

QUANTITATIVE ANALYSIS OF OCCLUDED GASES IN UO_2 PELLETS BY QUADRUPOLE MASS SPECTROMETER AND ITS APPLICATION IN QUALITY CONTROL OF NUCLEAR FUEL

O. Vega; H.G. Riella and C. Rodrigues

Instituto de Pesquisas Energéticas e Nucleares
Área de Processos Especiais
São Paulo - Brazil

An investigation on the amount of the occluded gases in sinterized, ceramic grade, UO_2 pellets as a function of temperature, is presented in this work. The total volume of occluded gases in UO_2 pellets is determined using a high temperature vacuum extraction system. The total volume of gases liberated from the pellets for a temperature of $1700^\circ C$ is in the range of $0.03 \text{ cm}^3/\text{g}$ which is less than the maximum limit of $0.05 \text{ cm}^3/\text{g}$ of UO_2 set by American Society for Testing and Materials. A quantitative determination of amount of gaseous components in UO_2 pellets is made using the mass spectrometric technique.

1. INTRODUCTION

In the fabrication of nuclear fuels the quality level is directly concerned with the safety and the lifetime of the nuclear plant. There are several lists of specifications to be rigorously observed for each lot of the fabricated fuel. In the UO_2 pellets fabrication, one of the chemical specifications to be observed is the quantity of occluded gases. The importance of this determination is based on the fact that when the fuel is subject to the operational temperature of the reactor, the released gases could cause considerable damage to the fuel cladding which in turn affects the reactor performance.

The main aim of the present work lies in the quantitative and qualitative analysis of different gaseous components (excluding water vapour) occluded in sinterized ceramic grade UO_2 pellets PWR type. A high temperature vacuum extraction system was utilized for the determination of the total volume of the gases, whereas the qualitative analysis of the gaseous components were carried out by the mass spectrometric technique.

2. EXPERIMENTAL PROCEDURE

The sinterized ceramic grade UO_2 pellets utilized in this work were fabricated by Nuclear Metallurgical Centre of the Instituto de Pesquisas Nucleares (IPEN), São Paulo. Two lots of pellets fabricated with the same material and by the same process were used. The average density of the sinterized pellets is 10.6 g/cm^3 for the first lot and 10.2 g/cm^3 for the second lot, 96% and 93% of the expected theoretical density values, respectively.

The high temperature gas extraction and analysis apparatus were designed and assembled for sequential analysis of up to four uranium dioxide pellets (Figure I). The system consists of three major units. The whole system is evacuated to a final pressure of less than 10^{-5} Torr using

a mercury diffusion pump and a mechanical pump. The outgassing unit consists of a pellet loading and unloading arm with an externally operated magnet feed, a quartz furnace glass tube heated with induction coil from a "Politron" model 1-5 (450 KHz - 10 kW) induction furnace. The transfer unit, consisting of two glass diffusion pumps and a cold trap cooled to a temperature of $-96^\circ C$, is capable of transferring the liberated gas into the analytical unit. The analytical unit consists of a Toeppler pump and calibrated McLeod gauge.

A weighed pellet is transferred into the outgassing unit for subsequent dropping into a platinum-rhodium (90% - 10%) or graphite crucible which is heated inductively up to $1700^\circ C$ during 20 minutes¹. The released gases are immediately transferred from the outgassing unit to the analytical unit passing through a cold trap ($-96^\circ C$) to remove water vapour.

The gases are transferred to a previously calibrated volumetric bulb where the total pressure and temperature are determined. For an accurate measurement of the low gas pressure a McLeod gauge is used. A blank measurement of the whole system is carried out before each run. The gas content in the pellets at S.T.P. conditions is calculated from the measured volume, pressure and temperature of the gas mixture by applying the ideal gases equations. The lower detection limit of this technique is $0.002 \text{ cm}^3/\text{g}$ of UO_2 (S.T.P.)

Quantitative and qualitative gas analysis were performed using a Varian quadrupole mass spectrometer model VQA-100 (Figure II). The sample introduction system connected to the mass spectrometer consists of a one litre gas expansion bulb coupled to a cold trap, leak valve and a thermocouple gauge. The bulb can be evacuated and filled with gas at a desired pressure. The gas from the bulb enters the vacuum inlet of the ion source through a bakeable leak valve, that can operate from the atmospheric pressure to 10^{-11} Torr.

