

Forschungszentrum Karlsruhe
in der Helmholtz-Gemeinschaft

Wissenschaftliche Berichte

FZKA 6859

Tritium extraction from JET CFC tile samples

Detritiation techniques of first wall carbon materials
used in fusion machines

N. Bekris, C. Caldwell-Nichols, L. Doerr, M. Glugla, W. Nägele, R.-D. Penzhorn,
R. Rolli, H. Ziegler

Hauptabteilung Versuchstechnik
Institut für Materialforschung

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**Forschungszentrum Karlsruhe GmbH
Postfach 3640, 76021 Karlsruhe**

**Mitglied der Hermann von Helmholtz-Gemeinschaft
Deutscher Forschungszentren (HGF)**

ISSN 0947-8620

ABSTRACT

Tritium in first wall materials of fusion machines is a matter of concern not only for inventory purposes but also for safety reasons. In the first wall carbon tiles, tritium is found predominantly in a very thin co-deposited layer and/or implanted in the surface layers. Since the tiles must eventually be disposed off in a repository it is necessary to reduce the total tritium inventory in the tiles down to the corresponding Low Level Waste (LLW) category. In this context, the development of detritiation techniques for graphite and CFC tiles removed from the first wall of fusion machines is of paramount importance. However, the experimental techniques investigated until now are limited by the conditions and techniques permissible inside the torus. Nevertheless, for tiles removed from the reactor more severe treatment techniques are acceptable. Working in that direction, numerous screening tests have been carried out at the Tritium Laboratory in Karlsruhe (TLK).

Tritiumextraktion aus CFC-Kachelproben von JET

Verfahren zur Detritiierung von Kohlenstoffmaterialien für die erste Wand in Fusionsanlagen

ZUSAMMENFASSUNG

Tritium in Materialien für die erste Wand von Fusionsanlagen ist ein wichtiger Aspekt nicht nur für die Bilanzierung, sondern auch aus Gründen der Sicherheit. In den Kohlenstoffkacheln der ersten Wand liegt Tritium vornehmlich in einer sehr dünnen koabgelagerten Schicht und/oder implantiert in den Oberflächenschichten vor. Da die Kacheln schließlich endgelagert werden müssen, ist das gesamte Tritiuminventar der Kacheln auf die entsprechenden Werte für schwach-aktiven Abfall zu reduzieren. In diesem Zusammenhang ist die Entwicklung von Verfahren zur Detritiierung von Graphit- und CFC-Kacheln der ersten Wand von Fusionsanlagen von besonderer Bedeutung. Die bisher untersuchten experimentellen Verfahren sind allerdings aufgrund der Bedingungen im Torus nur von begrenztem Nutzen. Aus dem Reaktor entfernte Kacheln können dagegen strengeren Behandlungsverfahren unterzogen werden. Dazu wurden im Tritiumlabor in Karlsruhe (TLK) zahlreiche Screeningversuche durchgeführt.

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1. INTRODUCTION

In graphite tiles of the first wall of fusion machines operating with D-D or D-T plasmas, tritium is found predominantly in a very thin co-deposited layer and/or as an implanted layer with a thickness of few tens of micrometers. Smaller tritium concentrations are retained into the bulk of the tiles after diffusion via to the surface connected porosity and by transgranular diffusion. After a shut down of a fusion machine it will be necessary to reduce the tritium concentration in the tiles to very low levels either to allow their reuse or to condition them for final disposal. In the latter case it is important to reduce the total tritium concentration in the tiles down to levels corresponding to those of the category of "low level waste" (12MBq/kg in UK). To accomplish this it is necessary to develop simple, reliable, and effective detritiation technologies allowing the conditioning of a large number of graphite and CFC tiles.

Most activities to date in the field of graphite tile detritiation have concentrated on *in-situ* methods, i.e. those performed inside the reactor, having the main objective of reducing the total in-vessel tritium inventory. Correspondingly, the work has been limited to gas-solid treatments under conditions restricted by the parameters permissible inside of the reactor and by the current safety requirements. Deuterium or oxygen-helium glow discharge cleaning at moderate temperatures, disruption discharge cleaning, as well as air ventilation at moderate temperatures have been employed as well in TFTR [i, ii] as in JET [iii]. Another recently proposed approach is the treatment of the tile surface with an impinging laser beam under an inert gas atmosphere [iv v]. When dealing with the tiles outside of the reactor more severe treatment techniques are acceptable, not only because single tiles or packages can be treated, but also because no precautions concerning the structural parts of the machine need to be taken.

In this work the main effort has been directed towards a tile treatment *ex-situ* with a view to final disposal. For that reason not only gas/solid techniques have been examined, but also methods involving liquid phase treatment of the tiles.

2. EXPERIMENTAL TECHNIQUES

The experimental techniques employed to investigate graphite detritiation are described briefly below:

2.1. The preparation of samples

To determine the actual concentration of tritium in the bulk of a tile the face opposite to the plasma exposed side was first cleaned with alcohol to remove all surface particles possibly contaminated with tritium. Next, a 7.8 mm cylinder was cut starting from this face of the tile using a fresh core drill. The cylinder produced was then retrieved and twelve, nearly equal sized 1 mm thick disks were cut from this cylinder (Fig.1 and 2).

Each disk removed from the plasma exposed side of the tile (A1 sample), was submitted to a detritiation technique among those mentioned below and then fully oxidised with moist synthetic air at 850°C employing a technique described in detail below, in order to determine its total tritium content. To completely exclude cross contamination from previous tritium analyses, the glass/quartz apparatus was thoroughly cleaned after each measurement and a full background determination was performed to confirm it as tritium-free. The tritium released by slow and complete combustion was collected in a water bubbler and analysed by liquid scintillation counting.

2.2. Methods for sample characterisation

2.2.1. The thermogravimetry

For the thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of graphite disks or their fragments, a Netzsch STA409 thermobalance equipped with a PU 1.851.01 power unit and a TASC414/3 controller was used. Temperatures were measured with a PtRh10-Pt thermocouple placed axially at the bottom of the ceramic sample holder. The instrument allows heating of the sample up to a temperature of 1300°C. Heat treatments were carried out either under inert gas (argon or nitrogen), air, or vacuum. In runs with samples containing tritium the exhaust gas was passed through water bubblers.

2.2.2. The full combustion

For graphite combustion, the technique proposed by Vance et al. [vi] was followed. The glass experimental arrangement used at the TLK is shown schematically in Fig. 3. Either a stream of laboratory air pumped with an oil-free Metal Bellows pump type MB 158E or synthetic air from

pressurised cylinders was used with a flow rate of approx. 15 cm³/min. Passing the air through a bubbler containing water humidified the carrier gas. Graphite or CFC disks were introduced via a joint into a small receptacle placed on top of the combustion zone and isolated from this zone by a glass-to-glass seal. To introduce the graphite disk into the combustion zone the seal was lifted from the outside with two appropriate magnets. The combustion zone itself consists of a vertical quartz tube heated from the outside with a cylindrical Ströhlein oven designed for temperatures of up to 1500 °C. The actual sample temperatures were determined with a thermocouple placed inside of the quartz tube. The combustion tube itself contained approx. 20 -30 g of a wire packing consisting of a Cu₂O core with CuO on the surface supplied by Merck, Darmstadt. The packing is secured between two pieces of quartz wool packing, on top of which the disk to be analysed drops by gravity when the seal is open. The copper oxide ensures complete oxidation of all molecular hydrogen isotopes and all hydrocarbons released during the combustion of the disks. The effluent gases are then passed through a water bubbler (about 200 cm³) via the shortest route. By this procedure the quartz tube, extending from the combustion zone down to the water level in the bubbler, remains at all times at comparatively high temperature. The experimental evidence indicates that most of the tritiated water is retained in this bubbler. To ensure quantitative trapping of the tritiated water, a second water bubbler, was placed downstream.

After each combustion water aliquots were taken from each of the bubblers using calibrated syringes. These aliquots were mixed with 15 cm³ of a scintillation cocktail and analysed for total tritium with a liquid scintillation counter (LSC). The LSC instrument employed at the TLK is a Tri-Carb 2300TR Liquid Scintillation Analyser from Packard. Upon completion of an analysis the surface contamination remaining on the tubing inserted into the water of the first bubbler was removed by rinsing thoroughly several times with fresh water. Frequent blank tests without sample or with virgin graphite disks were carried out to verify that no cross contamination had taken place.

2.3. Detritiation methods tested in the TLK

2.3.1. Tritium removal with an adhesive tape

In a few runs the co-deposited layer was removed employing an adhesive tape. The tape was applied three times to the plasma-exposed surface of graphite cylinders of 7.6 mm diameter drilled from JET tile No 004/2-20 and then combusted together with the adhered co-deposit. The results were very erratic as a large fraction (25 - 50 %) of the co-deposited layer can be easily

removed by this procedure depending on the tape quality and the way that it is used (one or several times applied at the same surface) for the removal of tritium.

2.3.2. Ultrasonic bath treatment

The graphite or CFC disks were introduced into a 250ml Erlenmeyer flask provided with a cap and containing either water or hydrogen peroxide and then placed into the water of an ultrasonic bath (Super Sonorex RK103H). The disks were treated at temperatures in the range 50 - 70°C for a period of up to one hour.

2.3.3. Detritiation with moist air or nitrogen

To investigate the detritiation of graphite tiles with moist air or nitrogen, A1 disks (the first millimetre from the surface of the plasma-exposed side of a graphite tile) were introduced into a quartz tube inside an oven as described above.

The sample was placed inside the Vance apparatus and kept above the oven first at ambient temperature while moist air was passed over it (10 cm³/min) for a specified period. At the same time the oven was kept hot (>220°C) to assure complete combustion of all the released hydrocarbons. After a specified period the same graphite disk was then introduced into the heated zone of the oven while the temperature was increased in steps up to 400°C.

