RETAINED GAS ANALYSIS SYSTEM

Paper presented at the CEC Hot Laboratories and Remote Handling Meeting at Chinon (France), June 1993

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HYDROGEN CONTENT IN ZIRCALLOY CLADDING

HELIUM CONTENT IN BERYLLIUM SAMPLES

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Contents.

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1. Summary.

The residual gas analysis method applied at the Laboratory of High and Medium level Activity (LHMA) at the Nuclear Research Centre SCK/CEN in Mol, Belgium, is a Hot Vacuum Extraction Method based on ASTM E146. Solid samples are introduced in a tungsten crucible positioned in a quartz tube under high vacuum and heated by R.F. induction. Released gases are transfered into a calibrated volume, the pressure is measured accurately and the gas composition determined by mass spectrometry.

The method allows to analyze 0.05 to 1 g samples in the range 1 to 6000 ppm (in the case of H_2). The precision amounts to 3 %.

Both integral gas content determinations and time-temperature dependent gas release measurements can be performed. An example of both methods is given :

- the integral bulk hydrogen content in zircalloy cladding of irradiated nuclear fuel rods and its correlation with the hydrides as revealed by metallographic examination ;

- the amount of transmutation helium formed in irradiated beryllium and its release characteristics.

2. Experimental method.

2.1. Apparatus.

The residual gas analyser (RGA) is a high vacuum - high temperature furnace equipped with appropriate gas handling and gas measurement devices. The apparatus (Fig. 1) consists mainly of four parts :

1. The sample introduction part allows to load up to five specimens, which can be analyzed sequentially. This specimen section is evacuated (down to $\leq 1 \times 10^{-6}$ mbar) by a turbomolecular pump backed up by a mechanical vacuum pump. During loading, this part is isolated from the other high vacuum parts of the apparatus and precautions are taken to prevent contamination of the inner walls. In this way, the background in the apparatus can be maintained very low, even after loading the specimens.

2. The heating part is a quartz tube surrounded by a high-frequency copper coil. It allows the heating of a tungsten crucible up to 2200 °C. The crucible can be transported remotely between the quartz tube and the sample introduction system where it can discharge and pick up the specimens.

3. The analytical part is composed of a gas collection system and a high accuracy pressure measurement system. A mercury diffusion pump transports the extracted gases quantitatively into a well defined volume. The resulting pressure rise is measured by a MKS Baratron capacitance manometer pressure sensor which has an accuracy of 0.1%. Evacuation of the analytical part (down to $\leq 5 \times 10^{-5}$ mbar) is carried out by a second mercury diffusion pump backed up by a mechanical vacuum pump.

4. The quadrupole mass spectrometer is coupled directly to the analytical part and allows to analyze the composition of the gas qualitatively and quantitatively. It is equipped with a batch inlet system, composed of a variable leak valve and a MKS Baratron capacitance manometer pressure sensor with an accuracy of 0.1%.

2.2. Test procedure.

Sample preparation.

Samples of appropriate dimensions, to cope with the crucible geometry and with the measurement range of the RGA instrument, are sectioned avoiding heating up to much the specimen since this may release some of the contained gases.

For a nuclear fuel rod cladding sample the fuel is removed out of its cladding. Fuel adhering to the inner cladding is mechanically removed by the action of a die. This operation is eventually backed up by supplementary longitudinal cutting if fuel cannot be removed easily. Residual fuel is dissolved by immersing the sample in boiling 10 N HNO_3 (eventually with some HF added) for six hours. After this, the ring specimen is rinsed with water. Then, the ring is cut in four equal segments of 90°, avoiding heating severely the sample.

The sample identification is recorded and the samples are ultrasonically cleaned with appropriate solvents, rinsed in acetone, air dried and weighted on an analytical balance to the nearest 0.1 mg (W_s, g).

Apparatus preparation.

The RGA is evacuated down to $\leq 5 \times 10^{-5}$ mbar in the analytical part and down to $\leq 1 \times 10^{-6}$ mbar in the sample introduction system. Baking of the system can be performed to promote the degassing of the inner walls for lowering the overall background of the instrument.

Once a good vacuum has been achieved, the samples (up to five) are loaded. For this purpose, the sample introduction part is isolated, heated at 50 °C and vented with dry nitrogen gas. The position of the samples in the numbered sample holders in the loading system of the RGA is recorded. The sample introduction system is sealed again, the heating stopped and evacuation performed by pumping overnight with the turbomolecular pump.

In the mean time the mass spectrometer is calibrated. At first the vacuum of the mass spectrometer ($\leq 1 \times 10^{-9}$ mbar) and its inlet system ($\leq 1 \times 10^{-4}$ mbar) are checked and a background scan is performed. If the background is to high, rinsing with He or Ar gas and/or baking of the mass spectrometer and its inlet system might be performed. Calibration is performed by admittance of pure gases (> 99.9 %) to the inlet system. The inlet pressure is measured with the MKS Baratron and the corresponding intensity of the main mass and the key fragments is determined. Thus a complete set of calibration factors is obtained. These are fed into the analysis matrix of the software which controls the mass spectometer. This calibration factor matrix is used to analyse qualitatively and quantitatively the mass spectrum of each subsequent mass spectrometric scan of a gas sample to identify the gas components and their relative concentrations.

