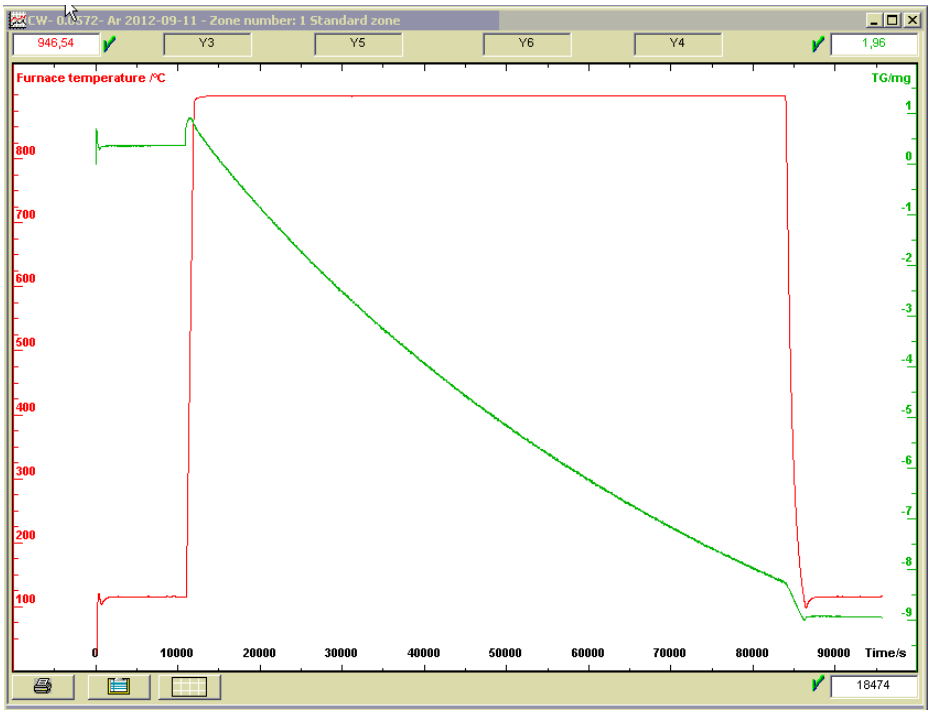

Figure 6. Typical result for Merlin powder exposed to 99.9999% Ar at 900°C with an adapted gas delivery circuit.

3.3 Additional tests on FJZ graphite powder (interlaboratory comparison)

Tests were performed, on the same type of non-irradiated graphite (GNP6), with three different TGA systems: our SETARAM TG 92-12, a newly acquired Netzsch STA 449 F1 Jupiter coupled to a mass spectrometer, and a SETARAM system at FZJ. The test procedure was as follows, after discussion between SCK-CEN and FZJ:

Quantity of graphite powder: 100 mg
Crucible: quartz crucible 1500µL

Day 1: start purge

evening: place crucible in oven of TGA, purge with Ar during night

- Flow 200ml/min Ar

Day 2: Baking out

morning: start baking out

- 1000°C over 7 hours with Ar-flow 30ml/min

Evening: end of baking out, start cooling down, Ar-flow 30ml/min stays on

Day 3: Blanco test

Morning (crucible is still in oven, flow is still 30ml/min Ar and remains so)

- Heating up to 300°C (slope 20°C/min)
- 3 hours at 300°C (take tarra at end of this period)
- Heating up to 900°C (slope 20°C/min)
- 7 hours at 900°C
- Cooling down to 300°C
- 3 hours at 300°C (take weight measurement at end of this period)
- Cool down to room temperature (= 20°C = temp cooling water), Ar-flow 30ml/min stays on

Day 4: Prepare test

Morning (crucible is still in oven, flow is still 30ml/min Ar):

- Open oven, take crucible out and fill crucible with 100mg of graphite powder (estimated time necessary 15min), place crucible back in TGA-oven
- Start flow at 200ml/min Ar (this flow will remain until day 5)
- Oven stays at room temperature

Day 5: Test with graphite powder

Morning (crucible is in oven, flow is still 200ml/min Ar)

