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TOTAL AND OCCLUDED RESIDUAL GAS CONTENT INSIDE THE NUCLEAR FUEL PELLETS

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ABSTRACT

This work describes three techniques available to measure total and occluded residual gases inside the UO_2 nuclear fuel pellets. Hydrogen is the major gas compound inside these pellets, due to sintering fabrication process but Nitrogen is present as well, due to storage atmosphere fuel. The total and occluded residual gas content inside these pellets is a mandatory requirement in a quality control to assure the well function of the pellets inside the nuclear reactor. This work describes the Gas Extractor System coupled with mass spectrometry GES/MS, the Gas Extractor System coupled with gas chromatography GES/GC and the total Hydrogen / Nitrogen H/N analyzer as well. In the GES, occlude gases in the UO_2 pellets is determinate using a high temperature vacuum extraction system, in which the minimum limit of detection is in the range 0.002 cc/g. The qualitative and quantitative determination of the amount of gaseous components employs a mass spectrometry or a gas chromatography technique. The total Hydrogen / Nitrogen analyzer employ a thermal conductivity gas detector linked to a gaseous extractor furnace which has a detection limit is in the range 0.005 cc/g. The specification for the residual gas analyses in the nuclear fuel pellets is 0.03 cc/g, all techniques satisfy the requirement but not the nature of the gases due to reaction with the reactor cladding. The present work details the chemical reaction among Hydrogen / Nitrogen and nuclear reactor cladding.

1. INTRODUCTION

The total and occluded residual gases inside the nuclear fuel pellets are a quality specification required by a quality assurance to assure the well function of the pellets inside the nuclear reactor. Hydrogen is the major gas compound inside these pellets, due to sintering fabrication process but Nitrogen is present as well, due to storage atmosphere fuel. Depend on what kind of nuclear reactor will be used the pellets, the specification must be clearly different. The thermal nuclear reactor and the fast nuclear reactor, require different specification in this item due to differences in the nature of the fuel and type of cladding.

During the manufactured process of the UO_2 nuclear fuel pellets, permanent gases like Hydrogen and Nitrogen are trapped in the interstitials spaces of the pellets. These trapped gases are know as total and occluded residual gases. In the sintering process, the pellets are set up at high sintering temperatures surrounding by a reducing gas environment, gases like Argon / Hydrogen or Nitrogen / Hydrogen are common sintering gases. During this cycle, some gases get trapped and will be released during the operation conditions of the reactor.

They may pressurize the clad, alter the thermal conductivity of cover gas, or react with the clad and cause damage. Hence, it is of importance to have a precise knowledge of the total gas content and its composition.

The scope of this work is to describe different types of gas analyzers for this purpose. It will be describes the Gas Extractor System of the occlude gases in the UO_2 pellets which determinate the total gas volume using a high temperature vacuum extraction system, which the minimum limit detection is in the range of 0.002 cc/g. The qualitative and quantitative determination of the amount of gaseous components employs a mass spectrometry or a gas chromatography technique. Another type is the total Hydrogen and Nitrogen analyzer which determinate H_2 and N_2 molecules by a thermal conductivity detector from the gases released by the UO_2 pellet inside a radio frequency extractor furnace, the detection limit of this analyzer is in the range 0.005 cc/g. The specification for the residual gas analyses in the nuclear fuel pellets is 0.03 cc/g, both techniques satisfy the requirement but not the nature of the gases due to reaction with the reactor cladding.

2. OCCLUDE RESIDUAL GASES IN THE UO_2 PELLETS

The technique of occlude residual gas analyses is based on the liberation of the occluded gases that are trapped inside a sinterized, ceramic grade, UO_2 pellet. The extraction is a function of temperature reached by a high temperature vacuum extraction system, simulating the nuclear reactor temperature. The determination of these gases is important to the quality control program of UO_2 pellets in Pressurized Water Reactor (PWR) [1].

2.1. The Gas Extractor System coupled to mass spectrometry – GES/MS.

The GES/MS is a home made extractor glass system built in the IPEN laboratory. The mass spectrometry is equipped with a quadrupole mass filter, electron impact ion source and a Faraday cup ion detector, it has a mass range from 1 to 100 Daltons and resolution of 1 Dalton.

