DEUTERIUM INGRESS AT ROLLED JOINTS IN CANDU REACTORS

V.F. Urbanic, G.M. McDougall, A.J. White and A.A. Bahurmuz

ABSTRACT

In CANDU nuclear reactors, the fuel bundles are contained in a lattice of horizontal Zr-2.5Nb pressure tubes. The pressure tubes, through which the heavy water coolant passes, are connected to out-of-core piping by roll expanding them into 403 stainless steel end fittings. The deuterium ingress into the pressure tube at the rolled joint is enhanced relative to the ingress in the main body of the tube. Because of the potentially deleterious effects of excessive deuterium buildup in the pressure tube, an understanding of the mechanisms of deuterium ingress at the rolled joint and a capability to predict deuterium buildup in the pressure tube is essential.

Deuterium ingress at rolled joints depends on a number of factors including: 1) the characteristics of the crevice between the end fitting and pressure tube, 2) chemical reactions in the crevice, 3) diffusion properties of deuterium in 403 steel, Zr-2.5Nb tubing and their oxides, and 4) mechanical aspects of the rolling process.

When a joint is rolled, some of the oxide on the outside surface of the pressure tube is removed and areas of metal-to-metal contact with end fittings are created. During reactor operation, the oxide damage is repaired except at these contact areas. The cathodic deuterium released during oxidation reactions in the crevice is the primary source for ingress; these reactions are enhanced both by galvanic coupling and unique crevice chemistry effects. Early in the life of the rolled joint, while oxide repair is occurring, deuterium can enter the pressure tube directly through unrepaired areas in the oxide. When only areas of intimate contact remain unrepaired, deuterium ingress occurs predominantly by diffusion through the end fitting to these contact areas.

A diffusional model was developed to predict deuterium buildup in the rolled joint region of pressure tubes. The model incorporates deuterium ingress at the rolled joint as well as pickup along the pressure tube due to corrosion on the coolant side and takes into account hydride precipitation effects. Deuterium analyses in pressure tube ends from 35 rolled joints removed from power reactors are used to determine deuterium ingress rates at rolled joints. The results, which show that the ingress rate is declining with time, are extrapolated to predict deuterium buildup in the pressure tubes still in the reactors.

Atomic Energy of Canada Limited
Chalk River Laboratories
Chalk River, Ontario KOJ 1J0

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1.0 INTRODUCTION

In CANDU nuclear reactors, Zr-2.5Nb pressure tubes, through which the heavy water coolant passes, are connected to out-of-core piping by roll expanding the tubes into 403 stainless steel end fittings. Some pressure tubes in Pickering NGS (Nuclear Generating Station) and Bruce NGS have failed by delayed hydride cracking (DHC). Most of these failures initiated at rolled joints due to high residual stresses remaining because of improper rolling procedures during construction [1]. More deuterium accumulates at the ends in the rolled joint region than in the main bodies of the tube. Since hydride* precipitation is a prerequisite for DHC, an understanding of deuterium ingress processes at the rolled joint and a capability to predict how the buildup of deuterium along the rolled joint region develops with time is essential to assure reliable operation.

The relative contributions of different sources and routes for deuterium ingress at rolled joints have been investigated by testing full scale and quarter sized assemblies in loops at both Whiteshell Laboratories (WL) and Chalk River Laboratories (CRL). Pressure tube-end fitting assemblies with different configurations were tested in out-reactor loops simulating both waterside and annulus side conditions that could exist in a reactor. Laboratory permeation experiments and small specimen tests in autoclaves have both provided additional insight into the mechanisms of deuterium ingress by investigating the consequences of galvanic coupling and water chemistry on the potential for deuterium ingress. Results from these programs are described and a hypothesis to explain deuterium ingress at rolled joints is proposed.

Pressure tube ends from thirty-five rolled joints removed from the power reactors have been analysed for deuterium. Significant differences in deuterium ingress between Bruce and Pickering rolled joints are observed. Analyses of the concentration profiles as a function of time have shown that

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* The hydrogen isotopes found in pressure tubes are protium (as-received hydrogen) and deuterium (picked up during service). The term "hydrogen equivalent" [= H + ½D where H and D are the hydrogen and deuterium concentrations by weight, respectively] is often used to refer to the total hydrogen isotope concentration. Although both zirconium hydride and zirconium deuteride may be present, the precipitated phase is generally referred to simply as "hydride" (for all practical purposes, the effects of zirconium hydride and zirconium deuteride on mechanical properties are identical).

the ingress rate is declining. A mathematical model has been formulated to predict deuterium buildup over a thirty year lifetime on the basis of these declining ingress rates. The model, its verification and predictions are described in detail.

2.0 DEUTERIUM INGRESS AT ROLLED JOINTS

2.1 Sources of Deuterium

There are three potential sources of deuterium that could contribute to the ingress at rolled joints:

(1) dissolved deuterium in the coolant, which is intentionally added to suppress oxygen production from radiolysis,

(2) deuterium in the annulus gas, which is present as an impurity from permeation of deuterium in the coolant through the stainless steel endfitting,

(3) deuterium generated locally within the crevice at the rolled joint due to galvanic coupling between the Zr-2.5Nb pressure tube and the 403 stainless steel endfitting.

The effect of dissolved hydrogen in the water was investigated by exposing small diameter rolled joints to water with dissolved hydrogen levels ranging from 0 to 30 cm^3/L at 300°C in the H3 loop at CRL. After 120 days exposure the rolled joints were removed and analysed for hydrogen pickup. The data presented in Figure 1 show the joint-to-joint variation inherent in rolled joint testing. Despite the scatter, the results show that the maximum hydrogen pickup at the tube ends is independent of the hydrogen concentration in the water.