The tritium released was oxidised and collected as HTO using two consecutive bubblers, each containing 200 ml of water, placed downstream of the reaction chamber.

The tritium remaining in the disk after the exposure to moist air to temperatures up to 400°C was measured by full combustion of the disk.

2.3.4. Detritiation with moist ozone

To determine the tritium release achievable by treatment with ozone, a disk from the plasma-exposed side of a graphite tile from JET was subjected to an oxygen stream containing ozone using an experimental apparatus shown schematically in Fig. 4. Ozone was generated with a Fischer ozone generator yielding approx. 1 g O₃/h at an oxygen flow rate of 30 l/h (≈ 1.6% O₃ in O₂). The oxygen/ozone stream was humidified by passing the gaseous mixture through a bubbler containing water. Downstream of the oven the exhaust gas was passed through two consecutive bubblers, a first one containing 50 ml water and a second one containing 20g/l potassium iodide (KI) dissolved in water (pH = 7). The ozone content of the gas stream exiting the reactor could be calculated from the iodine released by the reaction of ozone with potassium iodide and the integrated gas flow.

In general, graphite specimens were exposed to ozone for long periods of time and heated to temperatures in the range 25 - 220 °C. To investigate the effect of ozone, the bubbler immediately below the reactor was replaced repeatedly by one containing fresh water. The released tritium was measured by liquid scintillation counting.

2.3.5. Detritiation with moist noble gases employing radio frequency (RF) heating

A metal reactor with a feed through for a water-cooled RF coil was used for these experiments. A schematic drawing of the equipment is shown in Fig. 5. The volume of the reaction vessel was measured to be $(603 \pm 2) \text{ cm}^3$. Graphite samples were placed in a quartz tube placed axially inside of the copper RF coil. A quartz wool filter maintained the graphite specimen at the desired position. The quartz tube was joined to the inlet stainless steel tube via a metal/glass/quartz transition joint. The graphite itself was the susceptor for the RF heating power. By this procedure the graphite disks could be heated very rapidly to high temperatures measured with a pyrometer. The thermally released tritium is purged by humidified argon (99.999 % purity in entrance) used as carrier and passes sequentially through a heated quartz tube containing a BASF R3-11 catalyst bed ($\text{Cu}_2\text{O}/\text{CuO}$) where it is oxidised to water and collected downstream in 2 bubblers filled with 50ml water.

2.3.6. Detritiation by thermal desorption

The desorption studies were performed with a laboratory facility installed at the Institut fuer Kern- und Energietechnik (IKET). The experimental set-up basically comprises a purge gas supply and control, a high temperature stainless steel chamber containing the sample, a reduction bed containing granulated zinc operated at approx. 390 °C and a calibrated proportional counter for the detection of tritium. The sample chamber is heated from the outside with a controllable tubular furnace. The zinc bed converts tritiated water to molecular gaseous tritium (HT, DT, and traces of T_2). The tubing downstream of the ionisation chamber is trace-heated to about 300 °C. This heating contributes to minimise memory effects caused by tritiated water. Except for the pure gas supply and control, the whole system is contained in a glove box.

The purge gas used was helium containing 0.1 vol. % hydrogen. Typical flow rates were $50 \text{ cm}^3 \text{ min}^{-1}$. In normal operation, the sample temperature is initially increased linearly with time (reference rate 5 K min^{-1}) up to an end temperature of max. 1100°C, which is kept constant for a pre-determined time.

The purge gas flow rates, the sample temperatures and the tritium activity in the purge gas, which is derived from the count rate of the proportional counter, are continuously measured and

registered. The registered data are processed and evaluated with a PC data acquisition system. The count rate is corrected for the system background as determined at the start and the end of each run (sample at room temperature). The tritium release from the sample is obtained from the corrected count rate and the measured flow rate. The total released activity is calculated by integrating the release rate over the time region where a release is measurable.

2.3.7. Detritiation with an open flame

Another technique tested consisted of exposing the surface of the plasma-exposed side of a TFTR tile to the open premixed flame of a burner supplied with acetylene and nitrous oxide. The surface of the disk was treated for a few seconds with the hottest zone of the flame. The weight of the disk was determined before and after the treatment. The effectiveness of the treatment was derived from a comparison between the known mean tritium concentration of TFTR disks [vii] and the tritium concentration measured by full combustion after brief exposure to the flame.

3. RESULTS AND DISCUSSION

3.1. Thermal analysis (TGA and DTA)

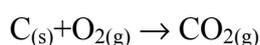
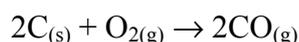
To determine optimised conditions for the combustion of graphite and of CFC specimen thermogravimetric experiments were first carried out with blanks (untritiated samples) under laboratory air. In a thermogravimetric analysis (TGA) the mass of the sample is recorded continuously as a function of the temperature of the sample that increased linearly with time, in a controlled atmosphere. A plot of mass or mass percent, as a function of the time, or the temperature, is called thermogram. Fig. 6 depicts such a thermogram showing the isothermal combustion of a CFC and of a graphite disk at temperatures between 700°C and 800°C. From these results it is apparent that a rapid combustion can only be achieved at very elevated temperatures (>750°C). For instance, for the complete oxidation at 800 °C of a 34 mg graphite sample, a total burning time of approximately two hours is required. At a temperature of only 100 °C less, the combustion time for only 22.8 mg of CFC increases significantly to more than 12 h. Of course, the combustion rates of the two specimens are different and will be discussed hereafter.

Fig. 7 compares thermograms obtained under identical experimental conditions of burning graphite and CFC disks. The samples were heated with a rate of 10 K min⁻¹ up to a final temperature of 780°C, which was thereafter held constant for about 15 hours (isothermal treatment). From the slopes of the straight lines it was possible to estimate the weight loss rates

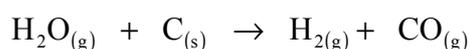
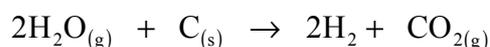
for pure graphite and CFC to be $(9.5 \pm 0.4) \text{ mg h}^{-1}$ and $(3.8 \pm 0.3) \text{ mg h}^{-1}$ respectively. Thus it is apparent that graphite oxidises much more readily than CFC. The time for the complete combustion of pieces from a disk is roughly proportional to the sample weight. Bigger the sample more time is needed for its combustion. For instance, while the burning of 24.15 mg of CFC is completed in about 400 min, that of 43.65 mg requires about 700 min. In both cases the combustion rate is nearly the same, i.e. 3.8 mg/h. This suggests that the rate of combustion is determined by the exposed surface. Grinding of the pieces would of course give rise to another rate.

In a differential thermal analysis (DTA), the difference in temperature between the sample and a reference material is measured as a function of the time while the sample and the reference are submitted to a controlled temperature programme. In a DTA plot, physical or chemical transformations are represented by characteristic peaks for each sample.

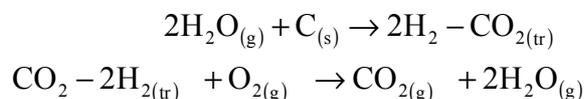
A comparison under vacuum and under air of the TGA and the DTA plots of graphite is illustrated in Fig. 8. When a sample of 14.85 mg of virgin graphite was heated up to 1300°C under an air atmosphere at a rate of 5 K min^{-1} the sample is oxidised with a progressively increasing rate of weight loss after the temperature reached values higher than 650°C . Complete oxidation took place after approx. 3 hours and a temperature of about 890°C . The DTA endothermic peak observed at approx. 437°C it is probably not due to a graphite re-crystallisation or phase transformation as such a phase transformation has been reported by Greenwood et al for temperatures higher than 1025°C . [viii]. Therefore, we attributed the DTA peak at temperatures below 600°C to oxygen chemisorption reactions leading to the formation of oxide surface complexes as it was already suggested [ix]. The broad endothermic DTA peaks registered during the oxidation phase with maxima at 837°C and 864°C , suggests that the oxidation of graphite to yield gaseous products takes place in more than one reaction pathway. Potential reactions include:



Moreover, it was establish that the presence of water increases significantly the combustion rate via the following proposed reactions:



or more probably via a reaction involving a transient species, where the oxygen atom of the water molecule is firstly fixed on the carbon substrate and only after the oxygen present in the gas phase removes the water hydrogen which also leads to the production of CO₂ [x].



3.2. Ultrasonic bath treatment

After the ultrasonic treatment the liquid was filtered out and analysed for tritium and the filter paper was analysed by full combustion. The tritium remaining in the disk was also determined by the same procedure, i.e. full combustion combined with liquid scintillation counting. The weight of the disk was determined before and after the ultrasonic bath treatment.

The results obtained from the ultrasonic bath treatment are described in Table I. As it is apparent, this treatment does not appear to be very promising.

To increase the efficiency of the method, water was replaced by hydrogen peroxide. Under these conditions the use of ultrasounds has the effect of producing oxidizing agents as hydroxyls and peroxide radicals which are more active in oxidising tritium.

Nevertheless, even in such a highly reactive medium containing 30 % hydrogen peroxide, only a relatively minor fraction (~ 11 %) of the tritium is liberated into the liquid. That amount probably reflects the reaction taking place at the interface between the carbon sample and the liquid while the majority of the radicals are destroyed by reacting with water or with themselves in the liquid phase. It was found that relatively little of the co-deposited layer is spalled off into the water (filtrate). The best results were obtained after prolonged ultrasonic treatment at 70 °C.

3.3. Detritiation with moist air or nitrogen

Prior to the detritiation runs, a graphite disk from the plasma-exposed side of tile 004/2-20 was placed in the Vance apparatus above the oven zone and moist air was passed over the sample at ambient temperature for a period of 10 hours (see Table II). The amount of tritium released under the first step was very small, (0.4%), indicating that at room temperature the tritium remains trapped. There is no weight lost during this step.

