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Basic investigation of graphite decontamination by TG-MS

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Document title

Basic investigation of graphite decontamination by TG-MS
Status report April 2011

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. To this end, we apply thermogravimetric analysis in combination with a ^{14}C measurement method based on liquid scintillation counting. The current report describes the experimental setup and the results obtained in nitrogen.

The main results from this task are as follows:

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	05/04/2011	First issue	Druyts SCK	Van Hecke SCK		von Lensa FZJ
02	dd/mm/yyyy	2nd Issue				

Table of Content

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. The current report describes the experimental setup used for these experiments, and the experimental results obtained so far.

2. Experimental details

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. As this change of technique had an impact on the starting date of our experiments, we will briefly discuss both QMS and the new batch technique and go into the details of the cause of the delay.

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 are 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 Quantachrome NOVA 1200 gas sorption analyser in an airtight glove box. 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:

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

Where S_t = total surface area of the sample [m^2]

N = Avogadro's number [$6.023\ 10^{23}\ mol^{-1}$]

A_{cs} = cross-sectional area of the adsorbate molecule [m^2]

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.

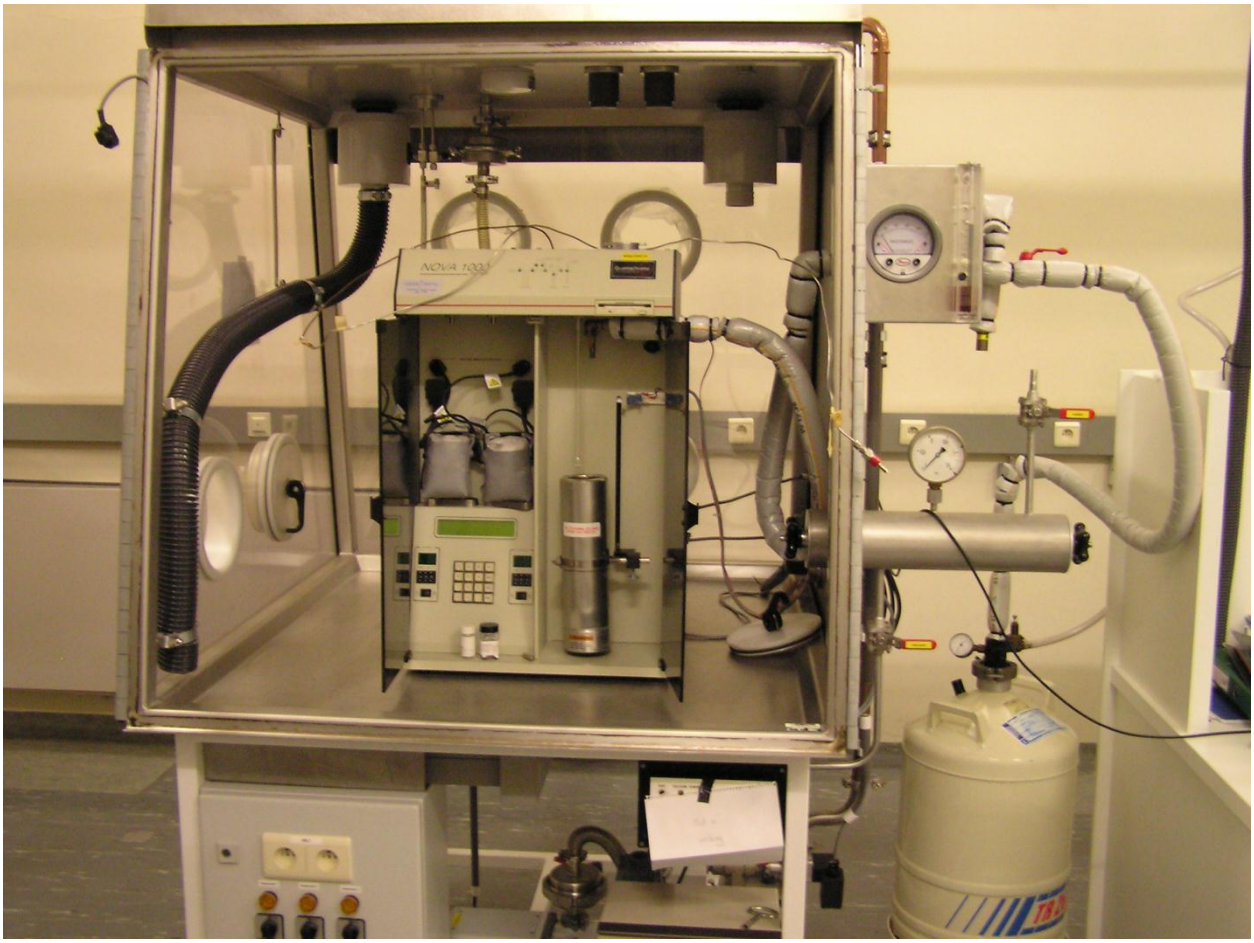

Figure 1. BET equipment for the measurement of the specific surface area of irradiated graphite.

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.