The GES/MS technique follows the forwards steps. The UO_2 pellets are inserting inside a borosilicate glass system denominate as Gas Extractor System – GES (Figure 1) in the compartment P, the GES is set up under a low pressure, vacuum in the order of 10^{-5} Torr. The pellets can be moved by a set of magnetic system and gravity force. A specific weighted pellet is located inside a graphite crucible that is moved up and down by a magnetic system and a tungsten wire. The pellet inside the crucible is set up inside a Radio Frequency furnace, in this way the pellet is heated up between 1500 to 1700 ^oC, measured by a pyrometer device. The gases liberated by the pellet is carry on by the first glass diffusion pump through a cryogenic trap to trapping the water molecules, then the gases are pump it up by the second glass diffusion pump into a mercury Toepler pump that introduce the gases inside a McLeod gauge. A aliquot of the gas is collected by glass containers and take it to a mass spectrometer device to measurement the composition of the occlude residual gas from the UO_2 pellets. The GES is a home made in IPEN, liked to a quadrupole mass spectrometry that have capability to detect and measurement the residual gases. The time lapse to performance one analyze takes 15 minutes. The minimum detection limit is in the order of 0.002 cm^3/g of UO_2 . A routine analysis of the occluded gas in the GES/MS of a set of UO_2

pellets is in the order of 0.020 to 0.009 cm^3/g of UO_2 with gas content of $H_2/CO/N_2/CO_2$ within, in part per million (ppm) at a range of 18/8/3/1 respectively [2].

The total volume in standard condition of temperature and pressure (STP) of the occluded residual gas content in the UO_2 pellets is measured by the equation 1.

$$\frac{P_1 \cdot V_1}{T_1} = \frac{P_2 \cdot V_2}{T_2} \tag{1}$$

where: P_1 is the pressure in mmHg exerted by the occluded gases; V_1 is the volume in mm^3 of the system into which the gases are collected; T_1 is the room temperature in Kelvin; P_2 is the normal pressure equal to 760 mmHg; T_2 is 273 K and V_2 is the occluded gas content at STP conditions.

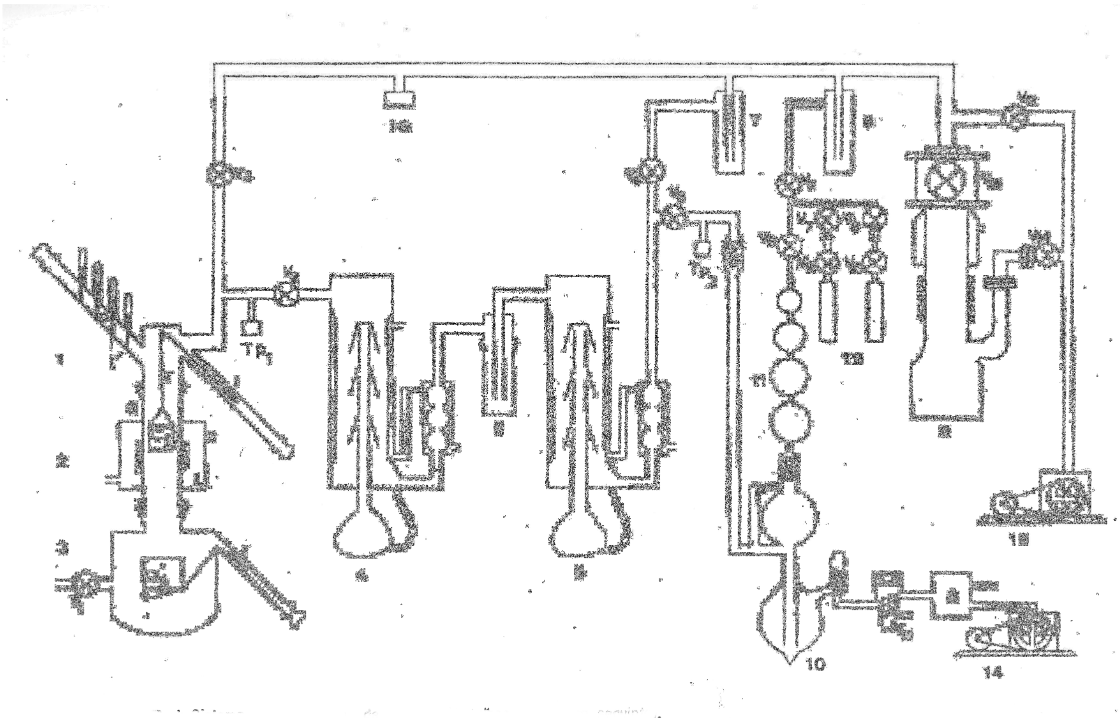

Figure 1: Gas Extractor System GES. 1) Sample inlet system. 2) Radio frequency furnace. 3) Sample outlet system. 4 & 5) Mercury diffusion glass pump. 6, 7 & 8) Traps. 9) Mercury diffusion metallic pump. 10) Toepler pump. 11) Mcleod gauge. 12) Glass containers. 13 & 14) Mechanical pumps.