Once the loaded RGA is evacuated and the mass spectrometer has been calibrated, the analytical part of the RGA is calibrated. This is performed by feeding dry nitrogen gas at an exactly known pressure ($P_c \cong 760$ mm Hg) and temperature ($T_c \cong 293$ °K) through a calibrated volume (geometrical volume = 44.2 ± 0.1 mm^3). In this way an exactly known amount of dry N_2 gas (V_c, μl at STP) is sampled :

$$V_c \ (\mu l \text{ at STP}) \ = \ 44.2 \times \frac{P_c \ (\text{mm Hg})}{760} \times \frac{273.15}{T_c \ (\degree K)} \qquad [1]$$

The corresponding pressure increase in the analytical part of the RGA is measured ($P_{rga,c}$, mbar), and the calibration factor is determined as :

$$C_{rga,v} \ (\mu l/mbar) \ = \ \frac{V_c \ (\mu l)}{P_{rga,c} \ (mbar)} \hspace{3cm} [2]$$

At least 3 calibrations are performed. The value obtained for $C_{rga,v}$ should be reproducible within 1 %. After a satisfactory calibration has been obtained, the analytical part is evacuated.

Sample measurement.

The vacuum of the RGA is checked again and the tungsten crucible is outgassed by transferring it into the RF coil and heating at 2000 °C for 5 minutes.

Background measurements are performed, each of them comprising the following operations and measurements :

* The loading of a sample is simulated by transferring the tungsten crucible to the sample introduction system and returning it into the RF coil without pick up of a sample.

* The crucible is heated at the analysis temperature (1200 °C for Zircaloy, 1250 °C for Beryllium and 1400 °C for the NBS Standards).

* The "blank rate" is followed during ten minutes (i.e. pressure rise in the analytical part as measured by the RGA baratron : $P_{rga,b}$, mbar). It should not exceed 1.5×10^{-3} mbar/min (corresponding to appr. 1 $\mu l/min$).
  If low gas contents are to be expected in the samples to be analysed (i.e. < 30 ppm), a satisfactory reproducible blank rate ($\leq 5 \times 10^{-4}$ mbar/min ± 10%) has to be obtained by several (at least three) background measurements.

* After each individual background measurement, part of the collected gas is fed to the mass spectrometer and analyzed for its composition ($F_{i,b}$ = fraction of gas component i in the gas). Thus the background of gas i can be obtained as :

$$V_{i,b} \ (\mu l \ at \ STP) \ = \ P_{rga,b} \ \times \ C_{rga,v} \ \times \ F_{i,b} \hspace{2cm} [3]$$

After the background measurements have been finished, the RGA is evacuated again.

The samples are analyzed as follows :
* After transferring the tungsten crucible to the specimen introduction system the sample is loaded. Then the crucible is returned into the RF

coil.

* The crucible is heated at the analysis temperature (1200 °C for Zircaloy,
  1250 °C for Beryllium and 1400 °C for the NBS Standards).

* The outgassing rate (i.e. pressure increase in the analytical part as
  measured by the RGA baratron) is recorded in function of time.

* Once the maximum pressure has been reached (normally after a few to up to
  ten minutes), heating is stopped. The final pressure is noticed
  ($P_{rga,s}$, mbar) and the total amount of gas released by the sample can
  be calculated as :

$$V_{t,s} \text{ (}\mu\text{l at STP)} = \{ P_{rga,s} - P_{rga,b} \} \times C_{rga,v} \qquad [4]$$

* A gas aliquot is fed to the mass spectrometer. A qualitative and
  quantitative analysis of the gas is performed by scanning the mass
  spectrum and using the calibration factor matrix to analyse the mass
  spectrum ($F_{i,s}$ = fraction of component i in the gas).

* The total amount of gas component i collected during the sample
  measurement can be obtained as :

$$V_{i,s} \text{ (}\mu\text{l at STP)} = P_{rga,s} \times C_{rga,v} \times F_{i,s} \qquad [5]$$

* Finally, on base of the background measurement results and on base of the
  sample weight, the weight ppm gas content of component i in the sample
  can be calculated :

$$C_i \text{ (weigth ppm)} = \{ V_{i,s} - V_{i,b} \} \div V_m \times W_m \div W_s \qquad [6]$$

where $V_{i,s} - V_{i,b}$ = volume of gas i liberated by the sample
(μl at STP)

V_m = molar volume = 22.4×10^6 (μl/mol at STP)

$W_{m,i}$ = molecular weight of gas component i (g/mol)

W_s = weight of the sample (g)

2.3. Qualification.

Qualification of the method is performed by analysing Certified
Unalloyed Titanium standards of the U.S. National Bureau of Standards.