The same graphite disk was then introduced into the heated zone of the oven while the temperature was maintained at 200 °C. After an exposure to a stream of 10 cm³ min⁻¹ moist air for a total of 96 hours a further small release of tritium, i.e. 6% of the total activity, was detected,

the weight of the sample remaining constant. Renewed exposure of the specimen to the same stream of moist air for another 22 hours caused no additional release of tritium but only an apparent slight weight loss of 0.35 mg.

The same sample was then reintroduced into the apparatus and the temperature raised up to 300 °C and then to 400°C.

Table II summarises the whole experiment. As this table shows, after exposure to increasing temperatures, the tritium release increases according to the temperature but independently of time. The largest fraction of tritium was obtained at 400°C. The comparatively large loss of weight observed during that step strongly suggests that letting the sample at 400°C in an oxidative atmosphere for a long period of time (>88h) leads to a substantial combustion of carbon without a further tritium release.

In a final run carried out at 800°C, the sample was completely combusted and the remaining fraction of tritium collected in the bubblers. Fig. 9 illustrates the whole experiment.

Another sample was thermally treated in a thermobalance (TGA apparatus). The specimen was first heated under a humidified nitrogen stream at 350°C for a total of five hours and then replaced by moist air keeping the other parameters constant. Under these conditions, 59 % of the trapped tritium was released in the first step and only an additional 3 % after the gas exchange, thus illustrating the importance of water regardless of the carrier gas.

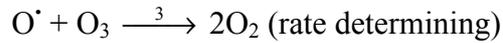
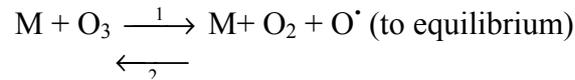
Similar observations have been reported by Causey et al. [xi, xii] in their studies with co-deposited and implanted material. Their tritium release results have been plotted in Fig. 10 together with those obtained in the above mentioned experiment.

Replacement of air by nitrogen does not appear to have a significant effect on the fraction of released tritium. According to Wampler [xiii] and depending upon the experimental arrangement a complete fractional release of tritium can be achieved after only 5 minutes. Thus for a rapid and quantitative liberation of the tritium co-deposited on a tile a short exposure to moist air at a temperature of the order of 400°C will have to be considered.

3.4. Detritiation with moist ozone

The general assumption was that ozone must be more efficient than oxygen concerning the detritiation of plasma facing components (PFCs). This was motivated by the fact that ozone is a powerful oxidant reagent, much stronger than oxygen. Nevertheless, passing ozone over a carbon disc has produced only minor releases of tritium (max 6%). This can be attributed to two facts, firstly the presence of water hinders the ozone reaction with the sample; e.g. ozone reacts preferentially with water rather than the sample. Secondly, passing ozone through a heated

quartz tube decomposes it thermally according to the modified Jahn atomic mechanism [xiv, xv, xvi]:



where M may be O₂ or O₃.

Using previous experimental results obtained by Axworthy and Benson [xvii] it is possible to calculate the decomposition of ozone in respect to the temperature and its dilution in oxygen. Fig. 11 shows the ozone decomposition as a function of temperature. Clearly, as the temperature is raised, the fraction of ozone available for reaction with the co-deposited layer becomes smaller. Curiously, working with bigger amounts of ozone will not increase the reaction yield. Indeed, as it is illustrated in Fig. 12 the ozone decomposition is markedly decreasing as the oxygen concentration is increasing. Moreover, as it was already pointed out, under the dynamic experimental conditions as ours (ozone is flowing and not in a static atmosphere) the decomposition is also independent of the concentration of the added nitrogen [xviii].

The small release of tritium observed could be caused by ozone, left after decomposition, exchange with moisture or some other oxidation mechanism. More work is needed to clarify this issue.

3.5 Detritiation with moist noble gases under RF heating

Under the assumption that the type of carrier gas for the moisture is of minor importance (see section 3.3) some tests were carried out using argon as carrier gas. The prospect of avoiding oxygen has the potential advantage of a tritium release without graphite combustion and therefore without damaging the tile. In addition, the need to deal with tritium contaminated carbon oxides in the exhaust stream is avoided.

In these experiments the specimens were heated by radio-frequency (RF) heating in a stainless steel apparatus (Fig.5). In the first run, an A1 disk (59.50 mg) obtained from the plasma exposed side of cylinder n°35 drilled from tile 004/2-20 was introduced into the axial quartz tube inside the apparatus. The whole reactor was then evacuated to remove oxygen. Then argon saturated with moisture was introduced into the reactor and the gas flowed through at a rate of 15 cm³ min⁻¹ over a period of 65 h. The temperature was measured pyrometrically. Only 0.3 % of the tritium was released under these conditions. The disk was then heated very rapidly by RF

heating up to 850°C. The fraction of released tritium with time was determined by periodically changing the bubblers, initially after 30 min and then after more prolonged periods of time (see Table III). Of the total activity in the disk, not more than 96.3% is liberated even after 24 hours at 850°C when moist argon is used as carrier gas.

When the reactor was opened it was observed that a very thin disk (weight 0.25 mg) had spalled off from the main disk (Fig 13). The registered weight loss of the thick disk was determined to be 6.7 mg indicating that a portion of the thin disk had been consumed. To determine the tritium content, both disks were combusted separately. The measured tritium concentrations in the two disks have been tabulated in Table IV.

It is seen that all of the remaining activity is concentrated in the thin disk. From this it could be concluded that the spalled off disk actually constitutes the co-deposited layer. It appears that under the prevailing conditions 850°C is sufficient to remove all the bulk tritium but not all of the tritium in the co-deposited layer. This supports previous suggestions that hydrogen in the co-deposited layer is strongly bound in the form of covalent chemical bonds [xiii].

3.6. Detritiation by thermal desorption

To improve the signal to background ratio in this thermal desorption investigation, a low purge of He with 1% H₂ flow rate of 10 standard cm³ min⁻¹ was used. To study the thermal release the sample temperature was raised up to 1100 °C employing a rate of 5 °C min⁻¹.

Altogether five disks from JET tile No 004/2-20 were heated under isochronal conditions and the results summarised in Table V. Only the disks obtained from the plasma-exposed side of the tile showed a significant tritium content of approximately 18-21 kBq per cm² of plasma-exposed surface. All other disks yielded tritium concentrations that were below the detection limit, i.e. 1.10 kBq cm⁻².

The sample temperature, the tritium release rate and the total tritium released from the A1 disk of cylinders 5 is depicted in Fig. 14. The two release curves are essentially similar, i.e. the release commences at about 700 °C, and the release rate reaches a maximum at approx. 850 °C. At still higher temperatures the release rate decreases rapidly. When a maximum temperature of about 1100 °C is attained the release rate drops to nearly zero, indicating that most of the tritium has gassed off. Similar observations have been reported by Sawicki et al. [xix]. The higher peak release rates are possibly caused by the higher heating rates employed by these investigators. They observed that neither a shift nor a broadening of the tritium depth profile could be detected within the accuracy of the measurements when graphite specimens containing tritium ion implanted at energies between 10 and 50 keV were heated to very high temperatures, i.e. ≤ 1700 K. This should be of significant importance as it suggests that tritium did not diffuse into the bulk of the samples but still needs to be confirmed with tiles recovered from a D-T operated machine.

Concerning the detritiation of graphite, the release data described above imply that only at temperatures above 700 °C will it be possible to liberate the tritium from the tiles via heating in a He + 0.1 % H₂ purge gas.

3.7. Detritiation with a flame

In a few runs, disks obtained from the plasma-exposed side of a TFTR tile were treated with an open flame for a few seconds and the remaining tritium measured by the full combustion technique. It was observed that with this hard but short treatment more than 98 % of the tritium can be liberated within a very short time. Thus, this treatment can be considered as highly promising for the detritiation of tiles before final disposal.

Conceivably, the tiles could be passed under a flame crown or exposed to a rectangular burner in an appropriate closed oven while continuously sweeping with an appropriate moist gas (or gas mixture) stream. A heated copper oxide bed downstream could ensure that all tritiated species and carbon monoxide are quantitatively oxidised to water and carbon dioxide. Water could be trapped very efficiently in a type 3A zeolite molecular sieve bed which do as not essentially retain carbon dioxide.

4. EVALUATION OF THE INVESTIGATED DETRITIATION TECHNIQUES

The ultimate goal of this waste conditioning investigation is an assessment of the effort needed to achieve the "solid low level radioactive waste category" for the graphite tiles of JET. In the UK, solid waste having a specific activity greater than 0.4 Bq g⁻¹ and below 12 MBq kg⁻¹ of non-alpha emitting radionuclides falls under this category [xx].

The most promising techniques appear to be:

- Abrasive removal of the co-deposited layer from a tile with a metal brush or an abrasive paper
- Treatment of a whole tile with humidified air at temperatures of 400°C or above
- Short treatment of the plasma-exposed side of a tile with an open flame or alternative flash heating procedures

In addition, the exposure of a RF heated tile to a humidified noble gas has also yielded encouraging results. These and other techniques, such the use of an argon torch [xxi], will now be tested in the near future on whole tiles or large fragments of them.

Table VI summarises the advantages and shortcomings of the various detritiation techniques used during this work.

5. CONCLUSIONS

Graphite tiles used in fusion devices such as JET operated with a D-D or a D-T plasma contain tritium. In graphite tiles most of the tritium (about 99 %) is found in a thin layer of less than 50 μm on the plasma-exposed side of the tile. The rest of the tritium (about 1 %) is evenly distributed within the bulk of the tile. For CFC tiles a large fraction of the tritium is trapped in the bulk. The detritiation techniques described in the paper (except full combustion) are almost exclusively dedicated to the detritiation of the surface co-deposited layer.