- Change flow to 30 ml/min Ar

Rest cfr blanco

- Heating up to 300°C (slope 20°C/min)
- 3 hours at 300°C (take tarra at end of this period)
- Heating up to 900°C (slope 20°C/min)
- 7 hours at 900°C
- Cooling down to 300°C
- 3 hours at 300°C (take weight measurement at end of this period)
- Cool down to room temperature

Figure 7 shows the result obtained in our equipment. After 7 hours at 900°C, the accumulated weight loss of the graphite sample was approximately 2.5 %, which is appreciably lower than with the earlier setup. Again, the weight decrease is linear during the entire test, suggesting that at long enough exposure the entire sample would be oxidated. Figure 8 shows the results obtained in the Netzsch equipment. In this case, the accumulated weight loss over 7 hours at 900°C was approximately 2%. Similar measurements, on the same graphite powder and following the same experimental procedure, at FZJ with a SETARAM system, yielded

accumulated weight losses of approximately 0.5 %. This indicates that the oxidation rates obtained at SCK•CEN are too high, indicating the presence of oxygen in the system.

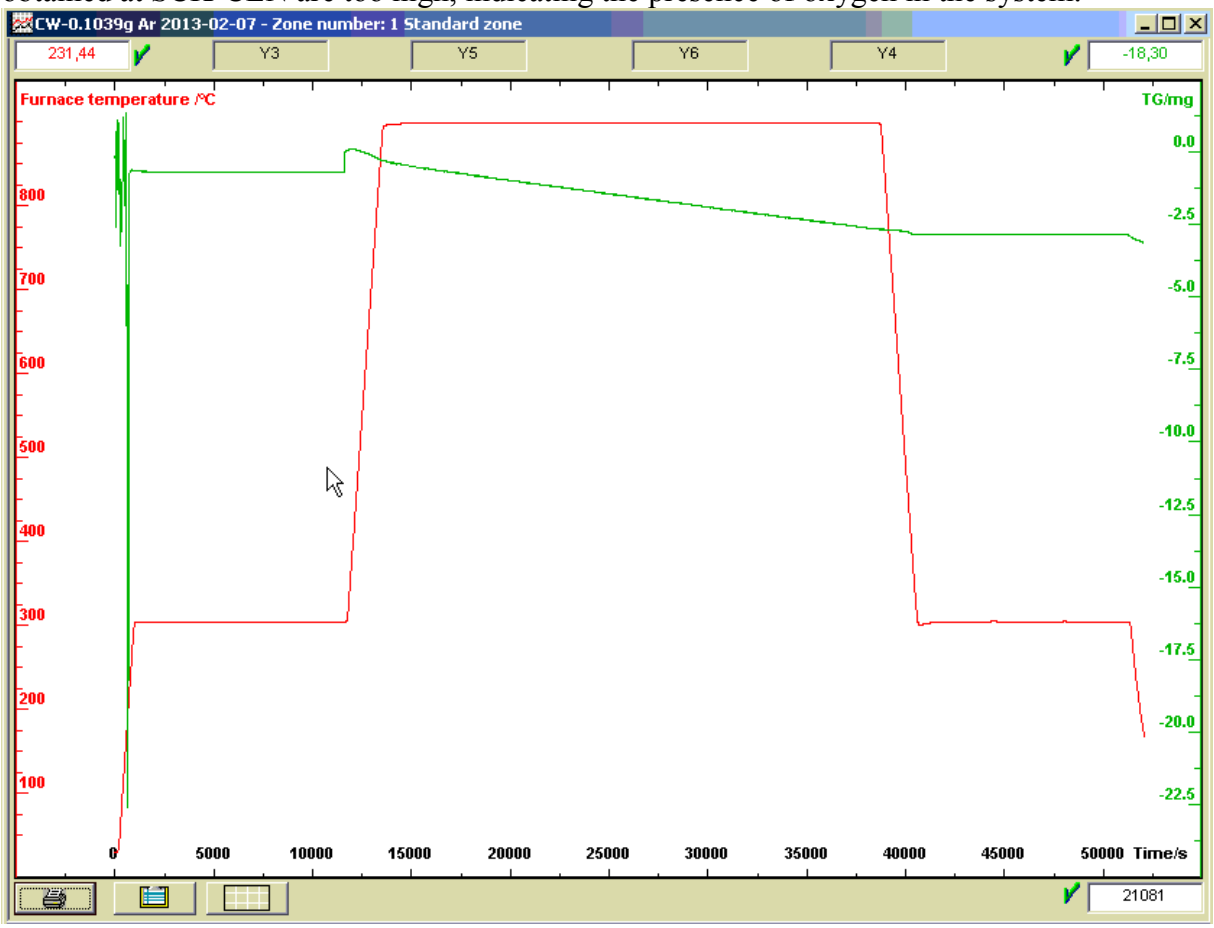

Figure 7. TGA results for GNP6 powder exposed to 99.9999% Ar at 900°C in the SETARAM TG92-12 equipment at SCK•CEN (initial mass 103.9 mg).

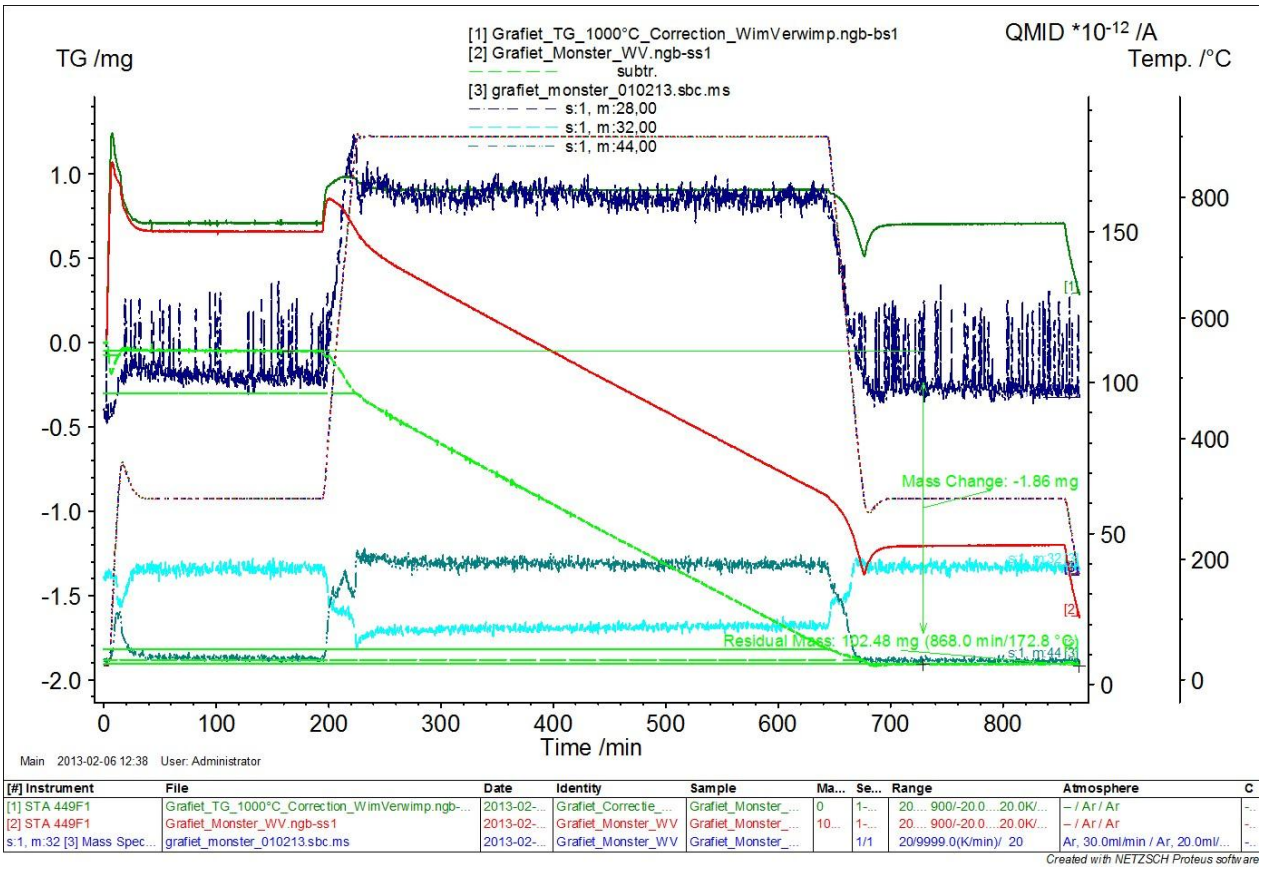

Figure 8. TGA results for GNP6 powder exposed to 99.9999% Ar at 900°C in the Netzsch STA 449 F1 Jupiter equipment at SCK•CEN (initial mass 102.48 mg).

