Characterization of Hydrogen, Nitrogen, Oxygen, Carbon and Sulfur in Nuclear Fuel (UO_2) and Cladding Nuclear Rod Materials.

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ABSTRACT

The importance of Hydrogen, Nitrogen, Oxygen, Carbon and Sulfur gases analysis in nuclear fuels such as UO_2, U_3O_8, U_3Si_2 and in the fuel cladding such as Zircaloy, is a well known as a quality control in nuclear industry. In UO_2 pellets, the Hydrogen molecule fragilizes the metal lattice causing the material cracking. In Zircaloy material the H_2 molecules cause the boiling of the cladding. Other gases like Nitrogen, Oxygen, Carbon and Sulfur affect in the lattice structure change. In this way these chemical compounds have to be measure within specify parameters, these measurement are part of the quality control of the nuclear industry. The analytical procedure has to be well established by a convention of the quality assurance. Therefore, the Oxygen, Carbon, Sulfur and Hydrogen are measured by infrared absorption (IR) and the nitrogen will be measured by thermal conductivity (TC). The gas/metal analyzer made by LECO Co. model TCHEN-600 is Hydrogen, Oxygen and Nitrogen analyzer in a variety of metals, refractory and other inorganic materials, using the principle of fusion by inert gas, infrared and thermo-coupled detector. The Carbon and Sulfur compounds are measure by LECO Co. model CS-400. A sample is first weighed and placed in a high purity graphite crucible and is casted on a stream of helium gas, enough to release the oxygen, nitrogen and hydrogen. During the fusion, the oxygen present in the sample combines with the carbon crucible to form carbon monoxide. Then, the nitrogen present in the sample is analyzed and released as molecular nitrogen and the hydrogen is released as gas. The hydrogen gas is measured by infrared absorption, and the sample gases pass through a trap of copper oxide which converts CO to CO2 and hydrogen into water. The gases enter the cell where infrared water content is then converted making the measurement of total hydrogen present in the sample. The Hydrogen detection limits for the nuclear fuel is 1 µg/g for the Nitrogen and Oxygen is 10 µg/g and for the C and S is 100 µg/g .The present work shows details of the methodology and data analysis of the nuclear fuel as well as Zircaloy cladding.

INTRODUCTION

The quality control program in the production of the nuclear fuels is a major item to assure that all these components will work as technical specifications in a nuclear plant. Among these fuel quality control, the gases in metals is the scope of the present work. The importance of Hydrogen, Nitrogen, Oxygen, Carbon and Sulfur gases analysis in nuclear fuels such as UO_2, U_3O_8, U_3Si_2 and in the fuel cladding such as Zircaloy, is a well known as a quality control in nuclear industry. In UO_2 pellets, the Hydrogen molecule fragile the metal lattice causing the material cracking. During fabrication of sintered fuel pellets, some permanent gases are occlude in the interstices. The gases, under the operation conditions of the reactor, get released and affect the performance of the fuel and clad. In Zircaloy material the H_2 molecules cause the boiling of the cladding. Zircaloy coolant channels of pressurized water reactor can become brittle due to the formation of hydride thus several limiting the life of these channels. Thus the ageing management of Zircaloy channels need to be addressed from the point of view of Hydrogen determination. An accurate method for Hydrogen determination in Zircaloy need to be established. Other gases like Nitrogen, Oxygen, Carbon and Sulfur affect in the lattice structure change. In this way these chemical compounds have to be measure within specify parameters, these measurement are part of the quality control of the nuclear industry. The scope of this work is to describe the gas analyzers in nuclear materials. It will be describes the H, N, O, C and S in the nuclear fuels, the detection limit of this analyzer is in the range 0.005 cc/g.

Hydrogen, Nitrogen and Oxygen analyses:

The analyzer is made by LECO model TCHEN600 (Figure 1) determines the hydrogen, nitrogen and oxygen content of a sample. It uses a self-contained electrode furnace for fusion. Hydrogen and Oxygen are measured by infrared detection as carbon dioxide, carbon monoxide and water vapor in an IR cell.

Nitrogen is measured by thermal conductivity in a TC cell. Analysis begins by placing an empty graphite crucible on the lower electrode. The electrodes close and atmosphere is purged from the crucible. High current passes through the crucible generating heat, which drives off gasses trapped in the graphite. This process is called outgassing. Next, a sample is dropped from the loading mechanism into the crucible. High current is again passed through the crucible driving off gasses in the sample. To prevent further outgassing during analysis, a current lower than outgas current is used.