Three types of NBS standard samples, of approximately 200 mg and containing a different certified hydrogen content, are used :

Standard Sample	Certified Hydrogen Content weight ppm
NBS 352	32 ± 2 (6.3 %)
NBS 353	98 ± 5 (5.1 %)
NBS 354	215 ± 6 (2.8 %)

Following typical results have been obtained :

Standard	Measured Hydrogen Content weight ppm	Accuracy
NBS 352	31.1	- 2.8 %
	32.5	+ 1.6 %
NBS 353	96.9	- 1.1 %
	97.3	- 0.7 %
NBS 354	217.7	+ 1.3 %
	220.4	+ 2.5 %

These results demonstrate that the accuracy of the method is well within the NBS standard specifications and that the precision amounts to ± 3 %.

At the beginning of each series of measurements, the performance of the apparatus is checked by measuring a NBS standard.

3. Hydrogen content in Zircalloy cladding.

Hot vacuum extraction hydrogen content determinations and quantitative analysis of the hydrides in metallographic specimens, as performed by means of a TAS Image Analyser, have been done on zircaloy cladded MOX fuel rods irradiated in a Boiling Water Reactor up to a discharge burnup of about 40 GWd/t_M. Different cross sections have been selected for metallographic hydride examination and two cladding samples, located in the vicinity of a

metallographic cross section have been selected for hot vacuum extraction analysis (H1 and H2). A correlation hydrides - hydrogen content has been established.

The measurement results of the hydrogen content analysis are given in the following table :

Sample		Hydrogen Content	
Identification	Weight (mg)	weight ppm	Accuracy
NBS 353	222.5	97	- 0.7 %
H1	152.0	113	± 5 %
H2	144.7	121	± 5 %

Photomicrographs of magnification x 500 have been used for the image analysis of the hydrides in the metallographic specimens. As an example Fig. 2 depicts two micrographs, one of a sample M2 (in the vicinity of the cladding sample H2) and one of a sample M4.

To obtain a correlation between the appearance of the hydrides in the metallographically examined cladding specimens and their hydrogen content, the amount of data obtained here is to small (i.e. two hydrogen content determination results in the vicinity of metallographically analysed specimens). In order to have more data for correlation literature data were used as well. To this end, the data contained in Ref. 1 are well suited. In this reference photomicrographs of transverse sections of Zircaloy tubes with various known hydrogen contents (from 10 to 11,600 ppm H_2) are depicted. The surface area of the hydride platelets on this photomicrograhs, in the hydrogen content zone of interest (from 50 to 330 ppm H_2), has been determined by image analysis. The precision of the determination of the area of hydrides in the photomicragraphs amounts to ± 20 %. The results are compiled in Table 1 and depicted in Fig. 3. From this figure it is clear that indeed, in the H_2 content range considered here, a linear correlation between hydrogen content and hydride platelets surface area can be obtained. This correlation is found to correspond to :

$$A = 31 \ x \ C_H \tag{7}$$

with A   = surface area of hydride platelets (in arbitrary units)
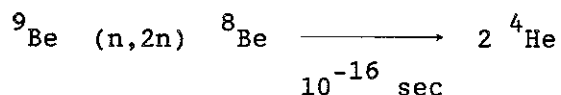
C_H = hydrogen content in weight ppm

The precision (1 σ) of the regression coefficient (31), as obtained from the least square fitting of the data, amounts to $\pm$ 2 (or $\pm$ 6.5 % relative).
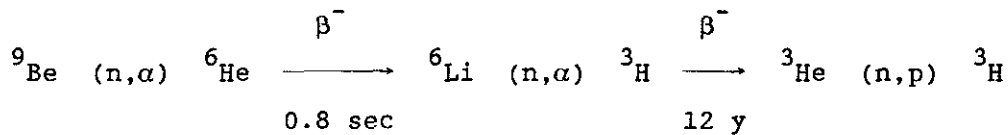
The results of the image analysis of the photomicrographs of the metallographic specimens of the MOX fuel rods are also compiled in Table 1. The results from samples M1 and M2, for which the hydrogen content is known from the hot vacuum extraction determination of the adjacent cladding specimens H1 and H2, are also depicted in Fig. 3. They correspond fairly well with the correlation as established on base of the literature data.

Finally, the hydrogen content of the cladding of all metallographic cross sections can be obtained by image analysis of the hydride platelets surface area and subsequent application of equation [7]. The results are also compiled in Table 1. From these results it is clear that the cladding of all metallographic cross sections contains almost the same hydrogen content, namely at around 110 $\pm$ 20 weight ppm. Thus it can be concluded that the cladding of the MOX rods, having a burn-up of approximately 40 GWd/t_M, shows only restricted hydrogen pick up.

