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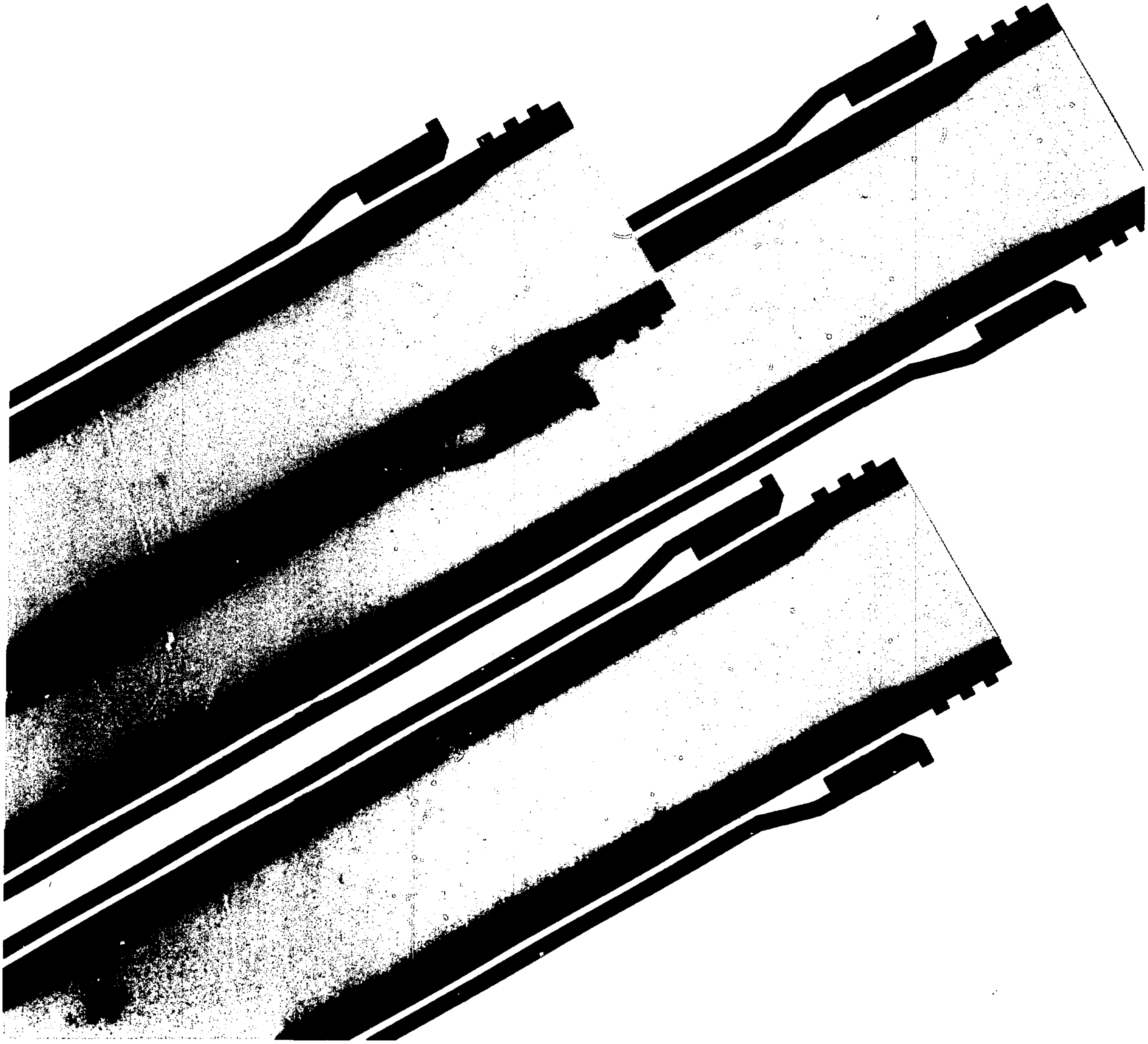
Highlights of the Metallurgical Behaviour of CANDU Pressure Tubes

by E.G. Price



Highlights of the Metallurgical Behaviour of CANDU Pressure Tubes

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Abstract

This paper is an overview of the service induced metallurgical changes that take place in Zircaloy-2 and Zr-2.5%Nb pressure tubes in CANDU reactors. It incorporates the findings of an evaluation program, that followed a significant pressure tube failure at Ontario Hydro's Pickering Nuclear Generating Station, and also provides valid reasons for continued confidence in the current CANDU design.

Faits saillants du comportement métallurgique des tubes de force des réacteurs CANDU

par E.G. Price

Résumé

Le présent rapport passe en revue les changements métallurgiques induits dans les tubes de force en Zircaloy-2 et Zr-2,5%Nb par leur service dans les réacteurs CANDU. Il incorpore les résultats d'un programme d'évaluation fait à la suite d'une rupture significative d'un tube de force à la centrale électronucléaire de Pickering, de l'Ontario Hydro et présente des bonnes raisons pour la confiance continue en la conception CANDU actuelle.

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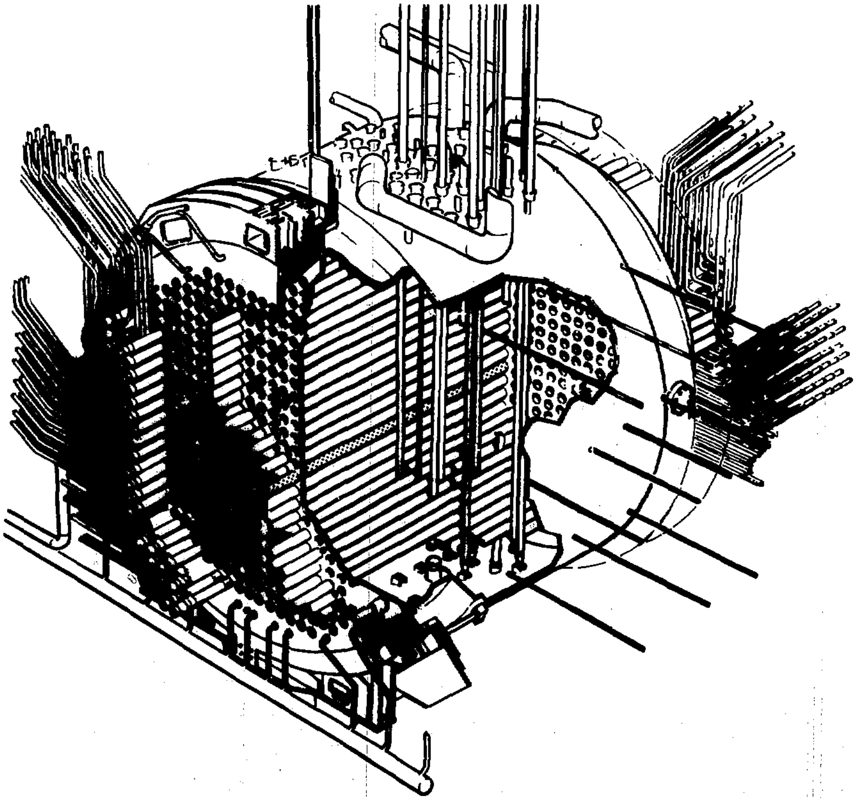
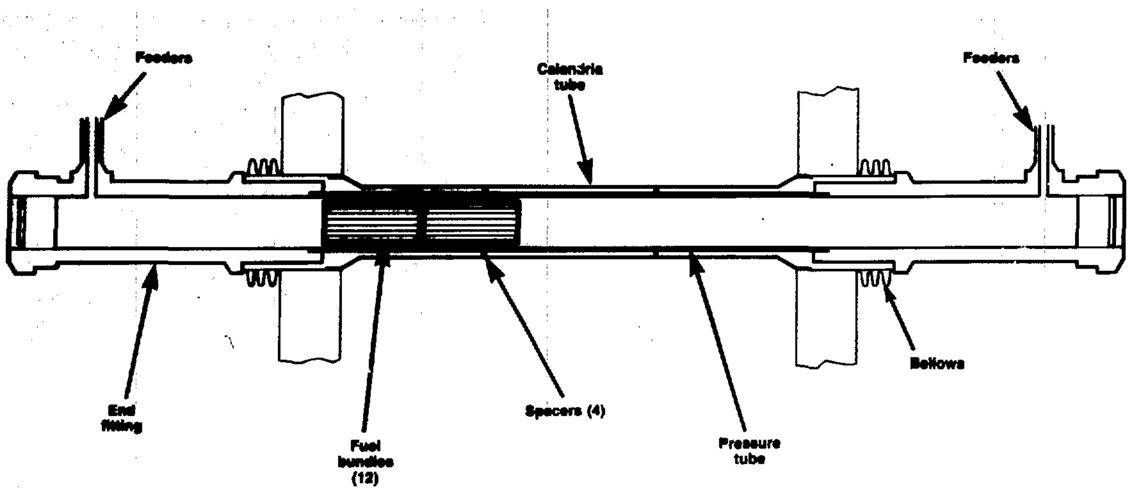
Introduction

Fast fracture of primary system piping is a failure mode that is rigorously analysed in all water-cooled reactor systems because of the potential for fuel damage through inadequate cooling. Such a fracture occurred in a pressure tube of a CANDU reactor (Pickering NSG, unit 2) in August 1983, yet no damage to the fuel sheaths occurred during the fracture, and consequently there were no radiation releases. The reactor was shut down with normal operating systems and procedures, without invoking the safety systems.

