Hydrogen Gas in CANDU Fuel Elements

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Abstract

One of the requirements in the Technical Specification for 37-element fuel bundles for a CANDU 6 reactor asks for "less than 1 mg of hydrogen gas in a fuel element". This is an important requirement. High contents of hydrogen gas may lead to cracking and to primary defects of fuel-element sheaths. In recent years, there have been some instances of this type of fuel defect.

In the paper, the definition of "hydrogen gas" is reviewed and the contributions from the usual sources of hydrogen gas in a fuel element (filling gas, pellets and the CANLUB layer) to the total hydrogen gas are assessed.

The paper discusses a model of sheath failure that is due to hydrogen gas and the principal processes related to it: ingress of hydrogen into the sheath, re-distribution of hydrogen in the sheath volume, formation of hydrides and changes in specific volume, and cracking.

Factors affecting the risk of defects are discussed: quantity of hydrogen gas as a function of fuel-element geometry, thickness of the CANLUB layer and the conditions of its curing; localized ingress and re-distribution of hydrogen; fuel-element uniformity in axial and circumferential directions.

The determination of hydrogen gas as a part of fuel inspection is reviewed.

The numerical value of the limit is discussed. The specification limit is separated from the defect threshold by a sufficiently large design margin. At the same time, product manufacturability requires a separation of the specification limit from the distribution of achieved values, i.e., satisfaction of a sufficiently low AQL (acceptable quality level).

1. Introduction

Early experience with CANDU fuel showed that excessive content of moisture inside the fuel elements may lead to defects. An appropriate requirement was therefore included in the specifications for fuel bundles [1, 2]. Because the incidents were linked to the presence of moisture in the fuel element, the requirement was first formulated as a limit of the contents of moisture (i.e., of H_2O). Only later was it changed to hydrogen gas in the fuel element, with the limit set below 1 mg of hydrogen per fuel element.

There were 2 incidents with fuel defects recently that were related to the presence of hydrogen gas in the gap of fuel elements. The cases are described in References 3 and 4. The post-defect deterioration is reviewed in Reference 5. This series of 2 incidents represents the most important excursion that has occurred with CANDU fuel during the last years, and while they were resolved by a correction of the manufacturing process, the topic of hydrogen gas in the fuel elements nonetheless deserves our attention.

The present paper reviews the concept of "hydrogen gas in fuel elements" and compares recent experience with the existing specification requirement.

2. Definition of "Hydrogen Gas"

As-manufactured CANDU fuel elements contain hydrogen. All fuel materials and parts contribute to this hydrogen content, and so we have to consider the following 4 components that make up the total hydrogen in unirradiated fuel elements:

1. hydrogen in the filling gas,
2. hydrogen in pellets,
3. hydrogen in the CANLUB layer, and
4. hydrogen in Zircaloy parts. This is mainly hydrogen that was present in the tubing used for sheath manufacture.

As is discussed later in more detail, only some of this hydrogen is present in elementary form. Significant fractions of the hydrogen content are bonded in compounds, such as water (moisture), zirconium hydride, or hydrocarbons.

In-reactor, the following 3 reactions occur that affect the content and distribution of hydrogen and deuterium in the sheath:

i. Hydrogen from the filling gas, from pellets and from the CANLUB layer is picked up at the inside surface (ID, inside diameter) of the sheath.
ii. Deuterium from the coolant is picked up at the outside surface (OD) of the sheath.
iii. Under gradients of concentration, temperature and stress, hydrogen and deuterium are redistributed within the sheath [6, 7]. Section 3 discusses this process.

For conditions in the reactor, reactions (i) and (ii) are essentially unidirectional. Hydrogen (and deuterium) that is present in Zircaloy cladding, either dissolved in the alpha solid solution or precipitated as hydride particles, has such a strong affinity with zirconium that it is not available for migration from the sheath into the gap.

As "hydrogen gas" in a fuel element we understand hydrogen, elementary or in compounds, that is present in the gap of the as-manufactured fuel element or enters the gap in-reactor within a short time after the element has reached its linear power, and is able to move freely within the gap.

In view of the unidirectional character of the reaction (i), there are 3 usual sources that contribute to the total hydrogen gas in a fuel element: filling gas, pellets and CANLUB.