The qualitative analysis result shows the presence of following components in the occluded gas: H_2, CO, N_2 and CO_2. A routine analysis of the occluded gas by the GES/MS in a set of UO_2 pellets is in the order of 0.020 to 0.009 cm^3/g of UO_2 with gas content of $H_2/CO/N_2/CO_2$ within, in part per million (ppm) at a range of 18/8/3/1 respectively. The quantitative analysis showed that Hydrogen is the major component in the gas phase extracted between, 1500 to 1700 ^oC. The presence of Hydrogen can be attributed to the absorption of the H_2 molecules by UO_2 pellets during the process of sintering, as the process is carried out in an atmosphere of Hydrogen. The presence of CO and CO_2 is due to the reaction of the O_2 present in the pellet and the carbon from the graphite crucible. The presence of the gases N_2 and O_2 is due to storage effect of the UO_2 pellets in the normal atmosphere.

2.2. The Gas Extractor System coupled to Gas Chromatograph – GES/GC.

The GES/GC system is a commercial gas analyzer VH-9 model, made by Leybold Hereaus. The gas extractor is a static ultra high vacuum system (Figure 2). The system is free from any contamination from hydrogenous material. Hence mercury diffusion pumps are incorporated in the system. Since the amount of total gas content is very small, the equipment should hold the vacuum under static conditions for several hours. The system is divided in two parts, sampling loading and gas extraction one. The system is evacuated to 10^{-5} mbar by means of mercury diffusion pumps and a mercury ejector pump supported by a backing pump. The sample is heated in a graphite crucible at 1500 ^oC by inducting heating. The gases released are extracted into a pre-calibrated volume by the mercury ejector pump. The pressure is measured employing McLeod gauge. The gases are introduced into a packet gas chromatography column with molecular sieve 5A stationary phase and Argon as carry gas. The gases are detected by a Thermo Coupled Detector (TCD). By this way the minimum detection limit is in the order of 0.001 cm^3/g of UO_2 [3].

The chromatogram analysis shows the presence of same components as the GES/MS, these are: H_2, CO, N_2 and CO_2. The presence of Hydrogen is attributed to the absorption of the H_2 molecules by UO_2 pellets during the process of sintering. The presence of CO and CO_2 is due to the reaction of the O_2 present in the pellet and the carbon from the graphite crucible. The presence of the gases N_2 and O_2 is due to storage effect of the UO_2 pellets.

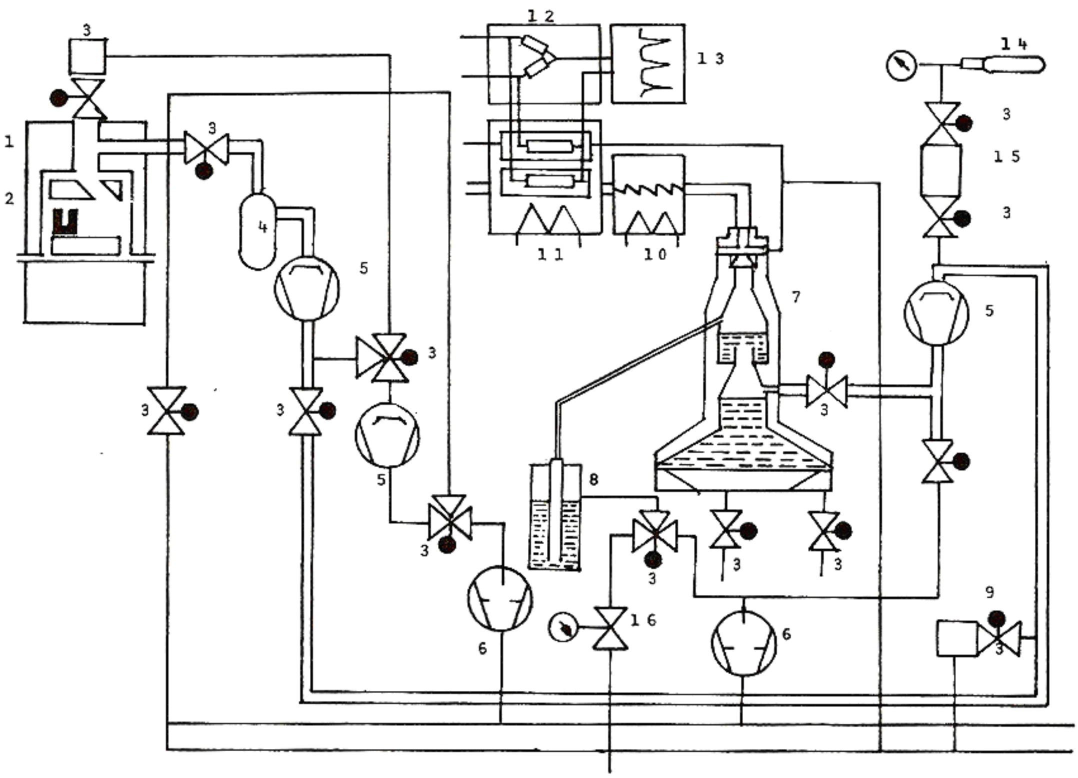

Figure 2: Evolograph VH-9. 1) Furnace 2) Graphite crucible. 3) Solenoid valves. 4) Trap. 5) Diffusion pump. 6) Rotary pump. 7) Transfer pump. 8) Mercury deposit. 9) Argon valve. 10) Gas chromatograph. 11) Detectors. 12) TCD. 13) Integrator. 14) Gas calibrator. 15) Volume chamber. 16) Pressurized air valve.

