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Abstract

An experimental program is described which was performed in the frame of a tritium technology task for the NET/ITER fusion fuel cycle. The aim was to investigate commercial gas purifiers containing metallic getters for the purification of gas streams such as the plasma exhaust gas.

Five purifiers with up to 3000g of getter material were tested in the PEGASUS facility mainly with respect to the removal of methane, which is known to be much more difficult to remove than other impurities like O_2, N_2, or CO.

Results are reported on

- the reaction rate constants for the sorption of methane as a function of temperature, gas flow rate, and getter material,
- the occurrence of cosorption effects caused by the presence of CO, N_2, and H_2 in the test gas,
- the enhacement of CH_4 sorption efficiency by continuous removal of hydrogen.

It was found that cosorption effects leading to the formation of additional methane can be suppressed by using two getter beds in series: the first operated at 250-300°C to remove O_2, CO, CO_2, H_2O, and some N_2; the second operated at 500-600°C to remove hydrocarbons and the residual amounts of other impurities (mainly N_2).

Additional emphasis was layed on the gettering and decomposition of water vapor. While gettering proceeds very effectively already at 100°C, temperatures beyond 500°C were found to be necessary for the recovery of hydrogen from the water molecules.

A proposal for a fuel cleanup method based on a combination of getter beds and Pd/Ag diffusors is presented as the main conclusion of the test program. The discussion of this method includes the aspects of flow rates, tritium inventory, and consumption of getter material.

Gasreinigung mit heißen Metallgetter-Betten

Im Rahmen einer Tritium Technology Task für den NET/ITER Brennstoff-Kreislauf wurde ein experimentelles Vorhaben durchgeführt mit dem Ziel, kommerzielle Gasreiniger, die nach dem Prinzip der Rückhaltung von Verunreinigungen an heißen Metall-Gettern arbeiten, auf ihre Eignung zur Reinigung von inerten Gasströmen, wie z.B. dem Plasma Exhaust Gas, zu untersuchen.

An der zu diesem Zweck gebauten PEGASUS-Anlage wurden fünf Gasreiniger mit bis zu 3 kg Gettermaterial eingesetzt, um vor allem die Rückhaltung von Methan zu bestimmen, das sich wesentlich schwerer abtrennen läßt als etwa O_2, N_2 oder CO.

Es werden Ergebnisse berichtet über

- die Reaktionskonstanten für die Sorption von Methan als Funktion von Temperatur, Gasdurchsatz und Gettermaterial,
- das Auftreten von Cosorptionseffekten durch die Anwesenheit von CO, N_2 und H_2 im Versuchsgas,
- die Erhöhung des Sorptionsvermögens für Methan durch kontinuierliche Entfernung des Wasserstoffs.

Die zur Bildung von zusätzlichem Methan führenden Cosorptionseffekte lassen sich durch den Einsatz von zwei Getterbetten in Serie vermeiden: das erste Bett ist bei 250°C zu betreiben, um O_2, CO, CO_2, H_2O und einen Teil des N_2 zu entfernen; das zweite bei 500 - 600°C, um die Kohlenwasserstoffe und das restliche N_2 abzuscheiden.

Ein weiteres Ziel der Untersuchungen lag in der Getterung und Zersetzung von Wasserdampf. Es zeigte sich, daß die Getterung bereits bei 100°C sehr effektiv verläuft, daß die Rückgewinnung von Wasserstoffisotopen durch die Wasser-Zersetzung aber Temperaturen von über 500°C erfordert.

Als Schlußfolgerung aus dem Versuchsprogramm wird ein Brennstoff-Reinigungsverfahren vorgeschlagen, das aus einer Kombination von Getterbetten und Pd/Ag-Permeatoren besteht. In der Diskussion dieses Verfahrens werden u.a. die Aspekte des Gasdurchsatzes, des Tritium Inventares und des Verbrauchs an Gettermaterial angesprochen.

Contents

2. Introduction

In the frame of the fusion fuel cycle many technical approaches for a fuel cleanup unit (FCU) have been discussed in the past years /1,2/. One method, which has attracted less attention than others includes the application of non-uranium getter beds in combination with Pd/Ag diffusors /3,4/. This method was investigated within a tritium technology task for NET and will be described in the present report.

According to the requirements for the NET/ITER Fuel Cleanup System /1/, the output from this system is expected to consist of two gas streams:

- a fuel stream containing no more than a few ppm of impurities, and
- a detritiated impurity stream containing no more than a few ppm of tritium.

The first of these demands can be satisfied by using a Pd/Ag diffusor which is an appropriate tool for the separation of molecular hydrogen isotopes. In addition, the purity of the extracted hydrogen stream is sufficiently high to allow a direct transfer to the Isotope Separation System (ISS). Diffusors are also used in other purification methods such as the HITEX process /5/, the cryogenic molecular sieve process /6/, the water-gas shift process /7/, and the fuel processing methods developed at JAERI /8/ and and at CEA /9/.

In this report it is presumed, that the first component of a purification process is a Pd/Ag diffusor, that removes the bulk of the molecular hydrogen isotopes, and that additional diffusors are used in later steps to complete the separation of these isotopes.

It is then the task of the metal getters to satisfy the second demand mentioned above.

The main properties of getter metals/alloys and intermetallic compounds (IMC)[1] can be summarized as follows:

They are able to remove atoms or molecules from the gas phase by chemical reactions (chemisorption) on "active" surfaces. At sufficient high temperatures, a permanent pumping effect is provided by diffusion of the sorbed atoms into the bulk of the getter. Chemical reactions with hydrogen isotopes proceed reversibly, i.e. hydrogen, deuterium, or tritium can be recovered. Chemical reactions with active gases such as O_2, N_2, CO, hydrocarbons, and water are irreversible due to the formation of stable oxides, nitrides, or carbides. No pumping effect is obtained for noble gases. Activation of the surface is accomplished by heating to at least 350°C under vacuum or inert conditions. An important property for the recovery of tritium is the ability of some getter materials to decompose molecules containing hydrogen isotopes like hydrocarbons or water[2].

When the present study was started in 1986, the experience with metal getter beds for impurity removal was limited to small scale applications and in the most cases to gases with sub-mbar pressures and small impurity concentrations /10-13,16/. The investigated getter materials were those of SAES Getters S.p.A./Milano (mainly ST-101, ST-707, ST-198) and uranium. It was known at this time that N_2, O_2, CO, CO_2, and H_2O can be removed at relatively low getter temperatures (<300°C) while higher temperatures are needed for the sorption of hydrocarbons. No information was available on the recovery of hydrogen from water vapour and on interactions between impurities and hydrogen isotopes during the purification process.

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[1] there is no large difference between alloys and IMC's; the latter normally exhibit a higher degree of homogeneity than alloys

[2] ammonia is not mentioned here because this species is decomposed already by the diffusor /14,15/

It was decided, therefore, to carry out a test program on the applicability of various metal getter beds for fusion gas purification with the following main objectives:

a) to find the most appropriate conditions for the sorption and decomposition of methane,

b) to study potential cosorption effects arising during simultaneous sorption of several impurities,

c) to investigate the sorption and decomposition of water.

In addition, it was intended to apply more realistic conditions with respect to gas flow rates, pressures and impurity concentrations than it had been done in the past. The test facility PEGASUS (Plasma exhaust gas purification system) was constructed in a semi-technical scale according to the standards of ultra-high vacuum technology and largely prepared for tritium tracer tests to be conducted in a later stage of the program. The test gases contained helium (the main impurity component of the plasma exhaust gas) as carrier gas together with up to 5% of hydrogen and up to 1% of the impurities N_2, CO, CH_4, and H_2O.

The tested getter beds were five commercial gas purifiers of SAES/Milano (Italy) and HWT/Mülheim a.d. Ruhr (Germany) containing 700g and 3000g of getter alloy; the latter were investigated for the first time for potential application in fusion technology.

3. Symbols

B1/2= Gas collection tanks
c = concentration of an impurity component in the gas
c_o = initial impurity concentration (at $t = 0$)
c_{in} = impurity concentration at getter bed inlet
c_{out}= impurity concentration at getter bed outlet
d = gas flow rate
f = purification factor ($0 \leq f \leq 1$)
F = effective cross section of the getter bed
FIC = Flow indicator and control
GC = Gas chromatograph
G1/2= Getter beds
HID = Helium ionization detector
HS = Humidity sensor
k = reaction rate constant
k_{Si} = Sievert's constant
L = effective length of the getter bed
p = test gas pressure
Δp = difference of test gas pressure between getter bed inlet and outlet
p_H = hydrogen equilibrium pressure
Q = hydrogen concentration in the getter
t = time
T = temperature
T_G = temperature of the getter bed
$t_{1/2}$ = half period of concentration decrease
t_{min}= theoretical minimum of $t_{1/2}$ (for $f = 1$)
V = test gas volume
w = avarage linear gas velocity
x = unit of effective length of the getter bed

4. Theory

The impurity absorption in a cylindrical getter bed can be described by using the formalism for chemical reactions in a stationary gas reactor: the amount of an impurity species absorbed per unit of time is proportional to the gas velocity and to the decrease in concentration per unit of length of the getter bed (mass balance equation):

$$\frac{dc}{dt} = - \frac{dc}{dx} \cdot \frac{dx}{dt} = - w \cdot \frac{dc}{dx} \qquad (4.1)$$

with c = concentration of the impurity component (mol%)
t = time (s)
w = linear gas velocity (cm/s)
x = unit of length of the getter bed (cm)

The kinetics of absorption is described by a first order chemical reaction

$$\frac{dc}{dt} = k \cdot c \qquad (4.2)$$

By using the assumption that the reaction rate constant k is independent of the impurity concentration in the gas and integrating equation (4.1) one gets the expression

$$k = \frac{w}{L} \cdot \ln \frac{c_{in}}{c_{out}} \qquad (4.3)$$

with L = length of the getter bed (cm)
c_{in} = impurity concentration (mol%) in the test gas at getter bed inlet
c_{out} = ditto at getter bed outlet

When sorption tests are carried out in the closed loop mode the decrease of the impurity concentration c in the gas collection tank is described by

$$\frac{\Delta c}{\Delta t} = - \frac{d}{p \cdot V} (c - c_{out}) = - \frac{d}{p \cdot V} f \cdot c \qquad (4.4)$$

With the assumption that the purification factor $f=1-c_{out}/c$ is independent of c (this is confirmed by the test results), the integration of equation 4.4 leads to

$$c(t) = c_o \cdot e^{-\alpha \cdot t} , \quad \alpha = \frac{f \cdot d}{p \cdot V} \tag{4.5}$$

where c_o = initial impurity concentration (at t=0)
c_{out} = impurity concentration at getter bed outlet
V = test gas volume (l)
p = test gas pressure (bar)
d = flow rate (bar·l/min)

The purification factor is an indicator of the purification efficiency of the getter at the working temperature and for a given impurity. Its maximum value f=1 is obtained, when the impurity is totally removed during a single passage of the gas through the getter. The factor f is evaluated from the c(t) curve as follows:

$$f = \frac{V \cdot p}{d} \cdot \frac{\ln c(t_1) - \ln c(t_2)}{t_2 - t_1} \tag{4.6}$$

A chacteristic variable of each test is the half period $t_{1/2}$ of the concentration decrease. It can be determined from the c(t) curve or according to

$$t_{1/2} = \frac{p \cdot V}{d \cdot f} \cdot \ln 2 \tag{4.7}$$

In the case of maximum purification efficiency (f = 1), the half period attains a minimum t_{min} which is equivalent to an upper limit of the purification velocity for a given set of experimental parameters.

If more than one impurity component is present in the carrier gas, characteristic c(t) curves and results for f and $t_{1/2}$ are obtained for each impurity, but only one value for t_{min}.

5. Description of Experimental Setup and Test Procedure

A schematic diagram of the PEGASUS facility is shown in Fig. 5.1. For simplicity, some components have have been omitted in the figure, e.g. the UHV pumping system, the manifold, and all normal valves. The test gas containing at least one impurity component in helium as carrier gas is prepared in one of the gas collection tanks B1 or B2. The circulation pump (Metal Bellows 151-DC) is used to transport the gas to the purifiers G1/G2, which can be exposed either separately or in series. The main technical data of five purifiers investigated in the test program are summarized in Table 5.1. Details of the construction of these purifiers can be seen in Figs. 5.2/3.

Constant gas flow rates up to 20 l/min are obtained by a flow control system FIC (Tylan). Selective removal of hydrogen can be achieved with a Pd/Ag diffusor (Leybold PA 150 with 290 cm^2 surface aerea). A gas chromatograph (Carlo Erba Fractovap 2700) with a helium ionization detector (HID) is used for quantitative gas analysis. It is placed in a bypass to the main loop and equipped with additional devices for pressure and flow control. The HID detection limit is 100 ppb for N_2, O_2, CO, CH_4, and 5 ppm for H_2.

When a higher sensitivity for the detection of H_2 is needed, an additional gas chromatograph (RGA 3 of Trace Analytics) is available. Its detection principle is based on chemical reduction of HgO by H_2 or CO, and subsequent measurement of the Hg vapor by use of a UV photometer. The detection limit is 10 ppb for H_2 and 2 ppb for CO.

Prior to each test, the composition of the gas mixture is determined by pVT measurements (during gas inlet into the collection tank) and by GC analysis which is carried out after 30 min of gas circulation through the loop to provide a homogeneous mixture.

The tests are normally conducted in the closed loop mode: the gas is circulated several times through the getter(s) until a given level of purity is obtained. Measurements of the impurity concentrations are carried out in two ways:

a) The concentration c_{out} at the outlet of the getter bed is determined in time intervals of 5 - 10 min, when the gas is passed through the (heated) purifier;

b) The concentration c_{in} at the inlet of the getter bed is determined in time intervals of 20 - 30 min, when the purifier is closed and the gas is directly transported from the collection tank B1/B2 to the GC.

Both methods are alternately used during each test to obtain results for both variables c_{in} and c_{out} as a function of time.

Humidity Generation and Measurement

The generation of humidity is accomplished by dehydration of $CuSO_4 \cdot 5H_2O$ (bluestone or Roman vitriole). The principle of the method is described in Fig. 5.4: A moisture generator consisting of a small stainless steel vessel with removable cover is mounted in a bypass of the experimental loop. An electrical heating plate including an automatic temperature control is used to heat the vessel to temperatures ≤ 200°C. The two filters (NUPRO SS-4TF-VCR) at the inlet and the outlet of the vessel are needed to retain hydrate particles during pump out or during gas flow through the vessel.

Before the humidity generation is started, the experimental loop and the bypass are filled several times with dry helium, which is circulated for at least 10 min and then pumped off to remove residual air and moisture from all components, in particular from the moisture sensors.

A continuous gas flow of 2 l/min at 1 bar helium is also maintained during humidity generation by slowly heating the sulfate hydrate. As shown in Fig.5.6, a moisture of about 1000 ppm is obtained in a volume of 106 l after 50 min at 50°C. The first plateau in the moisture curve is due to the release of two of the five water molecules from the hydrate. Upon further increase of the temperature to 80°C, the next two water molecules are released, and the resulting moisture is about 2000 ppm. When higher concentrations are required, it is preferable to increase the amount of hydrate rather than to go to complete dehydration, because temperatures >200°C are needed to release the last water molecule from the hydrate.

Quantitative analysis of the humidity is achieved by using a 4-channel hygrometer system of Panametrics (System 5). A moisture sensor (see Fig.5.6) is essentially an aluminium oxide capacitor, consisting of a small aluminium plate as a first electrode, a thin Al_2O_3 layer, and a gold film as a second electrode. Water molecules absorbed on the pore walls change the conductivity and the electrical impedance of the sensor. The latter is used for quantitative measurement of the water vapor pressure. Each sensor is surrounded by a porous sintered metal shield for protection.

In comparison with other types of hygrometer systems (dewpoint, electrolytical, or quarz hygrometers), the Panametrics system has some main advantages:

- fast response time for increasing humidity*)
- small volume of the sensor allows direct installation in the gas flow,
- large range of sensitivity (1....10^4 ppm).

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*) about 10 sec; during decreasing humidity and humidity concentrations <100 ppm, however, it was found to be at least ten times larger

6. Results

6.1 Sorption of Methane as a Function of Temperature

To investigate the sorption efficiencies for methane on the purifiers mentioned above, several tests have been carried out with getter bed temperatures ranging from 300 to 600°C, cf. Table 6.1. The gas flow rate was 1.0 l/min in the most cases. Results of tests with getter ST-707 are shown in Fig. 6.1. The semilogarithmic c(t) plots of the getter bed inlet and outlet concentrations were found to be straight lines, an indication that the reaction rate constant was independent of the impurity concentration in the test gas.

Increasing the temperature of the getter bed caused an increasing speed of the CH_4 removal and a decreasing ratio of the outlet/inlet concentration. At T_G = 600°C, the half period of the concentration decrease was 17.0 min. As this value is already close to the theoretical minimum (t_{min} = 14.5 min), no significant acceleration of the CH_4 removal can be expected at getter bed temperatures > 600°C, but smaller c_{out}/c_{in} ratios due to increased reaction rate constants k.