Many of these tests were conducted with a simulated gas annulus around the pressure tube - rolled joint combination. The annulus contained flowing nitrogen gas with up to 20 vol% deuterium added. Measurements of the deuterium concentration in these joints provided an indication of the importance of the annulus gas as a source of deuterium whereas the measured hydrogen concentrations represented pickup from the waterside. The results in Figure 1 show that in all cases the deuterium concentration was 1 $\mu g/g$ or less indicating that deuterium in the annulus gas is not a contributing factor to the overall ingress at rolled joints. The same conclusion was drawn from the results of similar tests conducted on three full size assemblies in the RD-5 loop at WL. In those tests, the simulated annulus gas was nominally CO_2 + 5 vol% D_2 but some joints also experienced exposures to 100 vol% D_2 as well.

Figure 1 also shows that hydrogen pickup was measured on a joint exposed in the H3 loop with no deliberate additions of hydrogen to the water. Pickup has also been seen on joints exposed to similar conditions in other loops. This indicates that dissolved hydrogen in the water is not a prerequisite for ingress at rolled joints and strongly suggests that cathodic hydrogen produced from galvanic coupling of the two components is important. The significance of galvanic coupling is shown by the results of permeation tests on type 403 stainless steel in water, Figure 2. The permeation of deuterium through steel is increased when the steel is physically coupled to Zr-2.5Nb alloy. This results from the additional production of cathodic hydrogen on the steel surface as a consequence of the coupling. In addition, the permeation of deuterium through steel is enhanced in a more alkaline solution when either uncoupled or coupled. Alkaline conditions could develop in power reactors due to lithium concentrating in the crevice regions between the pressure tube and the endfitting hub. The implication of strong galvanic effects from these results have been supported by loop test results which showed an appreciable reduction in deuterium ingress at rolled joints when the galvanic effects were eliminated or minimized by using either Zr-2.5Nb or titanium alloy endfittings.

The major source of deuterium ingress at rolled joints thus appears to be related to deuterium generation from galvanic effects on the waterside with contributions from the annulus side being insignificant.

2.2 Routes of Deuterium Ingress

Savatzky [2] originally identified five potential routes for deuterium ingress into rolled joints (Figure 3):

Route 1: deuterium entering from the inside surface of the pressure tube due to corrosion.

Route 2: deuterium migrating along the outboard crevice, between the pressure tube and the endfitting, and entering the pressure tube directly.

Route 3: deuterium on the surface of the endfitting migrating through the steel into the pressure tube.

Route 4: deuterium in the annulus gas migrating through the steel endfitting into the pressure tube.

Route 5: deuterium in the annulus gas migrating along the inboard crevice and entering the pressure tube directly.

As discussed above, routes 4 and 5 are now considered to be insignificant routes for deuterium ingress. Route 1 is the primary route for deuterium ingress in pressure tubes as a result of waterside corrosion and although it does not contribute to the additional ingress seen at rolled joints it does contribute a small amount to the total deuterium that is measured.

A variety of endfitting modifications that were designed to reduce deuterium ingress at rolled joints were tested on the RD-5 loop at WL. These included the placement of hydrogen sinks and barriers in the endfitting at the outboard crevice region. The barriers were intended to restrict hydrogen entering the pressure tube via the steel endfitting (Route 3) whereas the sinks were intended to absorb hydrogen in the crevice region and restrict both direct entry into the tube (Route 2) and entry via the steel endfitting (Route 3). The results of these tests, Figure 4, showed that the presence of the sinks and barriers did not affect the hydrogen ingress at rolled joints. However the results did demonstrate that hydrogen ingress at rolled joints was occurring at locations further inboard than these devices and possibly throughout the crevice region between the pressure tube and endfitting.

The three routes of deuterium ingress that are considered to be the main contributors to deuterium buildup at rolled joints are shown in Figure 5. For clarity, the Figure shows ingress by routes 2 and 3 at one location only; however, ingress could occur via these two routes at all locations under the hub where there are crevices and areas of metal-to-metal contact. The relative contributions of routes 2 and 3 are still the subject of investigation and will be discussed in the next section.

2.3 Mechanism of Deuterium Ingress

As a final stress relief step, Zr-2.5Nb pressure tubes are steam autoclaved. This introduces a 1-2 μm thick black oxide on the tube surface. Corrosion experiments indicate that this oxide is relatively impermeable to hydrogen. It has been suggested that capacitance measurements can be correlated with the 'protectiveness' of pressure tube oxides. A low capacitance value suggests that a large fraction of the oxide is present as an impervious or non-porous, protective layer closest to the metal/oxide interface [3].

Figure 6 shows the rolled section of two pressure tubes. The tube in Figure 6a was roll expanded into a 403 stainless steel end fitting, then removed. The tube in Figure 6b is from a rolled joint assembly fabricated in the same manner, then exposed to CANDU PHTS (Pressurized Heat Transport System) conditions. During rolling, some of the outside oxide on the pressure tube is broken up and areas of metal-to-metal contact with the end fitting are created. Figure 6a shows evidence of damage of portions of the black oxide from the area surrounding the grooves. The shiny appearance of the groove shoulders indicates complete loss of oxide at points of intimate contact with the end fitting.

During reactor operation, pressurized coolant (lithiated D_2O) can diffuse along the out-board crevice between the end fitting and pressure tube and re-oxidize exposed areas of the tube. In Figure 6b, areas which would typically suffer oxide damage during rolling (compare with Figure 6a) are covered with black oxide. However, further examination suggests that not all oxide damage is repaired; as well, in those areas where new oxidation has occurred, the resulting film may not be sufficiently protective. Figure 7 shows (qualitatively) the results of contact capacitance measurements on tube surfaces similar to those in Figure 6.

After rolling, areas of the pressure tube exhibiting damaged or removed oxide (for example, between grooves and at groove shoulders, respectively) show high capacitance values, indicating that the non-porous portion of any oxide present is rather thin. Conversely, areas in which the original oxide has been left intact (e.g., groove lands) show a low capacitance value (indicating a relatively thick non-porous component in the oxide film).