Treatment of plasma-exposed graphite in an ultrasonic bath containing water or hydrogen peroxide proved to be a rather ineffective detritiation method.

A humidified ozone/oxygen stream causes only minor liberation of tritium co-deposited with carbon at temperatures in the range 25-200°C. The ozone decomposition rates increasing with increasing temperatures (nearly complete at temperatures of about 200°C) constitute the limiting factor for this technique.

In laboratory experiments a sizeable fraction of the tritium in the co-deposited layer of tile sample is released by heating up to about 400°C under a stream of moist synthetic air or nitrogen. The release of tritium is predominantly determined by the temperature and to a lesser extent by the duration of the heating.

With RF heating at 850°C under a humidified noble gas stream it is possible to achieve high tritium decontamination factors. Further research shall uncover the full potential of the technique.

The quick treatment of the plasma-exposed side of a graphite specimen with an open acetylene flame proved to be very successful. Alternative flush heating procedures should also be explored, which may have reduced hazards associated with them.

6. ACKNOWLEDGEMENT

This work was performed in the framework of the Nuclear Fusion Project of the Forschungszentrum Karlsruhe and is supported by the EU within the European Fusion Program.

Table I. Detritiation of disks from TFTR tile using an ultrasonic bath

Conditions of the ultra-sonic treatment	Activity in water (%)	Activity in filter (%)	Rem. Activity (%)
50°C/15 min in H ₂ O	1	7	92
70°C/1h in H ₂ O	1	16	83
50°C/15 min in H ₂ O ₂	5	6	89

Table II. Tritium release with moist air from the A1 disk of cylinder No 30 from JET tile 004/2-20

Temperature °C	Disk mass [mg]	Heating time [h]	Total time [h]	Fraction of the released activity %	Total released activity Bq
25	81.20	10	10	0.4	0.4
200	81.20	96	106	6.0	6.4
200	80.85	22	128	0.0	6.4
300	80.85	22	150	17.0	23.4
400	80.80	18	168	63.2	86.6
400	78.70	19	187	0.0	86.6
400	77.60	69	256	0.0	86.6
800	76.50	4	260	13.4	100.0

Table III. Tritium release from a plasma-exposed disk obtained from cylinder 35 of JET tile 004/2-20 employing RF heating and a moist Argon sweep stream

Bubbler	Temperature (°C)	Accumulated heating period (h)	Fraction of released activity (%)	Fraction of activity remaining in disk (%)
1	23	65.0	0.3	99.7
2	850	0.5	49.3	50.7
3	850	1.0	80.7	19.3
4	850	1.5	89.4	10.6
5	850	2.0	92.6	7.4
6	850	2.5	94.1	5.9
7	850	3.5	95.1	4.9
8	850	4.5	95.5	4.5
9	850	6.0	95.9	4.1
10	850	24.0	96.3	3.7*

* *Fraction remaining in the thin disc*

Table IV. Tritium activity in the thick and the thin disk produced after RF treatment.

Disk mass [mg]	Released activity (Bq)	Mass specific activity (Bq/g)
52.55	0	0
0.25	123	$4.9 \cdot 10^5$

Table V. Thermal desorption measurements from JET graphite tile N° 004/2-20

Cylinder N°	disk N°	Mass g	Released tritium ^{***} Bq	Surface activity kBq/cm ²
5 [*]	A1	0.0792	9.516×10^3	20.96
	A2	0.0606	$\leq 5 \times 10^2$ [#]	≤ 1.10
	B1	0.0819	$\leq 5 \times 10^2$ [#]	≤ 1.10
6 ^{**}	A1	0.0785	$\leq 5 \times 10^2$ [#]	≤ 1.10
7 [*]	A1	0.0791	8.293×10^3	18.27

* A1 disks cut from cylinders N° 5 and N° 7 include the tile surface

** A1 disk cut from cylinder N° 6 was obtained from 1 mm below the tile surface

*** integrated between 2650 s (≈ 600 °C) and 10400 s (≈ 1100 °C)

detection limit

Table. V. Development of process for detritiation of plasma graphite tiles inside and outside of the torus

Technique	Maximum DF achieved	Merits	Short comings
Removal with organic solvents (alcohol, acetone).	1.0	None.	Very ineffective, production of secondary organic waste.
Treatment with moist ozone/oxygen.	1.0	Simple. Poor , activity reduced only few per cent.	Poor effectiveness, thermal decomposition of ozone begins at 150°C.
Ultrasonic bath with water or hydrogen peroxide at moderated temperatures.	1.1	None. Small activity reduction.	Very ineffective, tritiated liquid waste requiring further processing and/or disposal.
Treatment with moist air.	2.6 (350 °C) 7.5 (400 °C)	Simple and effective. Low DF	Requires high temperatures, produces tritiated gases that require further processing.
Removal of the co-deposited layer with an adhesive tape.	Maximum DF obtained 3.0.	Simple. Random , removal of significant tritium fraction.	Incomplete removal, not very useful in non accessible zones Depending to the tape and experimental conditions.
Mechanical abrasion with paper or a steel brush.	DF of 100 if a layer of 15 µm (or less?) is removed.	Simple, rapid will assure a large effect.	Production of hazardous tritiated powder containing beryllium. Large decontamination factors difficult to achieve. A uniform decontamination of tiles is difficult to guarantee.
Treatment with a noble gas at 800°C employing high frequency heating.	Assuming that the thin disk is constituted by the co-deposited layer, DF ≈ 50 - 55. No tritium was found in the bulk (single run!), i.e. high DF.	Simple from a safety point of view. High temperatures rapidly achievable without excessive heating or outer containment (only radiation heating).	Limited by the small exposed area. Production of tritiated carbon oxides requiring further processing.
Short exposure to an open flame.	DF = 50 , in few seconds.	Simple, effective and rapid. Appears not to cause significant change of structural configuration.	Requires a downstream process for the handling of tritiated off gases.
Treatment with an argon torch.	100 , in few seconds.	Could be performed under inert atmosphere	Small exposed surface area.
Full combustion.	Highest efficiency.	Very promising ex-situ solution. Full decontamination.	Large amount of secondary waste requiring additional process.



Fig.1. Cylindrical specimens and disks from graphite (left, darker) and CFC (right, striated metallic appearance) obtained by coring virgin JET tiles.

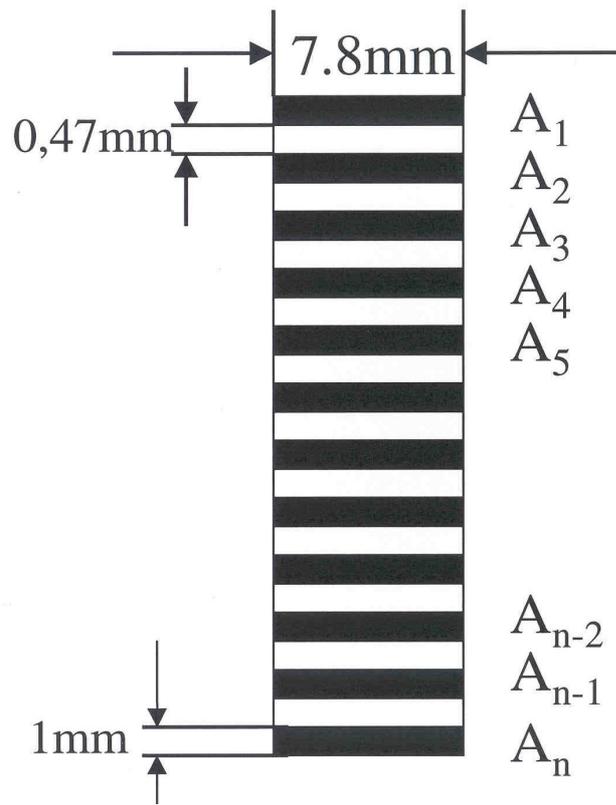


Fig. 2. Typical numbering for the cylindrical specimens and disks used for the tritium depth profile.

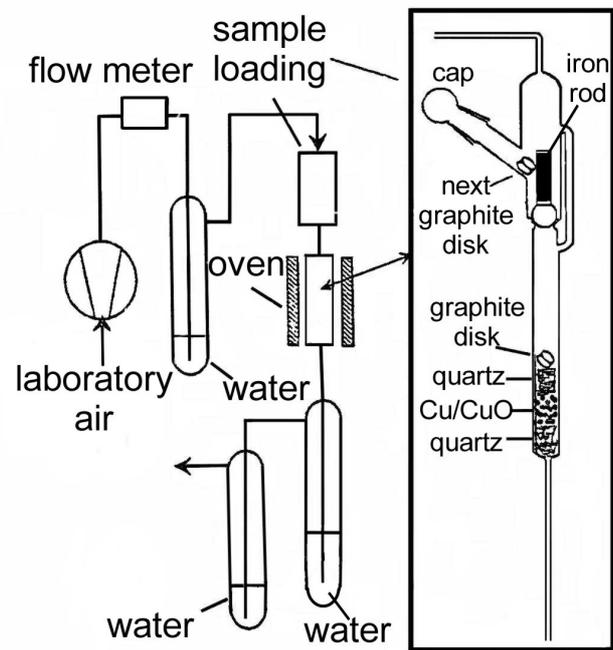


Fig. 3. Schematic view of the glass apparatus used for the combustion of graphite or CFC samples