Up to this time CANDU nuclear reactors had consistently demonstrated high reliability during the more than 100 reactor-years of operation. Ontario Hydro's Pickering and Bruce generating stations' units have led the world, with lifetime load factors averaging over 80%.



CANDU REACTOR – The CANDU reactor, unlike light water pressure vessel reactors, has a core that comprises hundreds of small (100mm) diameter pressure tubes containing natural uranium fuel. The tubes, through which flows the pressurized heat transport system heavy water, are separated from each other by a low pressure, low temperature heavy water moderator contained in a cylindrical tank called a calandria. Each hot pressure tube is surrounded by, and separated from, the cool moderator by a calandria tube and a gas filled annulus.



SIMPLIFIED DESCRIPTION OF A FUEL CHANNEL - Each fuel channel consists of a zirconium alloy pressure tube, sealed at each end with end fittings that have side port connections to the heat transport system. The gap, or annulus, between the pressure tube and the surrounding Zircaloy-2 calandria tube is filled with an insulating gas and contains four close-coiled helical spring spacers that provide physical separation between the two tubes and partial support for the pressure tube. The annulus is sealed at each end by bellows that accommodate relative axial movement between the fuel channel and the reactor end shields.

CANDU fuel channels, of which pressure tubes are the main component, were from the first units, designed to be replaceable. This resulted from the then current knowledge of in-core material behaviour, particularly of Zircaloy-2, which suggested that accurate predictions of service life contended with many unknowns. The fact that early units operated so well seemed to contradict this conservatism, but the failure of a pressure tube in Pickering Unit 2 re-inforced the correctness of the replaceability concept. Only Pickering Units 1 and 2 have pressure tubes made of Zircaloy-2, a zirconium-tin alloy and one of the first alloys developed specifically for reactor core operation. The remainder of the CANDU units use an alloy of zirconium and niobium (Zr-2.5%Nb) on which AECL has devoted an intensive research effort over the past 20 years and for which there is confidence that the service life will be the design life.

Table 1 Lifetime incapability of Pickering NGS-A and Bruce NGS-A to December 31, 1983

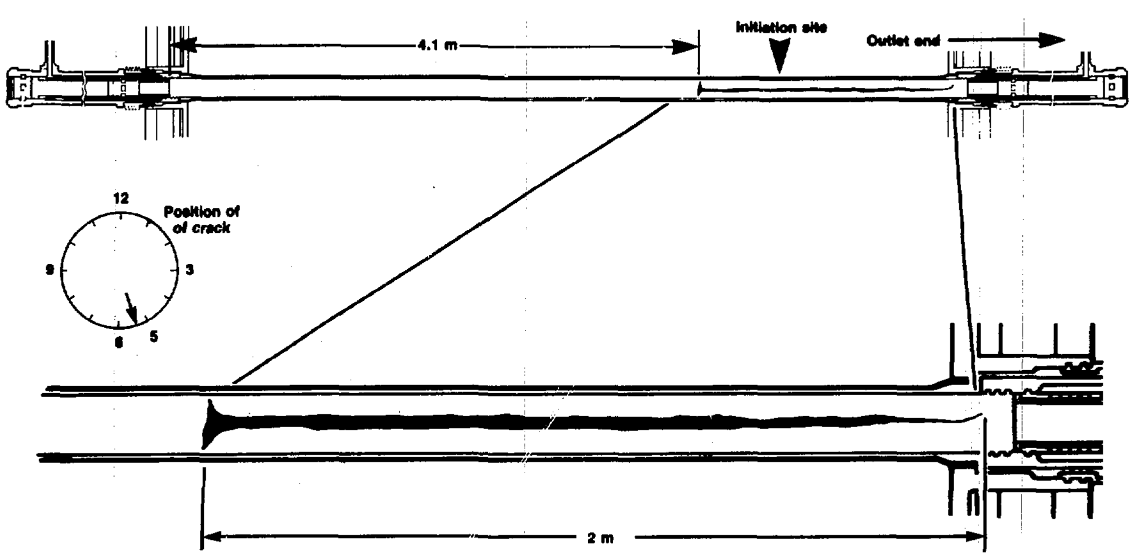
Cause of Incapability	Pickering NGS-A 4 Units, 45.6 Unit Years (Incapability %)	Bruce NGS-A 4 Units, 23.5 Unit Years (Incapability %)
On Power Fuelling	0.7	0.7
Fuel	0.1	0.0
Heat Transport Pumps	0.2	0.5
Pressure Tubes	5.3	1.4
Boilers	0.3	2.0
Turbine & Generators	6.8	5.0
Instrumentation & Control	0.7	1.5
Heat Exchangers	*1.1*	*0.1*
Valves	0.4	0.2
Other	3.9	3.0

While the failure of the Zircaloy-2 pressure tube at Pickering unit 2 initially caused a temporary lack of confidence in CANDU's ability to achieve economic pressure tube lifetimes, the subsequent investigations and examinations of Zr-2.5%Nb tubes from a number of reactors have renewed that confidence. The investigations and intensive examinations showed that the progressive deterioration, of the Zircaloy-2 pressure tube that fractured, was a characteristic that is limited to that alloy only. The Zr-2.5%Nb alloy tubes, on the other hand, are performing at or above the predicted design level. This review of the proven performance and the substantiated material characteristics of each alloy supports our continued confidence in the reliability of the CANDU reactor.

The Tube Failure

The pressure tube which failed on August 1, 1983, did so by developing a two metre-long crack near the coolant outlet end of the tube. Fast fracture took place without detectable prior leakage and, for this mode of failure, seemed to nullify the "leak-before-break" concept, which had been demonstrated on every previous occasion of pressure tube cracking.

A detailed analysis of the consequences of pressure tube rupture is an essential part of CANDU licencing documentation, and the tube failure at Pickering was in fact much less severe than that which had been allowed for in the design and in the safety document submissions. The flow of heavy water from the break, through the end bellows to the vault floor; the initial replacement from storage



FAILURE LOCATION - When the pressure tube failed in unit 2 at the Pickering Generating Station, it did so by fast fracture. The fracture extended from the point of origin, 4.1m in from the inlet end, to within a few centimetres of the outlet end of the 6.3m long pressure tube. The fracture progressed only a short distance towards the inlet end of the tube before bifurcating to form a T-shaped termination.

tanks; and the subsequent recirculation through recovery pumps back to the primary system — this was the scenario envisaged and aptly implemented by competent, well-trained operators. No heavy water was actually "lost" as a result of the failure, and while some fuel sheath damage occured during subsequent fuel removal, no sheath damage occured at the time of the pressure tube failure. The leaked heavy water from the heat transport system did not pose a serious radiation hazard to personnel entering the reactor building, and all necessary corrective and maintenance work was carried out after only a short delay. The drying out of the fuelling machine electrics, subjected to the effects of water and steam from the break, accounted for most of the delay period.

The design of the fuel channel was such that, following the pressure tube rupture, the leakage rate of the heavy water out of the primary heat transport system was determined by the clearance between the fuel channel bearings. Thus, although the end bellows ruptured, the gas annulus became pressurized to primary heat transport levels. The calandria tube however was able to sustain the loads placed on it without yielding.