Following exposure of an identical rolled joint assembly to CANDU PHTS conditions, many of the areas, especially between the grooves, which would typically exhibit high capacitance values prior to exposure, now show low values. This suggests an increase in the protective component of the oxide covering these areas. At the same time however, there is only a small decrease in capacitance in many areas typically forced into intimate contact with the end fitting during the rolling process (such as groove shoulders). Most notable is the rather small drop in capacitance characteristically observed for the out-board edge of the out-board groove, and the in-board edge of the in-board groove. The high degree of deformation observed at these locations suggests that, relative to other groove shoulders, a high proportion of the circumferential area of these shoulders must contribute to sealing of the rolled joint. This proportion likely remains high early in the life of the joint, and the fraction of shoulder area subject to coolant contact (allowing for re-growth of pressure tube oxide on the mating surface) will be a minimum. Later, thermal cycling of the rolled joint will create or enlarge localized gaps in the circumferential seal, allowing further coolant penetration and tube re-oxidation. It is postulated that for any pressure tube surface where the capacitance has not decreased to a uniform low value, either only a limited amount of re-oxidation has occurred, or that the type of new oxide present will offer only marginal protection from hydrogen ingress during subsequent exposure.

The primary source for hydrogen in rolled joints is the cathodic reaction attending oxidation reactions in the crevices formed between the pressure tube and 403 stainless steel end fitting. A significant factor is the galvanic coupling of the dissimilar pressure tube and end fitting materials. Under CANDU operating conditions, this favours the occurrence of the cathodic reaction on the steel half of each crevice; the deuterium generation on this surface will likely assume a maximum value near points of intimate contact between the end fitting and pressure tube. In addition, a unique electrochemical environment may exist in rolled joint crevices, giving rise to a 'crevice effect'. The nature and impact of such an effect is presently unclear, but is under investigation by the authors.

Figure 8 compares the contribution of both galvanic coupling and the 'crevice effect' to the overall deuterium ingress observed for three identical, bare Zr-2.5Nb rods corroded under CANDU conditions: 1) a Zr-2.5Nb rod by itself, 2) a second rod galvanically coupled to a 410 stainless steel sleeve, and 3) a third rod not only coupled to, but forming a tight crevice (25 μm ± 10%) with an identical sleeve. In the latter two types of samples, the rods were swaged into their respective steel sleeves to create an electrical 'contact area'.

Comparing the case of 'coupled only' and 'coupled and creviced' samples, two conclusions can be drawn. First, while all samples shared approximately the same degree of metal-to-metal contact (in terms of the length and integrity of their respective swaged areas) there was a drastic increase in the deuterium transferred into the Zr-2.5Nb rod at or near the contact area for the 'coupled and creviced' specimen. Second, the shape of the deuterium profile within the creviced region of the 'coupled and creviced' samples is somewhat different from the corresponding portion of the profile for the 'coupled only' samples. Since the terminal solid solubility (TSS) has been exceeded for that portion of the Zr-2.5Nb rod closest to and including the contact area for the 'coupled and creviced' specimens (TSS = 131 μg/g D at 300°C), this may have influenced some portion of the deuterium profile for the creviced Zr-2.5Nb rod. However, factors such as crevice geometry (length and gap) and chemistry (pD and Li concentration gradients) undoubtedly play an important role in the observed 'crevice effect'.

Deuterium evolved within a given crevice can follow at least two routes into the Zr-2.5Nb alloy. The relative contribution of deuterium from each ingress route to the total pressure tube concentration will be determined by the degree and adequacy of oxide repair which has occurred since rolling of the joint. We hypothesize that until oxide damage is repaired, the principal route for deuterium ingress is probably diffusion along the crevice to a point where it can enter the pressure tube through a 'window' of damaged or poorly protective oxide. Even after the pressure tube oxide in the crevice is adequately repaired, areas of intimate contact between the 403 steel and Zr-2.5Nb alloy may not be. Then, the largest fraction of ingress will be due to diffusion of the deuterium over short distances through the end fitting to closest point(s) of metal-to-metal contact.

Based on such a mechanism, one would predict an ingress rate which would be high initially then lower in the long term.

3.0 MODELLING DEUTERIUM BUILDUP IN PRESSURE TUBES AT ROLLED JOINTS

Deuterium picked up at the end of the pressure tube via rolled joint ingress diffuses inboard at reactor operating temperatures. Deuterium buildup in the pressure tube in excess of TSS leads to the precipitation of hydrides and a potential for DHC. Other necessary conditions for DHC include high tensile stresses and initiation sites (e,g., flaws). The high residual tensile stresses in the pressure tube just inboard of the rolled region (the edge of the rolled region is generally referred to as the burnish mark) is a critical region for DHC.

A model is being developed to predict deuterium buildup at the ends of pressure tubes. Progress in modelling deuterium buildup in the pressure tube is hampered by the fact that, at present, deuterium ingress rates at the rolled joint cannot be determined from first principles. Hence, ingress rates are currently determined from measurements on pressure tubes removed from the reactors and the emphasis is on understanding its transport in the pressure tube. This is discussed in detail in the next Section, followed by a description of the model used and its applications.

3.1 Reactor Data and Ingress Rates

Enhanced deuterium pickup at the rolled joint is illustrated in Figure 9 which shows deuterium distribution along the length of pressure tubes removed from Pickering NGS and Bruce NGS after approximately 10 years of exposure. The deuterium concentration profiles at the ends of the pressure tubes result from deuterium diffusion inboard from points of ingress at the rolled joint. At each end of the pressure tube, the part of the profile attributed to rolled joint ingress is confined to a small section of the tube (less than 50 cm from the pressure tube end). From the measured deuterium concentration profile and the extent of deuterium diffusion inboard, the total amount of deuterium picked up and the contributions from ingress at the rolled joint and pickup along the pressure tube due to corrosion can be determined as shown schematically in Figure 10. The results are shown in Figure 11 which plots the amount of deuterium picked up via rolled joint ingress as a function of time for 35 rolled joints removed from CANDU reactors. The data in this Figure, as well as data from the RD-5 loop experiments, indicate that the ingress rate is declining with time.