Corresponding results for the getter material ST-198 are shown in Fig. 6.2. Again a temperature of 600°C is needed to obtain a purification with a half period close to the minimum value for the given experimental conditions (p,V,d). The increasing slope of the two curves indicates an increase in purification efficiency at CH_4 inlet concentrations < 0.02%. A comparison of the SAES getters at T_G = 600°C shown in Fig. 6.3 does not reveal large differences in the purification efficiency between ST-198 and ST-707, whereas getter ST-101 appears to be somewhat less effective for the removal of methane.

The properties of the two HWT purifiers HTR-1/2 are illustrated in Fig. 6.4. The temperature dependence of the purification speed was similar to that of the SAES getters.

The higher retention efficiency of the purifier HTR-2 compared to that of HTR-1 can be explained by an increased cracking capability for CH_4 which is obtained by the catalytic property of the additional content of 7% nickel in the getter alloy.

6.2 Enhacement of Sorption Efficiency by Continuous Removal of the Released Hydrogen

The half period of 27.1 min measured in test PV-23 for the CH_4 removal at 400°C can be further decreased by additional provisions as applied in test PV-22. Before this test the getter was dehydrided at 450°C to a hydrogen equilibrium pressure of 0.36 mbar.

During the test, the hydrogen resulting from the remaining equilibrium pressure as well as from the cracking of CH_4 was pumped off with the Pd/Ag diffusor. In this way, the decomposition $CH_4 \rightarrow C + 2\ H_2$ was accelerated by continuously shifting the equilibrium to the right. The result is shown in Fig. 6.5. The output/input ratio decreased by a factor of two, and the half period of the CH_4 removal was now 18.3 min, which is even less than the corresponding value in test PV-9, where the purifier HTR-1 was operated at 500°C (cf. Fig. 6.4).

For the application of this method the getter must be sufficiently dehydrided to keep the hydrogen equilibrium pressure lower than the pressure expected from the cracking of CH_4.

6.3 Sorption of Methane as a Function of Flow Rate

Results on the influence of the flow rate on the sorption speed can be derived from tests PV-2b and PV-2d (cf. Fig.6.6): At a flow rate of 0.5 l/min a higher purification effect, i.e. a smaller value of the c_{out}/c_{in} ratio was found. This is due to the longer contact time of a given gas volume with the getter than at a flow rate of 1 l/min. On the other hand, the concentration in the buffer tank decreased more slowly, because the gas was less frequently pumped through the getter. In other words: The longer residence time in the purifier is overcompensated by the higher frequency of the gas circulation.

In analogue tests carried out with the HWT getter HTR-2 at flow rates of 1.0, 2.0, and 4.0 l/min, again a faster decrease in concentration was found with increasing flow rate (Fig.6.7). This effect is understood when the difference Δp of the gas pressure between purifier inlet and outlet is considered:

1 l/min : Δp = 42.3 mbar

2 l/min : Δp = 112.9 mbar

4 l/min : Δp = 205.4 mbar

Increasing loss of pressure means an increasing number of collisions between the gas atoms and the getter material and, as a consequence, also an increasing sorption rate. Although these results have been obtained for CH_4 only, it is assumed that they are also valid for other impurities like CO or N_2.

6.4 Cosorption Tests

To investigate the question of mutual interactions between different impurities during the sorption process two tests were carried out with H_2, CH_4, N_2, and CO as components of the carrier gas, cf. Fig. 6.8. Prior to the first of these tests the purifier HTR-1 was dehydrided during activation at 400°C.

At a getter temperature of 200°C hydrogen was gettered to a large extent in the beginning; however, the change in the slope of the curve at t = 40 min indicates an approach to the equilibrium condition where the rates of uptake become smaller. At 300°C the desorption pressure of the getter was already higher than the hydrogen partial pressure in the loop so that the concentration was found to increase.

For CO and N_2 a higher sorption speed was observed for 300°C than for 200°C, as expected. For CH_4 the getter temperature of 200°C was obviously too low to cause any measurable sorption effect. At 300°C, however, a surprising effect was found: an increase in concentration from 0.46% to 0.85% rather than the expected decrease. This can be explained by the formation of additional methane caused by an interaction of carbon monoxide and hydrogen which is catalysed by the hot getter:

$$CO + 3\ H_2 \longrightarrow CH_4 + H_2O$$

The corresponding amount of water was directly sorbed by the getter. From the form of the resulting curve and from the final amount of methane it can be derived that preferentially those CO molecules participated in the reaction that entered the getter together with the carrier gas. As there was a strong decrease in the CO concentration in the first 20 minutes of the test, the rate of CH_4 formation decreased also. The carbon sorbed in the preceeding test at 200°C was not involved in the reaction, otherwise the amount of the additional methane would have been much higher.

To further investigate the CH_4 formation by H_2 and CO an additional experiment (PV-10) was carried out with a test gas containing 0.8% CO and 3.8% H_2 in the carrier gas. The gas mixture was circulated through the getter for several time periods of 20 minutes during which the temperature was kept constant at 50, 150, 200,.., 400°C, respectively. The results of the gas analyses performed after each temperature step (see Fig. 6.9) contribute well to the understanding of the previous results:

a) CO was removed from the gas with an increasing sorption efficiency at higher temperatures; the outlet concentration was already lower than 100 ppm at 350°C.

b) First traces of CH_4 were found at 200°C; its concentration increased during the following steps up to a final value of 0.0325%. Most of this amount was formed at getter temperatures in the range of 250 - 350°C, where the CO concentration was still high enough and where the catalytic influence of the getter was already effective.

c) Throughout the test, the available amount of H_2 was higher than the demand for the CH_4 formation. Due to the sorption on the getter bed its concentration decreased to 0.13% at 300°C, but increased again at higher temperatures because of the rising desorption pressure of the getter.

6.5 Prevention of Cosorption Effects by Using Two Getter Beds in Series

The formation of additional methane is very undesirable from the view of gas purification. An appropriate way to suppress this formation is the application of two getter beds in series. The first bed has to be operated at about 250°C to reduce the concentration of CO and H2 and the second bed at a temperature of at least 400°C to effectively remove CH_4 and N_2.

Test PV-15 was carried out to verify this method. The resulting sorption curves are shown in Fig.6.10. The sorption speed for methane was almost as high as for CO and N_2. As can be seen from Table 6.1, the ratio c_{out}/c_{in} was 0.178, which is much better than the coresponding values of the tests PV-20/21. The H_2 retention capability of the first getter bed operated at 200°C was apparently higher than the H_2 removal capability of the Pd/Ag diffuser applied in tests PV-20/21. Thus, the equilibrium shift mentioned in 6.2 led to a stronger increase in the methane cracking efficiency of the second getter bed.

Additional tests (PV-16, PV-38) were carried out at 250/450°C and 250/500°C, respectively. In these cases the purification efficiency was considerably higher: the c_{out}/c_{in} ratios were about a factor of three lower than in test PV-15, see also Table 6.2 and Fig. 6.11. It can be concluded, therefore, that the combination of two getter beds in series operated at 250/500°C is a very effective method for the removal of methane, when H_2, CO, and N_2 are present as additional components of the test gas. If these components are missing (or have been removed by other methods) it may be sufficient to use a single HTR-2 purifier operated at 500°C like in test PV-34.

6.6 Identification of the Liberated Hydrogen

The hydrogen recovered from the cracked methane could not be measured because an unknown fraction of the formed hydrogen was sorbed by the getter. On the other hand, hydrogen was desorbed from the getter according to the equilibrium pressure resulting from the preceeding hydrogen uptake. It is impossible, therefore, to identify the origin of the measured hydrogen.

It would be necessary to use tritiated methane and a diffusor installed downstream of the getter bed to detect the liberated tritium after permation through the diffusor. While this is an on-line procedure, the identification could also be achieved off-line by isotopic swamping, i.e. by passing a helium/hydrogen mixture through the purifier and then by detecting the released tritium.

Similar difficulties arose in connexion with the cracking of water where additional attempts were made to identify the recovered hydrogen (cf. 6.9).

6.7 Evaluation of Reaction Rate Constants

The reaction rate constant of methane with the getter materials tested were calculated by using equation 4.3

$$k = \frac{w}{L} \cdot \ln \frac{c_{in}}{c_{out}}$$

The linear gas velocity w was derived from the gas flow rate by

$$w\ (cm/s) = \frac{d}{F} \cdot \frac{T_K}{273.15} \cdot ß$$

with
F = cross section of gas flow in the getter bed (cm^2)
T_K = temperature of the getter bed (K)
d = gas flow rate (l/min)
$ß$ = 16.667 = dimensional factor

The geometrical dimensions of the getter beds were

SAES getter beds (Model 101) : L = 1.4 cm, F = 152 cm^2

HWT getter beds (Model HTR) : L = 16.0 cm, F = 80 cm^2

The results of the calculations are compiled in Table 6.3. The highest rate constants were obtained for the getter materials St-707/St-198 at T_G=600°C and for the combination of two HTR-2 getter beds operated at T_G=250/500°C. This is shown also in Fig. 6.12, where the rate constants are plotted as a function of temperature.

The influence of continuous hydrogen removal obtained with the Pd/Ag diffusor is again apparent: the rate constants determined for these tests (PV-20...PV-22) are about twice as high as for test PV-23, where no diffusor was used.

6.8 Removal of Humidity

Sorption tests with water vapor were carried out to determine the removal capability of the getter HWT-HTR-2 as a function of gas flow rate and initial humidity concentration.

Results of three tests with initial humidity concentrations of 1000-3000 ppm are shown in Fig. 6.13, where the humidity at the getter inlet measured with sensor HS1 (cf. Fig. 5.1) is plotted as a function of time. The total gas volume was 20.7 barl·l in all cases. The removal factors calculated with equation 4.5 were in the range of $f = 0.97 - 0.99$. This means a very good retention of the moisture by the getter, at least for inlet concentrations ≥ 200 ppm.

At lower inlet concentrations, a decreasing slope of the curves was observed for the tests with gas flow rates of 4 l/min. This was mainly caused by the increasing response time of the moisture sensor. The humidity removal from the aluminium oxide layer of the sensor was not fast enough to allow a correct measurement of the decreasing humidity in the gas.

An additional effect might have been the desorption of water molecules from internal surfaces of the loop which leads to a delay in the humidity removal if the amount of desorbing water vapor is of the order of some ppm/min.

No influence of the sensor response time has been observed in test PV-26, where the gas flow rate was 1 l/min. However, the test has only been extended to a humidity level of 60 ppm. Similar effects as described above might have occured for smaller inlet concentrations.

Humidity values measured with sensor HS2 at the getter bed outlet are shown in Fig.6.14a/b for tests PV-27 and PV-28. Before these tests were started, the humidity of sensor HS2 had been removed by evacuation to levels of 5.4 ppm and 1.1 ppm. As can be seen from Fig.6.14a, the c_{out} curve decreases very slowly from the initial level, while in Fig.6.14b there is at first a fast increase and then a slow decrease. These findings again reflect the behavior of the sensor as described in Chap. 5.

Although the measurements are somewhat uncertain for small moisture levels, there is no doubt, that a humidity of a few thousand ppm can be reduced by two orders of magnitude during a single passage of the gas through the getter bed. This conclusion is also confirmed by the results of test PV-32 (Fig.6.15) which was carried out with an initial humidity of 6150 ppm, and by an additional test, where a getter bed temperature of 25°C was employed.

No sorption tests were carried out with the SAES purifiers because results on the reaction of these getter materials with water vapour were already available from the literature /16-21/.

6.9 Decomposition of H_2O

The investigation of hydrogen recovery by cracking of the H_2O molecules during interaction with the getter material was the second part of the humidity tests. The formation of H_2 was determined by two methods:

- by analysis of gas samples with one of the gas chromatographs described in Chap.5,
- by continuous measurement of the total pressure in the loop.

During H_2O sorption tests at 100, 200, and 300°C no additional hydrogen beyond that from the equilibrium pressure of the getter could be detected. In addition, the decrease of the total pressure was found to be quantitatively the same as the decrease of the H_2O partial pressure. At least a conversion of 80 ppm H_2O to H_2 would have been detectable, because this corresponds to a difference of 0.1 mb in total pressure.

To further investigate the question, the getter bed temperature was increased to 500°C. The H_2 equilibrium pressure, which was 15 mb at this temperature, was reduced by deloading the getter to $p(H_2) = 0.426$ mb. A known amount of hydrogen $\Delta Q = 210$ mb·l was then loaded onto the getter to determine the constant k_{Si} of Sieverts law /22/

$$p_H = k_{Si} \cdot Q^2$$

which describes the relationship between the equilibrium pressure p_H and the hydrogen concentration Q in the getter. After the getter was again deloaded to $p = 0.426$ mb, an amount of 3200 ppm H_2O was sorbed by the getter, while the temperature was still 500°C. By using the Sieverts constant, it was calculated that the hydrogen equilibrium pressure should have increased by 0.206 mb if all water molecules were converted to H_2. According to the experimental results, however, the hydrogen pressure increased only by 0.011 ± 0.005 mb. This means, that only 5% of the water molecules were cracked and that still higher temperatures than 500°C are needed for hydrogen recovery from water with the HWT purifier. Unfortunately, such temperatures could not be realized with the getter bed employed in this test series.

Similar results, i.e. the need of temperatures $\geq$ 500°C for hydrogen recovery have also been found for the getter materials St-707, St-199 (Zr_2Ni) /16-18,20/ and St-172 (Zr + St-707) /23/. However, G.Bonizzoni et al. /24/ have shown recently that a fast catalytic conversion of water to hydrogen can be obtained already at 300°C with the SAES getter ST-737 [$Zr(Fe_{0.5}V_{0.5})_2$]. Some of the results described in this publication are illustrated in Fig. 6.16.

7. Conclusions

Five commercial gas purifiers containing zirconium or titanium based getter alloys were investigated with respect to their applicability for the purification of inert fusion process gases. Because it had been known from the beginning that some of the expected impurities (O_2, N_2, CO, NH_3) can be removed without major difficulties, the test program was concentrated on the following questions

- to find the most appropriate conditions for the removal of methane,
- to study cosorption effects arising during simultaneous sorption of several impurities,
- to investigate the sorption and decomposition of water.

7.1 Highlights of the Results

1. All tested purifiers can be used for the removal of methane. A recomended minimum temperature is 500°C in all cases.

2. At 500°C, the SAES getter St-707 has the highest reaction rate constant for the sorption of methane. An extrapolation of the rate constant of the HWT getter HTR-2 indicates that this getter is equivalent to St-707 at 600°C.

3. The efficiency of the methane removal can be increased by suppressing the back reaction $C + 2H_2 \rightarrow CH_4$. This is achieved by using either a Pd/Ag diffusor or an additional getter bed at low operation temperature to remove hydrogen from the process gas before it is exposed to the hot getter bed.

4. The removal of hydrogen is also important to avoid the formation of additional methane due to the reaction between CO and hydrogen, which is catalysed by the getter at temperatures > 250°C.

5. It has been demonstrated successfully, that a combination of two getter beds with operation temperatures of 250 and 500°C can be used to prevent the formation of additional methane. Furthermore, the negative influence of other impurities on the methane removal efficiency of the second getter bed can be reduced by this method /25/.

6. A humidity of several thousand ppm (corresponding to several mbar of water vapor) can be removed very efficiently by the HTR-2 getter even at room temperature. At a getter temperature of 100°C and a gas flow rate of 4 l/min, a humidity of 6000 ppm was reduced by at least two orders of magnitude during a single passage of the gas through the getter bed.

7. Hydrogen recovery by chemical decomposition of water on the HTR-2 getter is not possible at temperatures below 500°C. Thus, temperatures of 600°C - 700°C are needed as reported in the literature for the getter materials St-707 and St-199 (Zr_2Ni).