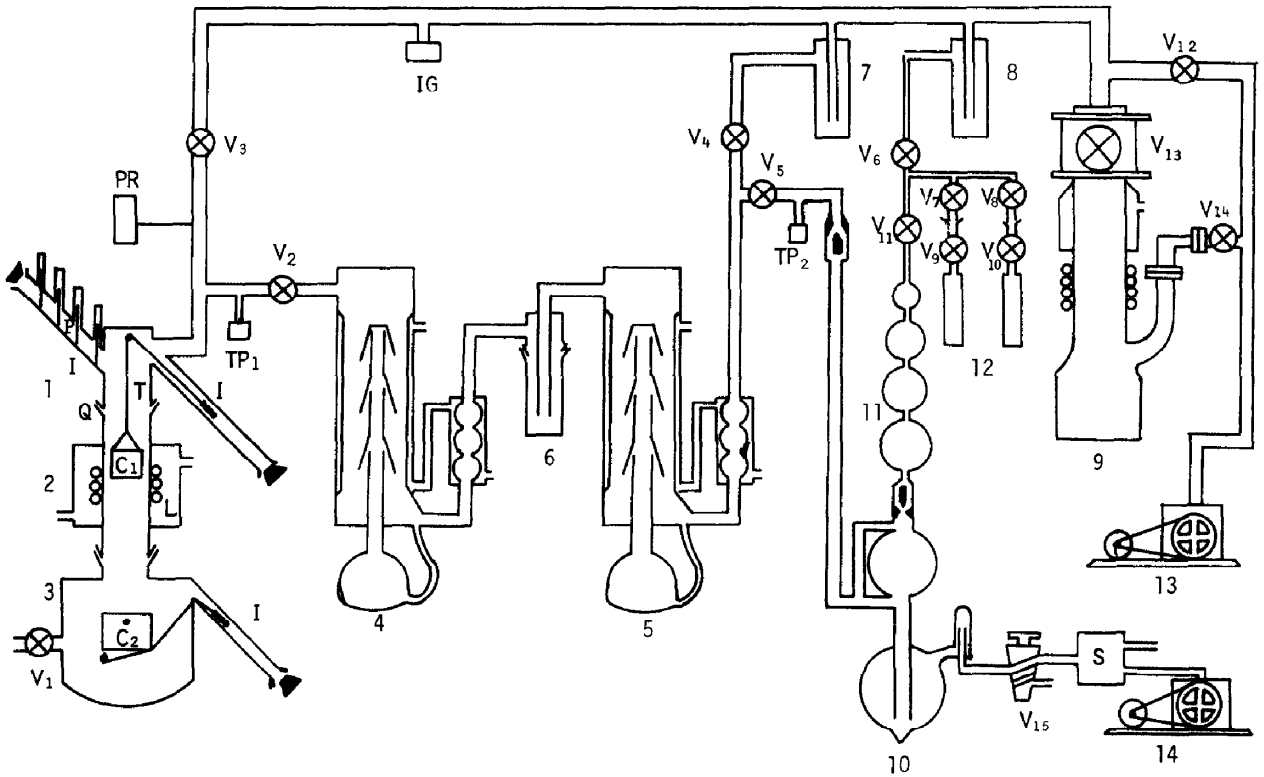


FIGURE I - VACUUM EXTRACTION SYSTEM, 1, PELLETS LOADING, 2, INDUCTION FURNACE, 3, PELLETS UNLOADING, 4, & 5, GLASS DIFFUSION PUMPS, 6, COLD TRAP (-96°C), 7, & 8, COLD TRAP (LIQUID NITROGEN), 9, METALLIC DIFFUSION PUMP, 10, TOE PLER PUMP, 11, McLEOD GAUGE, 12, CONTAINERS, 13, & 14, MECHANICAL PUMPS, I, MAGNETS, P, PELLETS POSITION, T, TUNGSTEN WIRE, C₁, GRAPHITE CRUCIBLE, L, WATER BUCKET, C₂, GLASS CRUCIBLE, TP₁ & TP₂, THERMOCOUPLES, IG, ION GAUGE, S, SOLENOID VALVE, V₁- V₁₁, STOPCOCK VALVES, V₁₂- V₁₄ STAIN LESS STEEL BELLOWS VALVES, Q, QUARTZ TUBE, PR, PIROMETER,

TABLE I - QUANTITATIVE ANALYSES OF SINTETIC GAS MIXTURE.

The minimum achieved leak is 1×10^{-9} Torr. litre/sec. The cold trap is used to remove condensable gases during analysis from the non condensable gases.

A weighted least squares procedure has been utilized to analyse the mass spectra of gas sample in order to determine the species and quantities of gases in the sample. This procedure needs a precalibration with various types of gas mixtures (H₂, Ar, N₂, CO and CO₂).