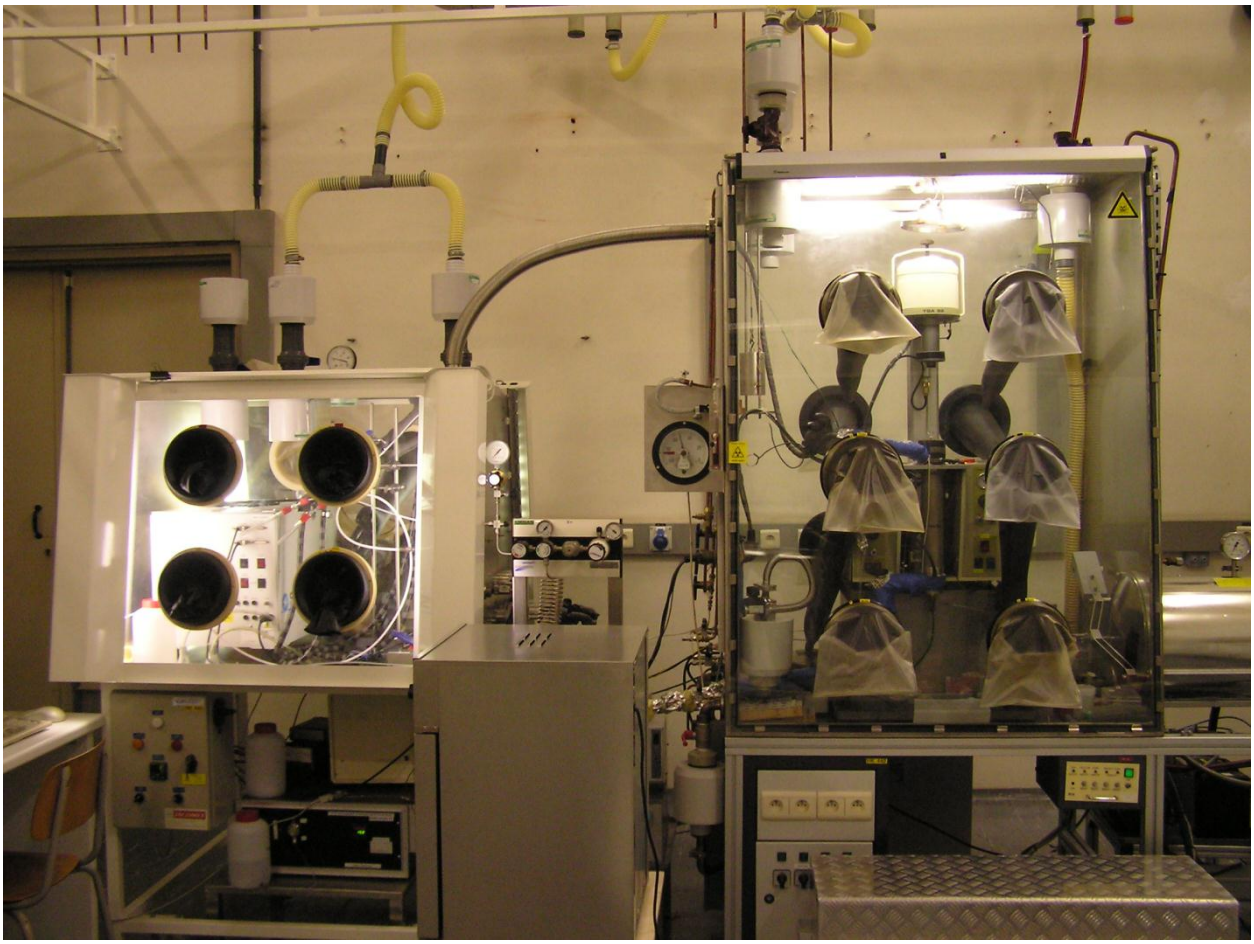

Figure 2. Overview of the airtight glove boxes with the TG/DTA furnace (right glove box) and quadrupole mass spectrometer (left glove box).

(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 we are at this moment considering two possible pathways:

(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. In the coming work period we will consider the specific advantages and inconveniences of the two techniques and then make a decision on which method we will apply for ^{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. Nitrogen as inert gas
2. Nitrogen with 2 % oxygen
3. Nitrogen with water steam
4. 100 % carbon dioxide (to study the Boudouard equilibrium)

The investigated temperature range will be 600-1000°C. Nevertheless, the first tests were at 900°C in order to duplicate previous tests performed at FZJ (these tests were batch tests in a tradional furnace without TGA capability).

The programme, that started in April 2008, has known considerable delay, related to the following problems:

- The i-graphite was delivered to SCK-CEN only in February 2010
- The original steam generator set-up was not succesful in delivering a steady stream of steam to the TGA furnace, thus provoking unacceptable instabilities of the TGA signal which made it impossible to reliably measure the weight loss of i-graphite powder.
- The procurement as well as the installation of new steam generator equipment caused additional delay.

The tests finally started in February 2011. It was decided, in agreement with the WP4 coordinator, to focus first on tests in nitrogen at 900°C, without the measurement of ^{14}C. The results of this measurement are shown in the next section.

3. Experimental results

Two experimental runs were made in pure nitrogen. After introducing the sample, the temperature was held at 110°C for three hours, and then the furnace was heated (at 50°C/min)

to 900°C, where the isotherm was maintained for seven hours. Figures 3 and 4 show the results of these tests. Figure 3 shows the result of test 1, for which 206,5 mg of i-graphite was used. There seems to be very little weight loss at 110°C, which indicates that there is little water present in the sample. At 900°C, the weight loss is erratic and proceeds almost steplike. The total weight loss is approximately 0,6 mg, or 0,3%. Figure 4 shows the result of test 2, for which 212,2 mg of i-graphite was used. Again, the weight loss at 110°C is negligible. At 900°C, a total weight loss of 0,5 mg is observed, which amounts to 0,23%.