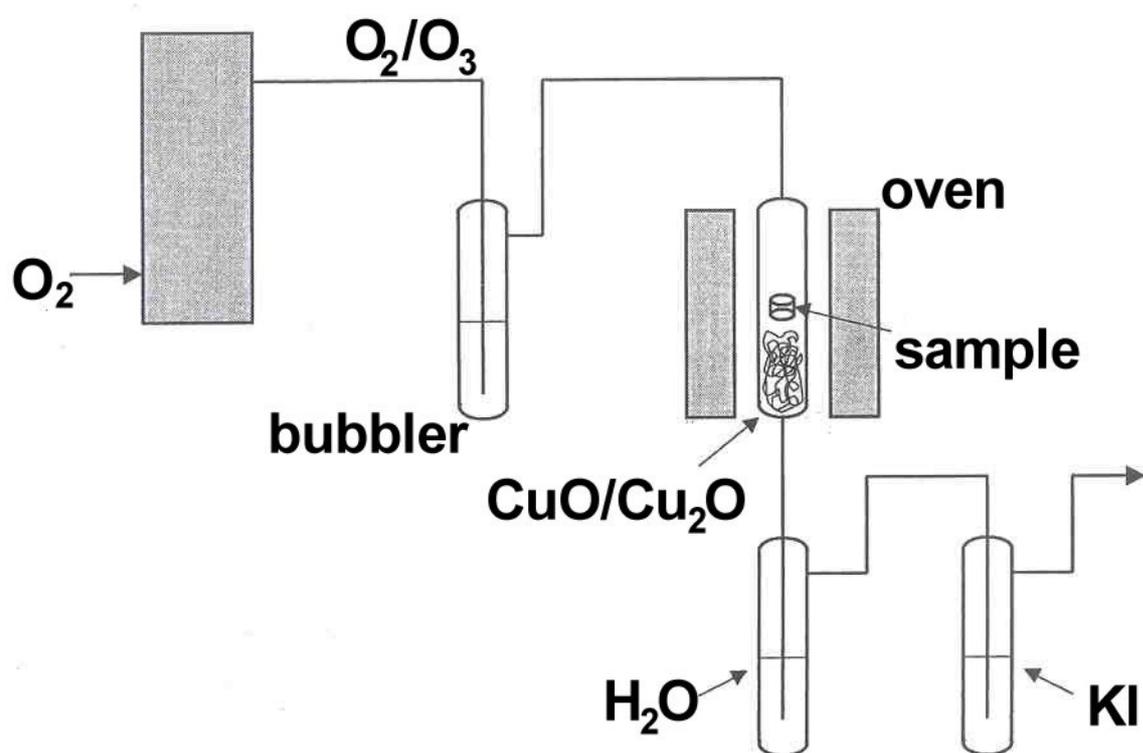


Fig. 4. Schematical representation of the experimental set-up used for the detritiation of carbon samples with ozone.

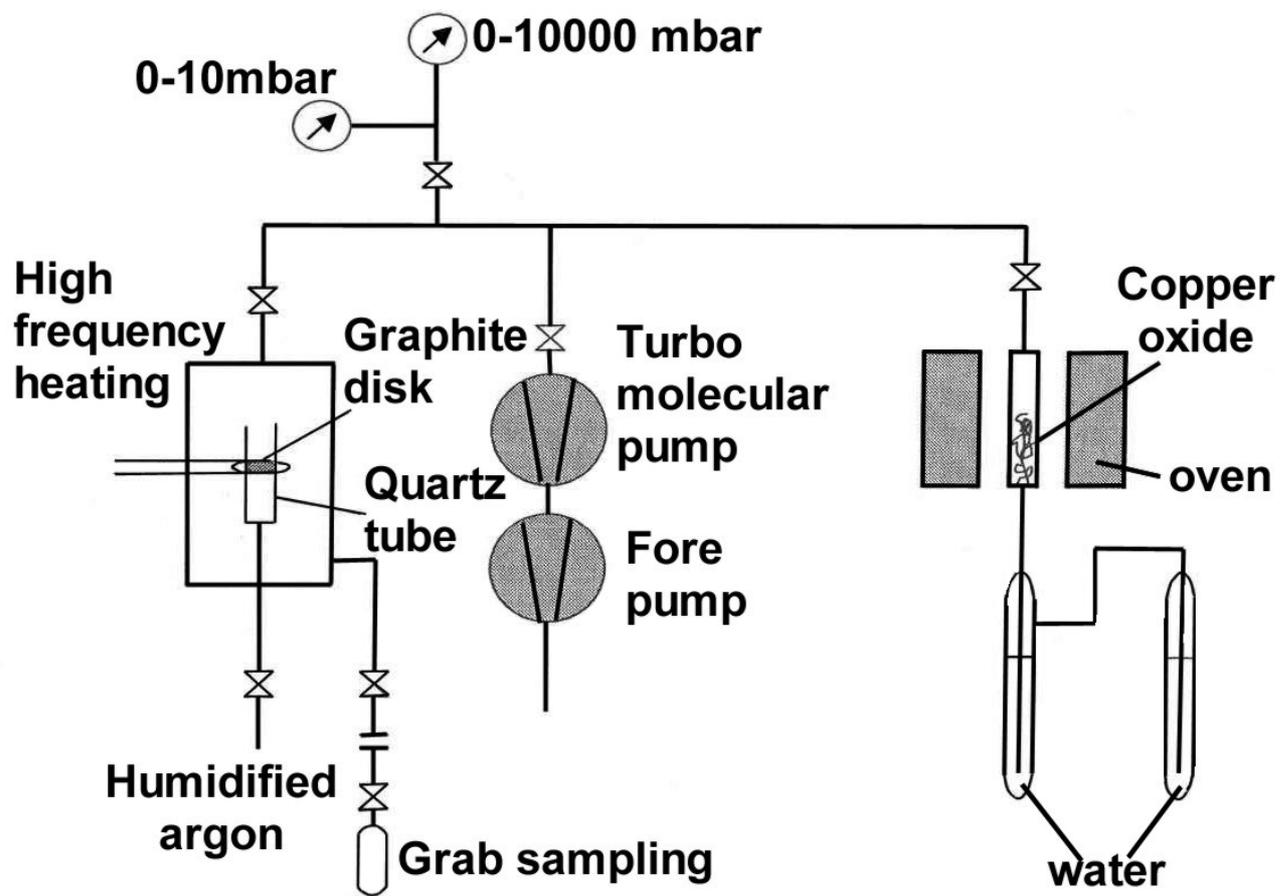
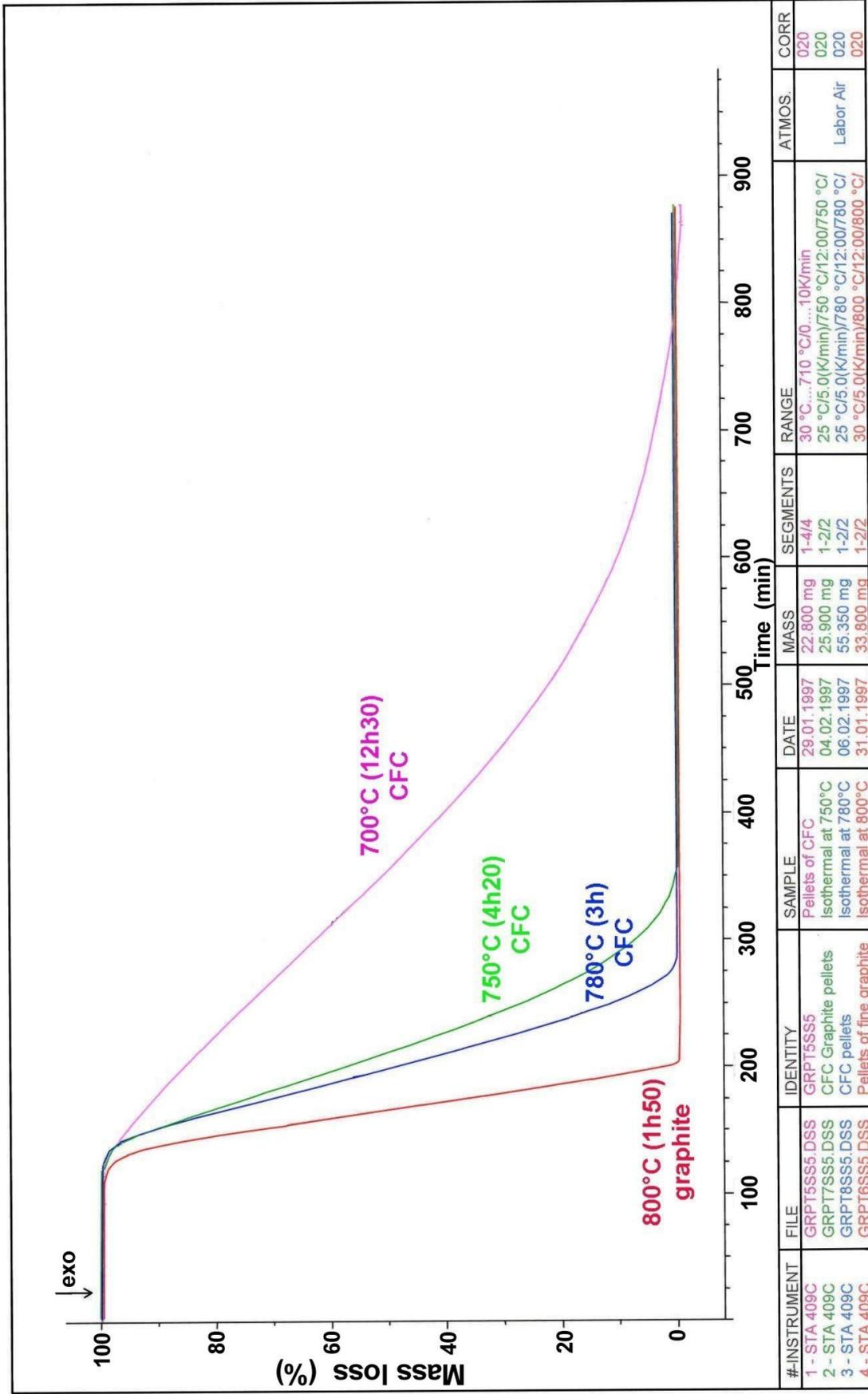
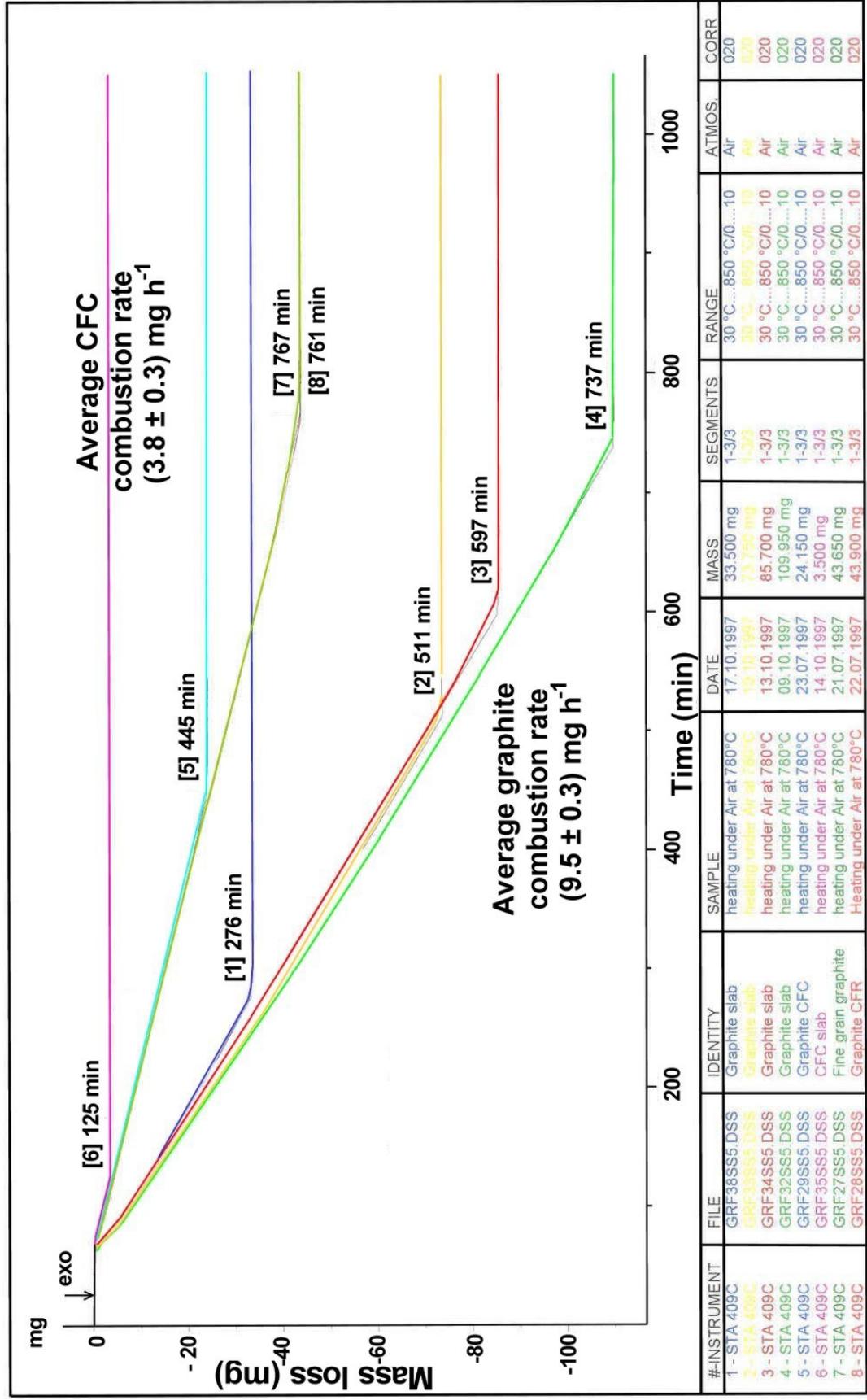