The functional form of the time dependence of the ingress rate is at present not fully understood. Initially, the decline in the ingress rate is thought to be due to the repair of oxide on the pressure tube in the groove-region damaged during rolling (the oxide damage provides the window for deuterium ingress into the pressure tube). For simplicity, the ingress rate is then assumed to be inversely proportional to the oxide thickness which in turn is assumed to grow according to the parabolic rate law commonly observed. The ingress rate, R, is thus taken to have a time dependence given by:

$$R(t) = \frac{1}{at^{1/2}+b} \tag{1}$$

where t is the time and a and b are constants to be determined from a fit to the measured deuterium mass picked up via rolled joint ingress. Integrating Equation (1), the deuterium mass M picked up as a function of time is given by:

$$M(t) = 2\pi rw\lambda\rho\beta[\alpha t^{1/2} - \ln(1 + \alpha t^{1/2})] \tag{2}$$

where $\alpha=a/b$ and $\beta=2b/a^2$. In the above equation, r and w are the pressure tube radius and wall thickness, respectively, λ is the length of the ingress region and ρ is the density of the pressure tube material. The values used for these parameters are r=53.73 mm, w=4.06 mm and ρ=6.49 g/cm^3. A nonlinear least-squares fit procedure is then used to obtain the coefficients α and β in Equation (2) and in turn these coefficients are used to determine the initial constants a and b which define the ingress rate in Equation (1). We note that Equation (2) is derived for a spatially uniform ingress profile and a scaling factor must be used to account for spatial variation in the ingress rate.

A striking feature in Figure 11 is the higher ingress rates observed in Bruce A compared to Pickering A. The difference between Bruce and Pickering cannot be explained by temperature differences since Pickering inlet ends operate at the same temperature as inlet ends of inner zone tubes in Bruce. A possible explanation is that the oxide on the outside surface of the 403 SS endfitting in the CO_2 annulus gas system (AGS) of Bruce units may be less permeable to deuterium than the oxide in the N_2 AGS of Pickering (before retubing) resulting in less deuterium escaping into the AGS and thus more deuterium getting into the ends of the pressure tubes in Bruce compared to Pickering. This is supported by the data from Pt. Lepreau and Pickering 8 which, like Bruce, have CO_2 annulus gas systems. As shown in Figure 11, the amounts of deuterium pickup in the Pt. Lepreau tube L1K05 and Pickering tube P8S15 are closer to rolled joints from Bruce A than Pickering A.

Because of the observed differences in the behaviour of inlet and outlet rolled joints and also differences between Pickering and Bruce, the data in Figure 11 are divided into 4 groups representing Pickering 3 and 4 inlets and outlets and Bruce 1, 2, 3 and 4 inlets and outlets. The results of the least-squares fit are shown in Figure 11 (the data from L1K05 and P8S15 were not included in the fit).

3.2 The Physical Model

A physical model for deuterium distribution in the rolled joint region of the pressure tube was first proposed by Sawatzky at WL [2]. Because it relied on an analytical solution, the model was limited by the form of the ingress function it could handle and an approximate way of treating hydride precipitation effects. To overcome these difficulties, a numerical model was developed by Urbanic and Burrill at CRL in which an attempt was also made to model deuterium transport through the endfitting into the pressure tube. In applying these models, ingress rates had to be adjusted to fit the measured deuterium profiles. The use of reactor data to determine ingress rates is adopted in the current model, as discussed below.

The physical problem being modelled is shown schematically in Figure 12. The exact extent of the ingress region and the actual form of the spatial variation of the ingress rate is not known at present. Based on the current understanding of the sources and routes of deuterium ingress outlined in Section 2, the ingress region is assumed to extend from the pressure tube end to the inboard groove and the spatial profile is assumed to have a peak at the outboard groove and to decline linearly to half the peak value at the ends of the ingress region as depicted in Figure 12. Deuterium entering the pressure tube builds up under the rolled joint and diffuses inboard. The redistribution of deuterium is governed by the diffusion equation:

$$\partial C(x,t)/\partial t = D\partial^2 C(x,t)/\partial x^2 + S(x,t) \qquad (3)$$

where C(x,t) is the deuterium concentration at the point x at time t, D is the diffusion coefficient for deuterium and S is a source term describing deuterium pickup at the rolled joint as well as pickup along the pressure tube.

The reference diffusion coefficient used is that of Sawatzky et al [4]. In the temperature range 250 to 500°C, the diffusion coefficient of hydrogen in Zr-2.5Nb is given by:

$$D = 1.17\times10^{-7}\exp(-8030/RT) \qquad \mathrm{m^2/s} \qquad (4)$$

where T is the absolute temperature (the gas constant R=1.987 Cal/K mole). The diffusivity of deuterium = $1/\sqrt{2}$ that of hydrogen (isotopic mass effect).

The redistribution of deuterium in the pressure tube is strongly affected by hydride precipitation, which occurs when the terminal solid solubility (TSS) is exceeded. Results of earlier calculations had shown that when TSS is exceeded the model overpredicts deuterium concentrations under the rolled joint and underpredicts deuterium concentration further inboard. This is because at constant temperature, no diffusion occurs in the 2-phase (α-Zr + δ-hydride) region first formed under the rolled joint, and this results in deuterium piling up at the pressure tube end. A mechanism which allows some supersaturation based on a 2-TSS model under thermal cycling was proposed to allow for greater deuterium flow inboard. The 2-TSS scheme assumes that deuterium in solution can supersaturate beyond the dissolution (heat-up) TSS and precipitation occurs after sufficient supersaturation or when the temperature drops substantially during a cold shutdown of the reactor. On subsequent reactor startup, deuterides will redissolve till the concentration of deuterium in solution reaches the heat-up TSS. Additional deuterium pickup is then allowed to supersaturate the matrix until a higher TSS level, referred to as the cool-down or precipitation TSS, is exceeded or the reactor shuts down again.