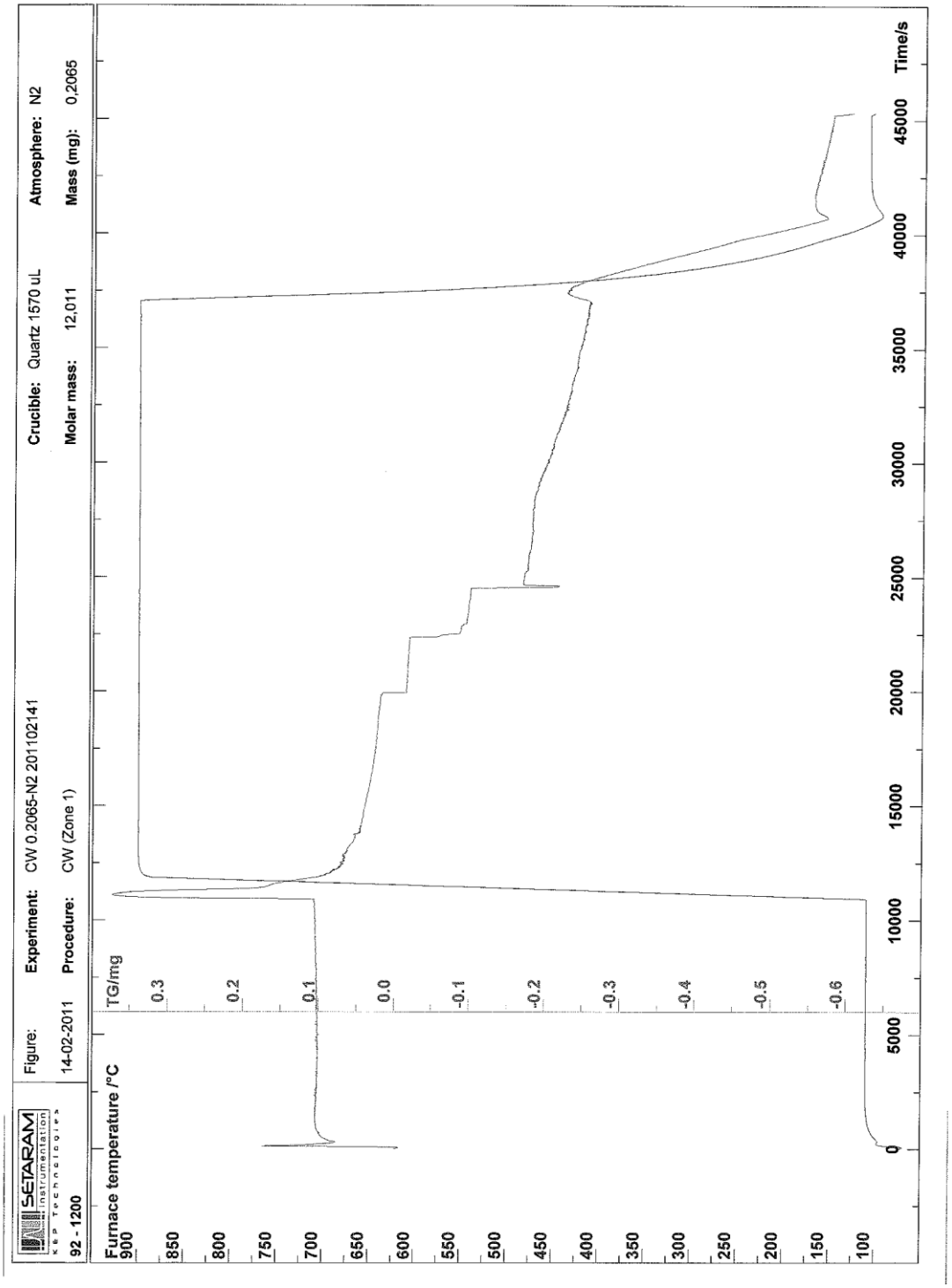

Figure 3. TGA scan (experiment 1) of i-graphite powder exposed to nitrogen at 900°C.