Fig. 5. Schematic set-up of the apparatus used to heat graphite samples by RF heating.



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Fig. 6. Thermograms for an isothermal heating of various CFC or graphite samples at progressively increasing temperatures



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Fig. 7. Isothermal heating of CFC or graphite samples at 780°C under air. For each sample is also given the time needed for the full combustion.

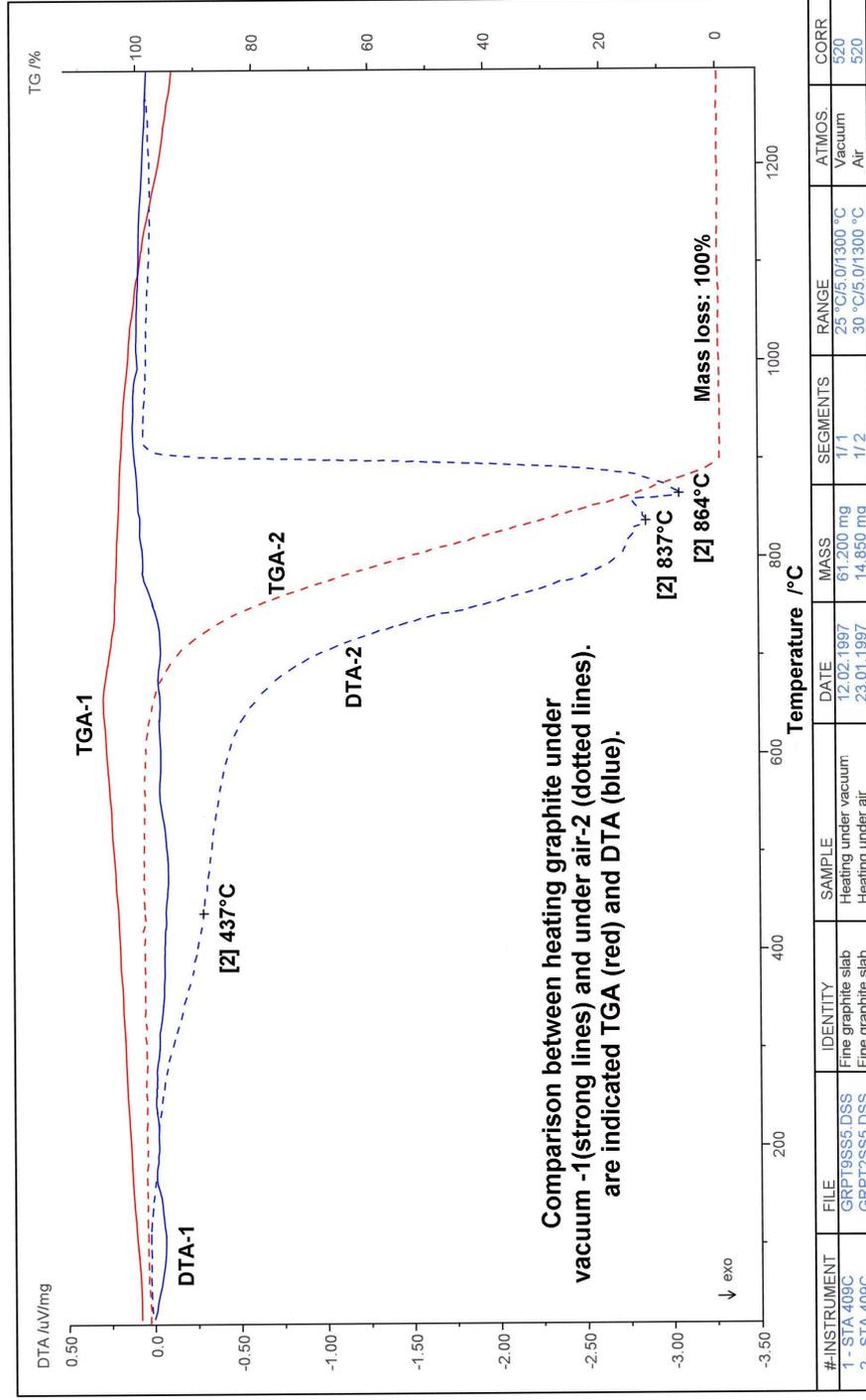


Fig. 8. Comparison between a thermogravimetric (red lines) and the differential thermal analysis (blue lines). The two thermograms are for a of graphite sample heated under air (broken lines) or under vacuum (solid lines)