The first component, hydrogen from the filling gas, is defined as the hydrogen available in the gap in an as-manufactured fuel element. It includes hydrogen-containing impurities from the filling gas itself (i.e., from helium plus accompanying residual air) and moisture, if any, from the components inside the fuel element.

The second and third component of total hydrogen gas, i.e., hydrogen gas from the pellets and from CANLUB, enters the gap in-reactor when the fuel element is at power, i.e., at elevated temperatures and under neutron flux.

Pellets are exposed to a hydrogen-containing atmosphere in the sintering furnace, and contain hydrogen mainly in their porosity. In-reactor, this hydrogen migrates to the gap, mainly through the cracks that form in the pellets.

To produce the CANLUB layer, colloidal graphite in the form of a slurry is applied at the ID of the sheath. The slurry contains 2 hydrogen-rich constituents: the binder and the solvent [8]. During the first heat-treatment after the application of the slurry, drying, the layer loses most of the solvent. During the second operation, curing, the remaining traces of the solvent and a part of the binder are eliminated. A cured CANLUB layer should display no hydrogen releases below the curing temperature. However, cured CANLUB still contains a significant quantity of hydrogen that gets released at higher temperatures [9].

When considering hydrogen releases from CANLUB in-reactor, we should distinguish between short-term (instantaneous) and longer-term (gradual) changes in the layer.

Upon loading into the fuel channel, the fuel bundle reaches power and CANLUB is heated to a temperature range that is in many cases higher than was the curing temperature. This temperature increase and certainly the exposure to neutron flux lead to a release of hydrogen into the gap. Similarly, CANLUB temperature increases when the bundle is shifted from a low-power position to a high power position. The quantity of hydrogen gas released from the CANLUB layer depends on the temperatures of the CANLUB layer (that is, on the temperature distribution between the sheath and pellet surface), on the quantity of CANLUB (thickness of the layer), and also on the temperature, conditions and uniformity of curing.

In the longer term, gradual disappearance of the CANLUB layer with continuing burnup [10] likely leads to a slow transition of the residual hydrogen into the gap of the fuel element. Normally, this hydrogen is not included in the total of "hydrogen gas".

3. Sheath Failure Resulting from Hydrogen Gas

Defects by hydrogen gas in fuel elements are characterized by the formation of heavily hydrided areas ("blisters", also "sunbursts"), at sheath's inside surface [11]. Because of a large increase of volume that accompanies the transformation of alpha zirconium into zirconium hydride [12], the formation of a blister is accompanied by large tensile strains and stresses in the surrounding alpha microstructure. This condition, with the availability of hydrogen and its effect on crack propagation, leads to crack growth and eventually to fracture and a defect in the sheath.

The volume of the heavily hydrided microstructure that provokes cracking in the surrounding area is rather small. It typically contains up to 1 mg of hydrogen. In the 13-mm-diameter sheath, a hydrided ring at the sheath ID, with a width of 1 mm in the axial direction and a thickness of 0.2 mm in the radial direction, contains approximately 0.5 mg of hydrogen, assuming that the average composition is ZrH (that is, assuming hydrogen deficiency if compared to solid hydride [13]).

Two mechanisms can lead to the formation of a blister and to fracture:

- redistribution of hydrogen (and deuterium) in the zirconium alloy part, and
- localized pickup of hydrogen from the environment by the surface of the zirconium part.

The first mechanism is based on the redistribution of hydrogen (and deuterium) that is already present in the zirconium alloy, either in solid solution, or as particles of the hydride phase. Under temperature or stress gradients, hydrogen can migrate to cold areas or to areas under tensile stresses (Sawatzky [6, 7]) and form a blister. Leger et al. [13] demonstrated that the existence of a cold spot on the pressure tube outside surface can result in a blister. To apply this mechanism to sheath defects related to hydrogen gas, we would have to assume that the pickup itself of the hydrogen by the sheath ID does not produce blisters, that this hydrogen redistributes within the sheath after the pickup and concentrates in a small volume. Hydrogen present in the sheath since fuel manufacturing and deuterium picked up from the coolant earlier would participate in this process. Can this be the primary mechanism of blister formation in CANDU fuel sheaths?