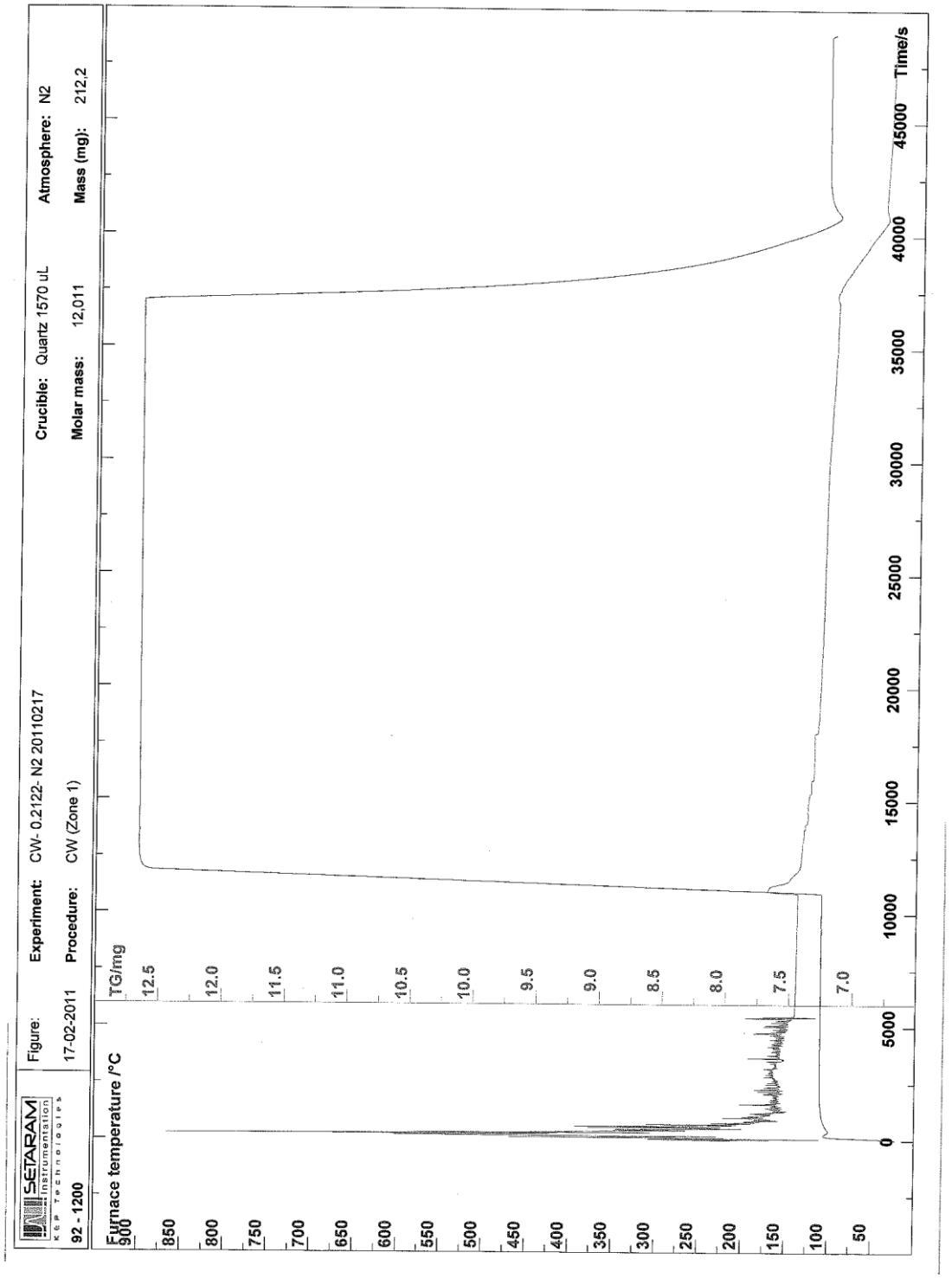

Figure 4. TGA-scan (experiment 2) of i-graphite powder exposed to nitrogen at 900°C.

4 Conclusions

In the framework of WP4 of CARBOWASTE, experiments were conducted to investigate the effect of nitrogen at 900°C on the decontamination of i-graphite. Two tests were run, with 0,3 and 0,23% total weight losses. These weight losses were smaller than previous, calculated weight losses observed in tests conducted at FZJ. During the next time period, tests will be conducted in nitrogen/oxygen and nitrogen/steam mixtures.