Oxygen is measured by infrared (IR) absorption. Sample gases first enter the IR module and pass through CO and CO_2 detectors. Oxygen present as either CO or CO_2 is detected. Following this, sample gas is passed through heated copper oxide to convert O to CO_2 and any hydrogen to water. Gases then re-enter the IR module and pass through a separate CO2 detector for total oxygen measurement.

This configuration maximizes performance and accuracy for both low and high range. The instrument automatically chooses the optimum detection range.

Nitrogen is measured by thermal conductivity (TC). Sample gases pass through heated copper oxide which converts CO to CO_2 and hydrogen to water. CO_2 and water are then removed with a Lecosorb/Anhydrone trap to prevent detection by the TC cell. Gas flow then passes through the TC cell for nitrogen detection.

Hydrogen is measured by infrared absorption. Sample gases pass through heated copper oxide which converts CO to CO_2 and hydrogen to H_2O. Gases enter the IR module and pass through an H_2O detector for total hydrogen measurement.

Before the sample gasses flow through the measure flow scrubber and TC cell, they pass through the Dynamic Flow Compensator. As CO_2 is trapped by Lecosorb, the sample gas flow rate is reduced. The dynamic flow compensator adds carrier gas to the sample gasses, maintaining a constant flow rate. In the presents of high oxygen, this process improves the nitrogen sample results. After the dynamic flow compensator, sample gasses flow through the measure flow scrubber where carbon dioxide is removed by Lecosorb to prevent detection by the TC cell. Water vapor is formed when carbon dioxide is trapped. Since water vapor can be detected by the TC cell, Anhydrone is used to remove it. Sample gasses then flow through TC cell producing the nitrogen result.

Infrared Radiation, Absorption and Detection

The infrared source (IR) consists of nichrome wire that is resistance heated to 850 °C. The IR source radiates visible energy as well as all of the wavelengths in the infrared spectrum.

Oxygen is detected in the IR cells as carbon monoxide or carbon dioxide. Carbon oxides absorb IR energy at a precise wavelength within the IR spectrum. Energy from the IR source is absorbed as the gas passes through the cell, preventing it from reaching the IR detector. All other IR energy is prevented from reaching the IR detector by a narrow band pass filter. Because of the wavelength filter, the absorption of IR energy can be attributed only to one carbon oxide. The concentration of carbon dioxide is detected as a level of energy at the detector.

One IR cell is used as both a reference and for measurement. The total oxygen, as carbon dioxide and carbon monoxide, is detected on a continuous and simultaneous basis. The cell consists of an IR source, a narrow band-pass filter, a condensing cone, an IR energy detector, and the cell body. Radiated energy enters the cell body through a window, travels through the cell body, and then exits through a second window and a precise wavelength filter. The selective filter passes only the carbon dioxide absorption wavelength into a condensing cone, which concentrates the energy at the detector. As the gas concentration increases the voltage to the preamplifier decreases.

The starting reference level, or "baseline," for the detector is established by running 100% helium through the cell. The pure helium environment permits the maximum amount of energy to reach the detector. This maximum energy level is coupled to the preamplifier where it is amplified and filtered. It is then sent to an analog

to digital (A/D) converter where it is converted to a digital signal. The nominal voltage when read at the cell output, via the Ambient Monitor, is 1.5 to 5 VDC.

Thermal Conductivity Detection

The Thermal Conductivity Cell can determine the differences in the thermal conductivity of gases, as shown in the Thermal Conductivity of Gases Table 1. The cell consists of two matched filaments that are maintained in a constant gas flow. Only the gas type is different. The reference filament is subjected to only carrier gas, while the measurement filament is subjected to the sample gas mixed with carrier gas.

Table 1: Thermal Conductivity of Gases

Gas	Symbol	Molecular Weight	Thermal Conductivity
Hydrogen	H_2	2	39.0
Helium	He	4	33.0
Water Vapor	H_2O	18	4.0
Neon	Ne	20	10.4
Nitrogen	N_2	28	5.6
Air (dry)	Air	29	5.4
Carbon Monoxide	CO	28	5.4
Oxygen	O_2	32	5.7
Argon	Ar	40	3.8
Carbon Dioxide	CO_2	44	3.3
Sulfur Dioxide	SO_2	64	1.6

The cell output is zero while both filaments are in identical carrier gas environments. The filament current causes the filaments to self-heat and keeps the filament temperature higher than the ambient oven temperature. The oven temperature is maintained at 50°C, which eliminates the effects from normal room temperature variations.