Gaseous mixtures of known compositions were analysed and the results are presented in Table I. The results obtained show that for gaseous mixtures Ar, N₂ and H₂, the deviation from the concentration listed by the suppliers of the gases

MIXTURES	NOMINAL CONCENTRATION GIVEN BY FABRICATED (%)	CONCENTRATION DETERMINED (%)
Ar- CO ₂	97.4 - 2.6	94.7 - 5.3
H ₂ - N ₂ - CO ₂	1.0 - 98.0 - 1.0	1.8 - 94.5 - 3.7
H ₂ - N ₂ - CO ₂	2.0 - 96.0 - 2.0	2.1 - 92.5 - 5.4
Ar- N ₂	96.5 - 3.5	96.4 - 3.6

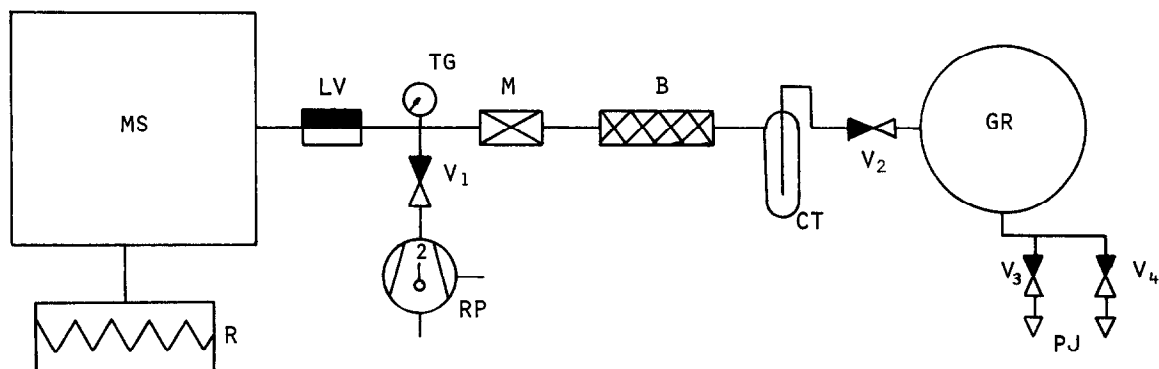


FIGURE II - INTRODUCTION SYSTEM, V₁- V₄, STRAIGHT-THROG STOPCOCK, TG,TERMOCUPLE GAUGE, R, RECORDE (SERVAGE GOERZ), MS, MASS SPECTROMETRE VGA-100, LV, LEAK VALVE (VARIAN MODEL N^o 9515100), CT, LIQUID NITROGEN COLD TRAP, GR, GAS RESERVOIR (1,0 LITRE), PJ, PYREX JOINT, M, MINI VALVE BAKEABLE, B, STAINLESS STEEL BELLOW, RP, ROTARY PUMP TWO STAGE,

is relatively small in comparison with mixtures which contain CO₂. This deviation may be due to the differential pumping speed and the cracking pattern of this component³.

3. RESULTS AND DISCUSSION

The total volume of gas occluded per unit mass in the sample at S.T.P. is calculated on the basis of the following equation^{1,2}:

$$V_t = \frac{1}{2.782M} \left[\frac{P_g V_g}{T_g} - \frac{P_b V_b}{T_b} \right]$$

where:

M = mass of the pellet

P_g, V_g and T_g = pressure, volume and temperature of the gas extracted from the pellet.

P_b, V_b and T_b = pressure, volume and temperature of the blank.

The total volume of the blank should not exceed 10% of the total volume of the gas extracted from the pellets. The minimum limit of detection for the extraction and measurement of the occluded gases in this work is found to be 0.002 cm³/g of UO₂. The results obtained for the volume of the gases liberated from the pellets as a function of temperature are presented in Table II and III for lots 1 and 2.

From Table II it can be seen that below 1400°C for different pellets from the same lot, the total volume of the gases liberated vary considerably (as much as 100%). Whereas above 1400°C the deviation is less, this can be explained as due to complete extraction above 1400°C.

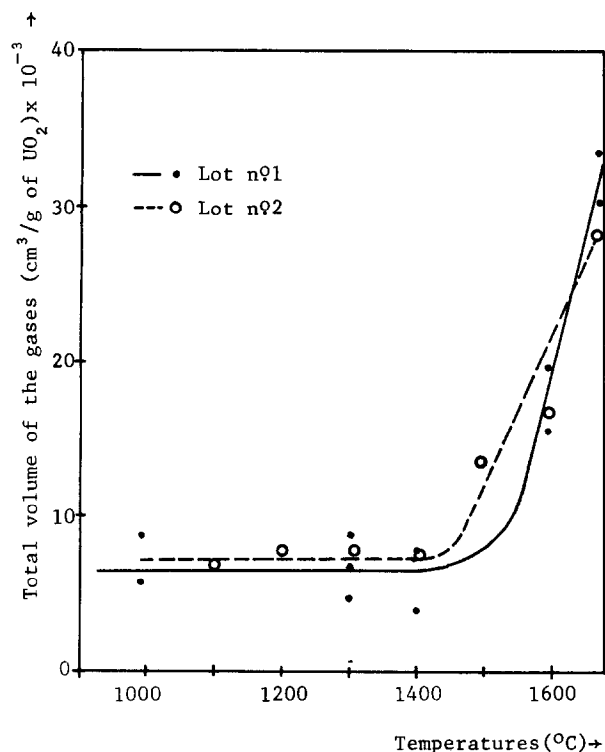


FIGURE III - VARIATION OF TOTAL VOLUME OF GAS IN RELATION TO THE HEATING TEMPERATURE OF THE UO₂ PELLETS FOR LOT 1 AND 2.