4. Helium content in Beryllium samples.

Beryllium, being a low-Z material with excellent neutron thermalisation and multiplication capabilities and good thermal characteristics, is a candidate material for the first wall and blanket in fusion devices. A crucial point for the choice of beryllium is its behaviour under high neutron fluences. The most important effects of irradiation on beryllium are associated with the high quantity of transmutation helium which is formed through the following reactions :

$$^9Be \ (n,2n) \ ^8Be \ \xrightarrow[10^{-16} \ sec]{} \ 2 \ ^4He$$

$$^9Be \; (n,\alpha) \quad ^6He \xrightarrow[\text{0.8 sec}]{\beta^-} \; ^6Li \; (n,\alpha) \; ^3H \xrightarrow[\text{12 y}]{\beta^-} \; ^3He \; (n,p) \; ^3H$$

Both reaction sequences lead to the production of two helium atoms. This helium generation has substantial effects on the mechanical properties, on the swelling characteristics and on the tritium retention and release characteristics (of the tritium formed in the second reaction sequence).

Beryllium samples have been irradiated in BR2, the material test reactor of the SCK/CEN in Mol, at 40-50 °C up to three different fast (E > 1 MeV) neutron fluences : 0.789 x 10^{22} n/cm², 2.767 x 10^{22} n/cm² and 3.925 x 10^{22} n/cm². Post-irradiation annealing of some of these specimens at 400 °C and 800 °C for periods of 1 h and 24 h has been performed.

The specimens were analyzed for their gas content with the hot vacuum extraction method. It was experienced that the specimens had to be heated at a temperature of 1250 °C, very near to the melting point of beryllium metal (1278 °C ± 5 °C), for release to occur quantitatively within a time period of 5-30 minutes. An advantage of the hot vacuum extraction method is that all permanent gases contained in the specimen as well as their isotopic composition can be measured. It has been found that the gases released by the beryllium specimens consists essentially (for appr. 99 %) of ^{4}He and ^{3}He. In addition some N_2, H_2 and ^{3}H was detected. Unfortunately, because of the high specific activity of ^{3}H, no calibration of the mass spectrometer for tritium can be obtained and consequently no quantitative determination of its content in the beryllium specimens can be derived from the RGA results.

The ^{4}He and ^{3}He content measurement results are compiled in table 2. The ^{4}He content in function of the neutron fluence is depicted in fig. 4. A linear correlation has been found :

$$C_{^4He} = (4878 \pm 86) \times \Phi \quad \text{appm} \qquad [8]$$

where Φ is the fast (E > 1 MeV) neutron fluence in 10^{22} n/cm². The helium production rate in beryllium irradiated in the BR2 reactor is in the range 2000-6000 appm/10^{22}n/cm² as reported for other fission reactors (Ref. 2-3).

The helium content measurements on the post-irradiation annealed

specimens (also compiled in Table 2) show that no helium is released at
400 °C for both periods considered, nor when annealed for 1 h at 800°C.
However, the specimen irradiated up to 0.789 x 10^{22} n/cm², when annealed
for a period of 24 h at 800 °C, released 70 % of its initial He (both
isotopes). Thus He produced during irradiation might be released during
annealing, even for the relatively short time periods considered here.

The release characteristics of the helium contained in the low
temperature irradiated beryllium has been investigated as a function of
temperature and time. The specimens were heated in a step-wise fashion at
800, 850, 900, 950, 1000, 1050, 1100, 1150, 1200 and 1250 °C for steps of
30-50 minutes (until a constant release rate was observed). The gas release
was measured and recorded continuously : Fig. 5. The He-contents obtained
at the end of this time dependent measurements correspond very well with
the results of the direct total helium content measurements. They are
compiled also in Table 2.

The time dependent release characteristics are similar for all three
specimens (fluences) examined : at first a "burst type" release is observed
at a lower temperature; this is followed by a "steady state" release at
intermediate temperatures; and finally a second "burst type" release leads
to a complete removal of all helium contained in the specimen at a
temperature near to the melting point of beryllium metal. The higher the
fast neutron fluence, the lower the temperature at which the first "burst
type" release is observed. The fraction of helium released at this first
"burst type" release is almost the same for all three specimens (± 20 %).
The intermediate "steady state" part is much shorter for the lowest
irradiated specimen, where the second "burst type" release starts already
at 1000 °C while this second "burst type" release appears at higher
temperatures for the other two fluences (1200 to 1250 °C). It has to be
remarked that the temperatures at which the different release
characteristics have been observed have only a relative value and no
absolute one. Indeed, time also plays an important role as shown by the
annealing experiments where the sample irradiated up to 0.789 x 10^{22} n/cm²
released already 70 % of its initial He content at 800 °C after 24 h.

Concerning helium release characteristics of irradiated beryllium, no
data are reported till now in the literature. However, some data on the
release characteristics of tritium have been reported (Ref. 3-5). They show
some similarity with the He release characteristics as observed in this

work : a "burst type" release of most of the 'H at higher temperatures, preceded by a "steady state" release has been observed. This indicates that the release of both 'H and He might be interconnected as suggested by M.C. Billone et all. (Ref. 3) who stated that the 'H might be vented through the interconnected pathways created by He bubble interlinkage.