As long as both resistors remain in the same environment, the cell output will remain at zero. Any disturbance of this environment will result in a change or increase in output. The output is zero when helium flows in both chambers of the cell. The introduction of nitrogen will cause the temperature of the measure filaments to increase because nitrogen has a lower thermal conductivity than helium. This causes the current through the filament to change producing an output. The magnitude of the output will vary due to the concentration of nitrogen.

Like the IR cell, the output from the TC cell is fed to a preamplifier. This, in turn, is fed to an analog to digital converter. The output, a digital signal, is then fed to

the computer where it is processed, displayed, and stored as the nitrogen measurement result.

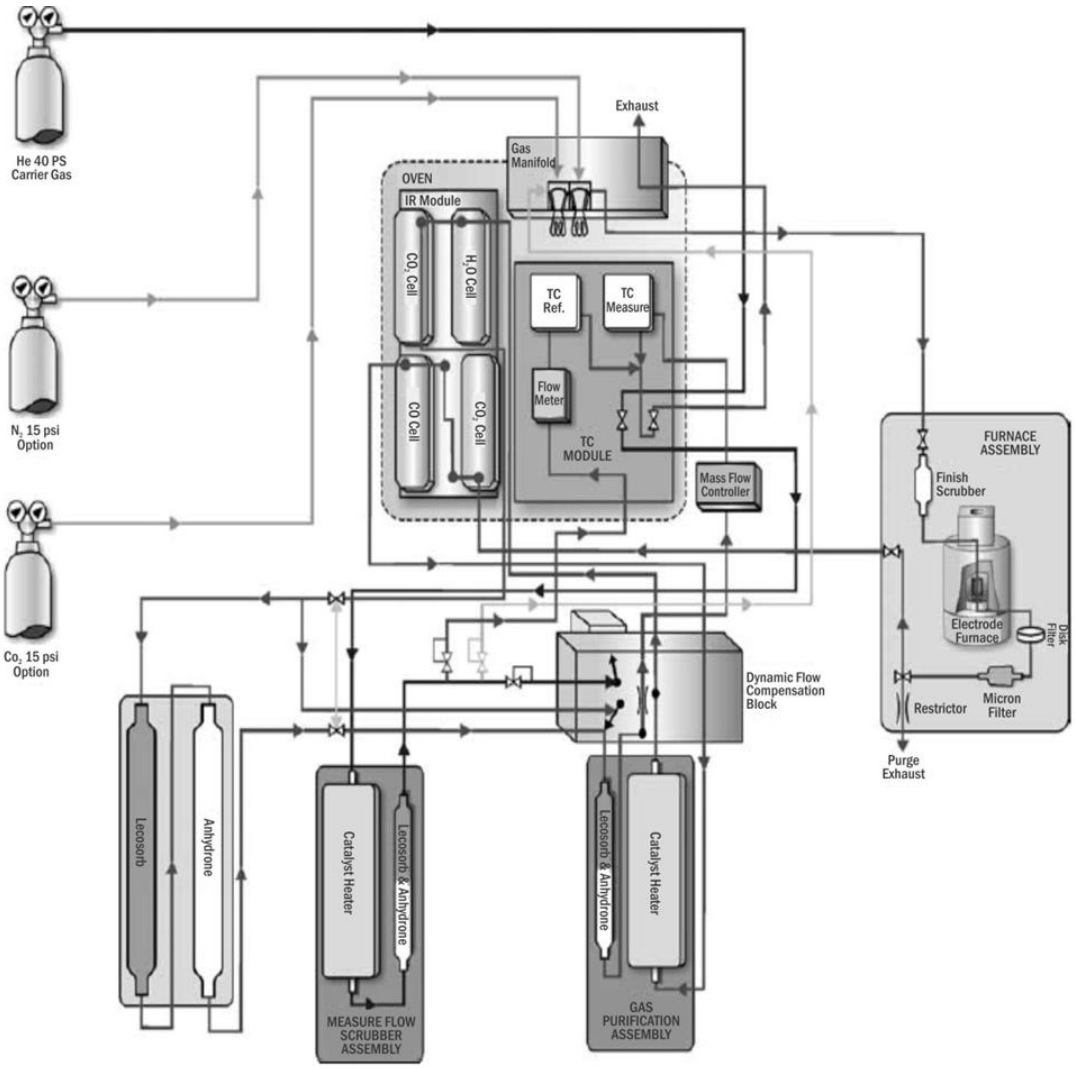

Figure 1: The H, N and O analyzer LECO model TCHEN600. Flow diagram.

Conclusions

The quality specification of the chemical compounds H, N, O, C and S 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. The specification for the residual gas analysis in the nuclear fuel pellets is 0.005 cc/g. The analytical method presents in this work satisfy the requirement.

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