Total gas analysis of nuclear fuels

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Total/occluded or residual gas content of sintered nuclear fuel pellets is an important specification. The specification of the gas content depends on the nature of the fuel and type of the reactor. The total gas content and its composition were determined employing hot vacuum extraction followed by quadrupole mass spectrometry. Detailed investigations carried out on the determination of total gas in various types of nuclear fuels used in different types of reactors are reported in this paper. Oxide pellet is heated at 1650°C for 15 min while carbide pellet is heated at 1000°C for 30 min for the determination of total gas content. The overall measurement error is ± 5% and the detection limit is 0.005 cc. The main constituent of the gas is hydrogen (> 95%) in all the types of fuel pellets.

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During the manufacture of high purity metals and alloys permanent gases like hydrogen and nitrogen are trapped in the interstitial spaces. These trapped gases are known as total/occluded or residual gases. If the pressure of these gases increases over a certain critical value, the intergranular structures of the above materials are suddenly deformed, which in course of time lead to embrittlement. To evaluate the implications of these gases in the material or the material surrounding it, it is also essential to find out the composition of these gases released.

In nuclear industry, various types of ceramic materials of U, Pu and Th are employed as fuel in the reactor. The fuel has to meet stringent specifications, for both major and minor constituents. The trace constituents, if exceed the specified limits, affect the fuel properties and hence its performance under conditions prevailing in an operating reactor. These fuel pellets are enclosed in appropriate cladding material and the gap between the pellets and the clad is filled by suitable cover gas.

Natural UO₂ is the fuel for Pressurised Heavy Water Reactors (PHWR). Mixed oxide (MOX) with appropriate composition of U and Pu can be used in PHWRs to increase the burn-up1,2. Enriched UO₂ is the fuel for Boiling Water Reactors (BWR). MOX fuel with Pu composition 3 to 5% is considered an alternate fuel for these types of reactors3. Mixed carbides and nitrides are promising fuels for the fast breeder reactors. In the Fast Breeder Test Reactor (FBTR), India, mixed carbide (MC) (U,Pu)C has been successfully used as the fuel. The first charge had 70% Pu, since the reactor core was partially charged with the fuel4. Subsequently MC with 55% Pu has been used. Low density MC of this composition is presently used as the fuel, to retain the fission products, released at very high burn-up.

For Prototype Fast Breeder Reactors (PFBR), MOX with 30% Pu and 49% enriched ²³³U is considered as the test fuel. These fuel pellets are fabricated with an annular hole to effectively transfer the heat from the centre of the pellet to the clad5.

In thermal reactors i.e., PHWRs and BWRs, zirconium alloy is employed as cladding material to take care of the neutron economy. In the fast reactors i.e., FBTR and PFBR, stainless steel is employed as clad material.

During the fabrication of these fuels, to maintain specified oxygen to metal ratio (O/M) or carbon to metal ratio (C/M), they are subjected to high temperature sintering in reducing gas environment (Ar + 8%H₂ or N₂ + 8%H₂). During this cycle, some gases get trapped and are released during the operating conditions of the reactor. They may pressurise 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

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composition. In case of nuclear fuels, the total gas content is defined as the amount of non-condensible gases released when the pellet is heated under vacuum at required temperature and time and converting the gas content to STP\textsuperscript{6}. Depending upon the nature of the fuel pellet, the temperature to which it is heated is arrived at. This temperature is arrived at based on the central line temperature of the fuel pellet during the operation of the reactor, and the ease with which the gases are released from the pellets by diffusion. For example, the centre line temperature of the oxide and carbide fuel pellets reaches 1650 and 1000 °C respectively. Also, since the oxide pellets are highly sintered and have high density compared to the carbide pellets, high temperatures are required to extract the gases from the interstitial spaces in the oxide pellets. The specifications of the total gas content in various types of fuels are given in Table 1.

\textit{Vega et al.\textsuperscript{7} have determined occluded gases in UO\textsubscript{2} pellets, while Iwai et al.\textsuperscript{8} and Maeda et al.\textsuperscript{9} have made studies on (U_{0.8} Pu_{0.2})C pellets.}

The present paper deals with the detailed studies, on the total gas analysis of various types of fuel pellets employing hot vacuum extraction technique, over the past two and a half decades. The implications of the gas content are also discussed.