Historically, the total and occluded residual gases inside the nuclear fuel pellets where develop by D. Vance et al. [6] in Los Alamos Scientific Laboratory in 1970. In Brazil, specifically in IPEN/CNEN, the SEG/MS where built in the year 1977 by H. Riella et al. [7], the SEG/GC where set up in the 1982 by O. Vega et al. [3]. K. Ferrari [8] has been study the storage oxide nuclear fuel at different atmospheres in 1995. In Japan A. Maeda et al. [9] where develop a SEG in 1985. In India, Y. Sayi et al. [10] where develop a SEG in 1990.

3. TOTAL HYDROGEN AND NITROGEN IN THE UO_2 PELLETS

The technique of total Hydrogen and Nitrogen analyses is based on the liberation of these gases inside sinterized UO_2 pellet as function of temperature made by a radio frequency furnace. These analyzers are commercially available, the detection of H_2 and N_2 is made by a thermal conductivity detector. The principle is based on such as the mayor gas liberated by the sintered UO_2 pellets is hydrogen and nitrogen then only these two gases is measured in the UO_2 pellets. The total H_2 and N_2 analyses it runs in a short time period of time, 2 minutes, compare to the GES/GC or GES/MS system that it takes 15 minutes.

3.1. The cladding nuclear rods and the OU_2 fuel pellets.

The PWR (Pressurized Water Reactor) nuclear reactor has a cladding made by a zirconium alloy well know as Zircaloy. During the first seconds of burn up, the occluded residual gas from the UO_2 pellets is liberated. If the volume of these gases is higher than the specification the cladding could be physically be damage given a consequently accident inside the nuclear reactor. In this way the measurement of the amount of occluded residual gases inside the UO_2 pellets is a mandatory quality control measurement in the production of nuclear fuel. In this way, if the pressure of these gases increases over a certain critical value, the intergranular structures of the cladding is suddenly deformed, which in course of time lead to embrittlement. To evaluate the implication of these gases inside the PWR cladding tubes, it is also essential to find out the composition of these gases released.

The possible chemical reactions between the Zircaloy cladding and the occluded residual from the UO_2 pellets are presents in equation 2.

$$\begin{aligned} 2\,Zr &+ N_2 \rightarrow 2\,Zr\,N \\ Zr &+ O_2 \rightarrow Zr\,O_2 \\ Zr &+ H_2 \rightarrow Zr\,H_2 \\ Zr &+ 2\,H_2O \rightarrow ZrO_2 + 2\,H_2 \end{aligned} \qquad (2)$$

There is another thermodynamic effect when these gases are liberated inside the nuclear bars. Depends on the qualitative and quantitative of the occluded gases will reduce the thermal capability of the Helium gas between the cladding and the UO_2 pellets, that means will reduce the transfer heat from the nuclear fuel to the pressurized water inside the nuclear core [4].

Few types of ceramic material such as U, Th, and Gd oxides are employed as fuel in the nuclear industry. All these fuels have to be meet stringent specifications for total volume of occluded residual gases besides identification both major and minor constituents.

In the fast nuclear reactors, stainless steel is employed as cladding material. In this way, another type of fuel/cladding reaction will take a place instead of those have been depicted in formula 2. Hydrogen embrittlement stainless steel within different hydrogen concentrations. At 25 ppm of hydrogen, 304 stainless steel loses 10% of its original mechanical strength and 20% plasticity [5]. Means that hydrogen damages the performance of 304 stainless steel significantly even at very low levels consequently damage the cladding nuclear rods.

4. CONCLUSIONS

The quality specification of the total and occluded residual gases inside any sintered oxides nuclear fuel pellets it has to be carefully be establish by the quality assurance, depend on the purpose of these fuel will be employee. If this fuel will be used in a Zircalloy or stainless steel cladding the quality control on total H_2 and N_2 has to be specify and this will be different due to the reaction between these gases and cladding. Even though, the total volume of these gases has to be measurement to avoid excess gases inside the nuclear rods during fuel burn up.

The specification for the residual gas analysis in the nuclear fuel pellets is 0.03 cc/g, both techniques SEG and total H_2 and N_2 satisfy the requirement but not the nature of the gases due to reaction with the reactor cladding. The H_2 and N_2 analyses runs in a short time period of time, 2 minutes, compare to the GES/GC or GES/MS system that takes 15 minutes.

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