In-reactor, a pronounced temperature gradient exists across the sheath wall. Related to the heat transfer from the pellets to the coolant, the temperatures in the sheath are the highest at the ID, and the lowest at the OD. This gradient is responsible for the typical hydrogen and deuterium distribution in the sheath wall, with the highest concentrations at the sheath OD and the lowest concentrations at the sheath ID. However, blisters in the sheaths have always been observed to start forming at the ID. In the axial direction, much smaller temperature gradients exist. A steep increase of hydrogen concentration that accompanies the formation of a blister, cannot be related to the small temperature gradients in the axial direction. Therefore, the temperature gradient can be excluded as the primary driving force for blister formation in fuel sheaths.

Sheath ID can be exposed to high tensile stresses and strains. This exposure occurs, for example, when the pellets expand under a high linear power of the fuel element. In fuel elements with a low burnup, the contents of hydrogen and deuterium in the sheath is small (0.5 to 1 mg); to locally accumulate a quantity of hydrogen and deuterium needed for a blister, diffusion over considerable distances would be needed. This process would require very long times. Also, we cannot assume the existence of significant stress gradients stretching over substantial parts of the fuel-element length. In fuel elements that have reached high burnups, the combined contents of deuterium and hydrogen are sufficiently high - typically, 5 to 10 mg [14]. For comparison, the highest contents of hydrogen gas reported for fuel that was involved in the recent excursion [3] was 4 mg. Yet blisters do not routinely form at the sheath ID in intact high-burnup fuel elements.

We can conclude that the redistribution of hydrogen and deuterium within the sheath is not the primary mechanism in the formation of blisters and blister-related defects in fuel sheaths, at least for burnups used with CANDU fuel today. Of course, hydrogen in the sheath may assist the formation of a blister or crack propagation as a secondary factor. The effect of burnup on the critical power of blister formation reported in Reference 3 supports such an interpretation.

The second mechanism, hydrogen pickup at the surface of the zirconium alloy part, can lead to a blister if the rate of pickup is so high that the localized influx of hydrogen cannot be balanced by its diffusion away from the pickup area.

Two conditions make a high rate of hydrogen pickup possible. They are

- easy access of hydrogen gas to the metallic surface of the sheath; and
- availability of a sufficient quantity of hydrogen locally.

With respect to the first condition, it is worth noting that normally the surface of Zircaloy is protected by a layer of oxide. The oxide at the sheath ID is porous (Cox [11]), but obviously slows down the rate of hydriding sufficiently: Fuel elements with high quantities of hydrogen gas do not develop blisters and defects, as long as they operate at low linear powers [3]. When an element is brought to a high linear power, its pellets expand and strain the sheath to such a degree that the layer of oxide cracks. Then, the unprotected surface of Zircaloy metal picks up hydrogen at a high rate, and a blister forms. Once the blister starts growing, its larger specific volume keeps the surface area expanding and the oxide film cracking.

The second factor, availability of sufficient quantities of hydrogen, depends on the total quantity of hydrogen gas in the fuel element and on the number of locations at the sheath ID where it gets picked up. Both circumferential and axial distribution of such locations should be considered.

In view of the cylindrical symmetry of the pellets and most parts of the sheath, similar conditions for fast pickup exist along the circumference of the sheath, and ring-like hydrided areas form.

In the axial direction, similar configurations and conditions repeat in the fuel element. There are only minor differences between most of the pellets with respect to their density or diameter, and with respect to their power, burnup, densification, hourglassing and swelling in-reactor. Thus several locations in a fuel element, such as circumferential ridges at pellet interfaces will have similar profiles and will be accompanied by similar strains of the sheath material.

For these conditions, the pickup of hydrogen gas will likely proceed simultaneously at several locations in a fuel element. Unless the total content of hydrogen gas is high, its supply will get exhausted before a critical degree of hydriding sufficient to promote cracking and fracture has occurred in one location.

To summarize, a fast and localized pickup of hydrogen at the sheath ID is the most important process that leads to blisters in fuel sheaths. Availability of sufficient quantities of highly mobile hydrogen gas in the gap of the fuel element, and tensile plastic strain, especially if it is localized in a small percentage of the sheath surface, are the principal factors in this mechanism of blister formation.

4. Determination of Hydrogen Gas for Inspection

As was reviewed in Section 2, three components make up the total hydrogen gas in a fuel element. Chemical analysis for these 3 components is therefore included in the Inspection and Test Plan for the fuel elements. The procedure and methods used for this inspection are described in Reference 15.

All 3 components of hydrogen gas should be extracted from the fuel element under conditions that yield quantities of hydrogen equal to or greater than those that are present in the fuel-element gap in-reactor and may be involved in the fast localized pickup by the sheath.