5. Conclusion.

The RGA Hot Vacuum Extraction equipment operational at the Hot Laboratory of the SCK/CEN is proven to be a very versatile instrument in analysing solid samples for retained gas content :
- the integral content of different gases in different solid samples can be analyzed ;
- both integral and temperature/time dependent gas release characteristics can be determined.

Futhermore, reliability is shown to be very appropriate as demonstrated
- by the analysis of certified standard samples ;
- by the intercomparison with literature data and results obtained with other measurement techniques.

6. References.

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1. B.Z. Hyat

Metallographic standards for estimating H_2 content of Zry-4 tubing

WAPD-TM-1431

National Technical Information Service, U.S. Department of Commerce,

5286 Port Royal Road, Springfield, Virginia 22161

February 1982.

2. J.M. Beeston, L.G. Miller, E.L. Jr. Wood, and R.W. Moir

Journal of Nuclear Materials 122-123, 802-809 (1984).

3. M.C. Billone, C.C. Lin, and D.L. Baldwin

Fusion Technology 19, 1707-1714 (1991).

4. W.G. Wolfer and T.J. McCarville

Fusion Technology 8, 1157-1164 (1985).

5. D.L. Baldwin, O.D. Slagle, and D.S. Gelles

Journal of Nuclear Materials 179-181, 329-334 (1991).

Table 1 : Surface area of hydride platelets and hydrogen content.

Sample [*]		H$_2$ Content [**] weight ppm	Area hydrides (arbitrary units)	H$_2$ Content [***] weight ppm
Ref. 1		50	1503	-
		80	1083	-
		100	3463	-
		150	5287	-
		220	6207	-
		330	9951	-
M1	0°	113 (H1)	2844	92
	180°		3976	128
M2	0°	121 (H2)	4148	133
	180°		4148	133
M3	0°	-	4166	134
	180°	-	4656	150
M4	0°	-	2680	86
	180°	-	3132	101
M5	0°	-	3072	99
	180°	-	4172	134

* 0° and 180° = at two opposite locations on the circumference.

** as determined by hot vacuum extraction of adjacent section.

*** as obtained from equation [7].

Table 2 : *Helium measurement results on irradiated Beryllium.*

fast (> 1 MeV) neutron fluence in 10^{22} n/cm²	Annealing		He-content(appm)			
	Temp.(°C)	time(h)	integral meas.		time/temp. dep.	
			^{4}He	^{3}He	^{4}He	^{3}He
0.789	–	–	3798	164	3980	173
	800	1	3880	167	–	–
	800	24	1163	49	–	–
2.767	–	–	12830	254	12720	265
	400	1	12994	260	–	–
	400	24	13333	267	–	–
3.925	–	–	20670	110	20630	96