TABLE II - QUALITATIVE AND QUANTITATIVE ANALYSIS OF THE OCCLUDED GASES PRESENTS IN UO₂ PELLETS. LOT 1.

PELLETS Nº	TEMPERATURE OF GAS EXTRACTION (°C)	TOTAL VOLUME (cm ³ /g of UO ₂)	QUANTITATIVE ANALYSIS (ppm)			
			H ₂	CO	N ₂	CO ₂
1	1000	0.009	1	11	2	<1
2	1000	0.006	2	8	<1	<1
3	1300	0.009	3	10	<1	<1
4	1300	0.005	1	5	1	2
5	1300	0.007	1	8	<1	2
6	1400	0.008	1	9	1	2
7	1400	0.004	1	4	<1	<1
8	1600	0.016	10	9	3	<1
9	1600	0.020	14	12	2	1
10	1700	0.034	16	11	3	2
11	1700	0.031	18	8	3	1

TABLE III - QUALITATIVE AND QUANTITATIVE ANALYSIS OF THE OCCLUDED GASES PRESENTS IN UO₂ PELLETS. LOT 2.

PELLETS Nº	TEMPERATURE OF GAS EXTRACTION (°C)	TOTAL VOLUME (cm ³ /g of UO ₂)	QUANTITATIVE ANALYSIS (ppm)			
			H ₂	CO	N ₂	CO ₂
1	1100	0.007	2	4	2	1
2	1200	0.008	3	4	2	1
3	1300	0.008	3	6	1	1
4	1400	0.008	3	4	3	1
5	1500	0.014	11	<1	2	1
6	1600	0.017	11	1	3	2
7	1700	0.029	22	2	3	1

The variation of the total volume of the liberated gases as a function of temperature is presented in Figure III, which shows similar type of liberation of gases from the UO₂ pellets of the two different lots. It can also be seen that the major portion of the gases are liberated above 1400°C for both lots of pellets.

The total volume of the occluded gases liberated for both lots for a maximum temperature of 1700°C is less than the maximum limit of 0.05 cm³/g of UO₂, as established by American Society for Testing and Materials.

This indicates that the pellets are within the norms established for nuclear fuel as far as the quantity of the total gases occluded.

The mass spectrometric analysis reveals the presence of H₂, CO, N₂ and CO₂ in the gas mixture. In Table II and III the concentrations of these components is presented in parts per million (µg/g of UO₂). It can be seen from the Tables that the major part of H₂ is liberated at higher temperature.

The results of this study indicate that the control of the occluded gases present in the UO₂ pellets can be made by measuring the concentration of hydrogen alone. The liberation of hydrogen causes major damage as it reacts with zirconium forming zirconium hydrate, a highly corrosive compound, which can alter its mechanical property and generate cracking.

4. CONCLUSIONS

1. In the present work the total volume of gases liberated from UO₂ pellets at 1700°C was found to be 0.034 cm³/g of UO₂ and 0.029 cm³/g of UO₂ for the first and the second lot respectively, which are below the limit established by ASTM (American Society for Testing and Materials).

2. The mass spectrometric technique employed for the qualitative and quantitative analysis of the occluded gases shows the presence of H₂, CO, N₂ and CO₂ in the gas mixture.

3. The variation in the quantity of the gases liberated from UO₂ pellets as a function of temperature show that CO, N₂ and CO₂ are totally liberated at temperatures of 1000°C whereas the hydrogen is liberated above 1500°C and at 1700°C is the major component in the gas mixture liberated. Hence the measurement of hydrogen alone at a temperature of 1700°C may be sufficient for the total volume measurement of occluded gas from the point of view of quality control.

REFERENCES

1. H.G. Riella, "Determinação de Gases Residuais em Pastilhas de Dióxido de Urânio". Master Thesis, Instituto de Energia Atômica, São Paulo, Brasil (1978).
2. Standard Specification for Sintered Uranium Dioxide Pellet, American Society for Testing and Materials, 1979, ASTM C 776-79.
3. J.O.W.V. Bustillos et al., Measurement of Mass and Isotopic Sensitivity of a Quadrupole Gas Analysis for Noble Gases; International Mass Spectrometry Conference, Oslo, Norway, (1979).