Therefore, the following applies:

a. Filling gas and moisture: Compared to the other 2 components of hydrogen gas, the sample of this component is obtained at the lowest temperature. However, the extraction should be done in such a manner that no moisture or gas belonging to this component is left behind and lost while the element is being sampled for the other 2 components.

b. Hydrogen gas from CANLUB is extracted at a temperature that is not lower than the highest temperature of CANLUB in-reactor. Hydrogen gas in the sample should be comparable with the "instantaneous" quantity of hydrogen released from CANLUB in-reactor (see Section 2).

c. Pellets: The extraction is done at a temperature representative of pellet temperatures in-reactor.

If the extraction is done at temperatures higher than those characterized above which represent the minimum values, the inspection becomes conservative. The quantity of total hydrogen gas found by analysis will be higher than what corresponds to the condition of fuel elements in-reactor. First of all, higher quantities of hydrogen are extracted from CANLUB. Also, if the sample consists of CANLUB plus the sheath, some hydrogen may be extracted from the sheath at high temperatures [9].

As long as such analyses give acceptable results and the conditions of high-temperature extraction are understood, similar conservative procedures may be used. However, one must be aware that the inspection conditions may make the detection of a drift difficult.

Data published in Reference 9 may be used as an illustration. If minimum extraction temperatures were used that conformed to the requirements described above, total hydrogen gas was found in the range of 0.25 to 0.3 mg. However, the currently established inspection method included hydrogen extraction from CANLUB at 1800°C. For this condition, total hydrogen gas was determined as 0.8 to 0.9 mg. A process drift resulting in an increase of hydrogen gas by 0.1 mg, for example, is much easier to detect in the first case.

5. Discussion: Specification Limit for Hydrogen Gas

A specification limit should provide for a sufficient design margin (difference between the specification limit and the defect threshold). At the same time, manufacturing should yield a distribution of parameter values separated from the specification limit by a satisfactory manufacturing margin; that is, the distribution should conform to the specification limit at an adequate AQL (Acceptable Quality Level).

With respect to hydrogen gas, the specification requirement ("hydrogen gas content in a fuel element less than 1 mg") can satisfy both criteria. When the samples for hydrogen gas determination are extracted under conditions described in Paragraphs (a) to (c) of Section 4, the 3 components of hydrogen gas give a total that is comfortably lower than the limit (See Section 4). With respect to the design margin, very large quantities of fuel elements (exceeding 40 million) have been irradiated and no defects related to hydrogen gas were noted, except for 2 manufacturing excursions. This demonstrates a sufficient distance from the defect threshold.

In an element of the 37-element design, a typical blister contains less than 1 mg of hydrogen (see Section 3). For a specification limit that is comparable to this critical quantity, the rationale for the acceptability of such a limit is that the total hydrogen gas does not accumulate in a single location of the sheath:

i. Hydrogen gas that is available for pickup by the sheath immediately after the fuel element has reached a critical level of linear power is absorbed at several locations of sheath ID.

ii. Hydrogen gas that is released gradually within longer time intervals (e.g., from the CANLUB layer) gets picked up by the sheath at a low rate and has time to dissipate within the sheath material.

iii. A residual content of hydrogen gas remains in the gap. Its partial pressure is reduced so that the pickup rate drops to very low values.

A factor that is related to item (i) and affects the defect threshold is the uniformity of the fuel element with respect to hydrogen gas pickup. Hydriding of end caps and welds in the Bruce 3 fuel in 1983 [14] may be mentioned here as an example of localized hydriding of a single region that was exposed to strains higher than the rest of the cladding.

6. Conclusions

1. Hydrogen gas in the fuel element is the primary source of hydrogen for blisters in intact fuel sheaths. Hydrogen in as-manufactured sheath and deuterium from the coolant can affect the formation of blisters in the sheaths as secondary factors.
2. Existence of high tensile stresses and tensile strains at the sheath inside surface make fast and localized pickup of hydrogen gas possible, thus assisting in the formation of blisters.
3. For a given quantity of hydrogen gas, simultaneous pickup of hydrogen gas at several locations of the sheath ID makes the development of a blister less likely.
4. In the specification for CANDU-6 37-element bundle, the requirement limiting the content of hydrogen gas provides adequate margins for defect-free operation and for manufacturing.

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