In the modelling, the value for the heat-up or dissolution TSS, denoted by TSS(D), is taken to be that given by Kearns [5] while the precipitation TSS, denoted by TSS(P), is taken to be that given by Sawatzky [6]:

$$\mathrm{TSS(D)} = 1.2\times10^{5}\exp(-8550/RT) \qquad (\mu g/g \text{ hydrogen}) \qquad (5)$$

$$\mathrm{TSS(P)} = 8.5\times10^{4}\exp(-7600/RT) \qquad (\mu g/g \text{ hydrogen}) \qquad (6)$$

We note that for the 1-TSS model the single TSS is designated simply as TSS and corresponds to the heat-up or dissolution TSS. We also note that in μg/g units, the TSS for deuterium is twice that for hydrogen.

3.3 Model Applications

To verify the model against measurements on removed pressure tubes, a database on 35 rolled joints removed from CANDU reactors has been compiled. The ingress rate for each rolled joint is given by the appropriate curve in Figure 11 but rescaled to pass through the measured data point (this ensures the amount of deuterium picked up corresponds to that measured for that rolled joint and allows the form of the profile to be compared with measurements). The results vary considerably from tube to tube but good fits are generally obtained except when TSS is exceeded and hydrides are precipitated. Good agreement is illustrated in Figure 13 for a pressure tube removed from Bruce fuel channel B2K03 after approximately 11 years of reactor exposure. At the inlet and outlet ends of B2K03, TSS at the operating temperature (261°C at the inlet end and 299°C at the outlet end) is only slightly exceeded and the results of model calculations are in good agreement with measured data. The discrepancy between measured data and model calculations when TSS is substantially exceeded is illustrated by the inlet rolled joint of B2U07 as shown in Figure 14 (the pressure tube was in the reactor for approximately 10 years and the inlet temperature was 250°C). The poor fit is thought to be mainly due to the poor treatment of diffusion in the presence of precipitated hydrides resulting from the combination of a high ingress rate and low operating temperature in this rolled joint. Two other inlet rolled joints from Bruce show fits as poor as that in Figure 14 and work is on-going to improve the fit.

Calculations were carried out to obtain life-time predictions of deuterium levels using the ingress rates given by Equation (1). A nominal corrosion rate of 1 μg/g (0.0045 at.%) deuterium per year and an initial hydrogen concentration of 15 μg/g (0.136 at.%) were assumed. Since all reactors now operate with a CO_2 AGS, the predictions are obtained using the ingress rates for Bruce in Figure 11. The operating temperatures used are 250°C (inlet ends of Pickering pressure tubes and inlet ends of inner zone pressure tubes in Bruce), 265°C (Bruce outer zone inlets), 295°C (Pickering outlets) and 305°C (Bruce outlets). The results are summarized in Table 1 showing the hydrogen isotope concentration under the rolled joint, in the high stress region and in the bulk of the pressure tube. More precise predictions will be provided as: 1) the database on rolled joints expands leading to more precise ingress rates, and 2) the model treatment of hydride precipitation is improved.

4.0 SUMMARY AND CONCLUSIONS

The main source of deuterium ingress at the rolled joints appears to be deuterium generation from galvanic effects in the crevice between the pressure tube and the end fitting. Deuterium ingress from the annulus gas side is insignificant.

The main routes responsible for the accumulation of deuterium at rolled joints are: 1) the direct deuterium ingress during repair of the damaged oxide, and 2) the diffusion of deuterium via the end fitting and into the pressure tube through the metal-to-metal contacts.

Based on current results, a hypothesis for the mechanism for rolled-joint deuterium ingress is developed. The hypothesis is based on the observation that the surface oxide on Zr-2.5Nb, which is normally a good barrier to deuterium ingress, is damaged by the rolling process and repaired during service. When a joint is rolled, some of the oxide on the outside surface of the pressure tube is removed and areas of metal-to-metal contact with end fittings are created. During reactor operation, water diffuses along the crevice between the end fitting and pressure tube and repairs the pressure tube oxide except at contact areas. The cathodic deuterium released during oxidation reactions in the crevice is the primary source for ingress. These reactions are enhanced by the galvanic couple between the pressure tube and end fitting at contact areas.

During the period of oxide repair, deuterium ingress occurs by both routes, whereas later in life, ingress is predominantly via the end fitting through the metal-to-metal contacts.

Pressure tube ends from thirty-five rolled joints removed from the power reactors have been analysed for deuterium. Rolled joint ingress rates are higher in Bruce than Pickering (before retubing). Analyses of the deuterium concentration profiles show that the ingress rate is declining with time.

A model for deuterium buildup in the rolled joint region of pressure tubes was developed. The model incorporates deuterium ingress at the rolled joint and pickup along the bulk of the tube and takes into account hydride precipitation effects.

Model calculations were carried out and compared with measured data on 35 rolled joints removed from power reactors. Good agreement is obtained between measured and calculated hydrogen isotope concentration profiles except in pressure tubes in which TSS is substantially exceeded.

The model was used to make life-time predictions of deuterium buildup in the rolled joint region of pressure tubes. The predictions are not yet accurate because of: 1) uncertainties in the deuterium ingress rates at the rolled joint, and 2) inability of the model to provide good fits to the data once TSS is substantially exceeded. Planned analysis of additional rolled joints to provide more precise ingress rates and on-going work to improve the model will provide better predictions.

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Table 1: Predicted hydrogen isotope concentrations at 15, 80 and 500 mm from the pressure tube end. The 80 mm mark represents the approximate location of the burnish mark.