4 Conclusions

TGA measurements were performed on Merlin i-graphite in 99.9999% Argon at 900°C, as part of a larger programme aimed at investigating the influence of gas composition on the decontamination of i-graphite. The weight losses in this high purity Argon were large and indicated the presence of oxygen in the TGA system. A comparison with other more recent TGA systems at SCK-CEN and FZJ confirmed that the oxygen level in our TGA equipment is too high to perform reliable decontamination tests. In this report, an experimental procedure is proposed that yielded good results at FZJ. In addition, it is important that

- The TGA furnace can be evacuated to obtain a vacuum
- The balance section can be purged with pure argon
- The distance between the argon bottle and the entrance of the TGA system is minimized

Appendix 1: TGA results

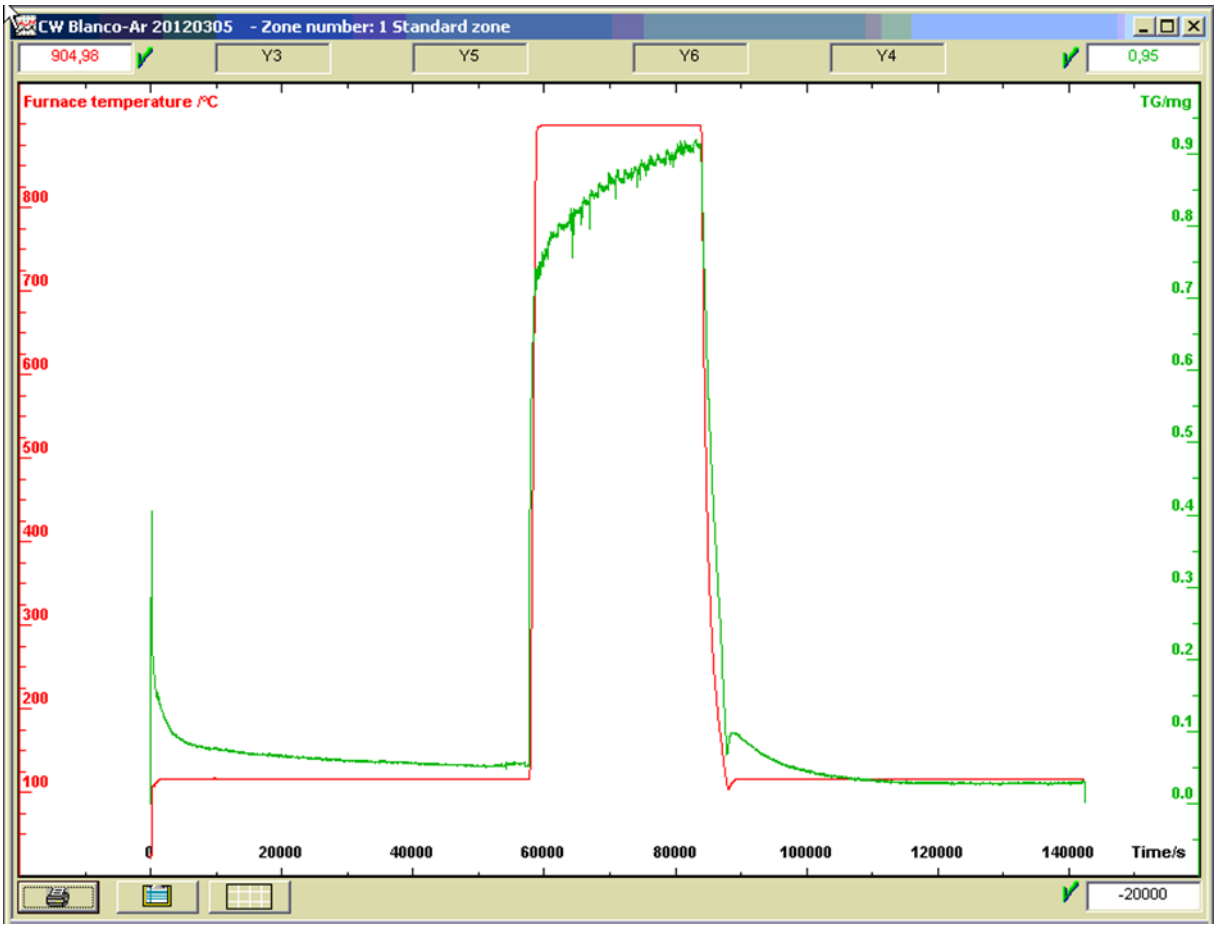

Figure A1.1. Blank test in pure Argon after 48 hours of purging with pure Ar.

Figure A1.2. Test with 234.8 mg Merlin graphite in Ar/steam after 12 hours of purging with pure Ar.

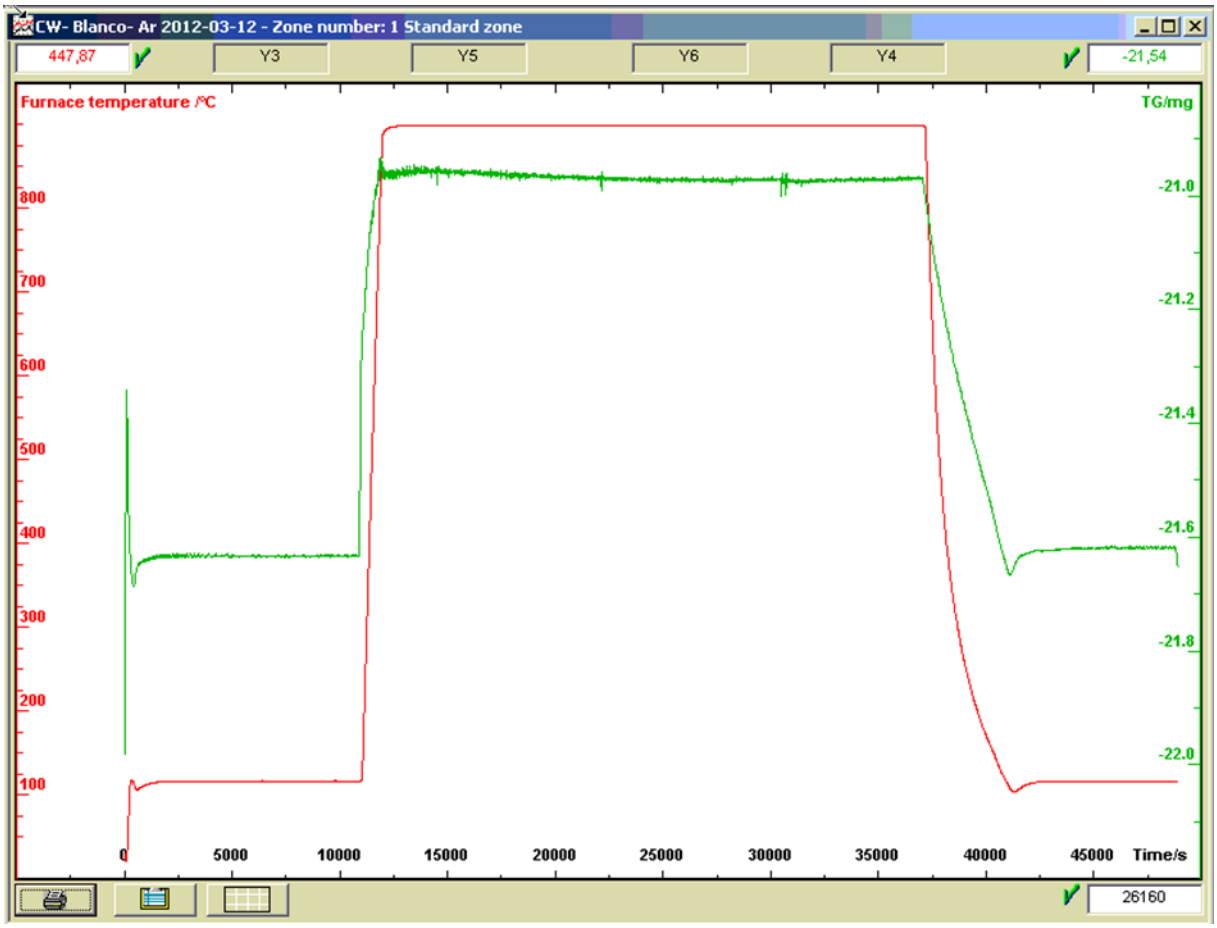

Figure A1.3. Blank test in 99.9999% Argon after 48 hours of purging in Ar.