Calibration
Gas

Quartz tube

HF Coil

Tungsten crucible

Sample
Loading system

Pressure transduser

Transfer pump

Turbo pump

Mass spectrometer

Diffusion pump

Prim.pump

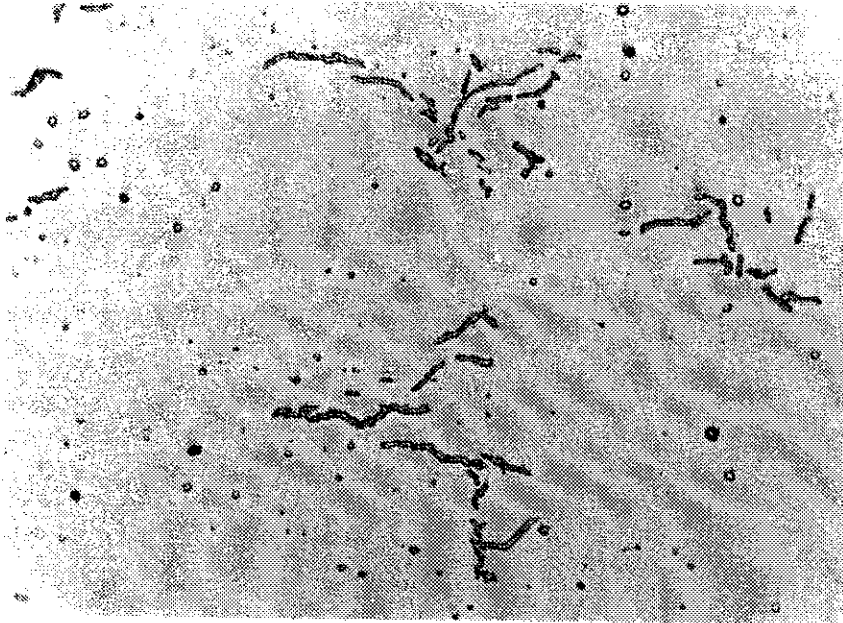Calibrated volume
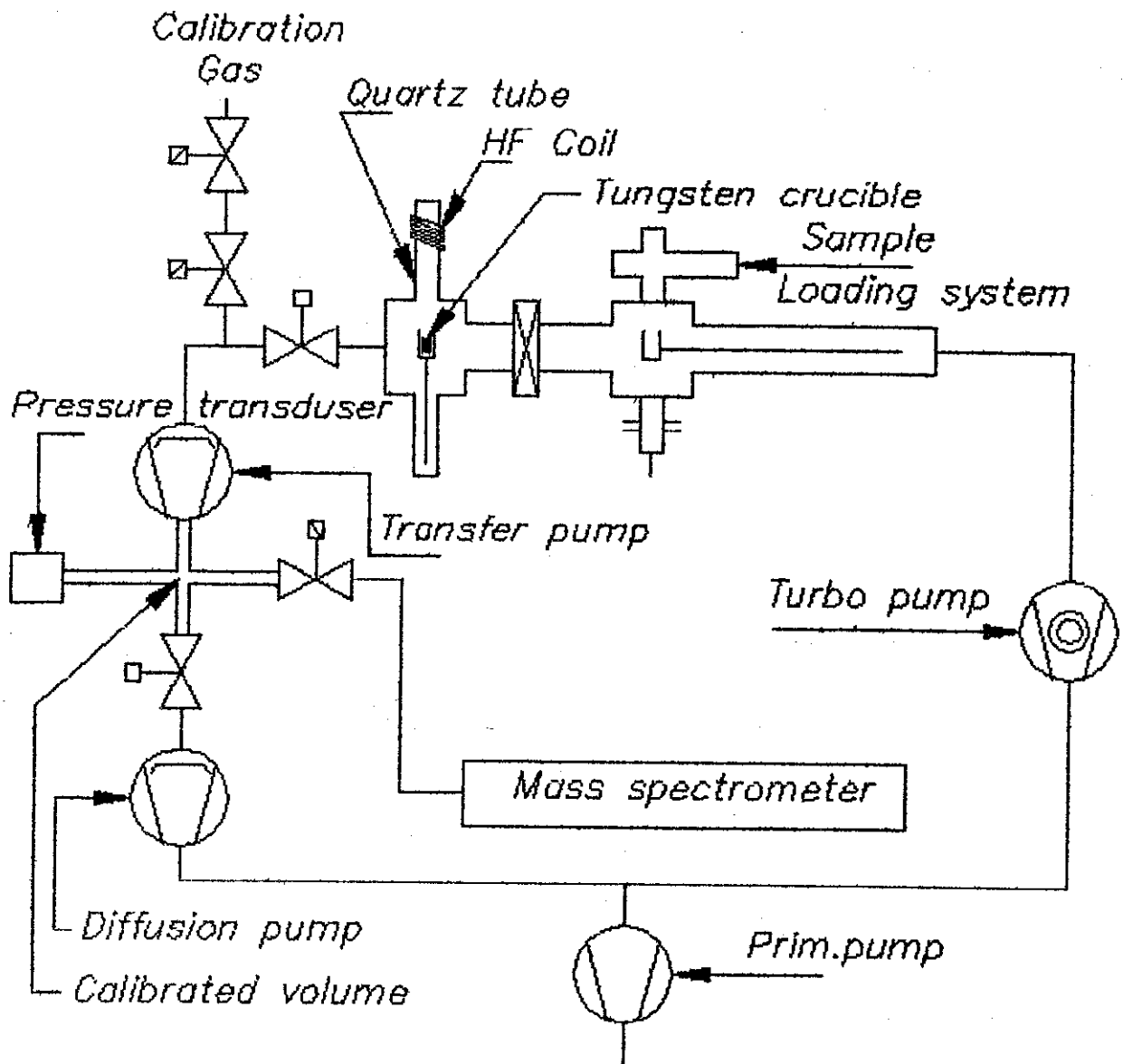
Fig. 1 : Residual Gas Analyser.

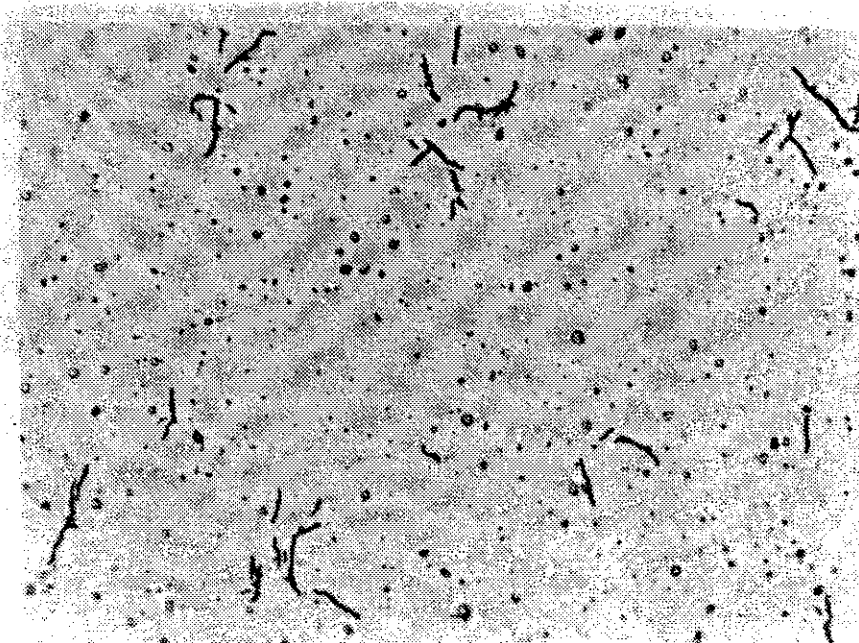*Fig. 2a* : Photomicrograph (x 500) of the hydrides in sample M2.