The Effects of Reactor Core Environment on Pressure Tubes

Pressure tubes are in the CANDU reactor's most severe environment, embracing conditions of high neutron, gamma and beta activity, relatively high temperatures, fluid pressure stress, and corrosion from the heat transport system heavy water. The pressure tubes have to support the weight of fuel, resist deterioration from the core environment and surface wear from fuelling operations, and must also be transparent to neutrons and be designed in such a way as to give maximum reactivity (a consequence of using natural uranium fuel). The materials which can adequately meet these specifications are dilute alloys of zirconium, a metal that, like titanium, has a hexagonal crystal structure at reactor operating temperatures, which results in single grain anisotropy (unequal physical properties along different axes). Anisotropy is also evident in the pressure tube alloys, since the individual grain resistance to deformation varies with direction and, during tube manufacture, will align the grains in preferred orientations.

Three significant changes take place in pressure tubes as a result of prolonged service in the core of a CANDU reactor:

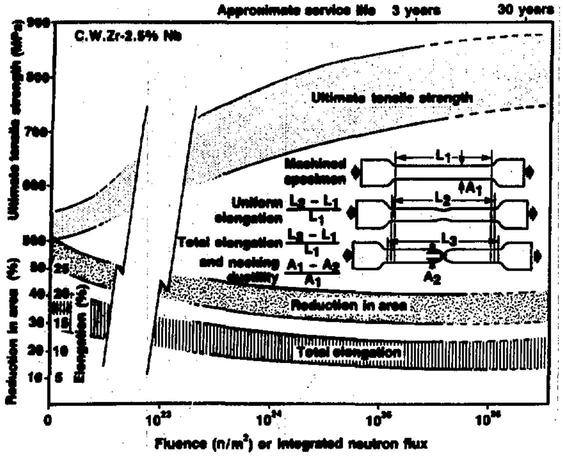
The mechanical properties change

The dimensions change

A small amount of the material is changed to oxide and hydride as a result of corrosion.

Mechanical Properties

The operating parameter responsible for changes in mechanical properties is the neutron flux. The neutrons have a spectrum of energies ranging from those below 500 eV (thermal neutrons) which cause the fission reaction in the fuel, to those above 500 eV (fast neutrons) which are the ones that cause changes in mechanical properties.



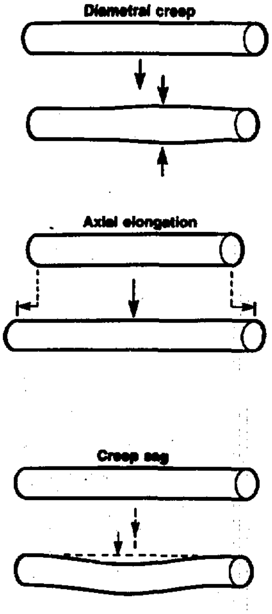
CHANGE IN MECHANICAL PROPERTIES AT 300°C DUE TO FAST NEUTRON FLUX – Strength and ductility of a material are commonly measured from the parameters of a machined specimen pulled to failure. Ductility can be determined from three of the test parameters: the total percentage elongation after failure, the extension which occures uniformly, and the localized deformation at the point of failure (reduction in area) which produces a fracture surface. In zirconium alloy pressure tubes, the changes in mechanical properties are a complex function of fluence, the grain orientation and the temperature at which they are irradiated. Generally the ultimate tensile strength of an irradiated tube increases by 45 percent over that of an unirradiated tube, while the yield strength increases by about 80 percent. The total percentage elongation, the uniform elongation, and the reduction in area are reduced by irradiation with fast neutrons, generally to about 50-60% of non-irradiated values.

The fast neutrons cause damage at the atomic level in the metallic structure of zirconium alloys. Lattice defects are created which, while strengthening the alloy, reduce its capability to extend in a tensile test. The capacity of zirconium alloys to plastically deform locally, as measured by the reduction in area of a tensile test, is not appreciably reduced by irradiation. In practice the strengthening of the alloy is an advantage, while the reduction in ductility due to irradiation is not great enough to be of concern. Thus zirconium alloy pressure tubes can, after a short service life, resist much higher short term loadings than they could immediately after manufacture.

Dimensional Changes

The dimensional changes that occur in pressure tubes are the result of the movement of small defects in the metal lattice. The movement of these lattice defects occurs in preferred directions in the lattice and, due to the anisotropic nature of the tube, results in differential dimensional changes in the tube's major directions. Lattice defects are generated during tube manufacture and during service by stress, and by fast neutron bombardment, while their mobility is mainly determined by temperature and stress on the metal. The gradual dimensional changes due to the stress induced movement of lattice defects from applied loads, is termed thermal creep. In pressure tubes that are not in a radiation field, thermal creep is minimal for operating stress levels. In a reactor environment, neutron bombardment induces more lattice defects in the tube and also accelerates the movement of those defects moving under the influence of stress, to produce larger dimensional changes than that of thermal creep alone.

The lattice defects, generated by fast neutron bombardment, can move within the tube during the neutron bombardment, without the application of external stress. The magnitude of the resulting dimensional change, or growth, is dependent on temperature, material factors, and the intensity of the neutron flux. The pressure tubes thus experience thermal creep, neutron enhanced creep, and irradiation growth. Analysis of the dimensional changes and correlation with laboratory behaviour determine the contribution of each.



DIMENSIONAL CHANGES IN PRESSURE TUBES – Pressure tube dimensions change over the years from the effects of stress, neutron flux, and reactor operating temperatures. A Pickering unit's pressure tube, unlike the exaggerated examples above, would, over a 30-year operating period, only increase in diameter by about 3mm and be 1 in 100 out-of-straight while extending 100mm over its total length of 6300mm.

The total effect on the tubes is that:

Diametral expansion occurs, mostly from irradiation enhanced creep due to the hoop stress in the tubes

The tubes elongate, mostly as a result of growth which occurs independent of the hydraulic pressure in the tube

The tubes sag, as a result of irradiation enhanced creep from bending stresses produced by the weight of fuel and the weight of heat transport system water in the tube.

Both Zircaloy-2 and Zr-2.5%Nb change dimensions in a similar fashion, but the greater strength of the Zr-2.5%Nb alloy resists creep deformation to a greater degree than Zircaloy-2. However, because of the superior mechanical properties of Zr-2.5%Nb, a thinner walled tube, with better neutron economy, is used,so that the total deformation for pressure tubes made of either alloy is similar in identical environments.

The data and the understanding developed from the behaviour of pressure tubes in commercial reactors has allowed fuel channel designs to be modified to accommodate predicted creep and growth in the latest reactors. However, in some of the early reactors, predicted dimensional changes, particularly axial extension, cannot be accommodated. On these reactors, modifications to bearings may be necessary to prolong pressure tube life or the tubes may have to be replaced before the intended design life.

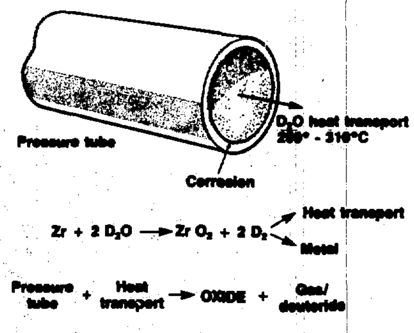
Corrosion and Deuterium Absorption

Contact with the heat transport system heavy water causes zirconium alloys to corrode by a chemical reaction which in its simplest form is: zirconium plus heavy water react to produce zirconium oxide plus deuterium. The corrosion, or oxidation over a period of 30 years could result in a 400 micron (0.016 inches) oxide layer on Zircaloy-2 tubes (assuming established oxidation rates continue without oxide spalling), whereas with Zr-2.5%Nb tubes it is predicted that the maximum oxide layer produced, over the same period, will be about 100 microns thick (about the thickness of this sheet of paper). This will be less than 3% of the wall thickness of a Zr-2.5%Nb tube, and such a loss is allowed for in the pressure tube design. The more complicated part of the chemical reaction is the disposition of the deuterium evolved by the oxidation reaction. Some of this deuterium will be absorbed by the metal and the remainder will be released to the coolant. Since deuterium is an isotope of hydrogen, the deuterium going into the metal is often described as 'hydriding' and quantitified as equivalent hydrogen. From oxide thickness measurements, the mass of oxide produced on a corroded tube can be calculated and an estimate of the total mass of equivalent hydrogen theoretically evolved can be made.