7.2 Comparison with Earlier Work

Investigations comparable to those described above are not very numerous. In particular, there is not one publication on the application of HWT getters for gas purification in fusion technology. The brief review of results described below deals mainly with properties of the SAES getters which appear useful for comparison or for additional information.

a) S.Prakash et al./26/ have studied the sorption behavior of a 5 mg sample of getter St-101 at temperatures up to 500°C. They found the sorption rates for different impurities to increase in the following order:

$$N_2 < CO < CO_2 < O_2$$

b) Similar results are reported by L.Rosai et al./27/. They found the same order of removal efficiencies for St-101 with the addition, that the sorption for CH_4 is still smaller than that for N_2.

c) L.C.Emerson et al./28/ used wafer modules of ST-101 to determine the pumping speed of four gaseous alkanes at temperatures up to 640°C. The pumping speeds were found to be 1 - 3 orders of magnitude smaller than that of active gases like H_2, O_2, or CO. In comparison with the pumping speed of CH_4 at 600°C, the pumping speed of C_2H_6 was found to be higher by a factor of 3 and that of C_3H_8 and C_4H_{10} even by a factor of 5. In addition, the pumping speed of CH_4 was found to be 10 times higher at 600°C than at 400°C. The latter result cannot be compared with the findings of the PEGASUS tests, as only one test was carried out with getter St-101. However, the temperature dependence of the reaction rate constants (Fig. 6.12) can be used to compare the factor 10 mentioned above with the ratio

$$\frac{k(T=600°C)}{k(T=400°C)}$$

which was found to be 3.1, 5.2, 29.5, and 9.4 for the getters St-707, ST-198, HTR-1, and HTR-2, respectively.

d) According to C.Boffito et al./29/ St-707 exhibits a better performance for the sorption of CO and CH_4 than ST-101. This statement is confirmed for CH_4 by the PEGASUS tests (Fig.6.12). (No results are available for CO). An additional advantage of St-707 is that lower activation temperatures are needed than for St-101 /30/.

e) W.J.Lange /31/ reports that a coiled tungsten filament operated at 2500 K can be used to crack some of the methane before the gas is sent through the purifier.

f) The sorption capacity of St-101 for CO, N_2, and O_2 has been determined by B.Ferrario et al./32/. The results of this investigation are also found in a general information sheet of SAES/Milano containing the following data:

Getter Alloy	Operation Temp.°C	Purification capacity (Torr·l/g) for CO	CO_2	O_2	N_2	CH_4	H_2O[a)]
St-101	700	2.2	2.2	11	2.2	N.A.	0.1
St-707	400	9	9	40	9	2.5	0.5
St-198	350	2.2	2.2	11	-	poor	0.9

a) depends on H_2 equilibrium pressure

These values, however, appear to be somewhat questionable, because they are far below the theoretical capacities. If, for example, a stochiometric uptake of N_2 or CH_4 is assumed for ST-707, and ZrN-V-Fe or ZrC-V-Fe is formed, the theoretical capacities are 45 Torr·l per g getter material for N_2 and 91 Torr·l per g for CH_4.

It has been shown by R.D.Penzhorn et al./33/ for the case of ZrCo that it is indeed possible to obtain saturation capacities for N_2 and CH_4 which are very close to the theoretical values.

g) Various intermetallic compounds (IMC's) such as

$Zr_{0.7}Ti_{0.3}Mn_2$, $ZrMnFeCr_{0.25}$, and $Zr(V_{0.8}Cr_{0.2})_2$

were investigated by V.G.Vasilev et al./34/ with respect to the sorption of O_2, N_2, and CO at temperatures up to 800°C.

They too noticed the formation of methane resulting from the reaction between CO and H_2 and mention the catalytic influence of the getter material. They propose a combination of 3 getter beds to separate impurities from hydrogen isotopes and helium:

1.bed: $ZrMnFeCr_{0.25}$ (T=700°C) for removal of N_2, O_2, CO
2./3.bed: $Zr_{0.7}Ti_{0.3}Mn_2$ (T=20°C) for absorption of hydrogen isotopes and separation of helium.

This method does not consider the presence or formation of methane. In addition, the handling of humidity and ammonia impurities is not discussed.

h) According to a literature evaluation carried out by A. N. Perevezentsev /35/ the IMC $Zr_{0.8}Ti_{0.3}Mn_{1.9}$ appears to have superior properties with respect to the removal of methane than the SAES and HWT getters investigated in the present report, cf. also /25/.

7.3 Significance of the Results to NET/ITER

It has been shown that metal getters can be used for efficient removal of the impurities occuring in the fuel cycle of a fusion reactor. However, the application of corresponding purifiers should be combined with the use of several Pd/Ag diffusors for the removal of molecular hydrogen during different steps of the purification process. A proposal for a purification method based on this principle is shown in Fig. 7.1.

According to /1/ the gas flow rate of the plasma exhaust is 75 moles/h in the burn and dwell mode. When the molecular hydrogen isotopes as the main components (95%) of the gas stream are removed by the first diffusor the remaining tritium radioactivity to be handled is less than 3% of the initial amount. In addition, the gas flow rate is reduced to 3.75 moles/h or 1.5 l/min, which corresponds very well with the flow rates applied in the PEGASUS tests.

Two relevant chemical reactions occur during the passage of the gas through the first diffusor: (a) the cracking of ammonia and (b) the formation of water, if unbound oxygen is available.

The next step of the fuel cleanup is the cracking of water molecules on the getter bed GB2 (St-737). A temperature of 300°C is recommended for this getter to keep the formation rate of additional methane by the Q_2/CO reaction as low as possible. (Some Q_2 is also available from the bleed of the preceeding diffusor). CO and CO_2 will be retained with high efficiency on the getter, while N_2 will be sorbed at a lower percentage (10 - 30%).

The second diffusor is used to reduce the Q2 concentration before the gas enters getter bed GB2, where the hydrocarbons are cracked (cf. 7.2,c). The getter material may be either $Zr_{0.8}Ti_{0.3}Mn_{1.9}$ or $Ti_{1.0}V_{0.3}Fe_{0.06}Ni_{0.3}Mn_{1.6}$(HTR-2). St-707 is not recommended, because this material becomes brittle after absorption of more than 25 mbar·l Q2 per gram.

The final diffusor separates the recovered hydrogen isotopes from the remaining gas which is now only helium since nitrogen is absorbed on the bed GB2.

The permeated hydrogen isotopes of all diffusors are conducted to the Isotope Separation System (ISS). The size of the diffusors, i.e. the effective surface area, is much smaller for the diffusors 2 and 3, because the amount of hydrogen isotopes to be separated is smaller by at least a factor of 50 than for diffusor No.1.

An estimation of the impurity load on the two getter beds during plasma exhaust purification (75 moles/h) is given in Table 7.1. If the integral purification capacity of the getters is assumed to be 15 mbar·l/g (cf.7.2f) the following consumption of getter material is obtained

GB1: 0.8 kg/h , GB2: 1.4 kg/h

It should be mentioned, however, that an uncertainty factor of 2-3 is involved in this calculation due to the lack of sufficient experimental data.

The main advantages of the proposed method are:

- Tritium inventory is reduced to less than 3% during the first step,
- Gas flow rate is reduced to 1.5 Nl/min at the same time,
- Getter beds BG1 and GB2 contain a low tritium inventory that can be extracted by heating and/or isotope swamping when the getters are exhausted,
- No introduction of additional gases,
- No need for electrolysis,
- Once through operation, if both getter beds are paralled by identical beds which are exchanged when their capacity is exhausted,
- Large, fully instrumented getter bed units commercially available (from SAES and HWT).

7.4 Suggestions for Future Investigations

The completion of the PEGASUS program which has covered many aspects concerning the applicability of metal getters does not yet mean that sufficient quantitative information is available for the layout of a getter based fuel purification facility for NET/ITER. Some important details to be investigated with respect to the cleanup procedure proposed above are:

- Construction and test of a Pd/Ag diffusor suited for gas flow rates of 30 bar·l/min and extremely high inlet concentrations of hydrogen isotopes (95%).

- Demonstration of the cracking of tritiated water by the getter material St-737 at 300°C in the presence of CO, N_2, and CQ_4.
- Identification of liberated hydrogen isotopes from the decomposition of methane and water, e.g. by applying the procedures proposed in 6.6.
- Additional tests with improved techniques for humidity measurements in the concentration range below 10 ppm.
- Additional comparative tests to select the most appropriate getter material for the cracking of hydrocarbons; these tests should be carried out with helium as carrier gas containing up to 25 % of hydocarbons and with getter beds that can be heated to 700°C.
- Determination of the purification efficiency as a function of impurity uptake, for St-737 as well as for the getter material selected for GB2.
- Determination of tritium desorption from the getter materials (decontamination).

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Table 4.1: Main technical data of the tested purifiers

Type	ST-101	ST-198	ST-707	HTR-1	HTR-2
Supplier	SAES	SAES	SAES	HWT	HWT
Alloy	Zr-Al	Zr-Fe	Zr-Fe-V	Ti-V-Fe-Mn	Ti-V-Fe-Ni-Mn
Content	700g	700g		3000g	
T_{max}	900°C	800°C[a)]		500°C	
p_{max}	10 bar	10 bar		10 bar	
d_{max}	2.5 l/min	5 l/min		16 l/min	
max. H_2-Sorption[b)]	15 bar·l	15 bar·l		-	

T_{max} = maximum working temperature

p_{max} = maximum input pressure

d_{max} = maximum gas flow rate

a) for purifiers without water cooling: $\leq$ 400°C

b) SAES getters have an upper limit for hydrogen uptake, beyond which embrittlement phenomena will occur; such a limit does not exist for the HWT getters

Table 6.1: CH_4 sorption tests with various purifiers

Test No.	Purifier	d (l/min)	T (°C)	c_o (%)	c_{out}/c_{in}
PV-2a	ST-707	1.0	300	0.45	0.68
PV-2b	"	1.0	400	0.80	0.36
PV-2c	"	0.5	400	0.70	0.31
PV-2d	"	1.0	600	0.50	0.15
PV-8	ST-198	1.0	400	0.46	0.71
PV-6	"	1.0	600	0.48	0.26
PV-5	ST-101	1.0	600	0.50	0.48
PV-4	HTR-1	1.0	400	4.81	0.56
PV-9	"	1.0	500	0.75	0.23
PV-20a)	HTR-2	4.0	400	0.30	0.70
PV-21a)	"	2.0	400	0.30	0.50
PV-22a)	"	1.0	400	0.30	0.25
PV-23	"	1.0	400	0.27	0.51
PV-34	"	1.0	500	0.10	0.015
PV-15b)	"	3.0	200/400	0.10	0.178
PV-16b)	"	2.0	250/450	0.10	0.064
PV-38c)	"	3.0	250/500	0.85	0.040

c_o = concentration at getter bed inlet at start of the test

c_{in}, c_{out} = concentration at getter bed inlet/outlet

a) with continuous hydrogen removal by use of a Pd/Ag diffuser

b) with two purifiers at different temperatures; initial gas mixture contained 0.5% H_2 and 0.1% of CO, N_2, and CH_4 in a total volume of 107 Nl

c) with two purifiers at different temperatures; initial gas mixture contained 5% H_2 and 1% of CO, N_2, and CH_4 in a total volume of 19.4 Nl

Table 6.2: Results of purification tests with two getter beds in series

Component	c_{out}/c_{in}		
	PV-15	PV-16	PV-38
CH_4	0.178	0.064	0.040
CO	0.066	0.024	n.d.
N_2	0.099	0.033	n.d.

n.d.: no data available

Table 6.3: Rate constants for methane sorption

Test No.	Type of Getter	T (°C)	d (l/min)	c_{out}/c_{in}	w (cm/s)	k (1/s)
PV-2a	St-707	300	1.0	0.68	0.230	0.063
PV-2b	"	400	1.0	0.36	0.270	0.197
PV-2c	"	400	0.5	0.31	0.135	0.113
PV-2d	"	600	1.0	0.15	0.351	0.476
PV-8	St-198	400	1.0	0.71	0.270	0.066
PV-6	"	600	1.0	0.26	0.351	0.338
PV-5	St-101	600	1.0	0.48	0.351	0.184
PV-4	HTR-1	400	1.0	0.56	0.5085	0.018
PV-9	"	500	1.0	0.23	0.584	0.054
PV-20[a)]	HTR-2	400	4.0	0.70	2.034	0.045
PV-21[a)]	"	400	2.0	0.50	1.017	0.044
PV-22[a)]	"	400	1.0	0.25	0.5085	0.044
PV-23	"	400	1.0	0.51	0.5085	0.021
PV-34	"	500	1.0	0.015	0.584	0.153
PV-15[b)]	"	200/400	3.0	0.178	1.525	0.165
PV-16[b)]	"	250/450	2.0	0.064	1.093	0.188
PV-38[c)]	"	250/500	3.0	0.040	1.752	0.352

w = linear gas velocity in the purifier

a) b) c) see footnotes of Table 6.1

Table 7.1: Estimation of the impurity load per hour on getter beds GB1 and GB2

Impurity	Feed Gas a,b) Mole Fraction	Feed Gas a,b) bar·l/h c)	GB1 bar·l/h	GB2 bar·l/h
He	0.033	59.4	---	---
C_xQ_y	0.0112	20.16	2.02	18.14
CO	0.0016	2.88	2.88	---
Ar	0.0008	1.44	---	---
CO_2	0.0008	1.44	1.44	---
N_2	0.0016	2.88	0.72d)	2.88
NQ_3	0.0008	1.44	---	---
O_2	0.0016	2.88	4.32e)	---
Q_2O	0.0016	2.88	---	---
Σ	0.053	95.4	11.38	21.02

a) data taken from Table IV-8 in /1/

b) gas flow rate including hydrogen isotopes: 75 moles/h

c) for 1 mol ≡ 24 l at 20°C

d) 20% N_2 including 20% of 0.72 bar·l/h from NQ_3

e) including 1.44 bar·l O_2/h from Q_2O

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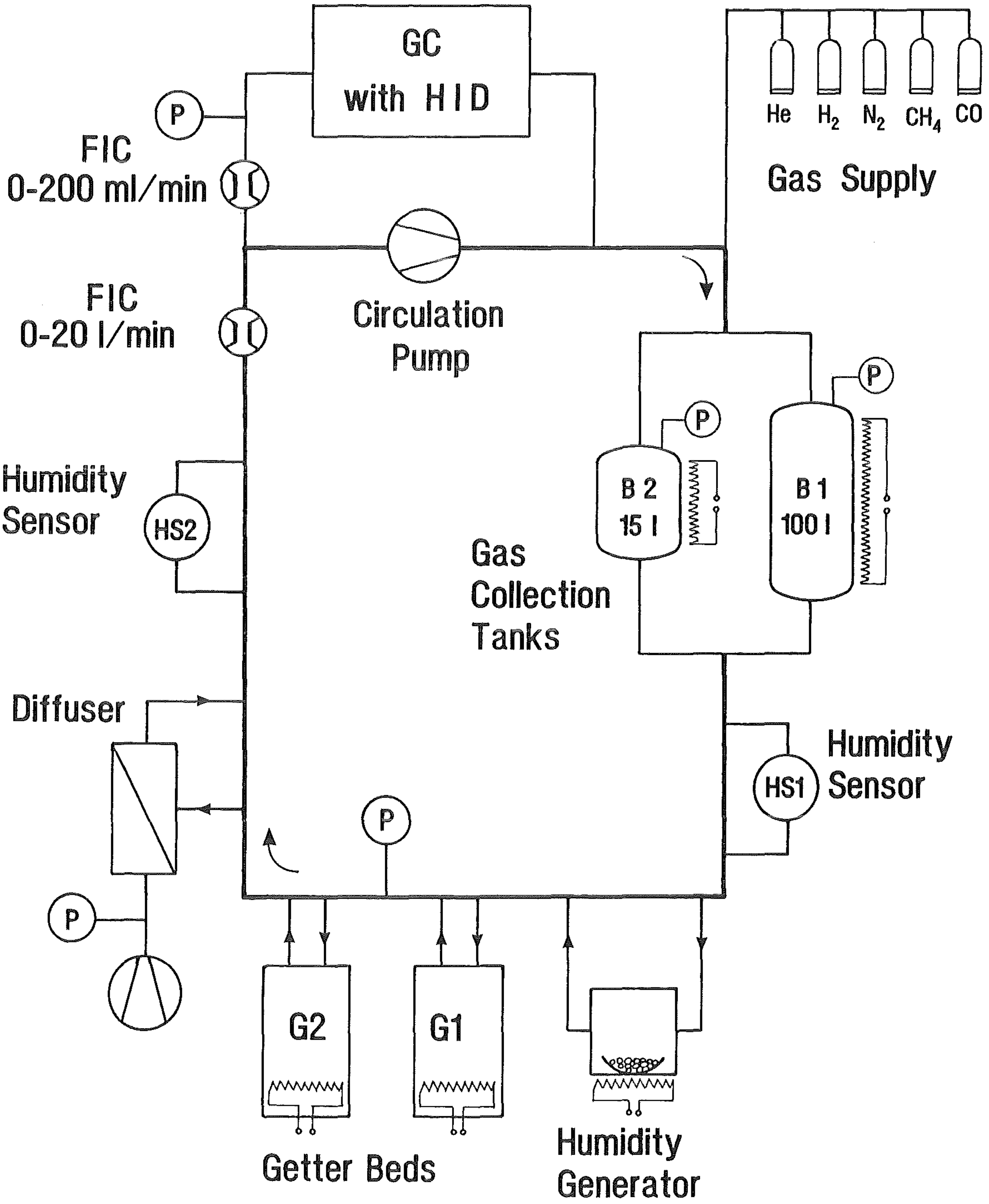


Fig.5.1:

DIAGRAM OF THE PEGASUS FACILITY

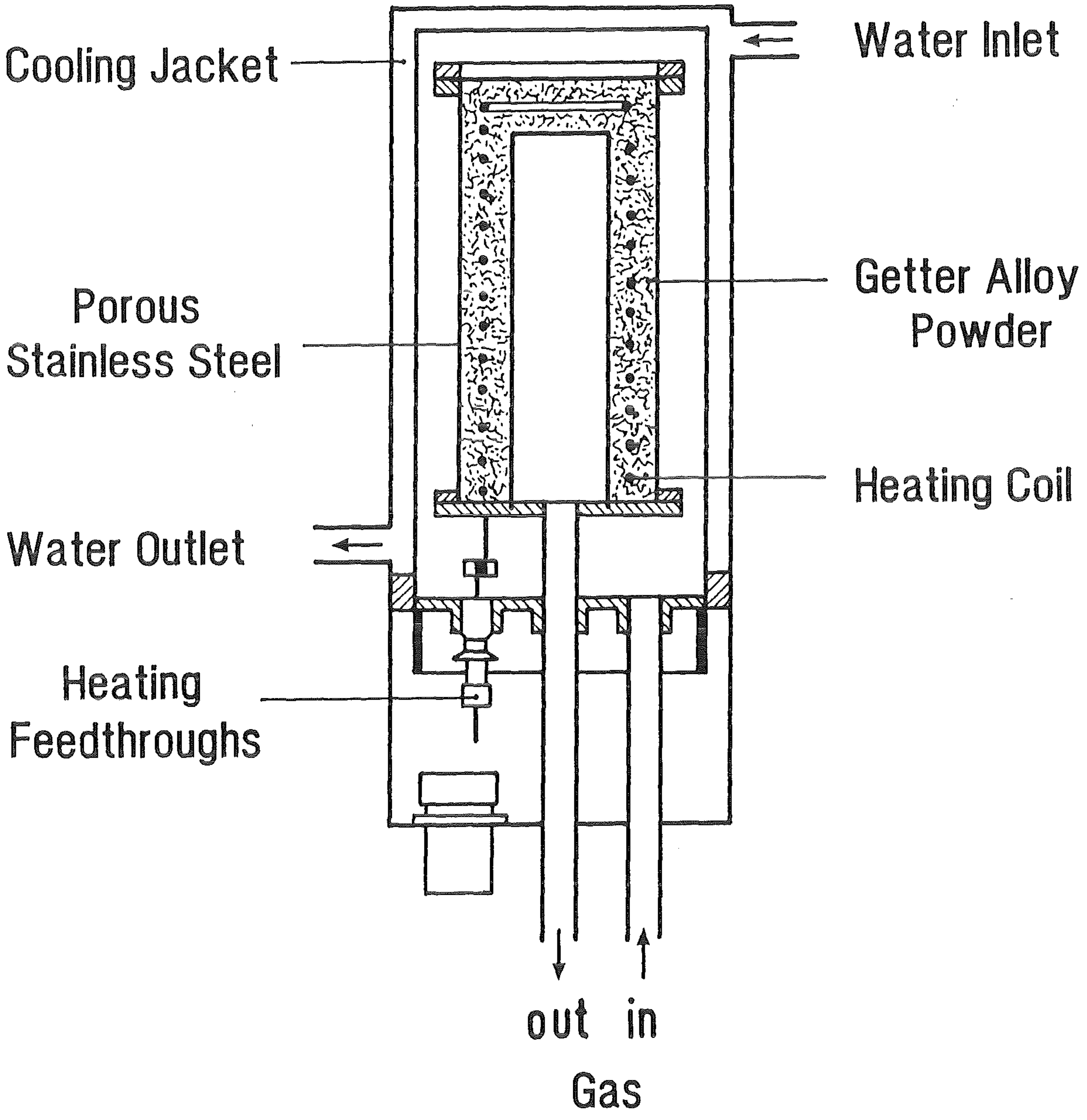


Fig. 5.2:

Construction of SAES Purifier 101/700

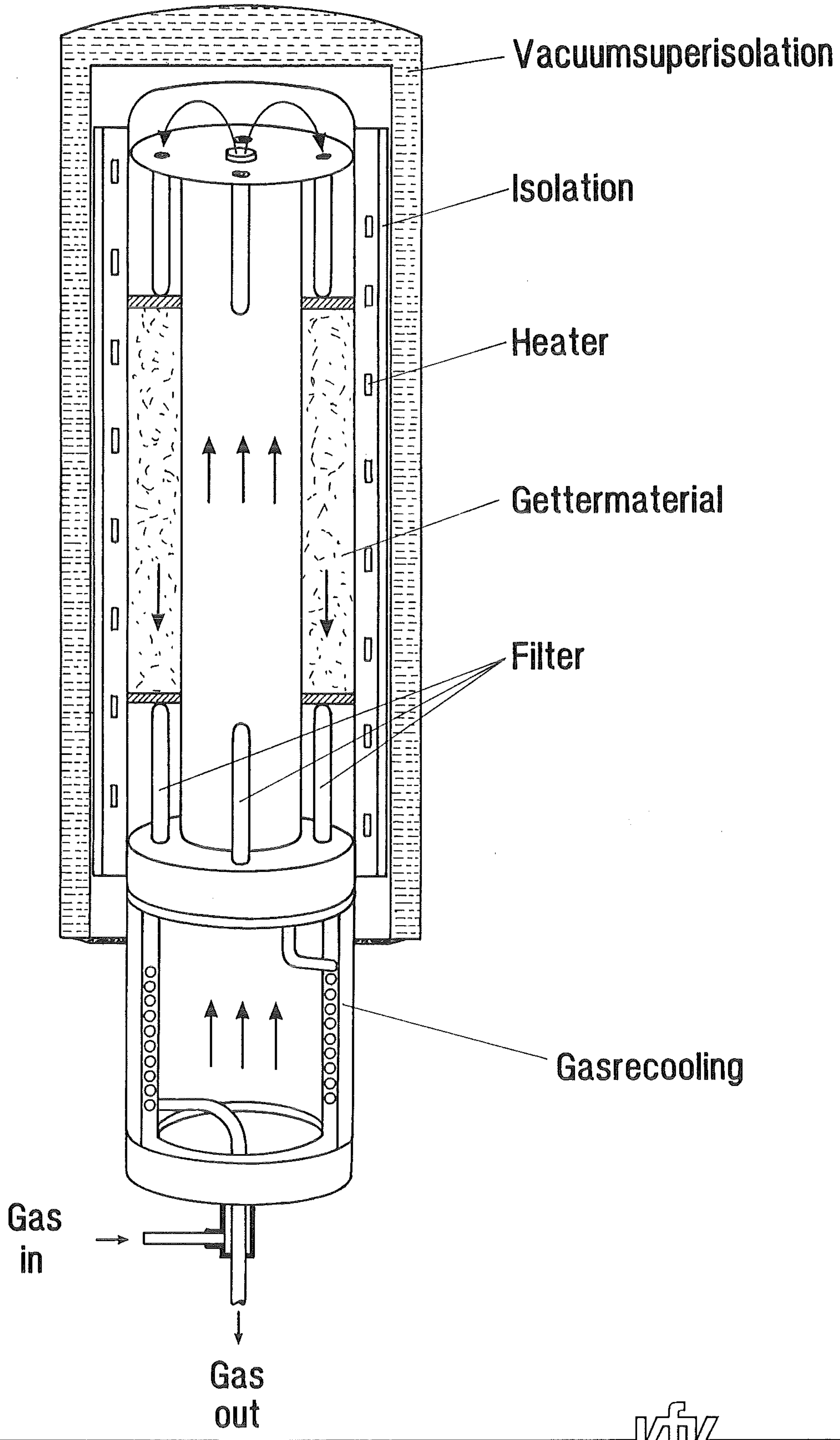
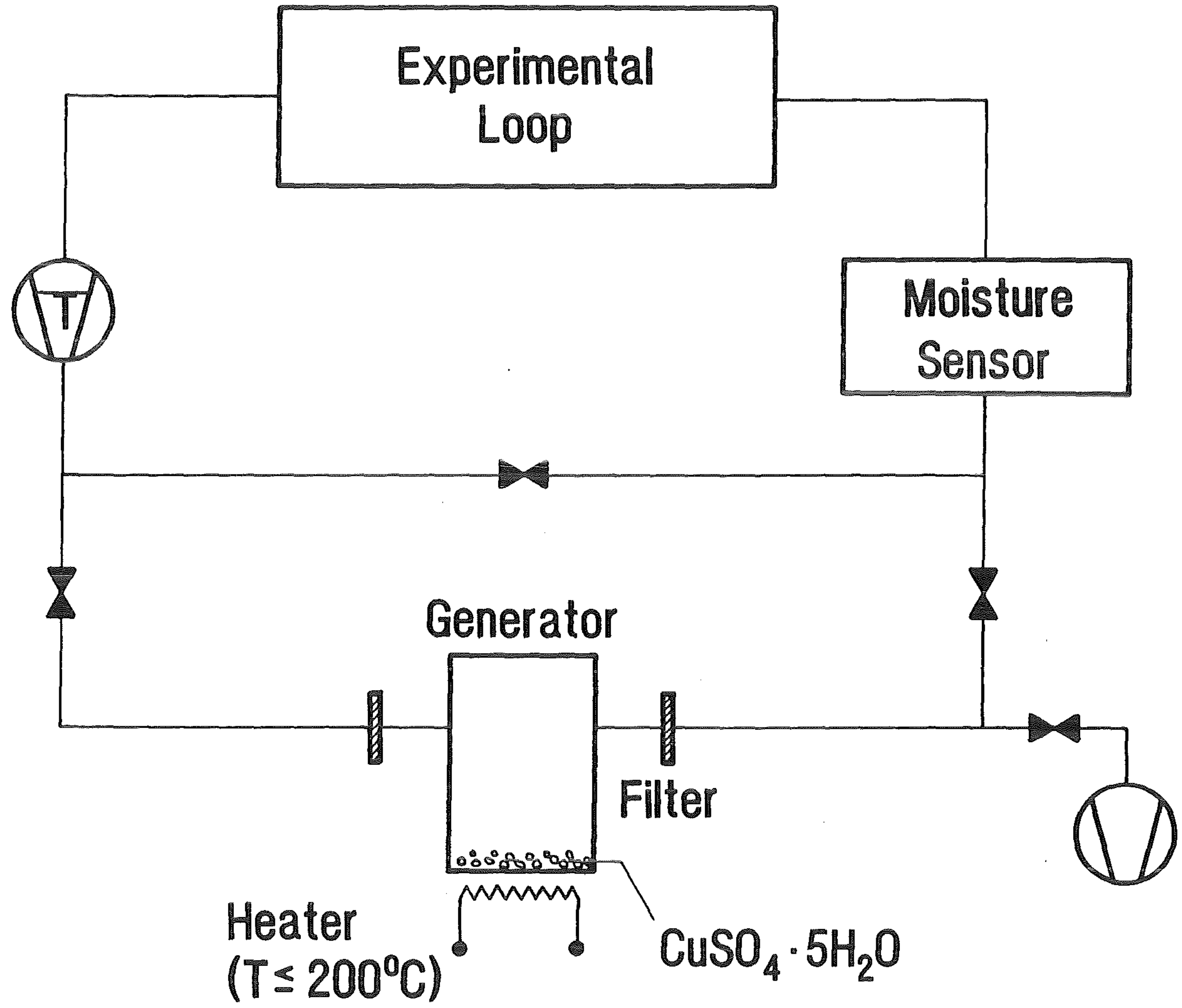


Fig. 5.3:

HWT Gas Purifier HTR



1 g $CuSO_4 \cdot 5\,H_2O$ → ≤ 4000 ppm moisture in 100 l He (1 bar)

Fig.5.4:

Principle of Moisture Generation

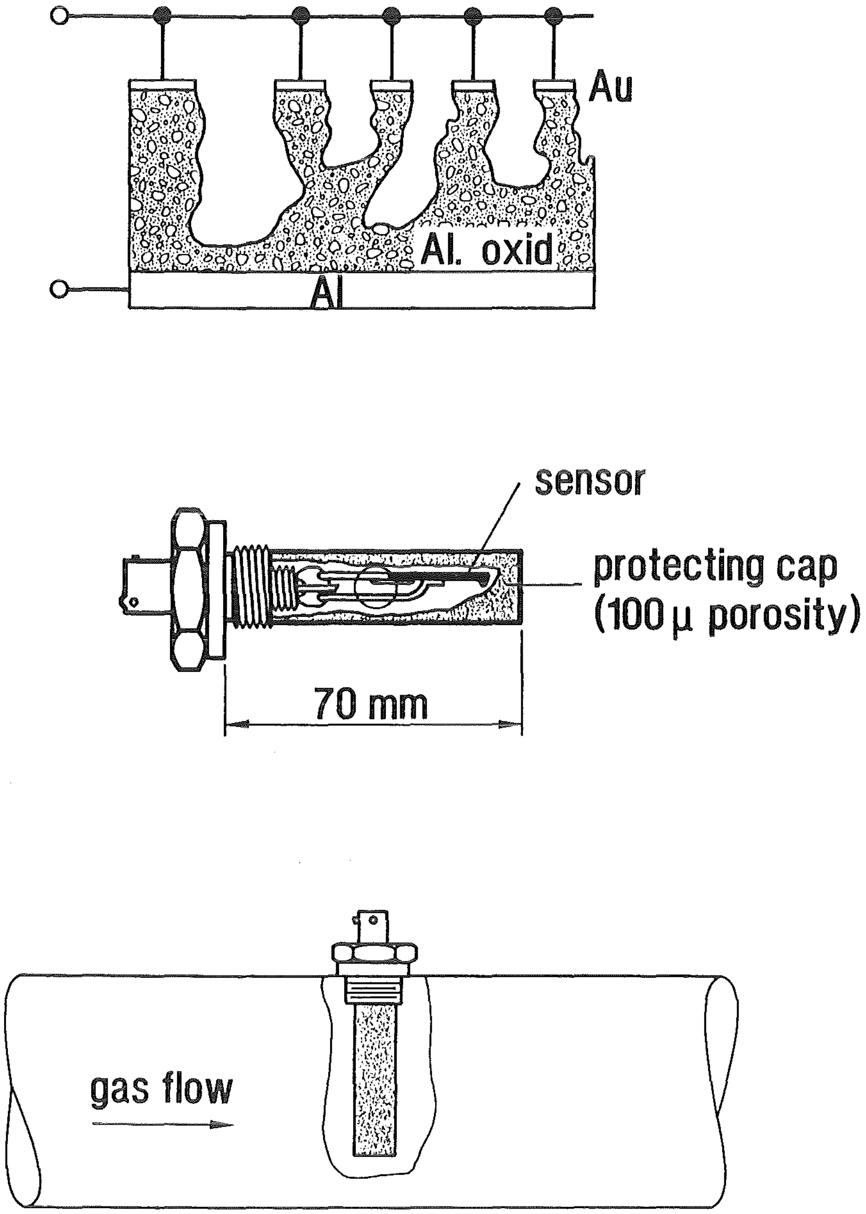


Fig. 5.5:

Construction and Application of the Panametrics Moisture Sensor

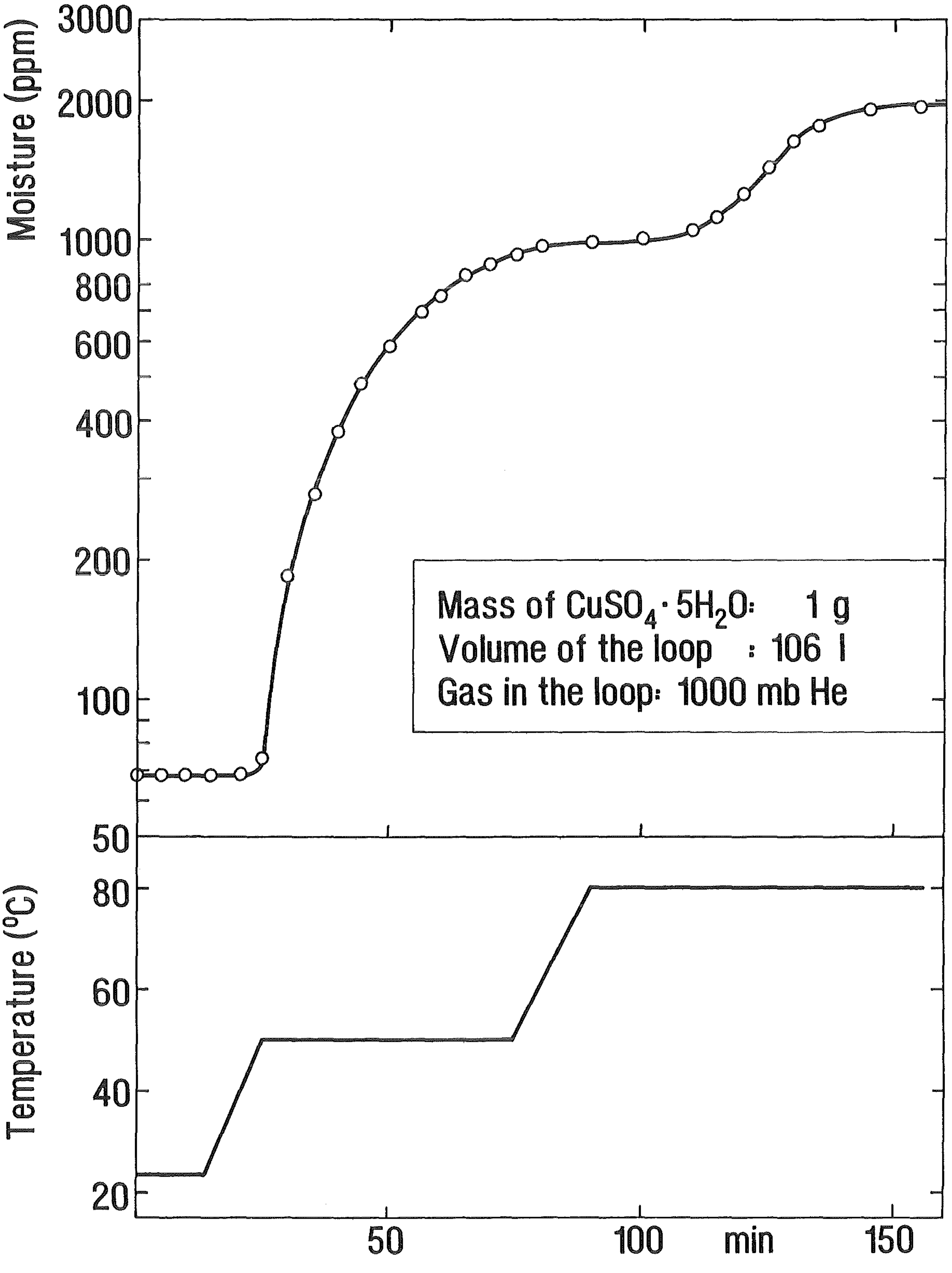


Fig. 5.6:

Generation of Moisture during Heat-up of $CuSO_4 \cdot 5\,H_2O$

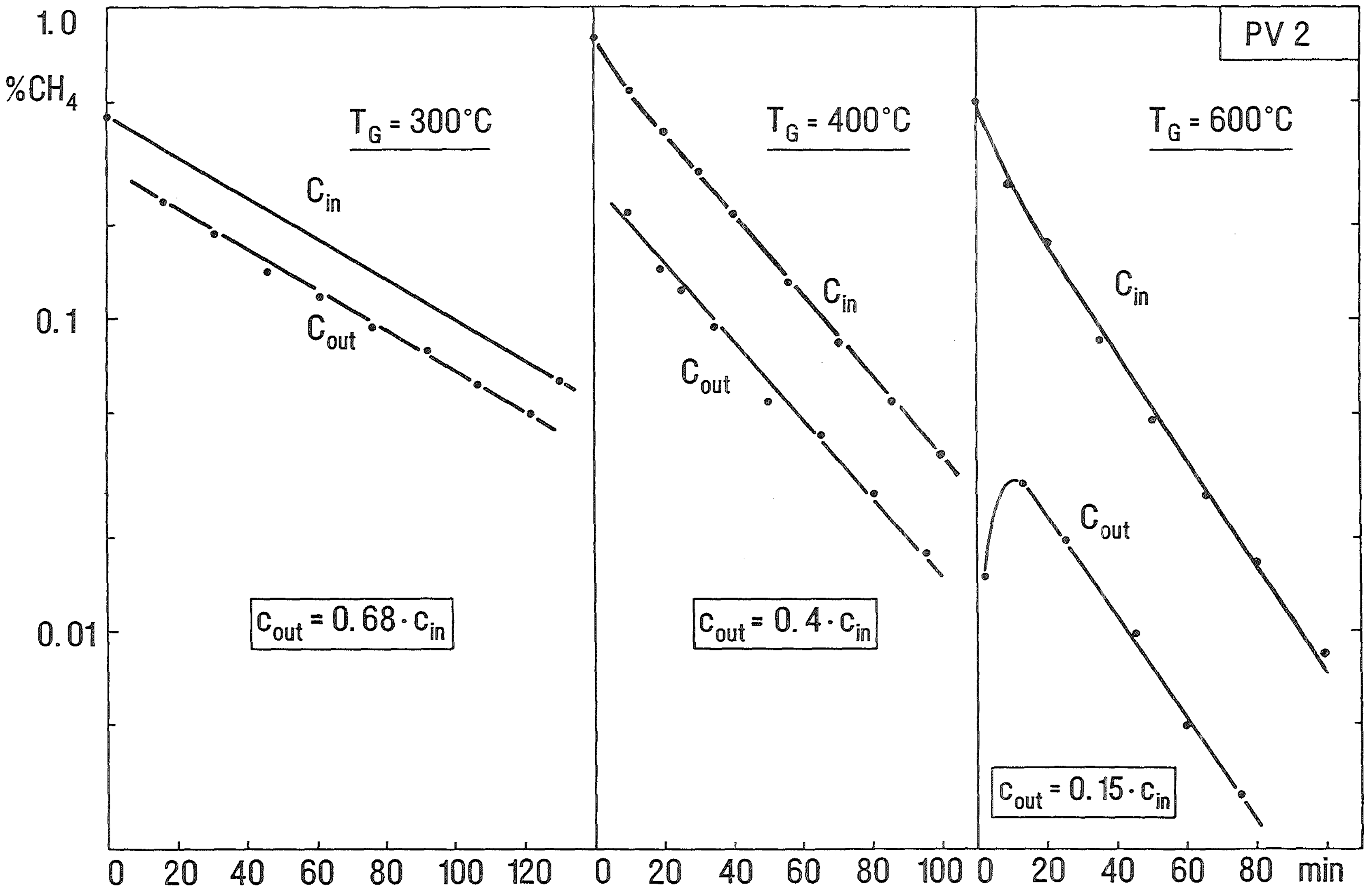


Fig. 6.1: Sorption of CH_4 on getter St-707 as a function of bed temperature T_G

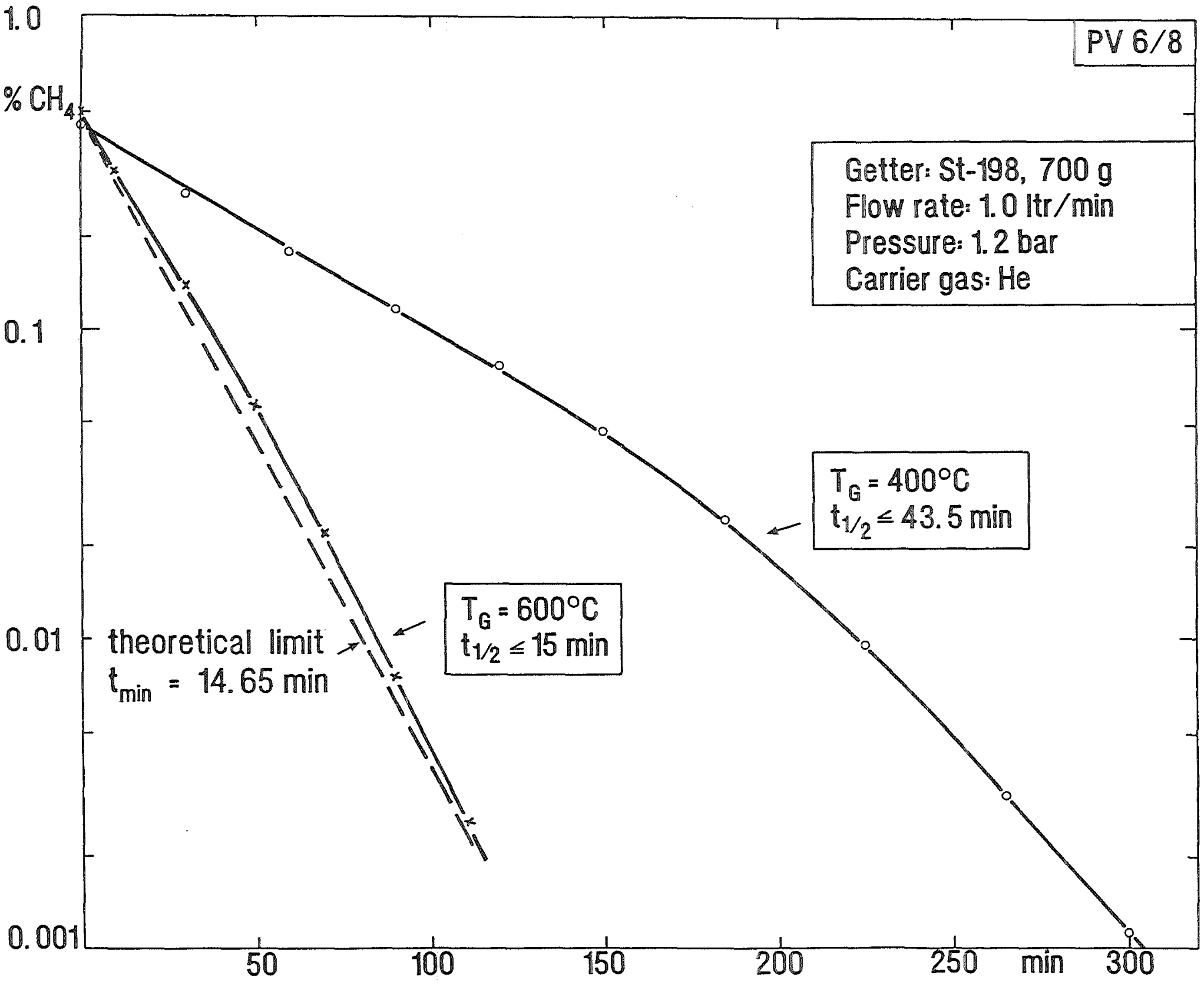


Fig. 6.2: Sorption of CH_4 on getter St-198 as a function of bed temperature T_G

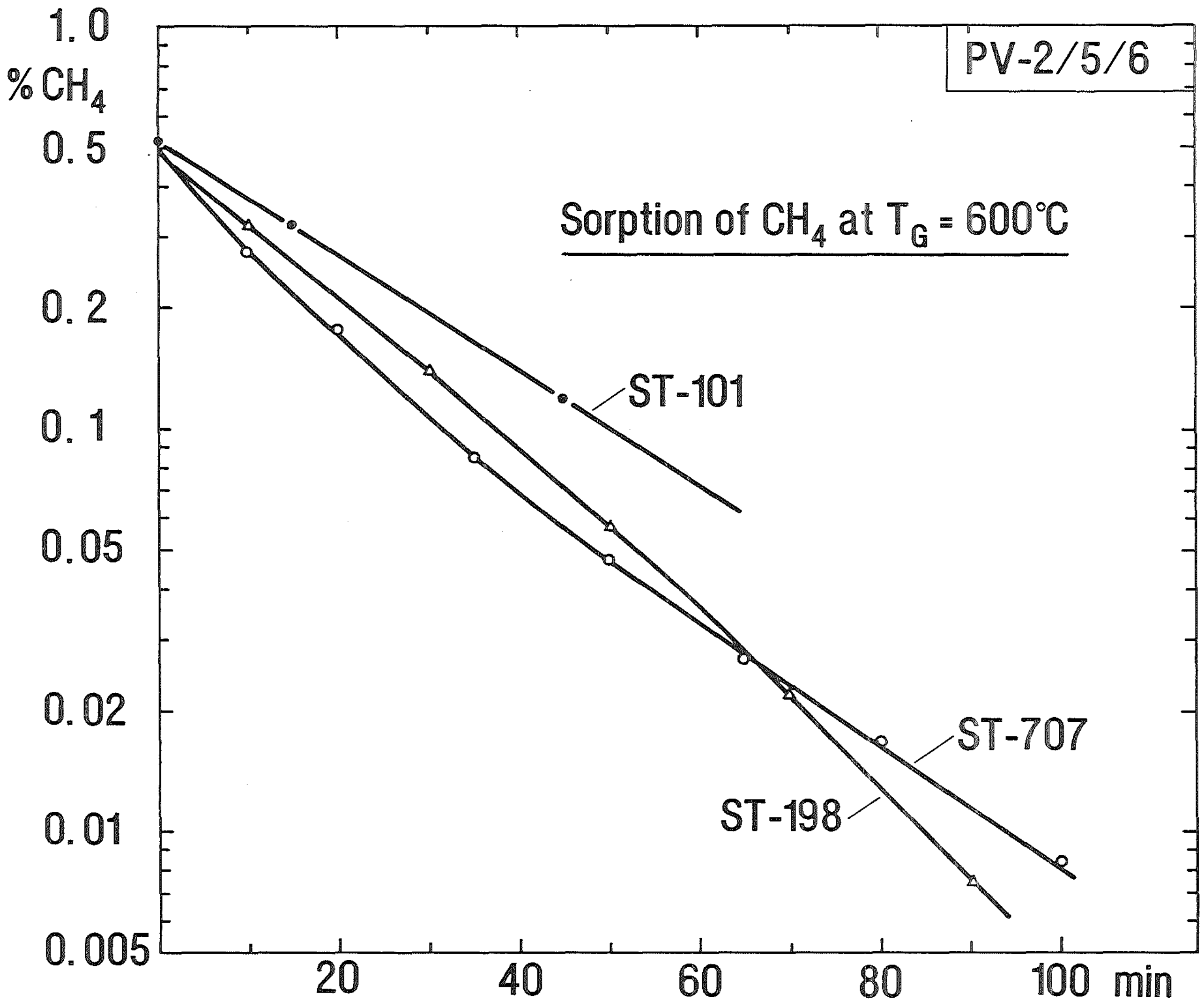


Fig. 6.3:

Comparison of SAES Getters

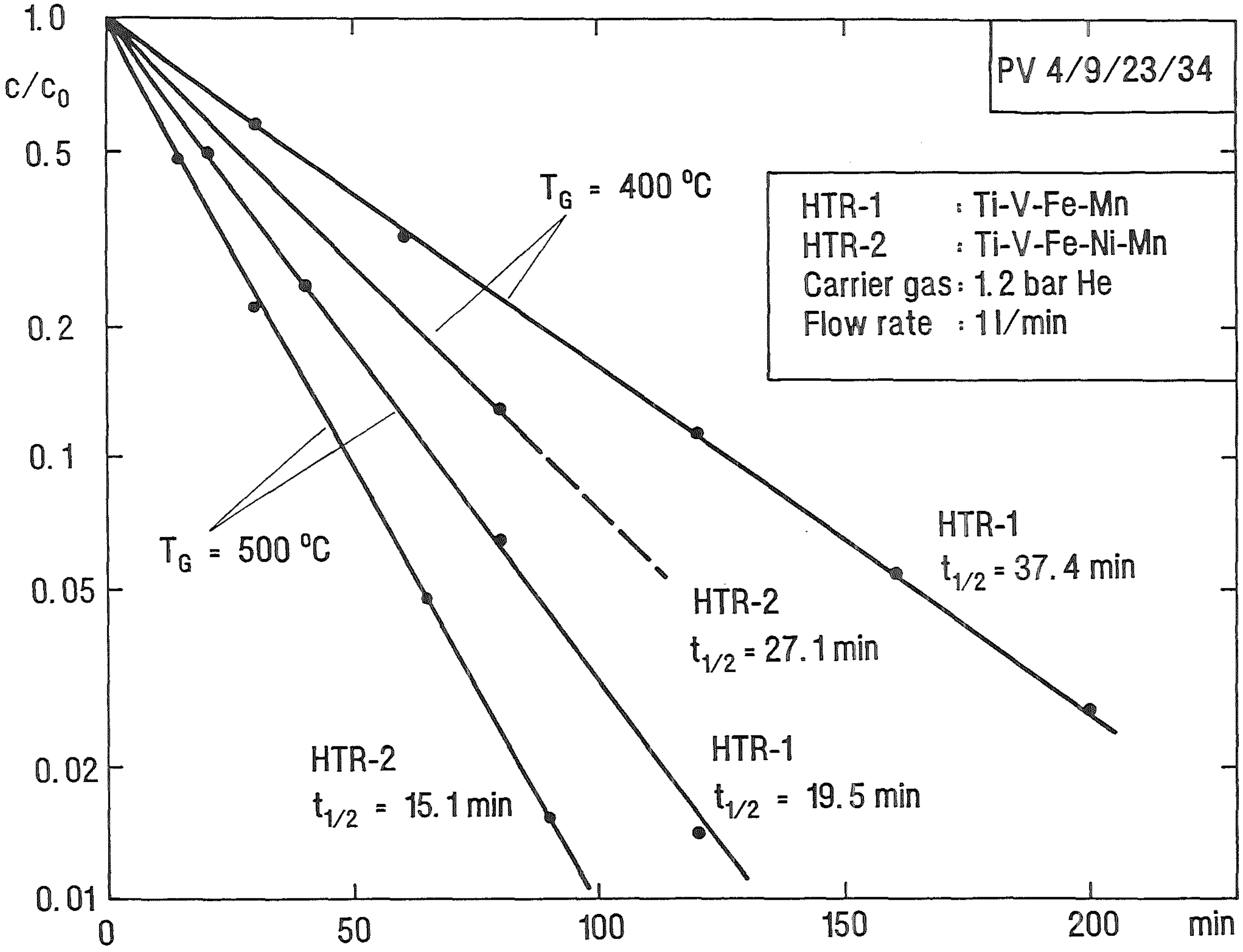
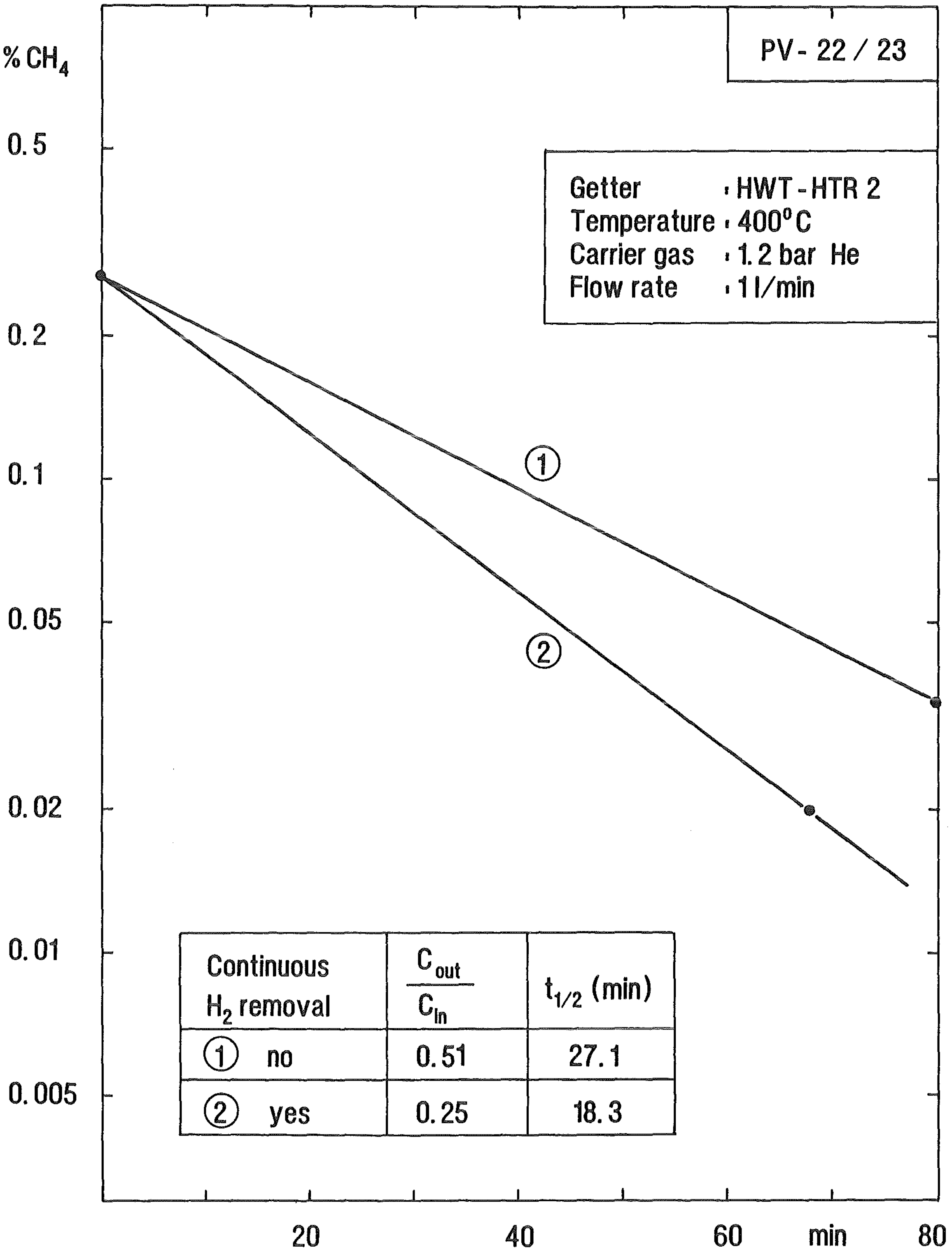


Fig. 6.4: Sorption of CH_4 on HWT getters HTR-1 and HTR-2



Continuous H_2 removal	$\frac{C_{out}}{C_{in}}$	$t_{1/2}$ (min)
① no	0.51	27.1
② yes	0.25	18.3

Fig. 6.5:

Sorption of CH_4 with and without continuous H_2 removal

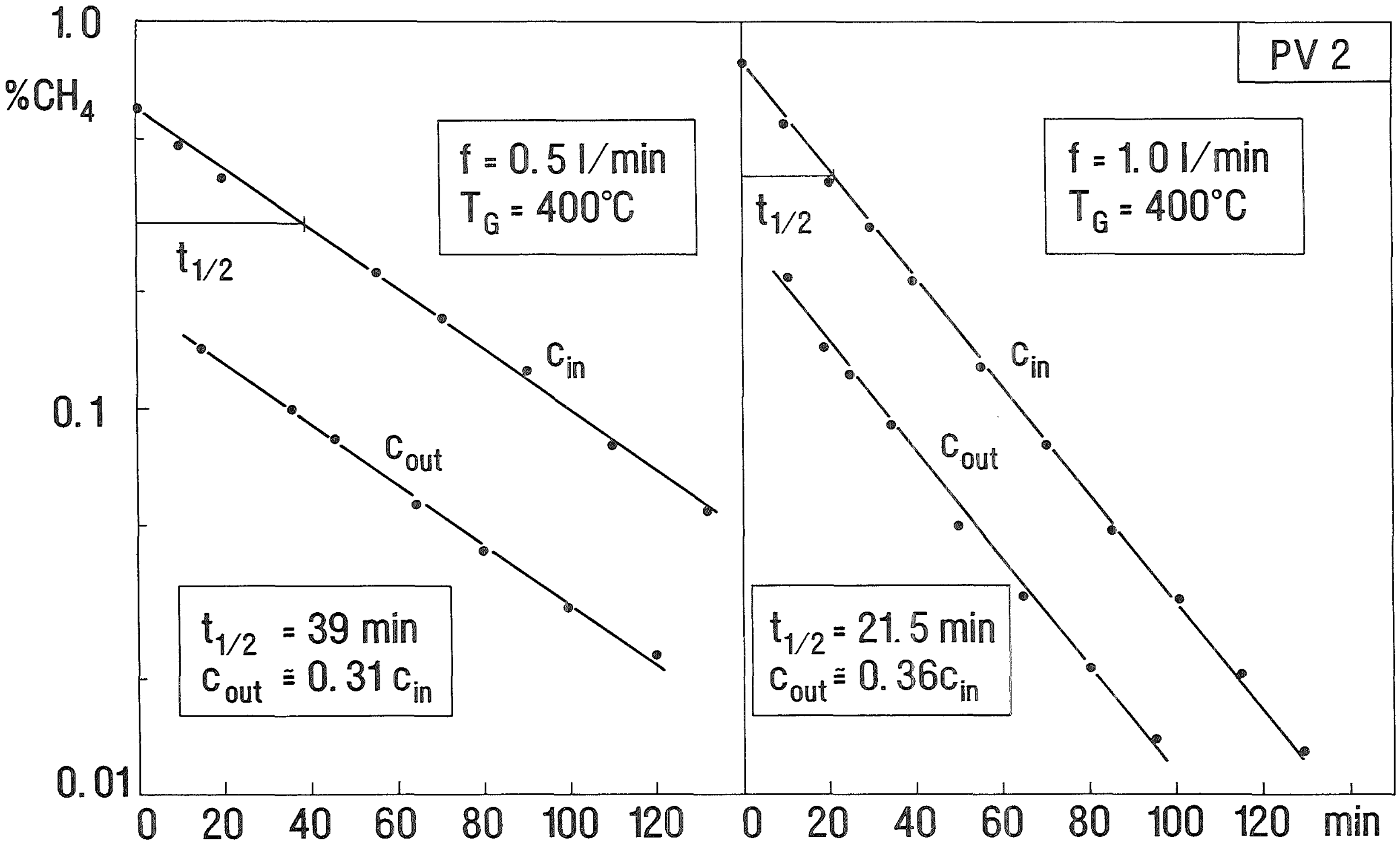


Fig. 6.6: Removal of CH_4 at different gas flow rates

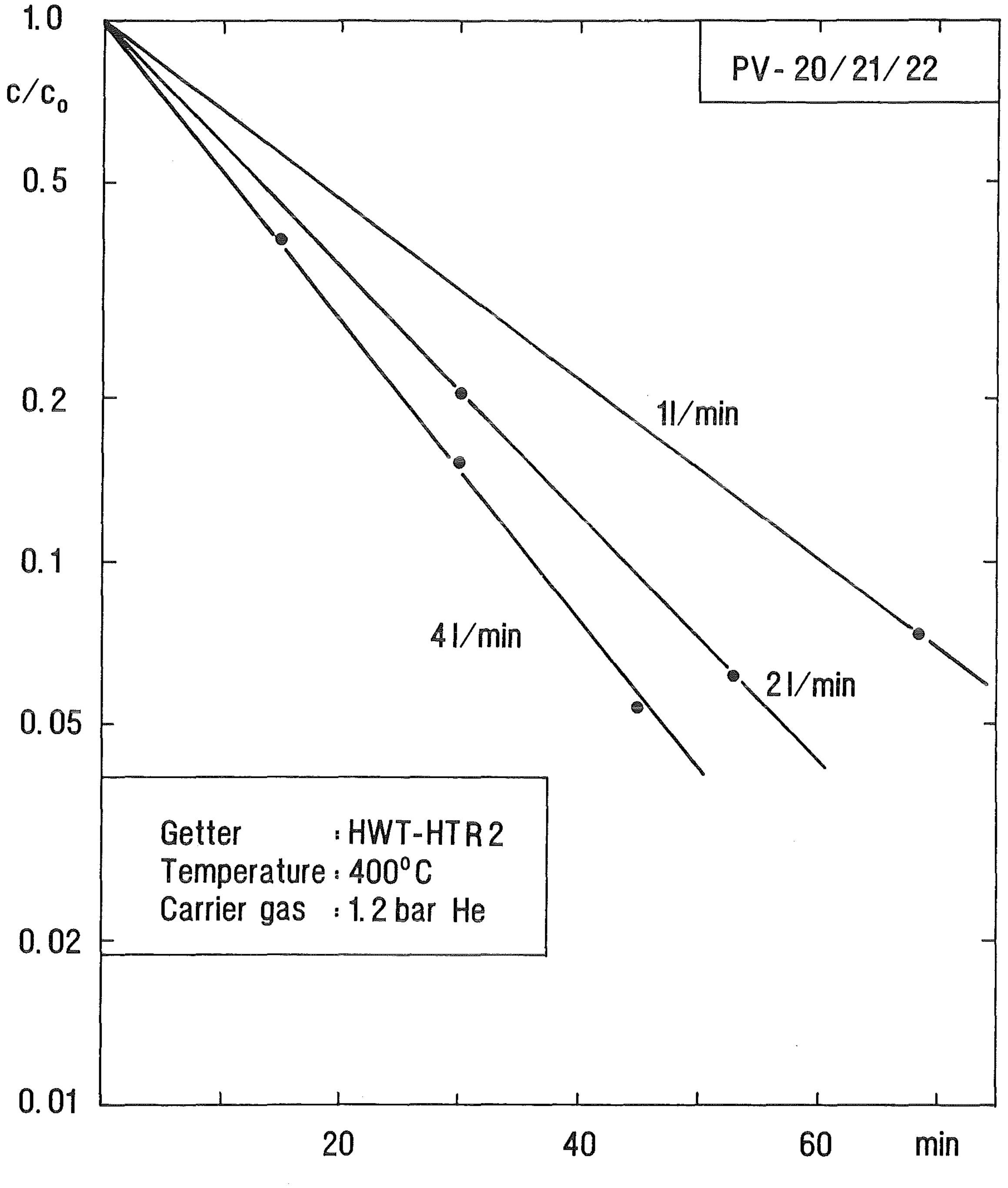


Fig. 6.7:

Removal of CH_4 at different gas flow rates

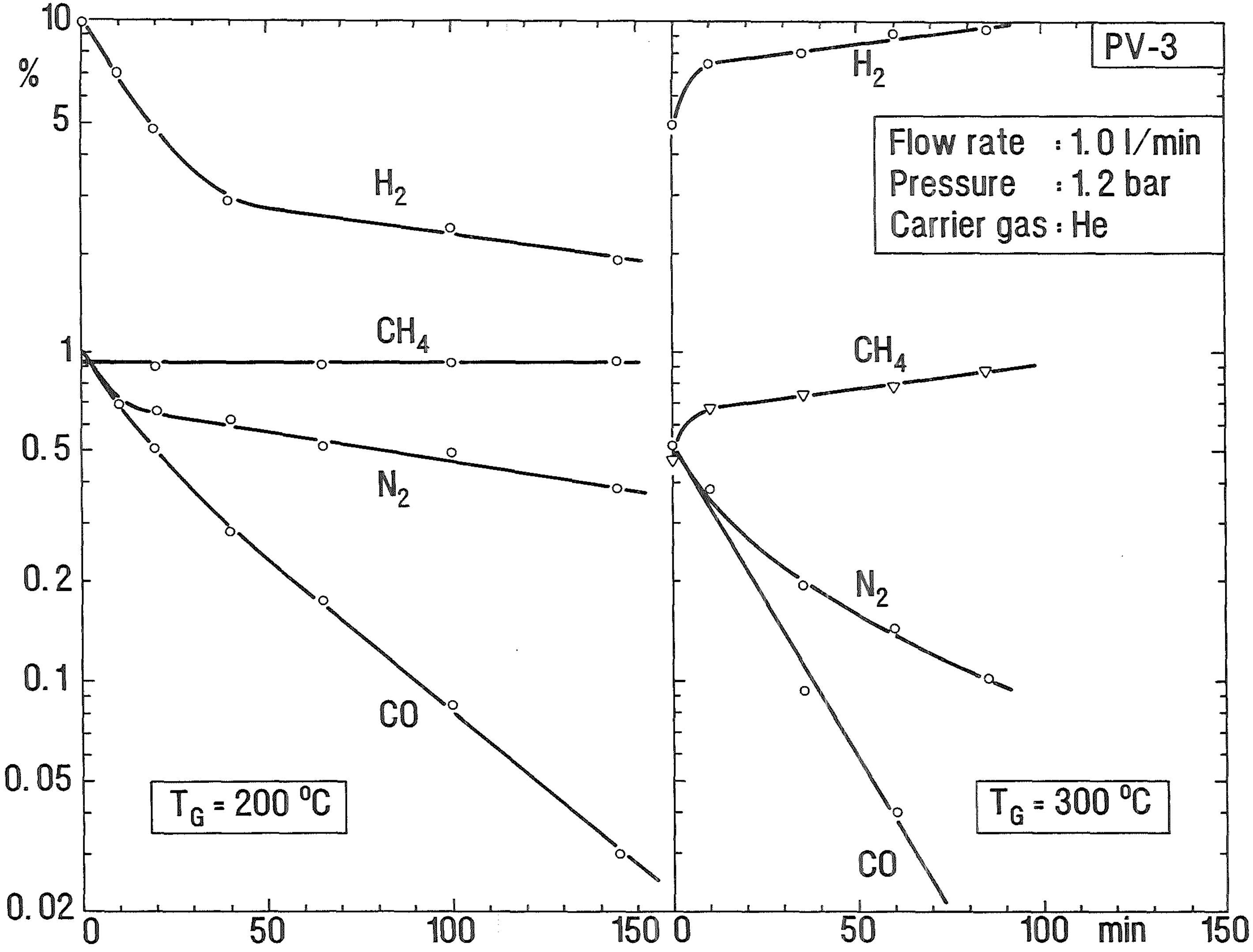


Fig. 6.8: Simultaneous sorption of various gas components on getter HTR-1

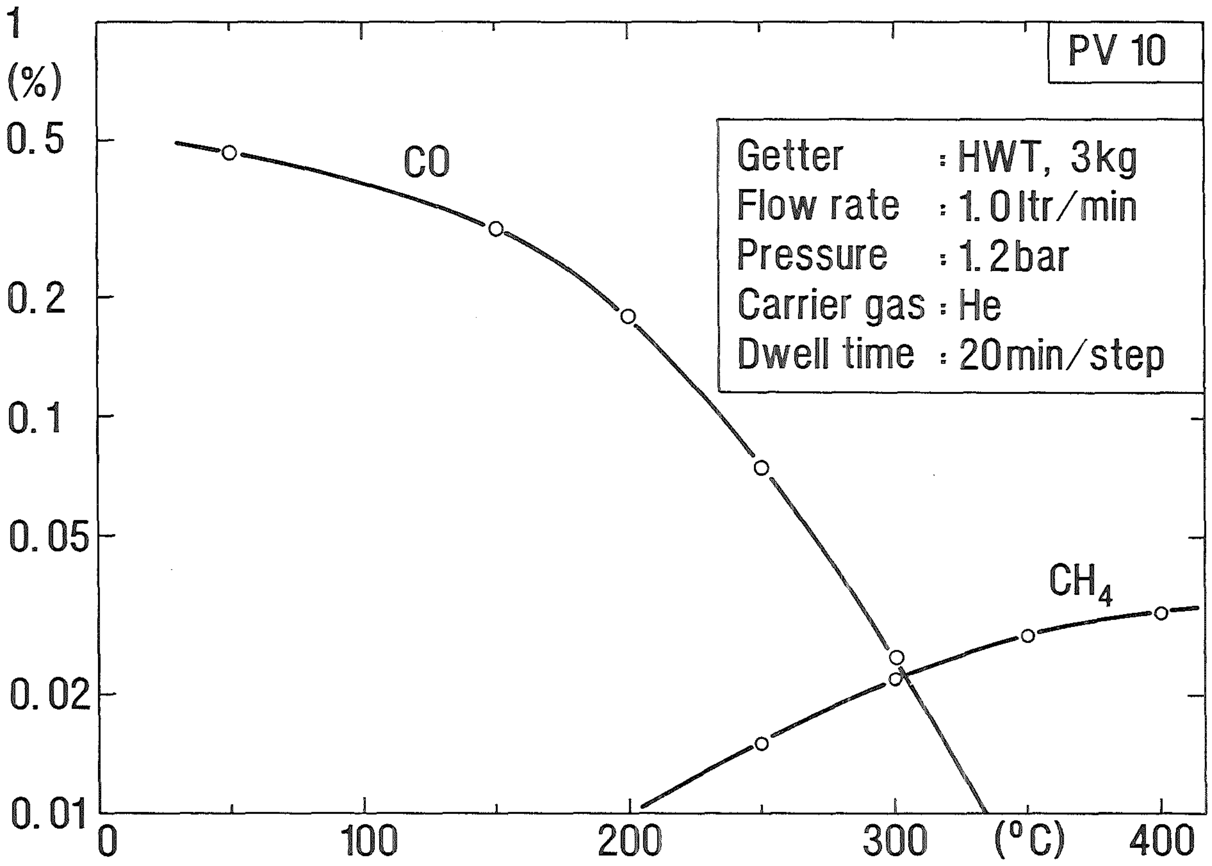


Fig. 6.9:

Sorption of CO and Formation of CH_4 during stepwise Temperature Increase

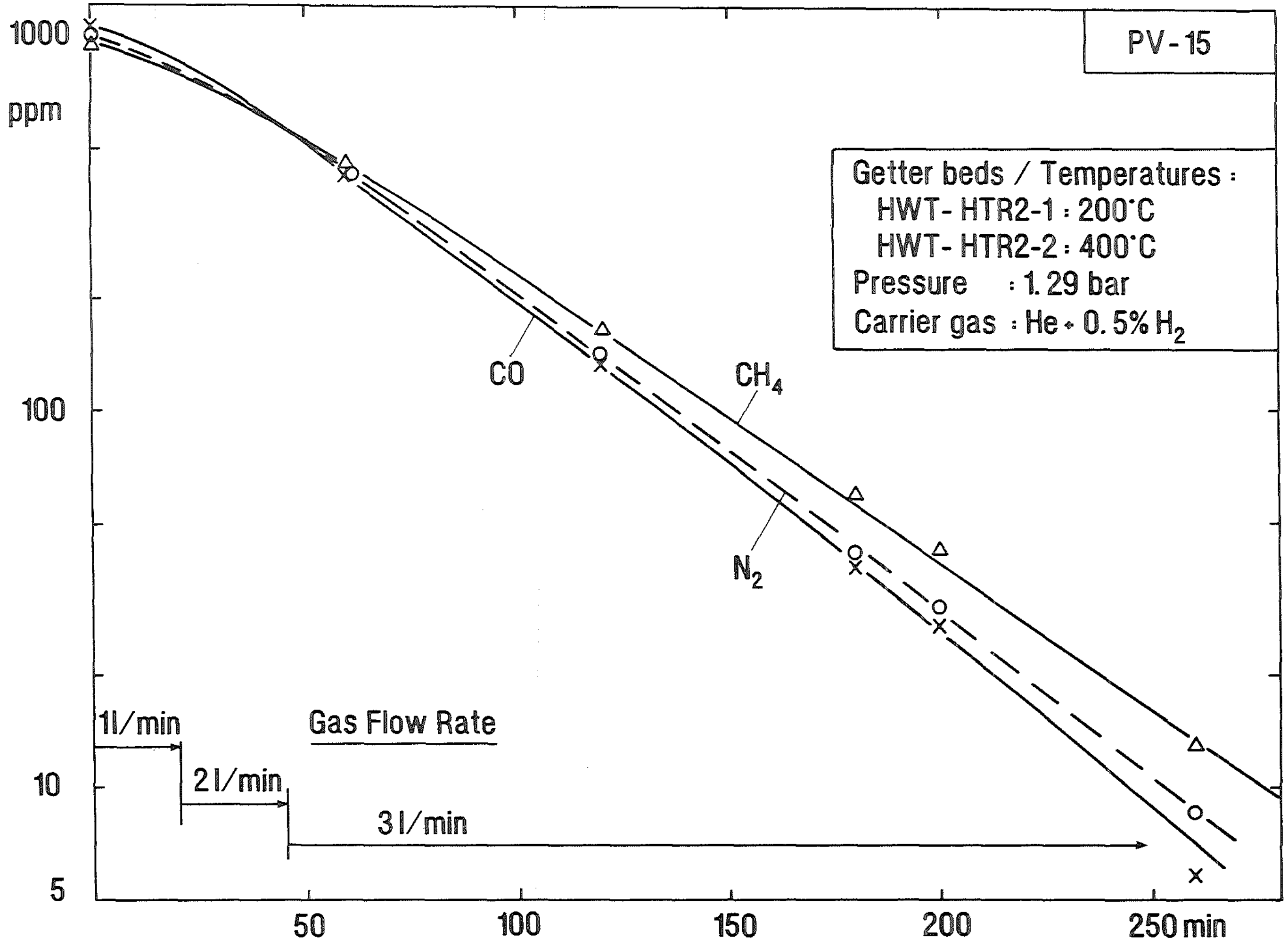


Fig. 6.10: Simultaneous Sorption of Impurities by two Getters in Series (Closed Loop Operation)

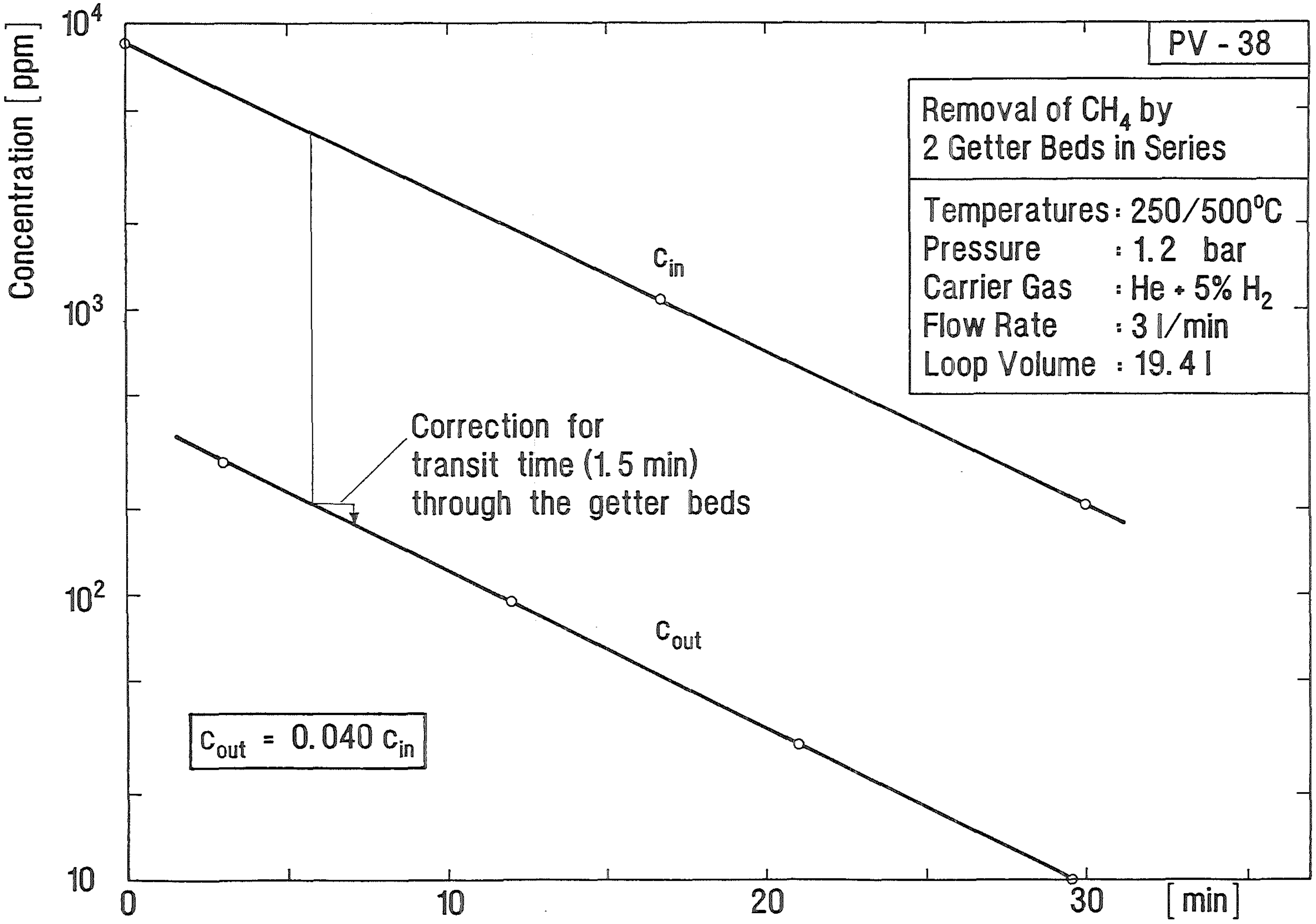


Fig. 6.11: Removal of CH_4 by two getter beds in series

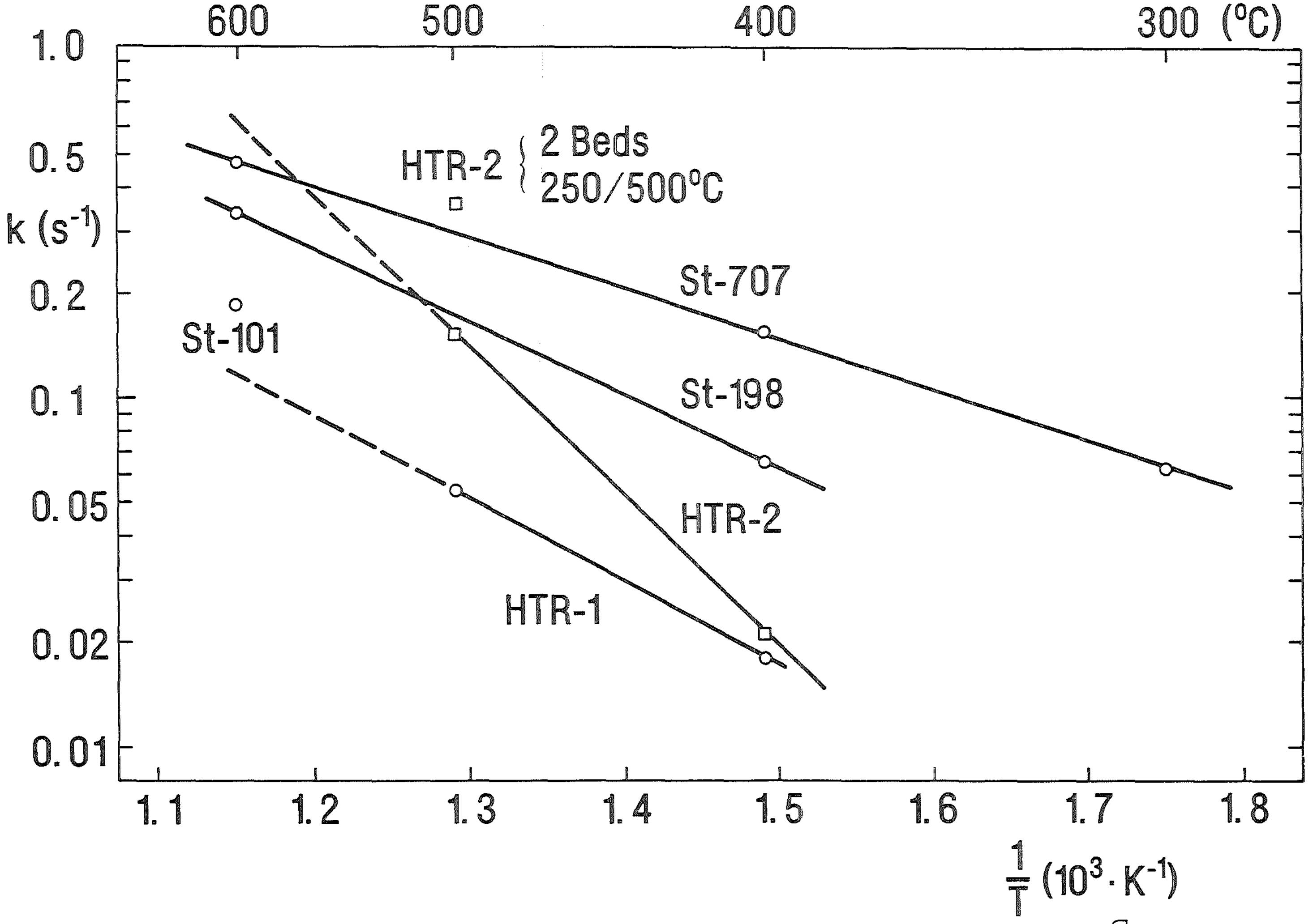


Fig. 6.12:

Reaction Rate Constants k as a Function of Temperature

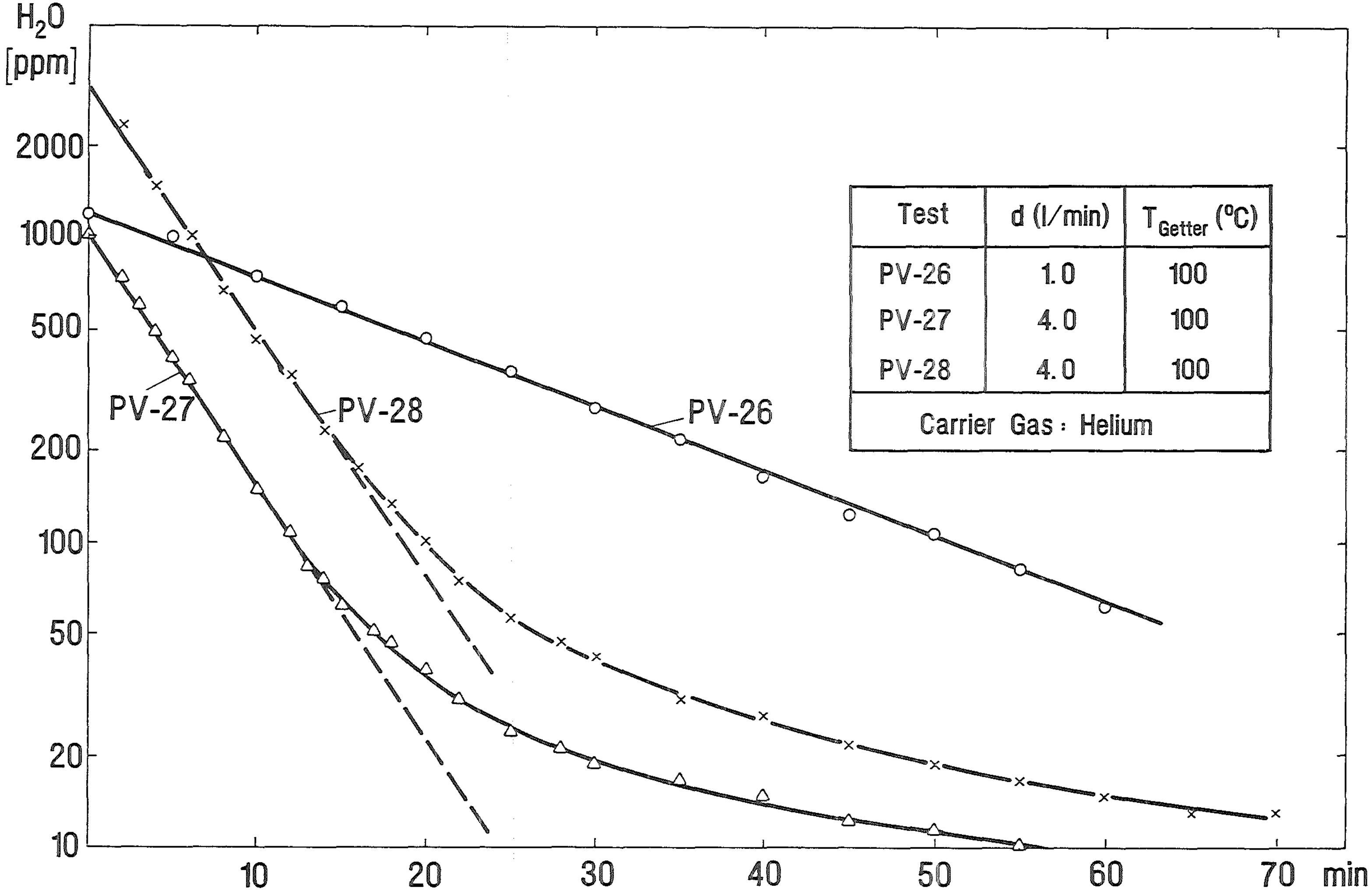


Fig. 6.13: Sorption of H_2O by the HWT Getter

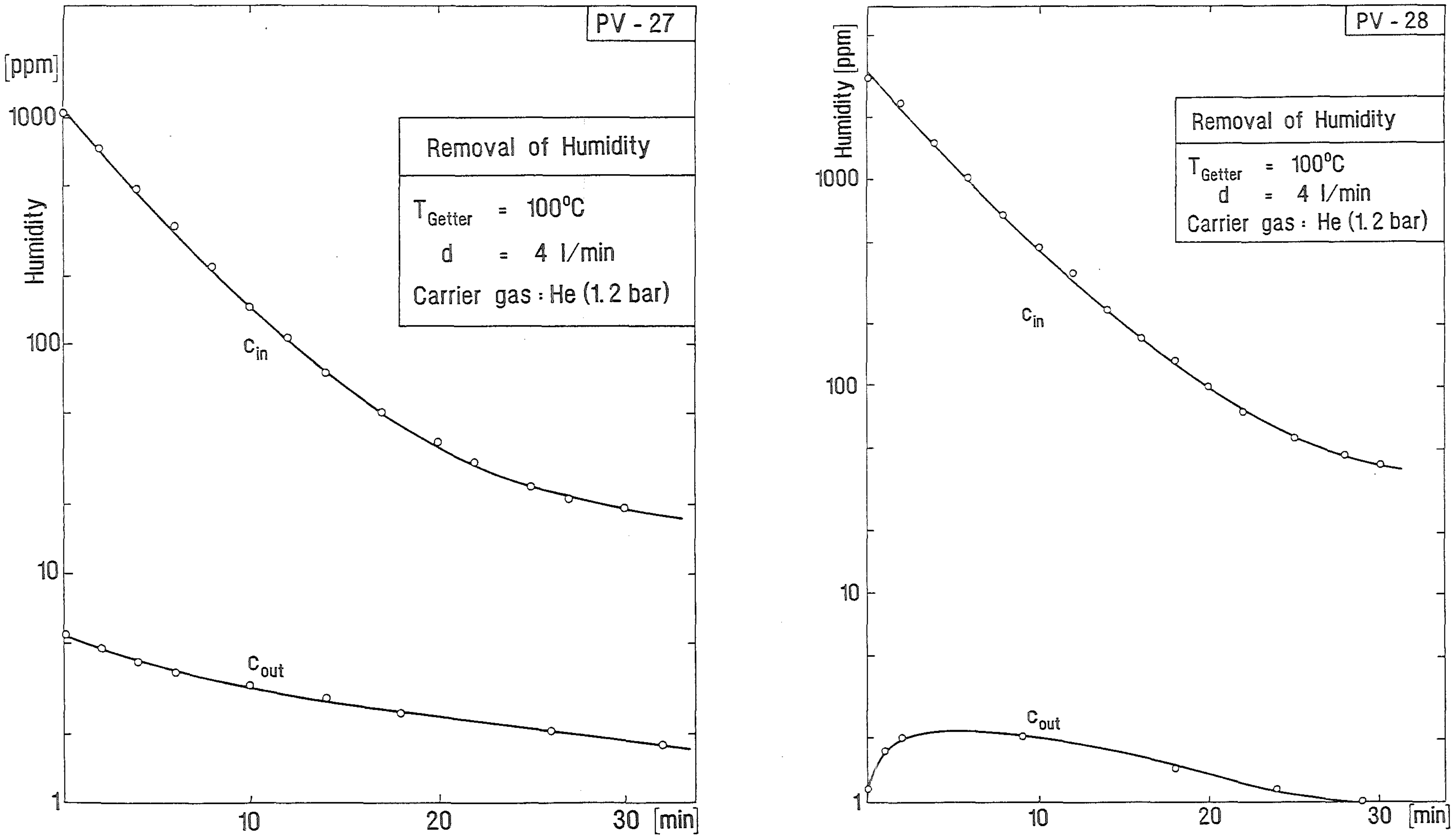


Fig. 6.14a/b: Removal of humidity (getter HTR-2, T_G = 100°C)

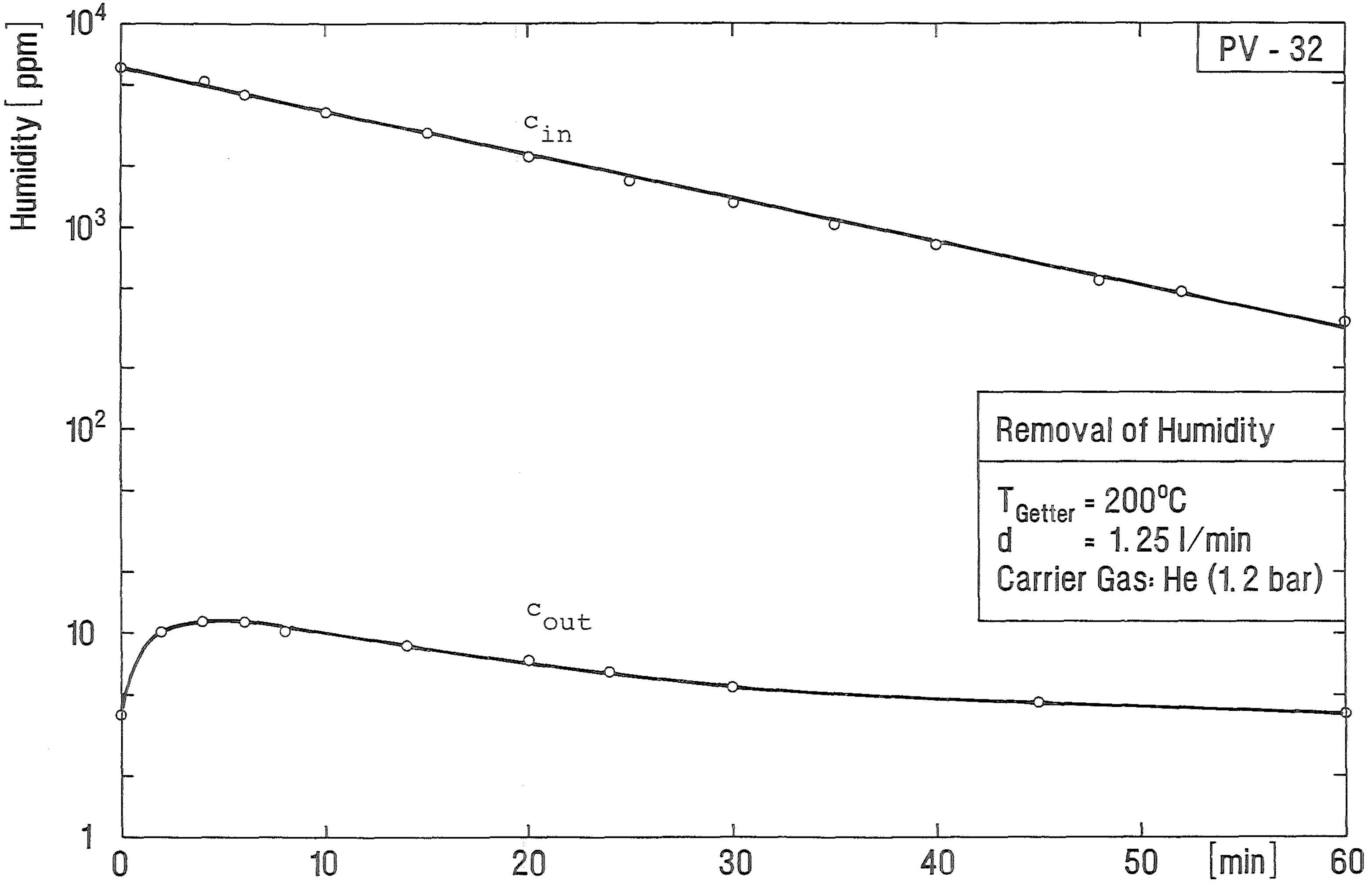


Fig. 6.15: Removal of humidity (getter HTR-2, T_G = 200°C)

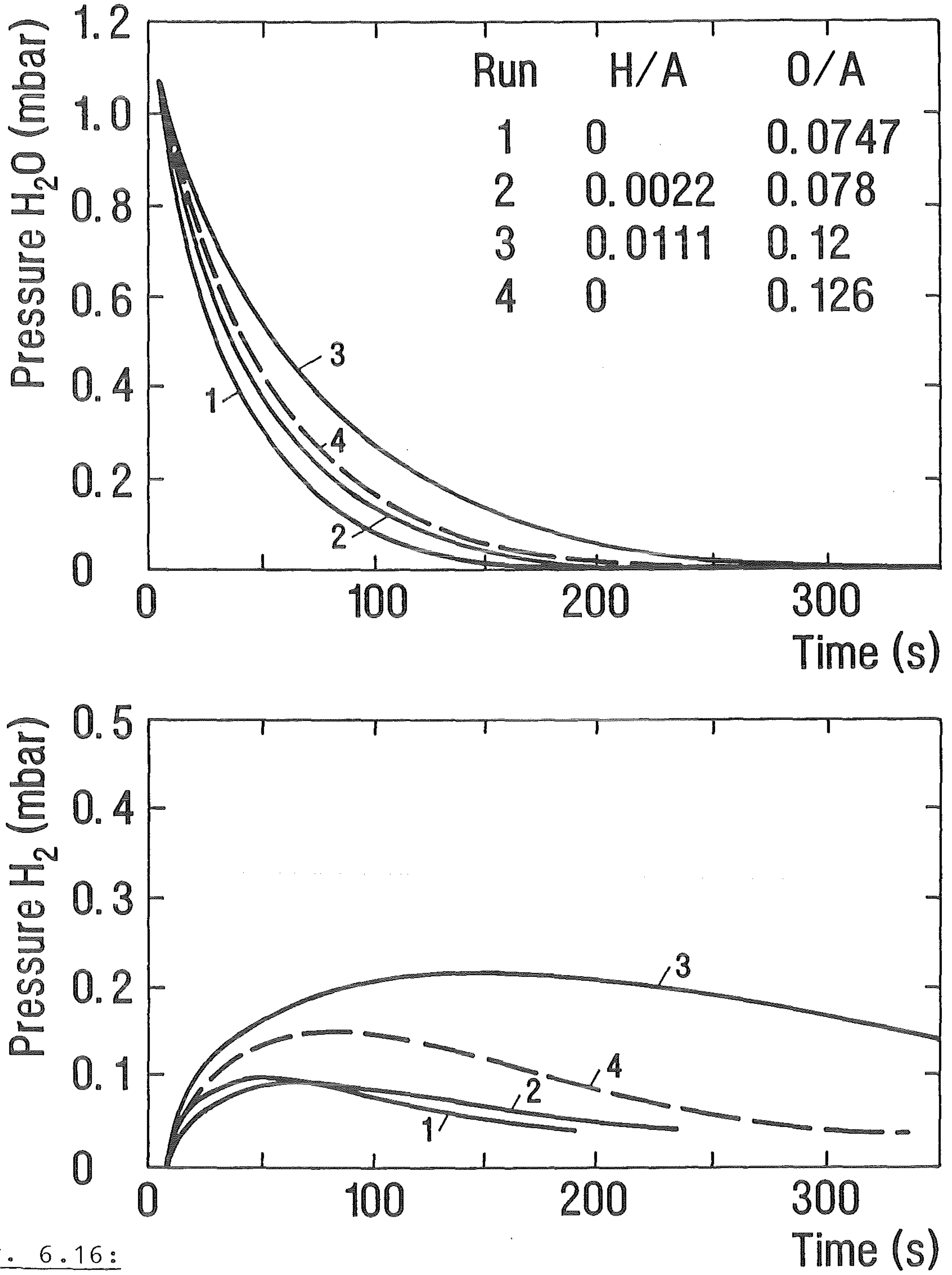


Fig. 6.16:

Results of Bonizzoni et al. for the conversion of water by using SAES getter St-737 at 300°C

Top: Time profiles of water vapor pressure in 4 different runs; H/A and O/A are the initial concentrations of hydrogen and oxygen in the getter alloy;

Bottom: Time profiles of the hydrogen pressure in the 4 runs indicating the cracking of water and the sorption of hydrogen by the getter

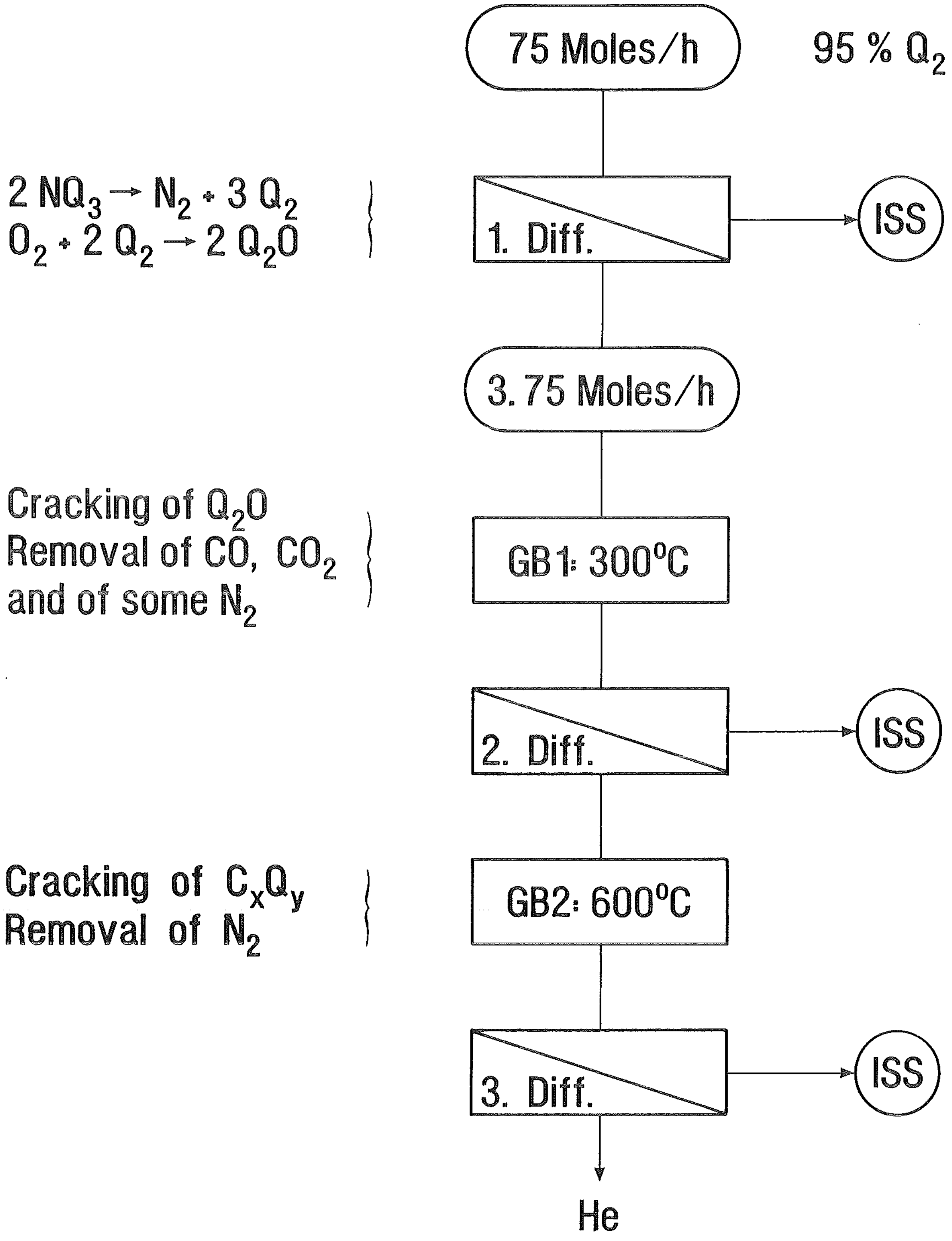


Fig.7.1: **Fuel Cleanup based on Diffusors and Getter Beds**