**Experimental Procedure**

**Equipment**

Leybold Hereaus, total gas analyser Model VH-9S has been employed in all the experiments. Optical pyrometer (PYRO micro optical pyrometer, USA) and Leybold Hereaus Quadruvac Q 200 and/or Dataquad DXM quadrupole mass spectrometer, UK were employed for measuring the temperature and composition respectively.

**Methodology**

The total gas analyser is essentially a static ultra high vacuum system. Schematic diagram of the system is shown in Fig. 1. The system should be free from any contamination from hydrogenous materials. 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 equipment can be divided in to two parts, viz., sample loading and gas extraction one. A gate valve separates these two parts. To load the sample, the sample port is opened in flowing inert gas atmosphere and the sample is loaded into sample dropping manipulator which can be rotated fully by means of vacuum rotational manipulator. This part is closed and evacuated to 10\textsuperscript{-7}mbar by turbomolecular pumping station. Tungsten crucible located in the gas extraction part of the system is brought to the sample loading side employing vertical, horizontal and angular vacuum manipulators after opening the gate valve. The sample is dropped into the tungsten crucible and taken back to the gas extraction part employing manipulators. The gate valve is closed. The crucible is taken into the induction coil zone employing the manipulator. The system is evacuated to 10\textsuperscript{-5} mbar by means of mercury diffusion pumps and a mercury ejector pump supported by a backing pump. The gas extraction part is made static by isolating it. The sample is then heated to the required temperature and time by induction heating. The temperature is measured by Optical Pyrometer. The gases released are extracted into a pre-calibrated volume by the mercury ejector pump, through a refrigerated cold trap, which condenses all condensible gases. The pressure is measured employing McLeod gauge. Small amount of this gas is then fed to the on-line quadrupole mass spectrometer through a micro leak valve. The quadrupole mass analyser has 90 mm long quadrupole having a resolution of $M/\Delta M \geq M$ at 10\% valley height. The resolution of the quadrupole mass spectrometer is determined by taking an equimolar 20Ne and 22Ne. It is found to be 45 at m/e 20. Ions are produced by an electron bombardment source with a tungsten/thoria quoted iridium filament having an electron energy of 80 eV. The mass range of the system is 1-100 amu. The ion currents are measured employing a Faraday cup detector. The peak heights at m/e 2 (H\textsubscript{2}), 12 (C\textsuperscript{−}), 14 (N\textsuperscript{+}/CO\textsuperscript{2+}), 16 (O\textsuperscript{−}), 20 (Ar\textsuperscript{2+}), 28 (N\textsubscript{2}\textsuperscript{+}/CO\textsuperscript{+}), 32 (O\textsubscript{2}\textsuperscript{+}), 40 (Ar\textsuperscript{+}) and 44 (CO\textsubscript{2}\textsuperscript{+}) are recorded.

**Table 1—Specifications of fuels for total gas content**

<table>
<thead>
<tr>
<th>Oxides (Thermal)</th>
<th>Oxides (Fast)</th>
<th>Carbides (Fast) (70%Pu)</th>
<th>Carbides (Fast) (55%Pu)</th>
<th>Oxides (Fast) Central hole:1.6 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04 cc/g at 1650°C for 15 min</td>
<td>0.09 cc/g at 1650°C for 15 min</td>
<td>0.1 cc/g at 1000°C for 30 min</td>
<td>0.1 cc/g at 1000°C for 30 min</td>
<td>0.1 cc/g (excl. H\textsubscript{2}) at 1650°C for 15 min</td>
</tr>
</tbody>
</table>
Calculations

From the volume of the system and the pressure exerted by the occluded gases, after making the correction for the blank, the total gas content is calculated employing gas laws,

\[ P_1 \times \frac{V_1}{T_1} = P_2 \times \frac{V_2}{T_2} \]

where in \( P_1 = \) corrected pressure in atm. exerted by the occluded gases

\( V_1 = \) volume of the system into which the gases are collected

\( T_1 = \) room temperature in K

\( P_2 = \) atmospheric pressure i.e., 1 atm.

\( T_2 = 273 \) K

\( V_2 = \) the occluded gas content at STP conditions = \( P_1 \times V_1 \times 273 / T_1 \)

From \( V_2 \) and the weight of the pellet, the gas content per gram of sample is calculated (\( V_2/wt \)).