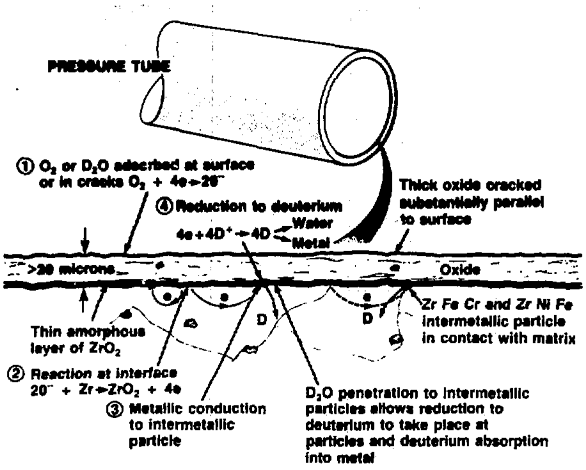
The hydrogen absorbed by the metal can also be measured by chemical analysis and the amount, expressed as a percentage of the total hydrogen evolved, is termed 'percentage pickup'. The actual percentage pickup is determined by heat transport heavy water chemistry and the thickness of the oxide and alloy composition. High temperature water that contains excess oxygen, (for example, in a boiling water reactor), produces a relatively high corrosion rate of Zircaloy-2, but the percentage hydrogen pick-up is low. For water that contains an excess of hydrogen, to suppress oxygen (reducing chemistry), the corrosion rate of Zircaloy-2 is low, but the percentage hydrogen pick-up can be relatively high. The situation is further complicated by the fact that thick oxides on Zircaloy-2 appear to corrode at higher rates in a neutron flux than do thin oxides, and that thick oxide behaviour may vary from alloy to alloy.

Researchers have, over the past few years, been able to assemble a considerable amount of information on the corrosion of the Zircaloys in a variety of water chemistry environments. (Zircaloy-2 and Zircaloy-4 are the main alloys used for fuel cladding in pressurized water and boiling water reactors.) The data have been derived from behaviour studies of fuel sheathing in the oxidizing chemistry of BWRs, and the reducing chemistry of PWRs, as well as the behaviour of the alloys in pressure tube reactors. The data generally falls into a fairly precise pattern, which can be used as a basis for predicting the effect various reactor conditions will have on zirconium alloys.

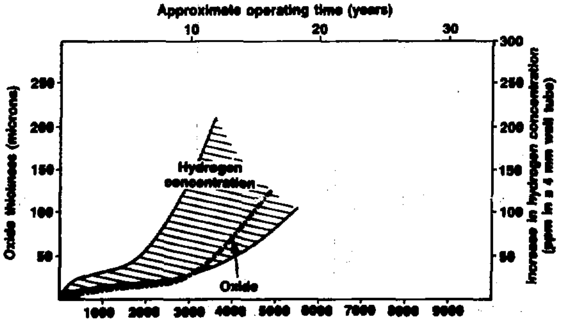
Thin oxides (less than 20 microns thick) on Zircaloy-2, in the reducing water chemistry of PWRs, and that of CANDU, pick up 30 to 50% of the theoretically evolved hydrogen.The pick-up for thin oxides of Zr-2.5%Nb is less than 5%. Thus, Zircaloy-2 tubes will absorb much



CORROSION OF PRESSURE TUBES AND BUILD-UP OF HYDROGEN – Corrosion of the inside surface of a zirconium alloy pressure tube, represented by the above equation, produces a thin layer of oxide and at the same time liberates deuterium into the heat transport system heavy water. Part of the liberated deuterium is absorbed by the tube. Deuterium is an isotope of hydrogen and its effect in zirconium is indistinguishable from that of hydrogen.



HYDROGEN ABSORPTION DURING CORROSION OF ZIRCALOYS - Zircaloys are nominally single phase alloys of zirconium and 1.5% tin. Small amounts of chromium, iron and nickel form inter-metallic compounds with the zirconium and exist as small particles in the alloy. These particles have a different electrochemical potential from the surrounding base alloy, which is tin dissolved in zirconium. It is theorized that where water penetrates the oxide, deuterium is evolved at these particles by cathodic reduction, following the sequence shown. The deuterium then has an easy path into the alloy through the particles.



THE CORROSION AND HYDROGEN INCREASE IN ZIRCALOY-2 PRESSURE TUBES AFTER REACTOR SERVICE - Corrosion of zirconium alloys typically shows an increase in oxide thickness that follows a cubic relationship to a transition thickness of about 2 to 3 microns. This pretransition oxidation is followed by a second stage, where the rate of corrosion increases with time. In the irradiation field of a reactor a third stage is developed, in reducing water chemistry, where at 15 to 20 microns there is a further transition to a higher rate of oxidation that is accompanied by an increase in percentage hydrogen pickup.

more of the corrosion hydrogen evolved than Zr-2.5%Nb tubes. This has been observed in both reactor and laboratory environments and, while the evaluation process continues, the most probable reason for the hydrogen pick-up difference between the two alloys is due to second phase particles, present in the Zircaloys. Such particles are theorized to act as sites for the cathodic reduction of hydrogen ions, and also facilitate absorption of the hydrogen by the base metal. Zr-2.5%Nb, on the other hand, is substantially free of second phase compounds.

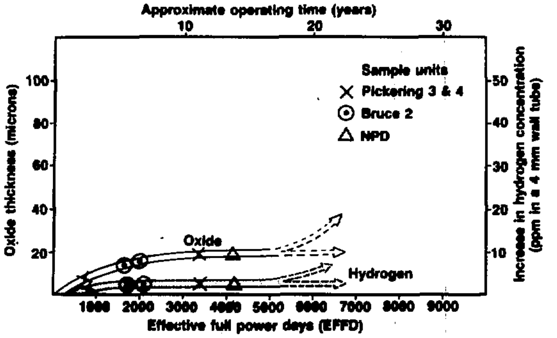
In the case of a thick oxide of Zircaloy-2 (i.e. thickness approaching 50 microns) the percentage pick-up, in reducing chemistry, appears to increase to values that are above 50%. The theory advanced to explain Zircaloy-2 behaviour is that a localized water chemistry is developed in the pores of thick oxides which is independent of the bulk chemistry conditions. In short, the thick oxide on Zircaloy-2 can produce conditions that exhibit the worst of both oxidizing and reducing chemistries — a high oxidation rate and a high percentage hydrogen pick up. With the exception of some minor localized regions, Zr-2.5%Nb tubes in reactor service have not exhibited oxide growth thicker than 20 microns, and even when oxide growth has reached this thickness there has been no evidence of increased hydrogen pick-up during reactor service. Thus from the limited laboratory evidence available on thick oxides of Zr-2.5%Nb the percentage pick-up does not appear to increase over the values for thin oxide. The thick oxides on both alloys form layered structures that have cracks running parallel to the interface with the base metal, and can spall when the tube is cut or its surface is damaged.

Pressure tube reactors operating with reducing chemistry have shown a consistent pattern of oxide growth on pressure tubes. In that for the first five years of operation in a reactor, both Zircaloy-2 pressure tubes and Zr-2.5%Nb tubes corrode at similar rates, then the two alloys exhibit different corrosion rates. The corrosion rate for Zircaloy-2 accelerates while that of Zr-2.5%Nb continues at a low rate for at least another nine years (or a minimum of about 14 years service). The acceleration in Zircaloy-2's corrosion rate occurs when the oxide thickness on the tube reaches about 15 to 20 microns. In fact the latest data suggests that, even with optimum control of the reducing chemistry, Zircaloy-2 tubes would enter a thick oxide condition in less than 12 years of service.

The hydrogen pick-up shows a trend similar to that of oxide growth. For Zircaloy-2 tubes, the hydrogen pick-up increases rapidly in the thick oxide regime, while Zr-2.5%Nb tubes show no evidence of either accelerated corrosion or hydrogen pick-up.

The 30-year prediction for corrosion and hydrogen pick-up for Zr-2.5%Nb tubes is based on analyses of current and historical data from a variety of sources, and as more service time is accumulated by the tubes, so will the degree of certainty increase. But, our interpretation of the data is that even if an acceleration in corrosion were to occur beyond 15 years service, the oxide thickness will not significantly exceed 100 microns. Similarly, while there is no evidence of increased hydrogen pick-up in thick oxides of Zr-2.5%Nb, an increased rate of hydrogen pick-up may only produce a maximum hydrogen concentration in the tube of about 45 ppm.