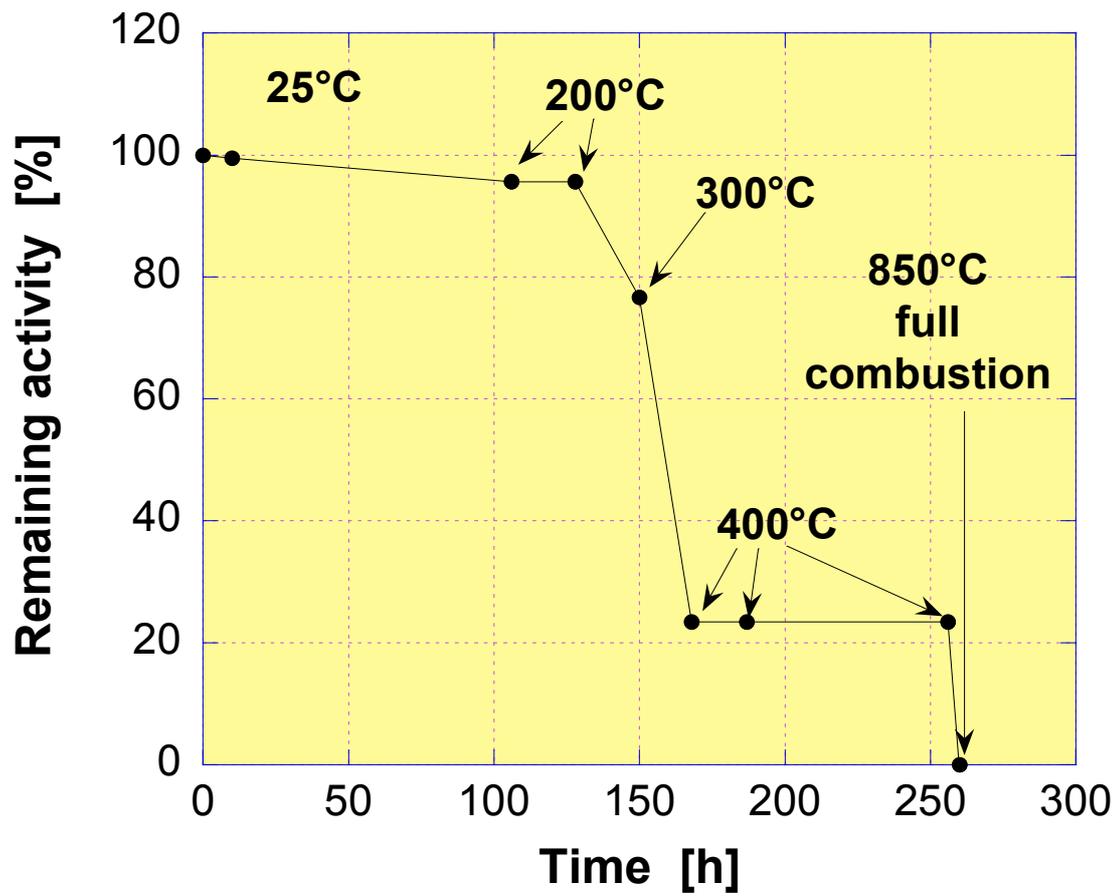


Fig. 9. Tritium release by sweeping the surface of a plasma-exposed graphite disk to moist air.

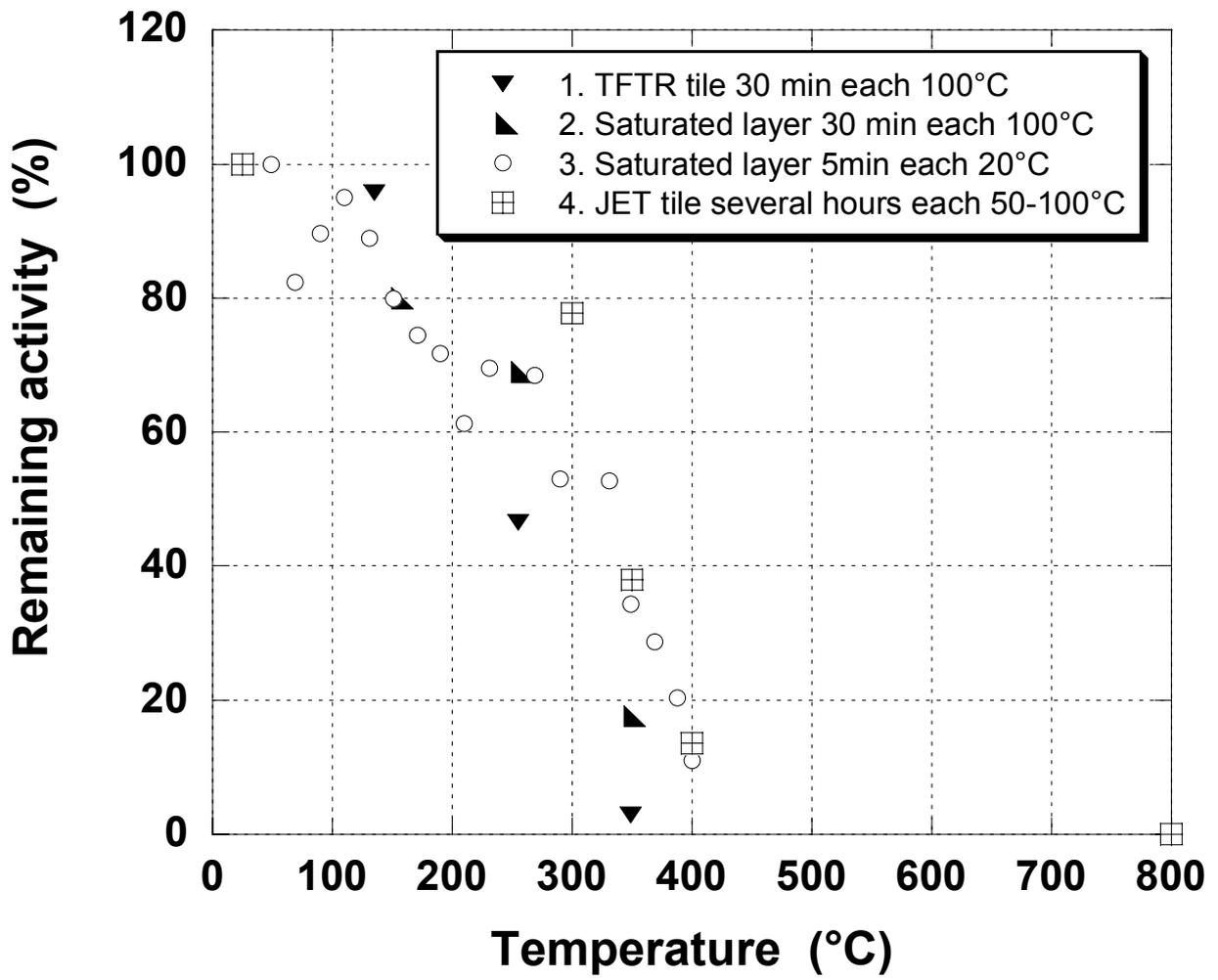


Fig. 10. Tritium release from saturated layers and co-deposited films from JET and TFTR. 1 to 3 ref. [xi, xii], 4 this work.

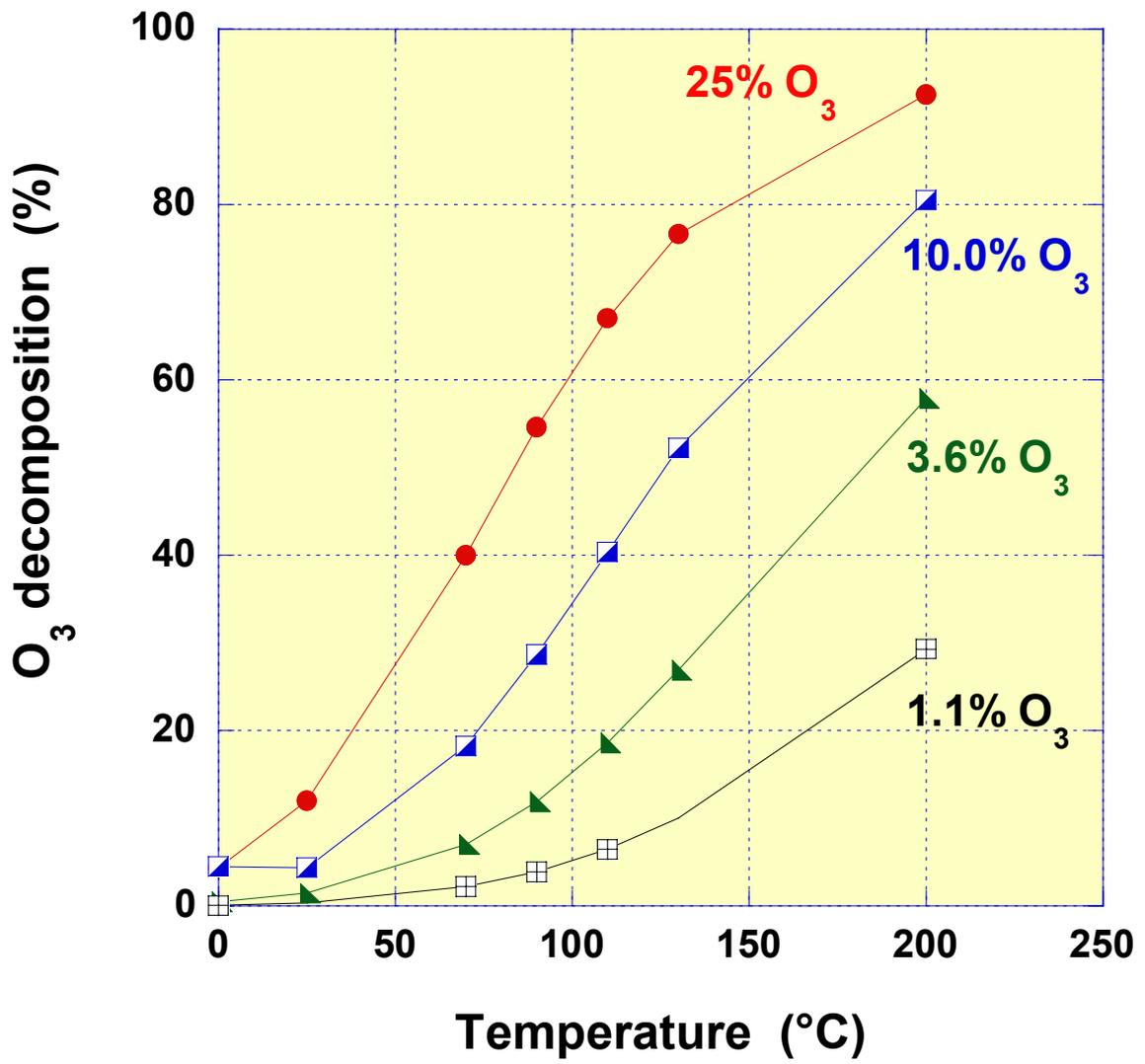


Fig. 11. Decomposition of ozone as a function of the temperature and its concentration in an oxygen stream.