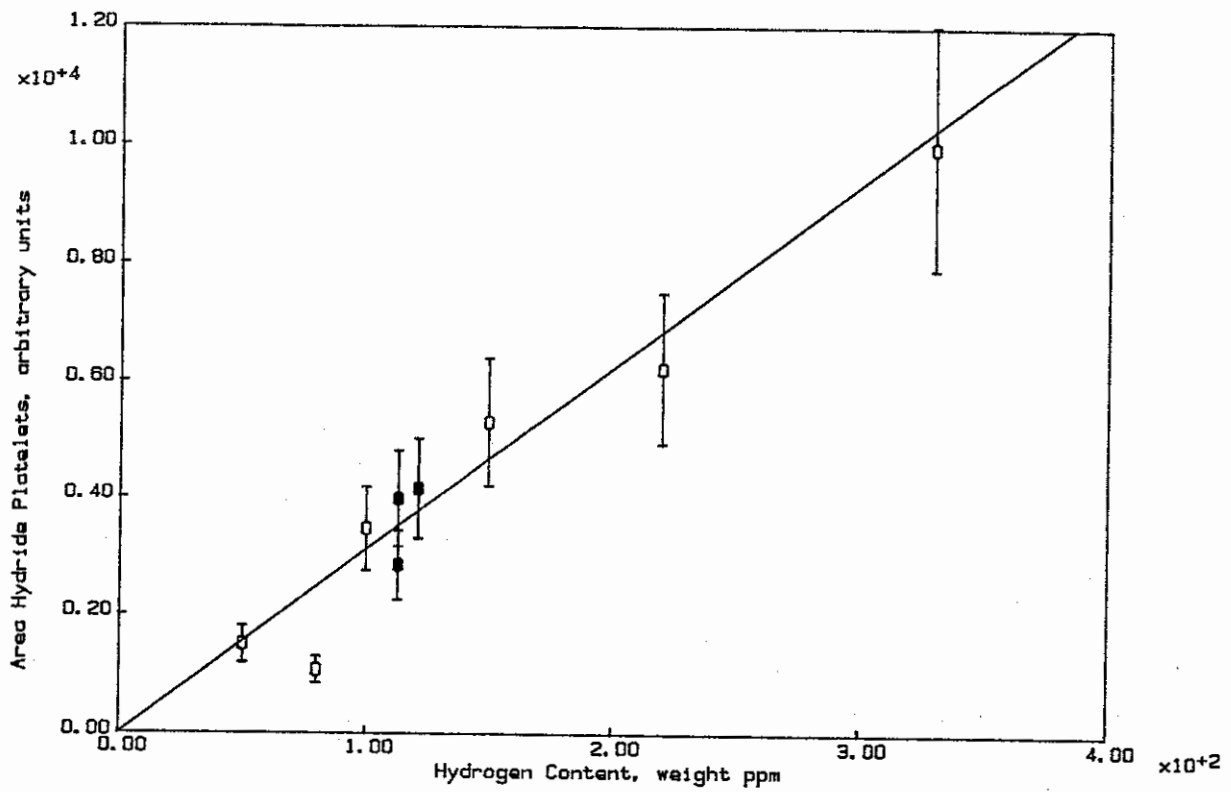*Fig. 2b* : Photomicrograph (x 500) of the hydrides in sample M4.

Fig. 3 : Surface area of hydride platelets, obtained by image analysis of
metallographic photomicrographs, versus hydrogen content.