Some oxidation was also predicted for the outside surfaces of the pressure tubes that are exposed to the annulus gas, but laboratory examination of the pressure tubes removed from Pickering and NPD revealed minimal oxidation on the outside surfaces of the Zircaloy-2 tubes, and negligible oxidation on the outside surfaces of the Zr-2.5%Nb tubes. Thus, it appears that in-reactor oxidized zirconium alloys are particularly resistant to continuing gaseous oxidation at temperatures up to 300°C. However, examination and analysis of pressure tubes, removed from operating reactors, indicate that thin oxide (less than 3 microns thick) on the outside surfaces of Zircaloy-2 tubes can be permeated by deuterium that may be present in the annulus. While we have no evidence to suggest a similar thickness of oxide on Zr-2.5%Nb tubes is permeable to deuterium, it is desirable to install pressure tubes with an adequate outside surface oxide thickness in a circulating annulus gas that is low in deuterium and which is oxidizing to the pressure tube.

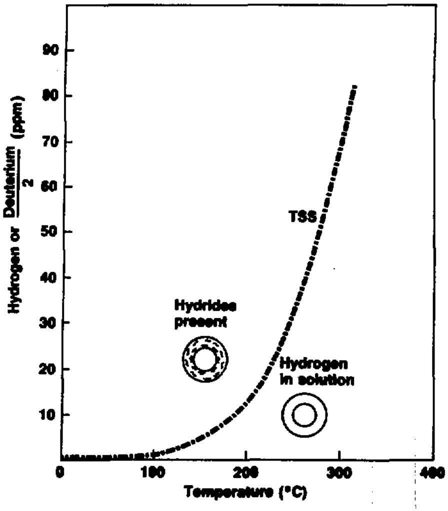


THE CORROSION AND HYDROGEN CONCENTRATION INCREASE IN Zr-2.5%Nb PRESSURE TUBES AFTER REACTOR SERVICE - The corrosion of Zr-2.5%Nb CANDU pressure tubes, at 4200 EFPD, has not progressed beyond a second stage of oxide growth at a nearly linear rate, and even if an acceleration in oxide growth (similar to that of zircaloy-2) were to occur, it would be unlikely to exceed a thickness of about 100 microns in 30 years. The low hydrogen pickup, accompanying the corrosion, supports the prediction that the total hydrogen equivalent will not exceed 45ppm after 30 years of reactor operation.

Deuterium and Hydrogen in Pressure Tubes

Hydrogen Concentrations

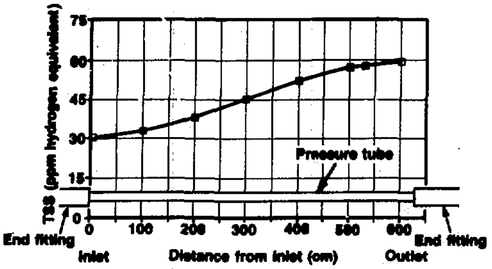
Pressure tubes normally contain between 5 and 15 parts per million (ppm) of hydrogen by weight when first installed in the reactor. After a 30-year residence in the reactor the equivalent hydrogen content of Zircaloy-2 pressure tubes was originally predicted to be about 90 ppm. Our revised 30-year estimate, now that better operational data has become available, is that the total equivalent hydrogen content would be much more than 1000ppm. Similarly, Zr-2.5%Nb alloy pressure tubes were predicted to pick up about 1 ppm hydrogen equivalent per year for a 30-year maximum concentration of about 45 ppm. This estimate for Zr-2.5%Nb now, in light of current data, appears to be high. The difference in the levels of hydrogen concentrations in the two alloys leads to 30-year projected material conditions (discussed later in the report) that are, in essence, severe embrittlement for Zircaloy-2 tubes, and structural soundness for Zr-2.5%Nb tubes.



SOLUBILITY OF HYDROGEN IN ZIRCONIUM ALLOYS - The limiting solubility of hydrogen in zirconium alloys at any temperature is called the terminal solid solubility (TSS). Some hydrogen will always be in solution, but at temperatures below 100°C it is less than 1ppm. This graph can be used to determine the amount of hydrogen in solution and the amount precipitated as hydride in the alloy, at a particular temperature, for any level of hydrogen concentration.

Hydrogen Solubility

Hydrogen (either as hydrogen or deuterium) is not appreciably soluble in zirconium alloys below approximately 100°C. It precipitates as small platelets of zirconium hydride, with the approximate chemical formula ZrH_2. In solution, hydrogen exists as individual atoms free to move in the zirconium lattice. Above 180°C, the solubility of hydrogen in zirconium increases rapidly and at typical



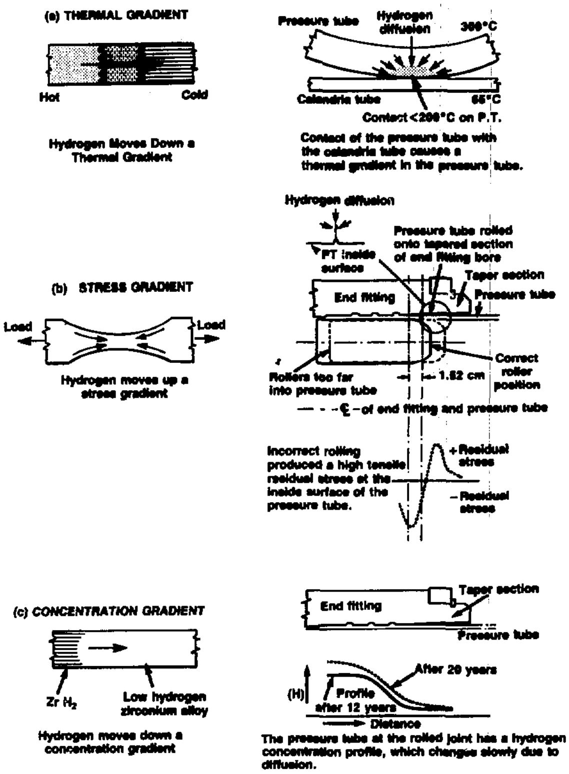
SOLUBILITY LIMITS OF HYDROGEN ALONG A FUEL CHANNEL – The temperature of the heat transport system heavy water increases, by about 46 degrees C, along the length of a Pickering unit fuel channel. Thus the pressure tube can hold less hydrogen in solution near the cooler inlet end of the tube than at the hotter outlet end. The amount of hydrogen that can be held in solution at a particular point of the tube, before hydrides are precipitated, is shown in the profile above, obtained from channel temperatures and reference to the TSS vs temperature graph.

Pickering N.G.S. fuel channel temperatures, about 30 ppm can be taken into solution at the inlet end of the tube, and about 60 ppm at the outlet end of the tube.

If the hydrogen concentration exceeds the solubility limit at fuel channel operating temperatures (between 250°C and 310°C, in later units), only the hydrogen in excess of the equilibrium concentration remains as a precipitate. On cooling, practically all the hydrogen precipitates out as a zirconium hydride platelets.

Hydrogen Movement

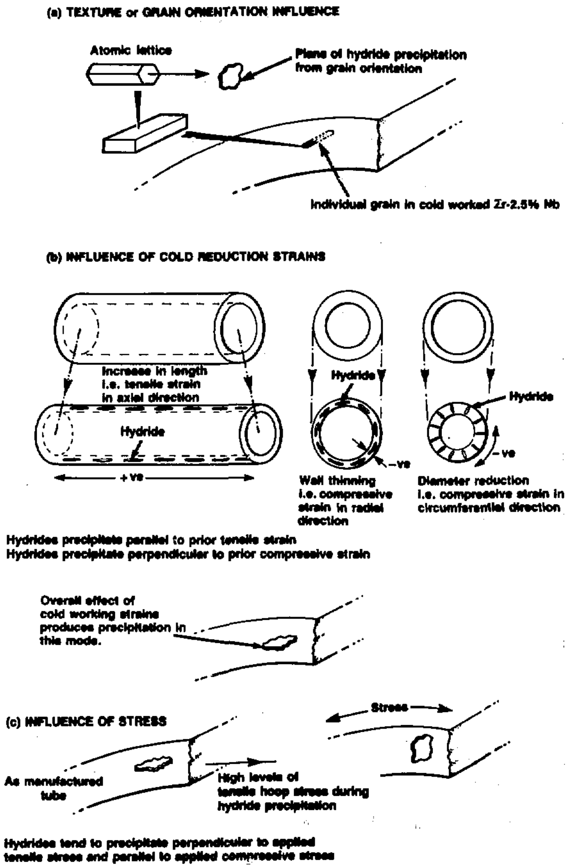
Hydrogen, when in solution in zirconium alloys, can be driven in certain directions, within the alloy, under the action of a number of gradients: thermal, stress, and hydrogen concentration gradients. Under CANDU conditions the most powerful of these is the thermal gradient, a phenomenon which moved hydrogen to create solid zones of zirconium hydride on the outside surfaces of Pickering units 1 and 2 pressure tubes. Thermal gradients have also concentrated hydrogen as hydride in regions of fuel cladding during reactor service.