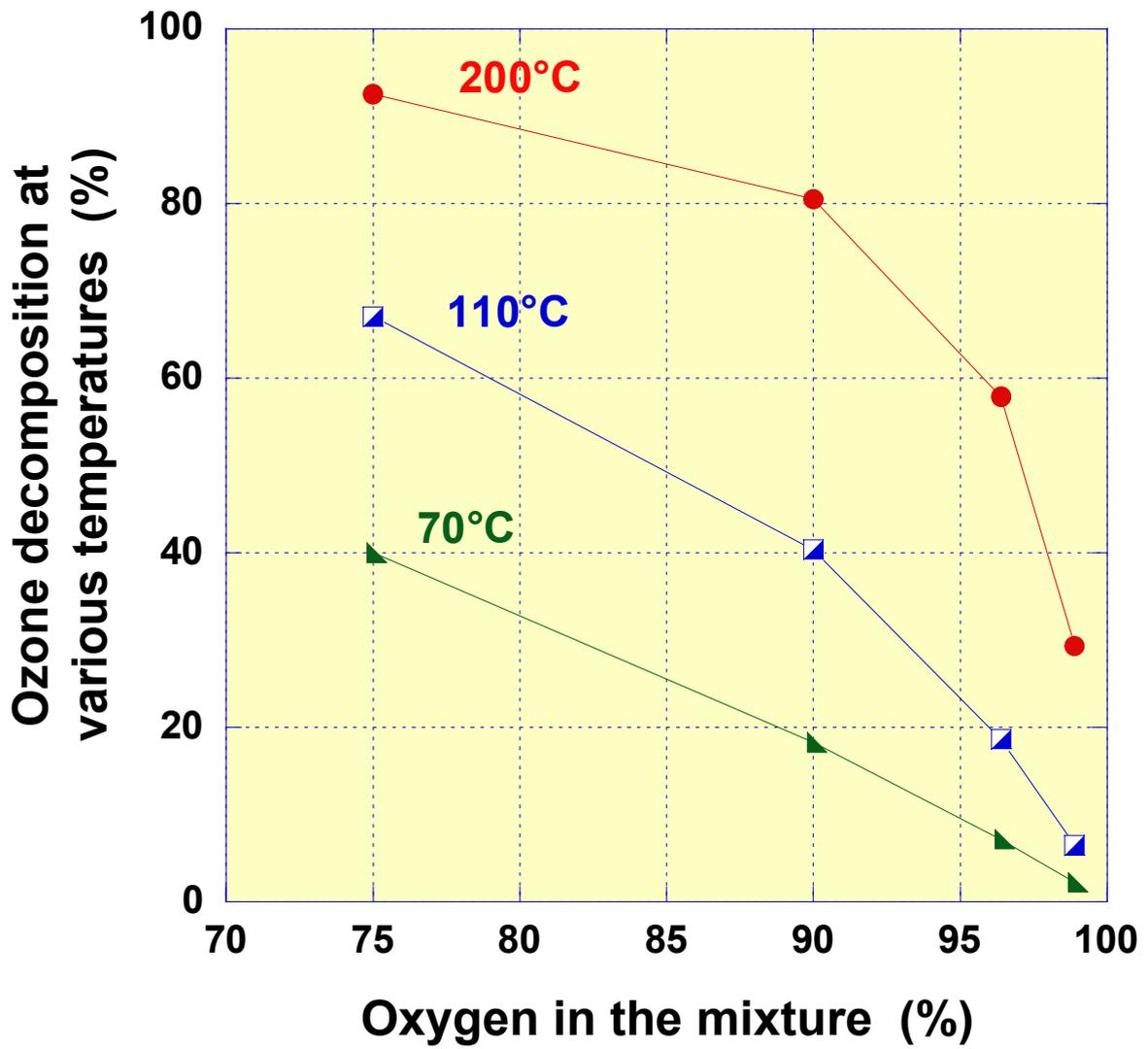


Fig. 12. Decomposition of ozone decreases when the oxygen concentration in the gaseous mixture increases.

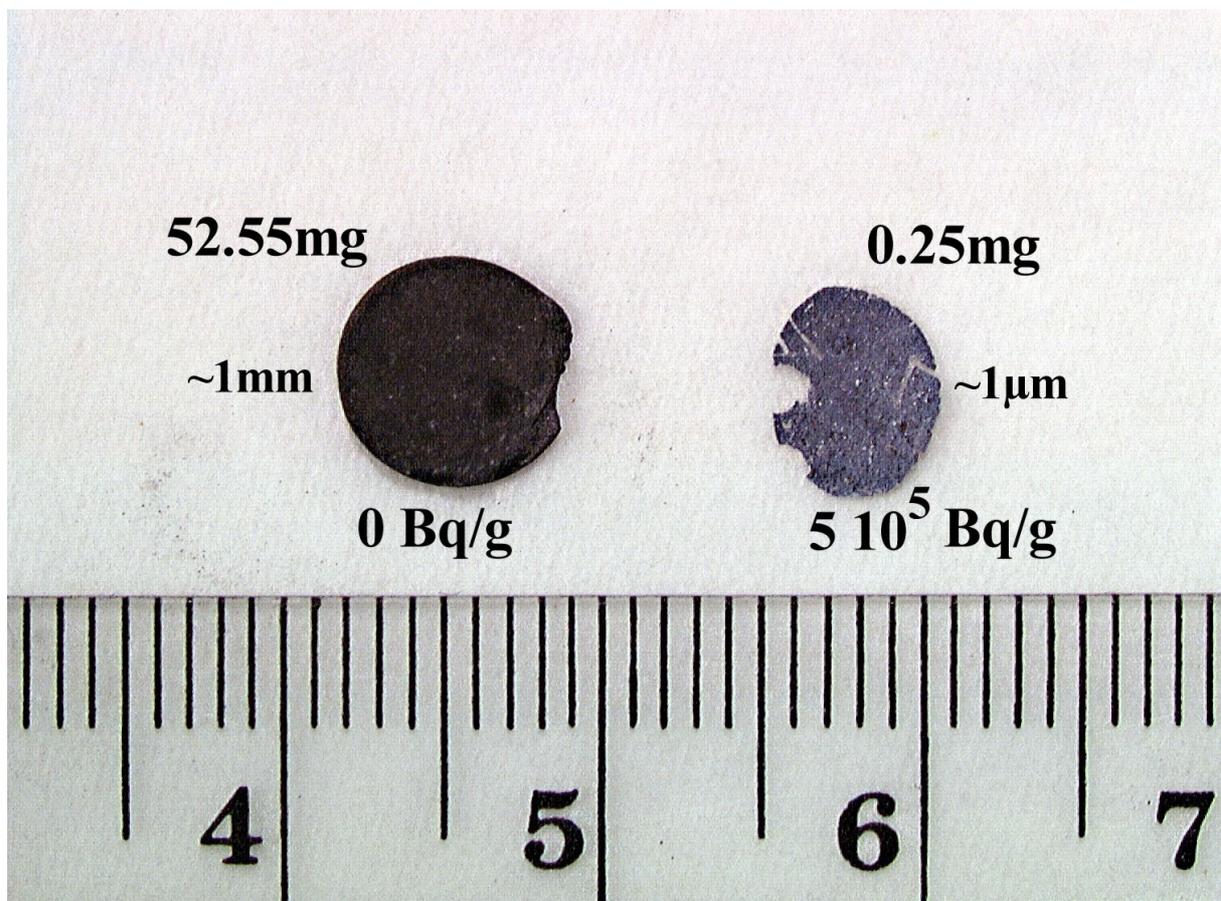


Fig. 13. Thick and thin disc after the RF heating under moist argon.

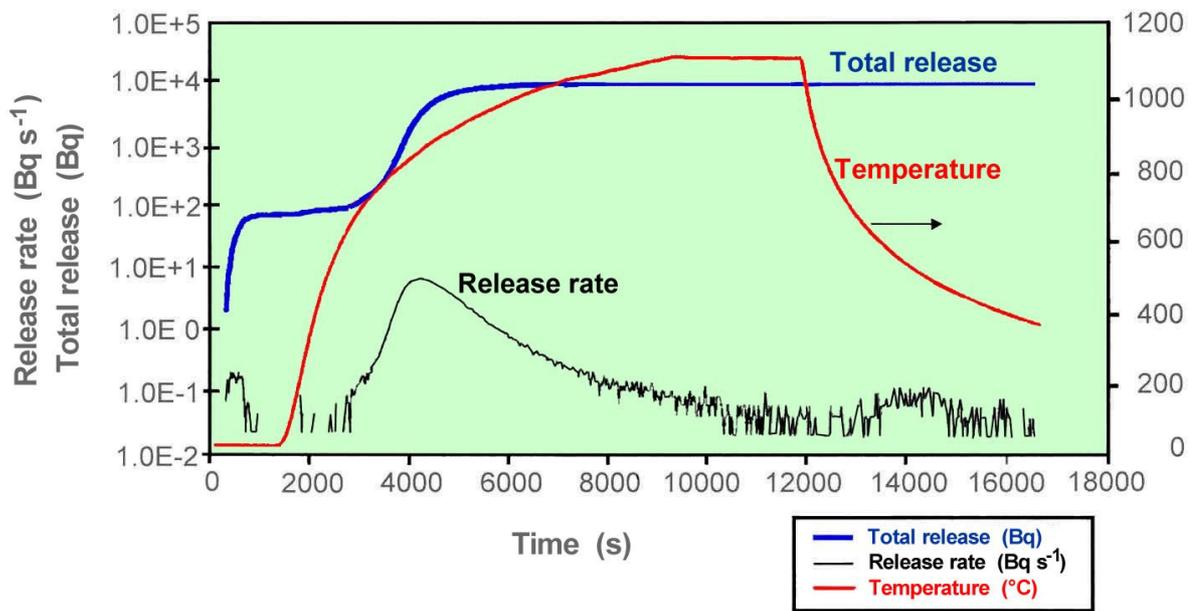


Fig. 14. Tritium thermal desorption spectrum of the A1 disk, cylinder 5 of a JET graphite tile 004/2-20.

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