TEMPERATURE	NUMBER OF YEARS	HYDROGEN ISOTOPE CONCENTRATION					
		15 mm		80 mm		500 mm	
		(μg/g)	(at.%)	(μg/g)	(at.%)	(μg/g)	(at.%)
250°C TSS=32 μg/g	5	72	0.65	29	0.26	18	0.16
	10	99	0.89	31	0.28	20	0.18
	15	122	1.09	32	0.29	23	0.21
	20	141	1.26	34	0.31	26	0.23
	25	159	1.41	38	0.34	28	0.26
	30	175	1.55	42	0.38	31	0.28
265°C TSS=40 μg/g	5	54	0.49	34	0.31	18	0.16
	10	75	0.67	37	0.34	20	0.18
	15	94	0.84	39	0.35	23	0.21
	20	112	1.00	40	0.36	26	0.24
	25	128	1.15	41	0.37	29	0.26
	30	144	1.29	43	0.39	32	0.29
295°C TSS=62 μg/g	5	54	0.48	40	0.36	18	0.16
	10	68	0.61	53	0.48	21	0.19
	15	99	0.88	57	0.51	24	0.22
	20	133	1.19	59	0.53	29	0.26
	25	167	1.48	60	0.54	33	0.30
	30	201	1.78	61	0.55	37	0.33
305°C TSS=70 μg/g	5	52	0.46	40	0.36	18	0.16
	10	63	0.57	52	0.47	21	0.19
	15	71	0.64	61	0.55	25	0.22
	20	90	0.81	65	0.59	29	0.27
	25	117	1.04	67	0.60	34	0.31
	30	145	1.30	68	0.61	39	0.35

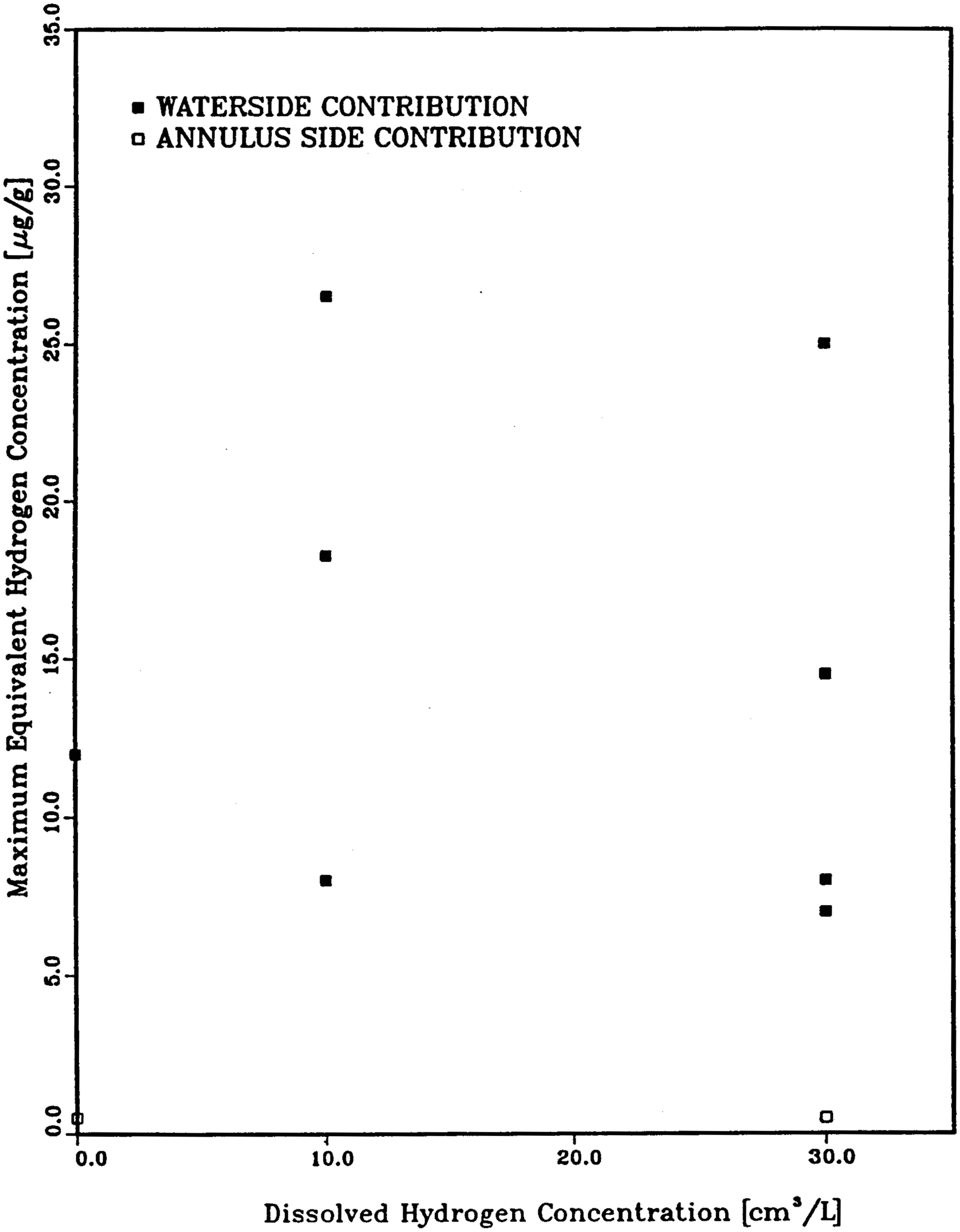


Figure 1: Hydrogen pickup at rolled joints exposed for 120 days at 300°C in the H3 loop.