Figure A1.4. Test with 233.8 mg Merlin graphite in 99.9999% Argon at 900°C after 4 hours of purging with pure Ar.

Figure A1.5. Test with 56.5 mg Merlin graphite in 99.9999% Ar at 900°C after purging with pure Ar for 2 hours.

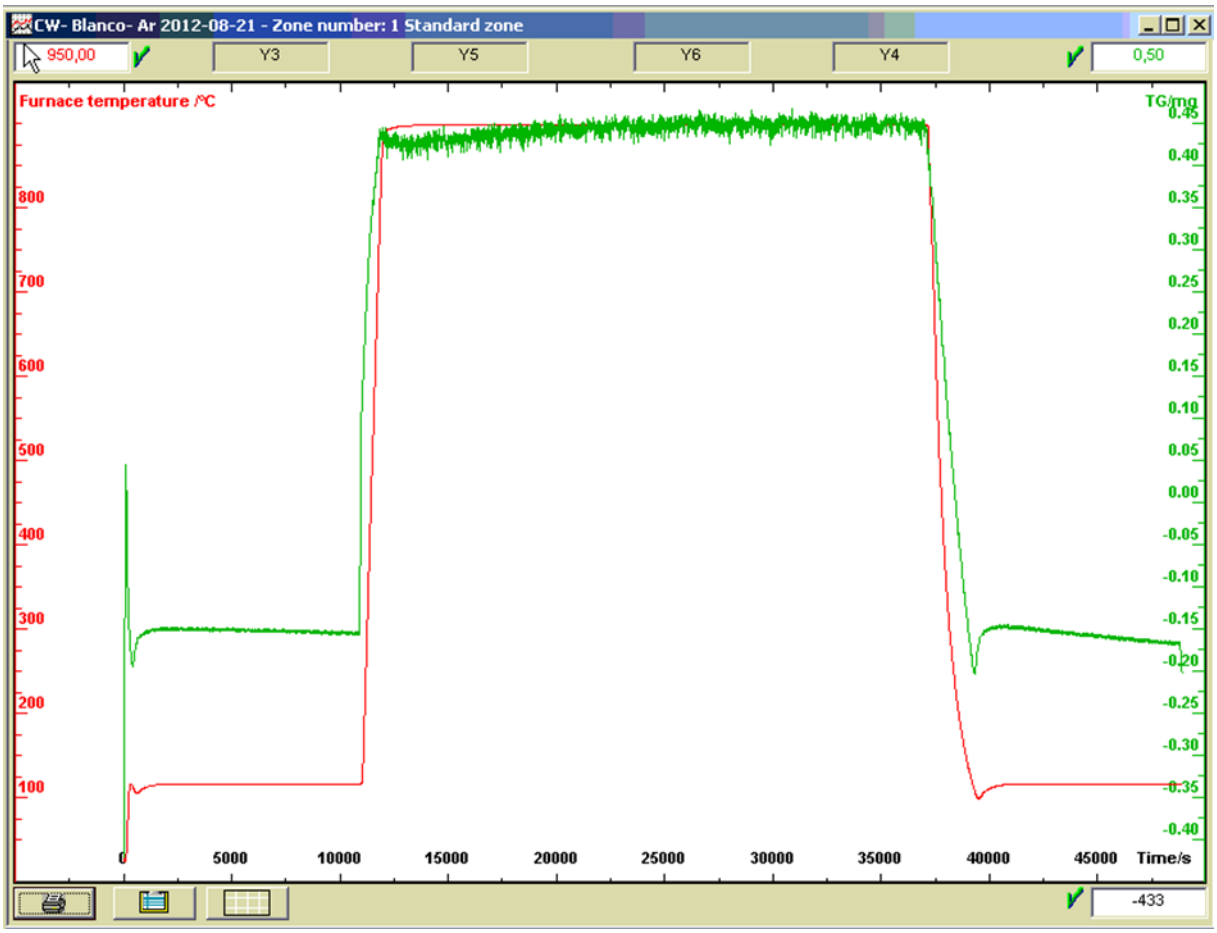

Figure A1.6. Blank test in 99.9999% Ar.