o : data from Ref. 1

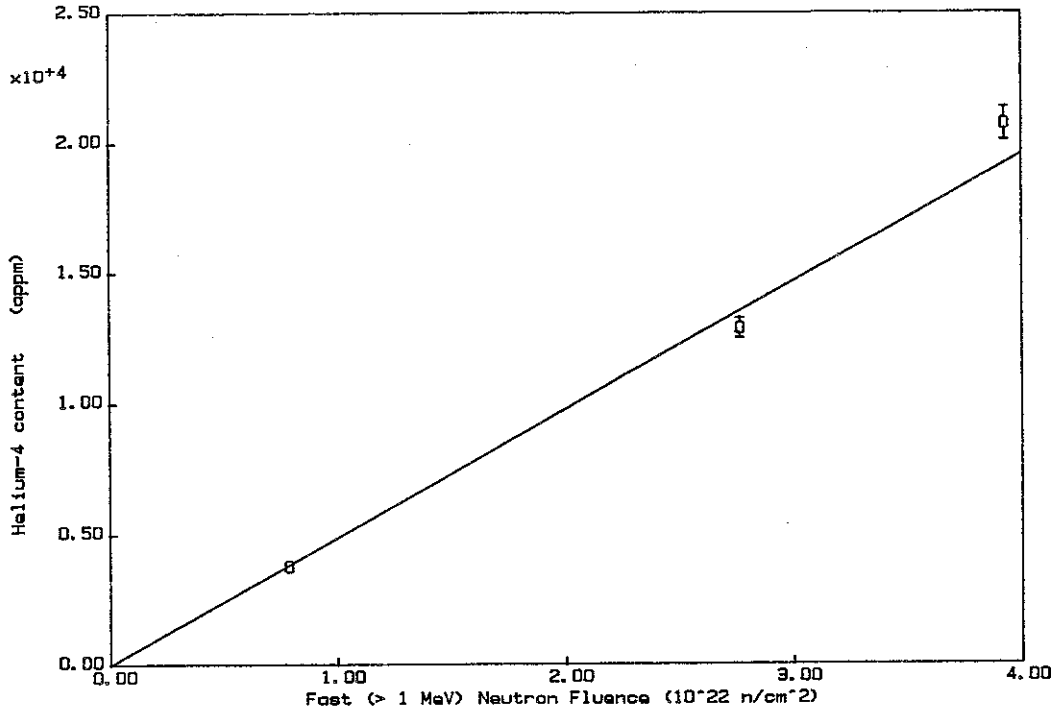• : data from the MOX fuel rods

(with 20 % error bars)

Fig. 4 : Helium production in irradiated beryllium as a function of the
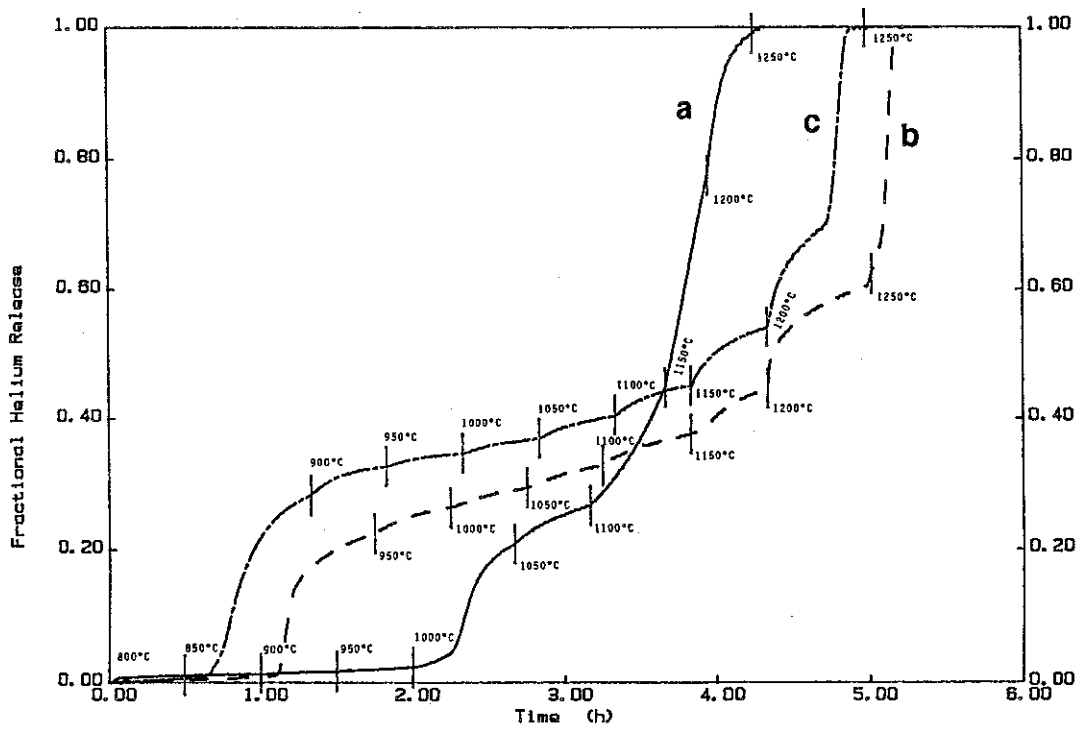fast-neutron fluence.

Fig. 5 : Fractional helium release in function of time and temperature at
three fast-neutron (E > 1 MeV) fluences : (a) 0.789×10^{22} n/cm^2
(b) 2.767×10^{22} n/cm^2
(c) 3.925×10^{22} n/cm^2