MOVEMENT OF HYDROGEN IN ZIRCONIUM ALLOY PRESSURE TUBING – Hydrogen, in solution in zirconium alloys is not fixed at particular positions in the metal, it is able to move under various driving forces. It will move down a temperature gradient, up a stress gradient, and down a concentration gradient. Hot pressure tubes contacting cold calandria tubes can produce temperature gradients that drive hydrogen to the outside surfaces of the pressure tubes. High levels of tensile stress, when present in pressure tubes, move hydrogen up the stress gradients to precipitate in a manner that would tend to relieve the stress. Finally there are concentration gradients that distribute hydrogen over limited distances in zirconium metal.

The movement of hydrogen under a stress gradient was the basis of the delayed hydride cracking phenomena in Zr-2.5%Nb tubes in Pickering Units 3 and 4, in 1974, and in Bruce A in 1982. The pressure tubes in these instances had been installed with a rolling procedure that left high levels of residual tensile stress near the end of the rolled section. The high stress caused hydrogen to migrate and precipitate, at small surface imperfections on the inside surface of the tube, as a hydride flake, perpendicular to the stress. This occurred during the interval between installation and reactor start up, and the continuing high stress caused the precipitated hydrides to crack. The process of stress gradient diffusion brought more hydride to the end of the crack, which in turn also cracked and the repeated process eventually penetrated through the tube wall to cause leakage. A number of the tubes in these units thus experienced cracks before reactor operation reduced the stress to a level where crack initiation would not occur. Current pressure tube installation employs a procedure that does not leave significant residual tensile-hoop stresses at the inside surface of the tube. However, there is the possibility that further pressure tube leaks, from delayed hydride cracking at rolled joints, may occur in older reactors.

During reactor operation, concentration gradients distribute hydrogen, produced by inside surface corrosion,



HYDRIDE ORIENTATION IN ZIRCONIUM ALLOY PRESSURE TUBES - Precipitated hydride platelets assume an orientation that is dependent on grain orientation and the type of cold working strains developed during tube manufacture. The relatively long pencil-like grains (0.2 x 4.0 x 8 to 10 microns) in cold worked (CW) Zr-2.5%Nb have an atomic lattice predominantly oriented with the axis of the hexagonal unit cell parallel to the circumferential direction. Hydride platelets prefer to precipitate on planes that are nearly perpendicular to the axis of the unit cell. Cold working strains developed in Zr-2.5%Nb tubes during fabrication cause axial elongation, wall thinning and slight diameter reduction. Fabrication processes that produce tensile strain, cause the hydrides to precipitate with the plane of the platelet parallel to the direction of strain. Processes that produce compressive strain (wall thinning) cause the hydrides to precipitate with the plane of the platelets perpendicular to the direction of strain. The overall result of cold working pressure tubes, is a hydride platelet plane orientation that is parallel to the surface of the tube. Tensile stress if sufficiently high can rotate the orientation of the platelets from the manufactured plane shown, to the radial-axial plane.

uniformly through the tube wall. Concentration gradient effects are also seen at the ends of tubes, where a greater ingress of hydrogen at the steel end fittings builds up higher concentrations in the rolled joint areas. The hydrogen diffuses slowly, almost imperceptibly, along the tube into the areas of lower concentration.

Precipitated Hydride

Precipitated zirconium hydride, has basically the structure of a near metal and its mode of formation and precipitation have an important influence on the strength, ductility, and fracture behaviour of zirconium alloys. Evaluations of the behaviour of precipitated platelets revealed that their orientation is affected by three main factors:

The predominant orientation of the grains in the tube

The direction of strains from cold working processes

The level, and type, of applied stress when the hydrogen precipitates as the solid zirconium hydride.

In the absence of other factors, a hydride platelet will tend to precipitate in the zirconium lattice in a plane that is close to the one that represents the end of the hexagonal prism (basal plane), the basic unit of the metal lattice. Since the grain orientation, or texture, in a pressure tube, has most of the grains with the basal plane close to the radial-axial plane (more so in Zr-2.5%Nb tubes than in Zircaloy-2 tubes), the preferred plane of hydride precipitation, from solely textural effects, will be in the same plane.

In fact recent observations of hydride precipitates at high magnification show that most precipitation is on the preferred lattice plane. Hydrides in other orientations, are made up of short platelets stacked of tne in a staircase mode but with each platelet precipitated in the preferred plane.

The cold working strains imposed upon pressure tubes during manufacture ensure that the hydrides lie in the circumferential plane, parallel to the pressure tube surfaces. The tubes are cold worked, after hot extrusion forming, by a plug drawing operation which elongates the tube, reduces the wall thickness, and slightly reduces the diameter. It is these strains, put into the tube during the cold reduction process, that influence hydride orientation. An empirical observation of hydride behaviour concludes that tensile strains during cold working, produce a condition where the preferred orientation of the plane of the hydride platelets will be parallel to the direction of tensile strain. Compressive strain will cause the plane of platelet precipitation to be perpendicular to the direction of the strain. Each of the cold reduction strains in pressure tubes can thus be analysed for its contribution to hydride orientation. Thus the axial elongation, or axial tensile strain induced by plug drawing would cause the hydride platelet to lie in a plane parallel to the tube axis. The wall thickness reduction, or compressive strain in a radial direction, will cause the hydrides to be parallel to the tube surface. While the limited diameter reduction, or compressive strain in the circumferential direction, would favour precipitation in the radial-axial plane, the axial and radial strains dominate this effect and the final preferred orientation of platelets, from cold working strains, is parallel to the tube surfaces.

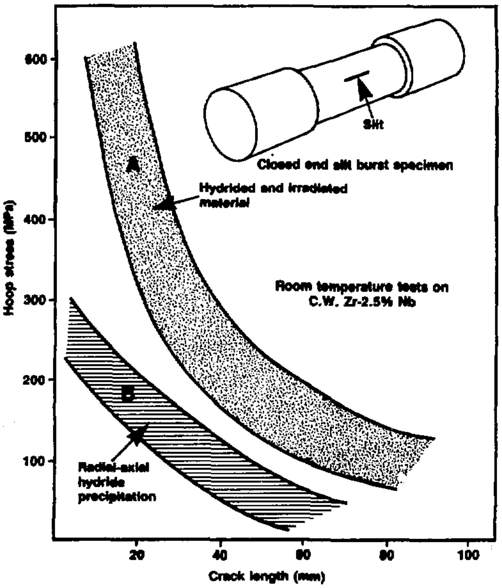
Hydrides precipitate either when the hydrogen concentration builds up beyond the solubility limit at operating temperatures, or when the reactor is cooling down. The action of stress under these conditions may cause a particular pattern of precipitation to emerge. Tensile stress, when it exceeds a particular level, depending on the alloy, will favour precipitation of the platelets perpendicular to the tensile stress direction. Compressive stress assists precipitation of the platelets parallel to the stress direction. Thus the major stress experienced by a pressure tube, the tensile circumferential or hoop stress, will, if high enough, tend to precipitate platelets in the radial-axial plane. It should be noted that radial-axial precipitation from circumferential tensile stress, reinforces the orientation of precipitated hydrides favoured by the texture. Conversely, tensile stress in the axial direction has to be considerably higher to acheive any level of hydride precipitation in the radial-circumferential plane and, in fact, such precipitation is seldom observed. The stress required to achieve radial-axial hydride orientation in Zircaloy-2 tubes, as used in Pickering units 1 and 2, is close to the operating stress. In Zr-2.5%Nb tubes, the stress required to achieve the same hydride orientation would be 40% higher than the operating stress. Thus, the stress in Zircaloy-2 tubes is more likely to precipitate hydride in the radial-axial plane, whereas in Zr-2.5%Nb tubes hydrides precipitate parallel to the tube surface.