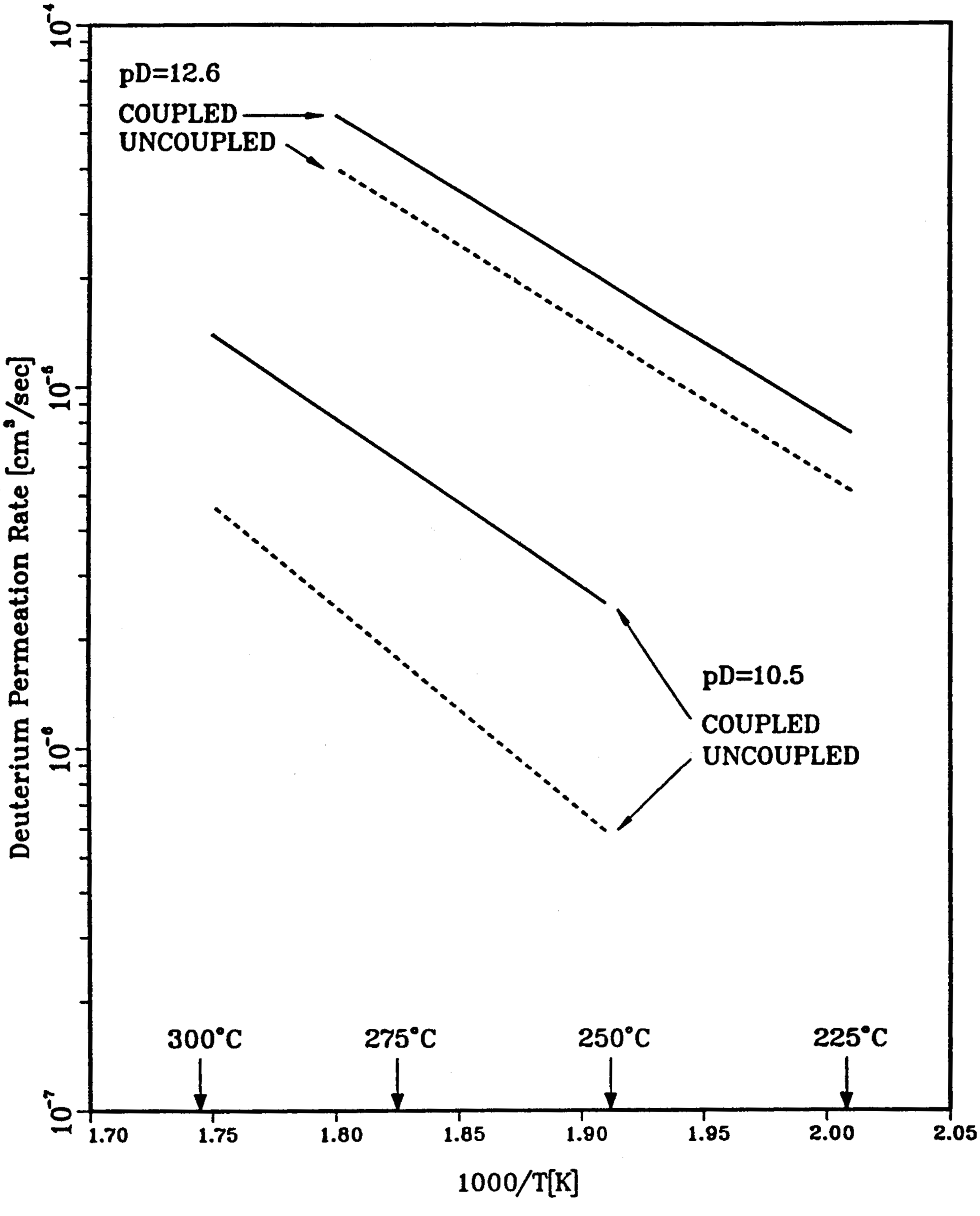


Figure 2: Permeation of deuterium through 403 stainless steel with and without coupling to Zr-2.5Nb in degassed D_2O.