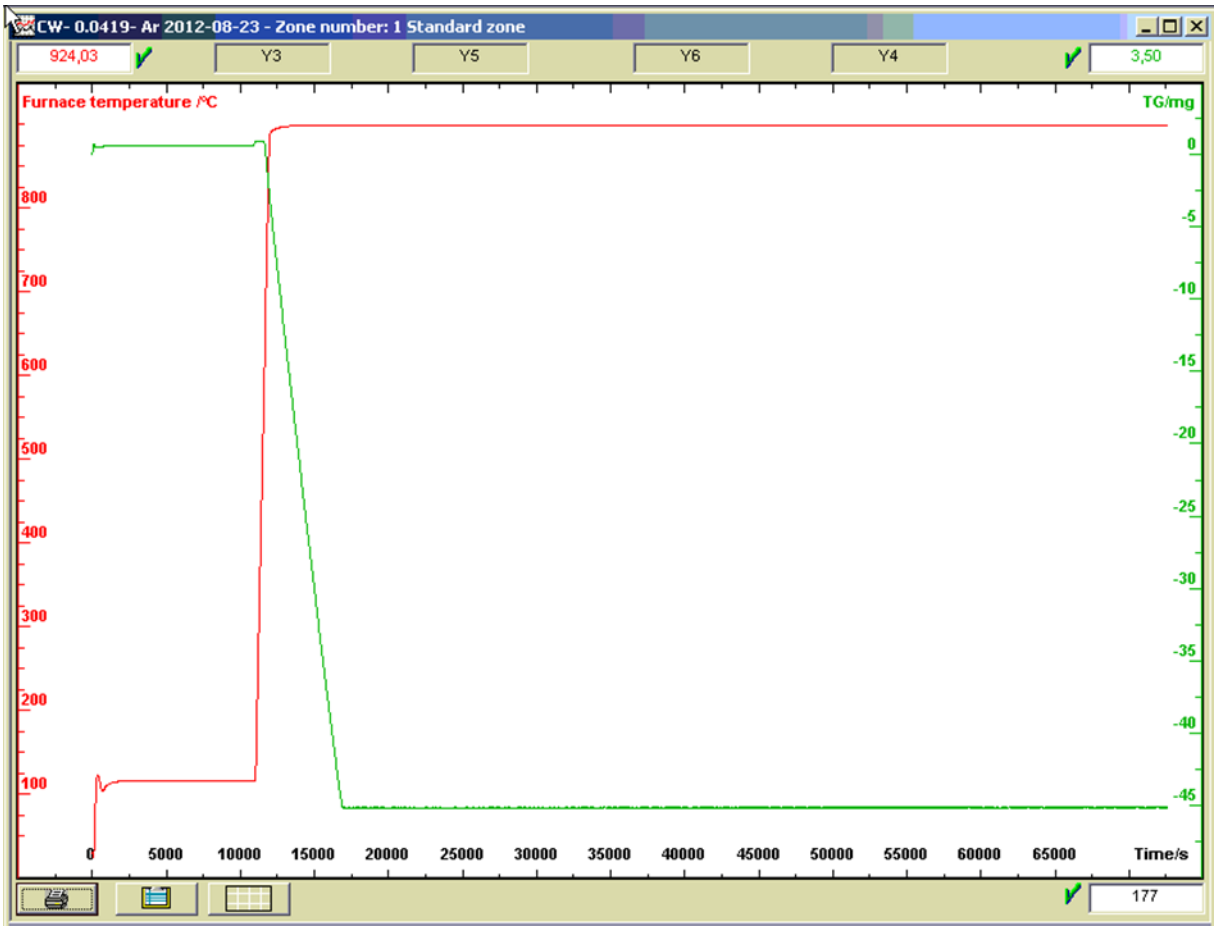

Figure A1.7. Test with 35.6 mg Merlin graphite in 99.9999% Ar at 900°C.