The gas composition is calculated from the peak intensities (ion current) at various m/e ratios after correcting for blank spectra. Necessary corrections are incorporated for the ion fractions arising due to the fragmentation of gas molecules. Since the ion current depends on the type of gas, they are normalised with respect to nitrogen whose sensitivity factor is taken as unity. All other species are multiplied by the respective relative sensitivity factors (RSF values for \( N_2 = 1 \); \( Ar = 0.8 \); \( H_2 = 2.45 \); \( CO = 0.92 \); \( CO_2 = 0.69 \)) to obtain the corrected peak intensities. From the corrected peak intensities (\( M_i \)) and total intensity (\( \sum M_i \)), the partial pressures of gases are calculated as Partial pressure of any species, \( p_i = \) Tot. pressure \( \times \) intensity at \( M_i / \sum M_i \)

Carbon monoxide and nitrogen have isobaric interference at m/e 28. These can be sorted out based on the fragmentation patterns of these gases\(^{10}\).

Results and Discussion

The total gas content (cc/g) = \( P_1 \times V_1 \times 273 / (T_1 \times wt) \)

The accuracy of the estimation is therefore reflected from the errors in measuring the volume, pressure and weight. The volume of the system is calculated by expanding known amount of dry nitrogen into the system and measuring the pressure changes for 20 times. It was found to be 16.14 \( \pm \) 0.10 L and is fixed in all the subsequent measurements. The error in measurement of pressure with McLeod gauge is \( 2 \times 10^{-6} \) m bar. For each determination, a full pellet is taken. Weight of the sample varies from 1 to 25 g depending on the nature of the fuel pellet and is weighed in an analytical balance that can read up to 0.0001 g. From all these individual errors, the
cumulative error comes to 3%. The detection limit is 0.005 cc. The precision of the measurement is determined by analysing several samples from same lot and was found to be $\pm 5\%$ at $3 \sigma$ level.

**Time of heating**

The total gas content, as a function of time, has been measured on UO$_2$, MOX and MC pellets. MOX pellets with and without annular hole were heated at 1650°C and the pressure of the gases evolved was monitored at regular intervals up to 2 h. The gas content was calculated at each time interval, after correcting for the blank. It can be seen from the Fig. 2 (without annular hole) and Fig. 3 (with annular hole) that within 10 min of heating all the gases were released. Hence, heating the pellet for 15 min was more than adequate for oxide pellets.

Similarly, the release pattern of gases in MC pellets was studied at 1000°C up to 4 h. It is obvious from the Fig. 4 that 30 min of heating and extraction was sufficient for the quantitative extraction of gases.

Hence, the time of extraction of gases released was confined to 15 and 30 min for oxides and carbides respectively.

**Gas composition**

After the measurement of the pressure of the extracted gases, the gases were fed to on-line quadrupole mass spectrometer through a micro leak valve. The peak heights at m/e 2, 12, 14, 16, 20, 28, 32, 40 and 44 were monitored both in blank and sample. After correcting for the blank, the composition of gases was computed. A typical mass spectrum of the gases released from oxide pellet, in bar graph mode, is given in Fig. 5. Typical data of the blank, gases released from oxide and carbide pellets (after incorporating the correction for the blank and the RSF) are given in Table 2.
It was observed that the main constituent of the released gases was hydrogen (>95%). The rest of the gases were a mixture of carbon monoxide, nitrogen and carbon dioxide. CO and N$_2$ can be resolved based on the peak intensities at m/e 12 (which is 8% of the parent peak) and 14 (which is 16% of the parent peak). However these intensities will be so small compared to peak intensity at m/e 2, the resolution of these gases could be carried out only when their contribution was more than 10% of the released gases.

**Effect of temperature**

Detailed investigations were carried out to determine the quantity of occluded gases released from the MOX pellets (for 15 min) and MC pellets (for 30 min), as a function of temperature. In the former case, the gas content increases slowly with temperature and reaches maximum at 1600$^\circ$C (Fig. 6). However, in the latter case, the plateau was obtained at 1000$^\circ$C (Fig. 7). Above this temperature, the gas content goes on increasing. Above 1300$^\circ$C, the gas content increases exponentially. The composition of the gas was determined in both types of pellets. In MOX pellets, at all temperatures and in MC pellets up to 1000$^\circ$C, the gas was mainly hydrogen. In MC pellets, above 1300$^\circ$C it was mainly carbon monoxide. Mixed carbide pellets are fabricated through carbothermic reduction route. In this process, calculated amounts of UO$_2$, PuO$_2$ and carbon are mixed and subjected to reduction at 1748 K under dynamic vacuum conditions. In the end product, invariably some oxygen will be left as an impurity (3000-6000 ppm). This oxygen will react with carbide to release CO gas$^{11}$. Hence the gases released above 1300$^\circ$C were the reaction products and not the occluded gases.