Table 2 Stress to reorient hydrides in cold worked zirconium alloy pressure tubes

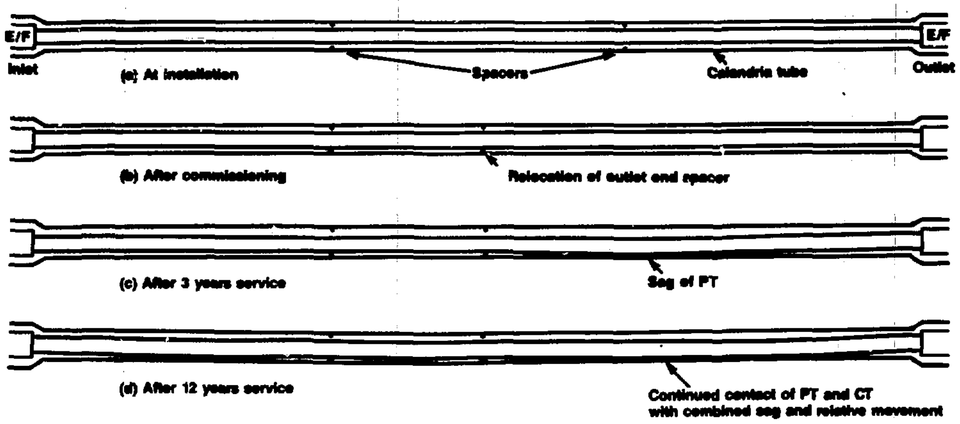
	Hoop stress to produce radial-axial hydride precipitation (MPa)	Operating stress (MPa)
Zircaloy-2	80 – 110	95 (Pickering 1/2)
Zr 2.5% Nb	180 – 220	130

The described parameters are not the only influences on mode of hydride precipitation. In Zr-2.5%Nb, the hydrides tend to nucleate in the grain boundaries, apparently influenced by the different grain structure in those regions. The hydrides then grow into the grains as stacks of individual platelets preferring to cross as few grain boundaries as possible. The grains in Zr-2.5%Nb are long, very thin plates, and thus the preferred direction of growth will be parallel to the circumferential surface boundaries of the grains. In Zircaloy-2 the grains are larger and grain boundaries have less influence on development of hydrides.

The other significant factor about solid hydride is its ductility. It is a compound of low ductility at temperatures below about 150°C. This hydride ductility has a negligible effect on alloy ductility when the concentration of hydrides is low, or when the hydrides are oriented parallel to the stress direction, as the surrounding metal can absorb the load. But, at high hydride densities, or when platelet orientations are perpendicular to the major stress direction, the ductility and fracture properties of the tubes are significantly affected, and the effect may extend to temperatures above 150°C. The radial-axial hydride orientation will be most adverse in pressure tubes for the predominant circumferential or hoop stress, since it can lower the defect strength of the tube by providing easy paths of crack propagation.



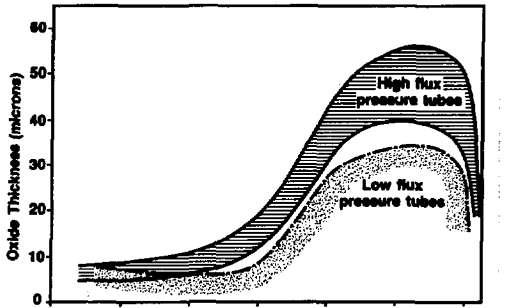
PRESSURE TUBE TOUGHNESS — Resistance to crack propagation in pressure tube material can be measured by pressurizing short lengths of tubing containing different lengths of through-wall cracks. Tests at room temperature, produce a relationship between the hoop stress at which a particular length of crack propagates and the initial crack length (band A). The effects of irradiation and circumferential hydride are not discernible in the band of data obtained, although other fracture toughness tests, using small specimens can show the limited effect of these parameters. At 250 - 300°C a cold worked (C.W.) Zr-2.5%Nb tube requires a nominal 75mm through-wall defect to become unstable at an operating pressure of 130MPa, although statistically there is a low probability that the "critical crack length" could be as low as 50mm. The parameter which has a significant effect on toughness is hydride precipitated on radial-axial planes, (band B), but this parameter only affects toughness below 270°C and when the hydrogen concentration exceeds the terminal solid solubility by more than 30 ppm. Normal operation does not produce radial-axial hydride precipitation in c.w. Zr-2.5%Nb.



CHANGES IN GEOMETRY ARRANGEMENT OF G16 FUEL CHANNEL IN PICKERING NGS UNIT 2 - The loose-fitting spacers in Pickering unit 2, were subject to movement from vibration during installation and commissioning. In channel G16, the outlet end spacer moved inboard 1.07m, leaving a long unsupported span over the hottest section of the pressure tube. Pressure tube sag produced contact with the calandria tube within three years. The continued sag combined with relative axial movement, between the pressure tube and calandria tube, localized the contact area.

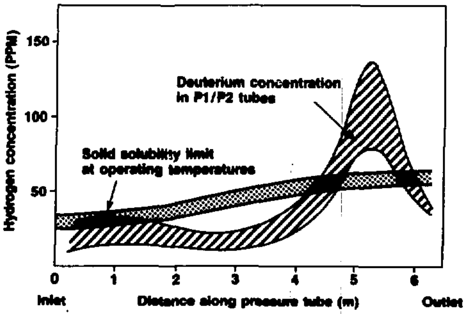
Reasons Why the Pressure Tube Failed

The intensive investigative studies of pressure tubes from Pickering units 1 and 2, both at the station and at AECL Chalk River Nuclear Laboratories, have provided enough information to positively identify the events that led to the failure of a pressure tube at Pickering unit 2:



CORROSION OF PICKERING 1 AND 2 ZIRCALOY-2 PRESSURE TUBES - The Zircaloy-2 pressure tubes in Pickering units 1 and 2 had peak oxide thicknesses towards the outlet ends of the tubes where the combination of temperature and fast neutron flux were most severe. At the outlet end, the tube corroded at a faster rate than the rest of the tube, to a threshold oxide thickness of 15 to 20 microns. Oxide thickness greater than the threshold sustained a local water chemistry that was not affected by the bulk water chemistry. This allowed radiolysis within the oxide pores to generate a separate oxidizing water chemistry.

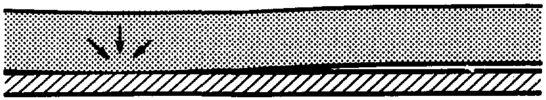
The Zircaloy-2 tube had oxidized to a thick oxide condition (greater than 20 microns), and acceleration of oxidation and hydrogen pickup had occurred which produced high deuterium concentrations near the outlet end of the tube. The oxidation peaked at the particular area of the tube which is subjected to the most severe combination of temperature and flux, conditions conducive to reaching a 20 micron oxide thickness at the maximum rate, and allowed an accelerated oxide growth and hydrogen build up to take place.



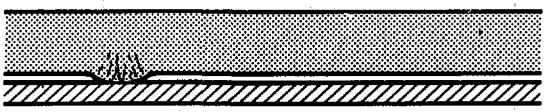
DEUTERIUM CONCENTRATION - The Zircaloy-2 pressure tubes in units 1 and 2 (P1/P2), of Pickering Generating Station, developed a particular deuterium concentration profile in channels in high flux zones. Analysis of the outlet ends of each tube showed an area of tube where hydride was present at operating temperature. Without the presence of hydride the defect could not have grown to a size where fast fracture occurred.

One of the two tube-to-tube spacers, in this early design, was displaced towards the centre during construction. The displacement produced a long unsupported span at the outlet end of the tube. The pressure tube, under the influence of fuel loads and irradiation, sagged at the outlet end and touched the calandria tube. This was also the region where the high hydrogen concentrations were later developed by corrosion.