**Rate of heating**

The pellet was subjected to the required temperature by induction heating. The temperature

![Table 2 — Peak intensities and gas composition](image)

<table>
<thead>
<tr>
<th>Channel No.</th>
<th>Mass</th>
<th>Blank</th>
<th>Oxide (1650$^\circ$C)</th>
<th>Carbide (1000$^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(After correcting for blank and RSF)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>$1.4 \times 10^{-8}$</td>
<td>$1.3 \times 10^{-5}$</td>
<td>$5.4 \times 10^{-6}$</td>
</tr>
<tr>
<td>2</td>
<td>12</td>
<td>$6.0 \times 10^{-10}$</td>
<td>—</td>
<td>$1.0 \times 10^{-9}$</td>
</tr>
<tr>
<td>3</td>
<td>14</td>
<td>$8.0 \times 10^{-10}$</td>
<td>—</td>
<td>$1.5 \times 10^{-9}$</td>
</tr>
<tr>
<td>4</td>
<td>16</td>
<td>$1.2 \times 10^{-8}$</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>$0.0 \times 10^{-10}$</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>6</td>
<td>28</td>
<td>$4.3 \times 10^{-8}$</td>
<td>$5.0 \times 10^{-7}$</td>
<td>$3.4 \times 10^{-7}$</td>
</tr>
<tr>
<td>7</td>
<td>32</td>
<td>$1.1 \times 10^{-9}$</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>8</td>
<td>40</td>
<td>$3.6 \times 10^{-10}$</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>9</td>
<td>44</td>
<td>$3.7 \times 10^{-9}$</td>
<td>$1.6 \times 10^{-9}$</td>
<td>$1.3 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

Fig. 6—Temp. versus TG (cc/g) in MOX pellet

Fig. 7—Temp. versus TG (cc/g) in MC pellet
was attained within a fraction of a minute. After the extraction of the gases for the specified time, the integrity of the pellet was physically examined. It was observed that all pellets were intact, barring the MOX fuel pellets with the annular hole. The shattering of these pellets may be due to the sudden thermal shock. Hence, experiments were carried out to find out the effect of rate of heating. It was observed that the rate of heating plays a major role on the integrity of the pellet and if the pellet was heated slowly it remains intact. In the reactor, it is expected that the temperature of the pellets raises slowly and hence the integrity of the pellet will not be lost.

Vacuum degassing

The total gas content of carbide in the early stages of fabrication and MOX fuel pellets with the annular hole was high (>0.3 cc/g). These fuel pellets are employed in fast breeder reactors, wherein the clad is stainless steel. It is known that hydrogen diffuses out of stainless steel at elevated temperatures. Hence there may not be pressure build up in the fuel pin due to the hydrogen released from the pellets. However, this hydrogen will enter the liquid sodium, the coolant in this type of reactors. Hydrogen forms bubbles in sodium. The radius of the bubble depends on the initial pressure of dissolved hydrogen and it decreases with temperature and time. Hydrogen may form NaH, which will again dissociate at high temperature to release hydrogen gas. These hydrogen bubbles may alter the thermal conductivity of the liquid sodium. Hence, it is advisable to minimise the release of hydrogen into liquid sodium. In the initial stages of fabrication of MC pellets, the total gas content was high (>0.2 cc/g, hydrogen being the main constituent). It was suggested to carry out vacuum degassing after sintering in the fabrication route of the pellets. After the inclusion of this step, the carbide pellets met the total gas specifications. On similar lines, the total gas content in oxide pellets, with annular hole, can be reduced by the introduction of vacuum degassing step.

Storage of pellets

The pick up of occluded gases in the sintered pellets with storage has been studied. It was found that in oxide fuel pellets, virtually there was no increase in the total gas content even if they were stored in argon atmosphere in dry box, additional pick up of the total gas was observed. Hence the carbide pellets, immediately after the fabrication, were loaded into the pin and welded.

Conclusion

Occluded gas is mainly hydrogen. Hence, it is more stringent specification in thermal reactors compared to fast reactors due to its reaction with the cladding material. The extraction of occluded gases is a diffusion phenomena, which is proportional to the temperature. The oxide pellets are heated at relatively higher temperatures compared to carbides and hence shorter time periods are sufficient for quantitative release of gases. Occluded gas content can be substantially reduced if a vacuum degassing step is incorporated at the fag end of the pellet fabrication.

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References