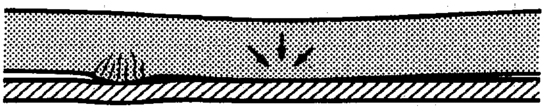
At the contact areas the outside surface of the pressure tube was cooled to below normal operating temperatures, and a thermal gradient developed in the pressure tube wall. Hydrogen then migrated down the thermal gradient to build first hydride layers, then semi-ellipsoidal solid hydride zones on the outside surface of the tube. These zones are termed 'blisters' because they are raised above the surface and the normal blue-grey colour of the surface oxide is thicker and whiter. Blister formation appeared to be the result of localized contact and the solid hydride of the blister penetrated about 1 mm into the tube wall.



(1) Cold spot developed on PT from contact with CT causing H_2/D_2 diffusion to cold spot.



(2) Blister develops and cracks from volume expansion of hydride.



(3) PT sags, blister indents the calandria tube and PT contacts at another spot down the tube

(4) Cracks, developed from blisters, link up and grow to an unstable size.

PROBABLE SEQUENCE OF CRACK DEVELOPMENT FROM PRESSURE TUBE (PT)/CALANDRIA TUBE (CT) CONTACT – Initial contact, between the pressure tube and calandria tube, will probably result in negligible hydrogen movement if pressure tube hydrogen concentrations are low and contact is not localized. On the other hand, if hydrogen concentrations or the thermal gradients produced are high, hydride layers may be formed. Hydride blisters appear to form from high thermal gradients, produced by localized contact, at general hydrogen concentrations above TSS or when intense thermal gradients occur at lower hydrogen concentrations.

The formation of solid hydride is accompanied by a 17% volume expansion which creates stress within and around the blisters. The stress then produced cracks, by a process still being investigated. The propagation of the cracks to a critical size, and the subsequent fast fracture were facilitated by both the high concentration of the precipitated hydrides and their radial-axial orientation. The hydrides were radial-axially oriented because both the hydrogen concentration exceeded the solubility limit and the stress for reorientation of hydrides was very close to the operating stress.

Pressure Tubes — Current and Future Reactors

The process resulting in failure of the Zircaloy-2 pressure tube in Pickering unit 2, took about 12 years in three separate stages:

Excessive sag of the pressure tube due to displacement of a spacer to allow tube-to-tube contact near the outlet end

Subsequent accelerated buildup of the hydrogen concentration over the outlet end. In the contact areas this resulted in the formation of solid hydride zones or blisters

Crack initiation and growth of the crack to a critical size that resulted in fast fracture. Probably due to stress induced delayed hydride cracking mechanisms.

The Zircaloy-2 tubes will all be replaced with Zr-2.5%Nb tubes during large scale retubing programs at Units 1 and 2. To prevent spacer displacement and the subsequent pressure tube to calandria tube contact, the spacers have been redesigned to ensure that they will remain in the design positions. This type of spacer, similar to a design used successfully for 22 years in the prototype reactor N.P.D., has already been installed in one unit under construction, and steps have been taken to ensure that spacers in CANDUs being commissioned are in the design locations. Some operating units, with original design spacers, may require spacer relocation at some time during reactor design life, but four spacers that are correctly positioned will prevent contact for the design life of the unit. When contact with the calandria tube is prevented, pressure tubes cannot develop the crack initiation mode experienced at Pickering Unit 2.

In contrast to that of Zircaloy-2 tubes, the hydrogen build-up in Zr-2.5%Nb tubes at Pickering Unit 3 is extremely low. After more than 12 years service, the hydrogen concentration in the tube increased by only 2 to 3 ppm due to corrosion of the tube. After 17 years service in NPD, a test prototype Zr-2.5%Nb tube had increased its hydrogen concentration by a similar amount. In addition, the Zr-2.5%Nb tube removed from Pickering unit 3, which had been in contact with the calandria tube, had no visible hydride concentration. Because of the low hydrogen concentration, the temperature of the pressure tube never dropped low enough to produce hydride concentrations. It is still possible that hydrogen diffusion may occur in some tubes, where tube-to-tube contact takes place, but the relocation of spacers will both eliminate such contact points and enable any hydride layers that may have formed to be gradually redissolved by concentration gradient-induced diffusion.

The levels of hydrogen currently contained in Zr-2.5%Nb tubes, and for a significant period into the future, will be in solution at the normal operating temperatures of the reactor and will have negligible effect on material properties. Should the levels of hydrogen exceed solubility limits, the hydrides will remain circumferentially oriented because the operating stress is lower than the threshold stress for re-orientation, and this is not detrimental to the fracture resistance.

Conclusion

Pressure tubes in all commercial CANDU reactors, other than Pickering units 1 and 2, are predicted to last the design life of the plant. Occasional problems may occur but, the Zr-2.5%Nb pressure tube material with its proven advantages over other zirconium alloys, and CANDU's controlled primary circuit chemistry to maintain low hydrogen pickup, along with the improved spacer design, will minimize the mechanisms that can concentrate hydrogen in undesirable modes or locations. Therefore, there is every reason to believe that, in terms of reliability and economy, CANDU reactors will continue to outperform all other reactor types.

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For further information, refer to the following papers:

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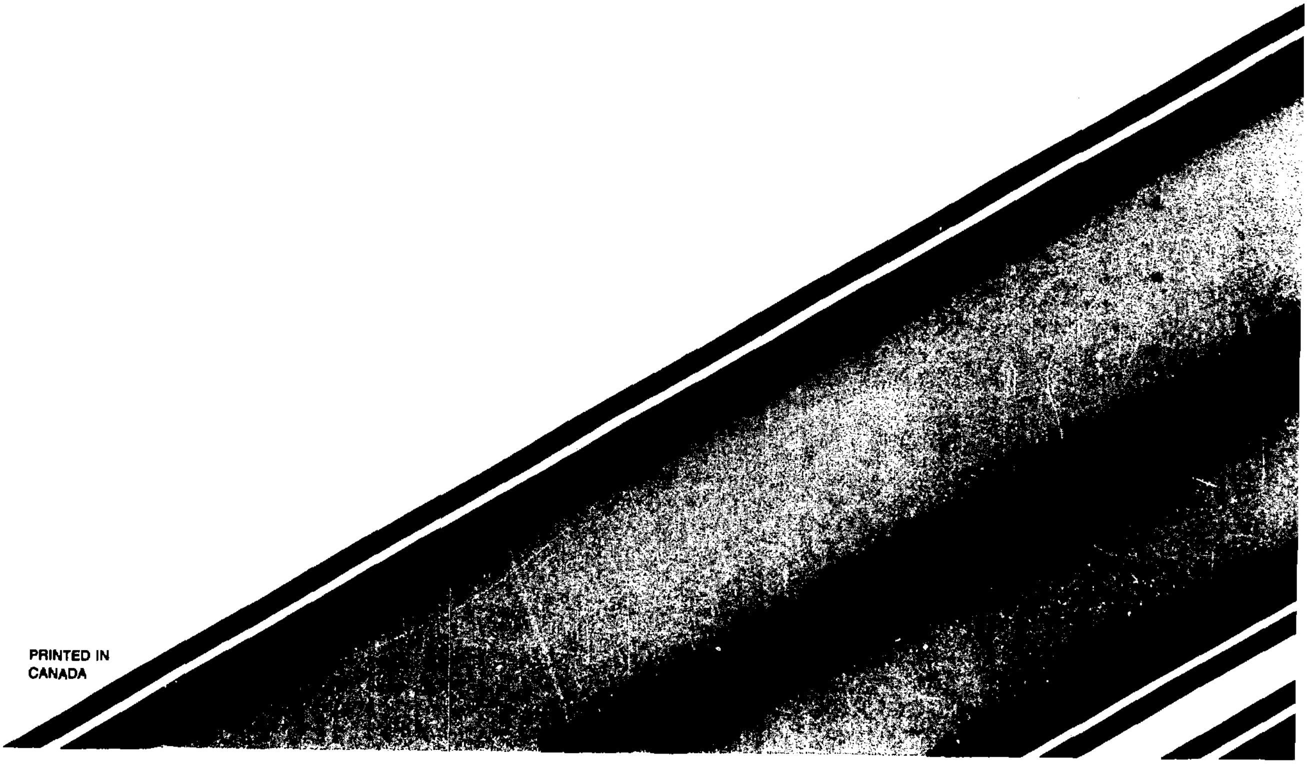

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