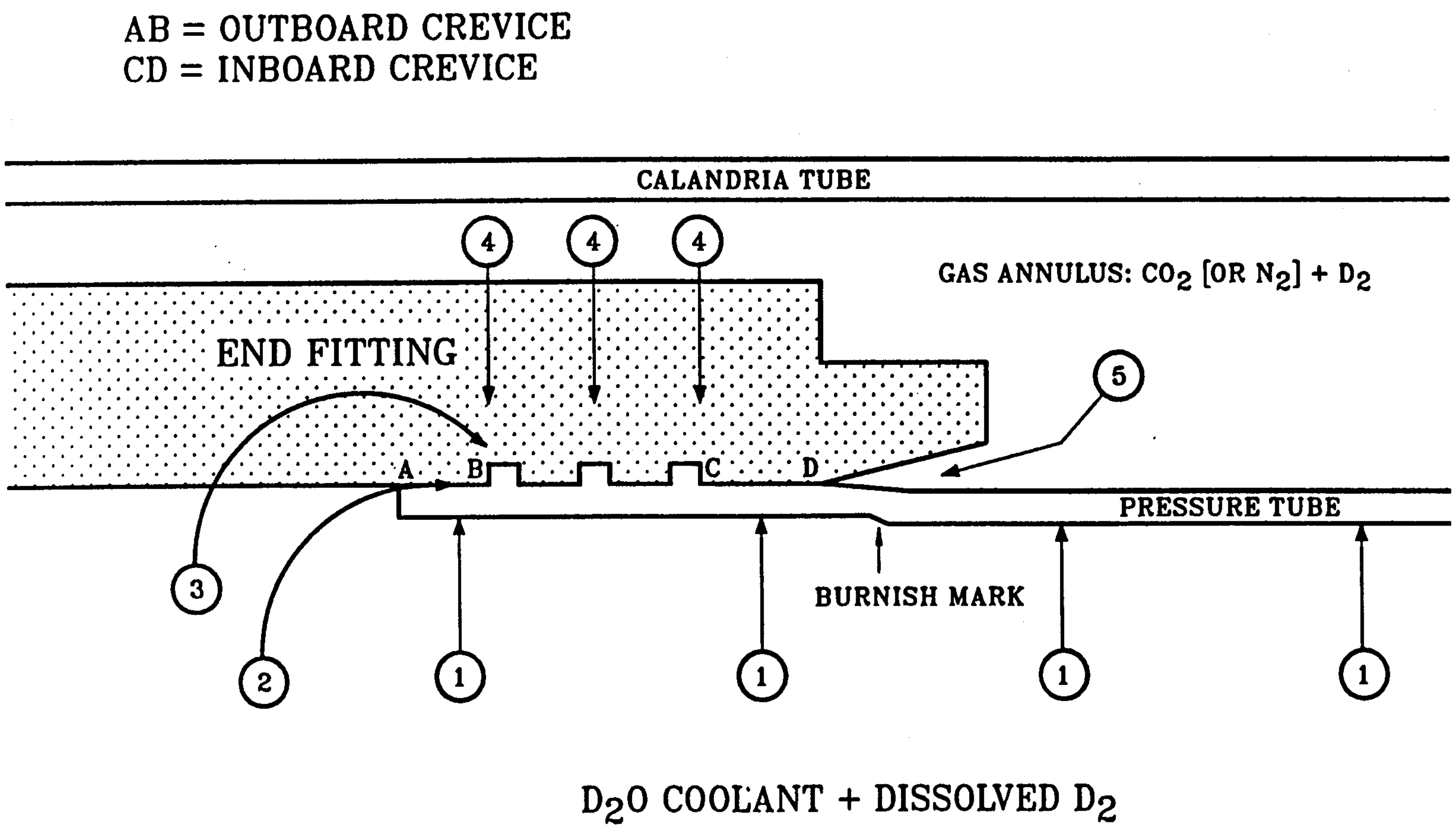


Figure 3: A schematic diagram of the rolled joint showing the five possible routes originally proposed for deuterium ingress into pressure tubes at rolled joints.

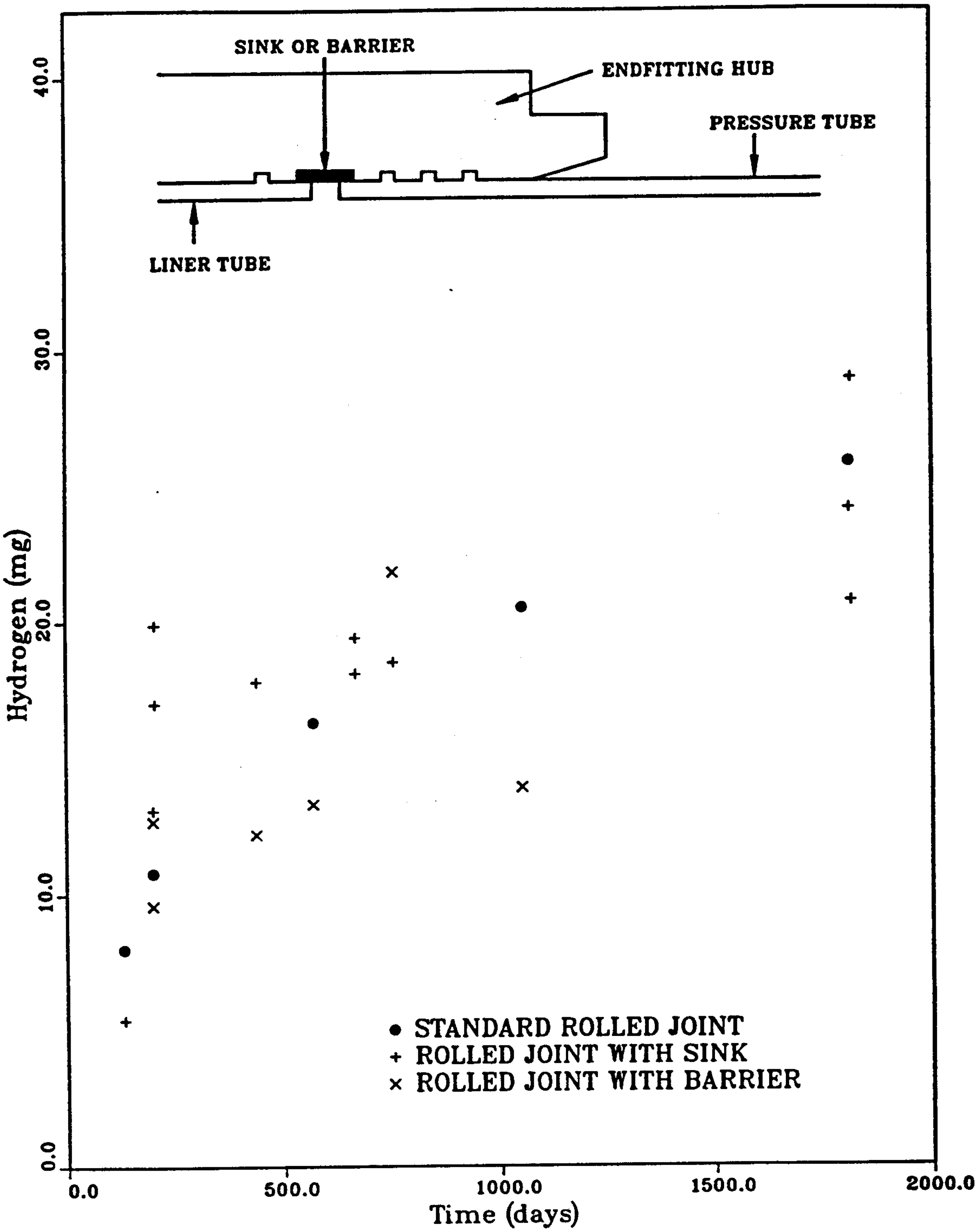


Figure 4: Hydrogen pickup at standard, sink- and barrier-type rolled joints exposed in the RD-5 loop at WL.

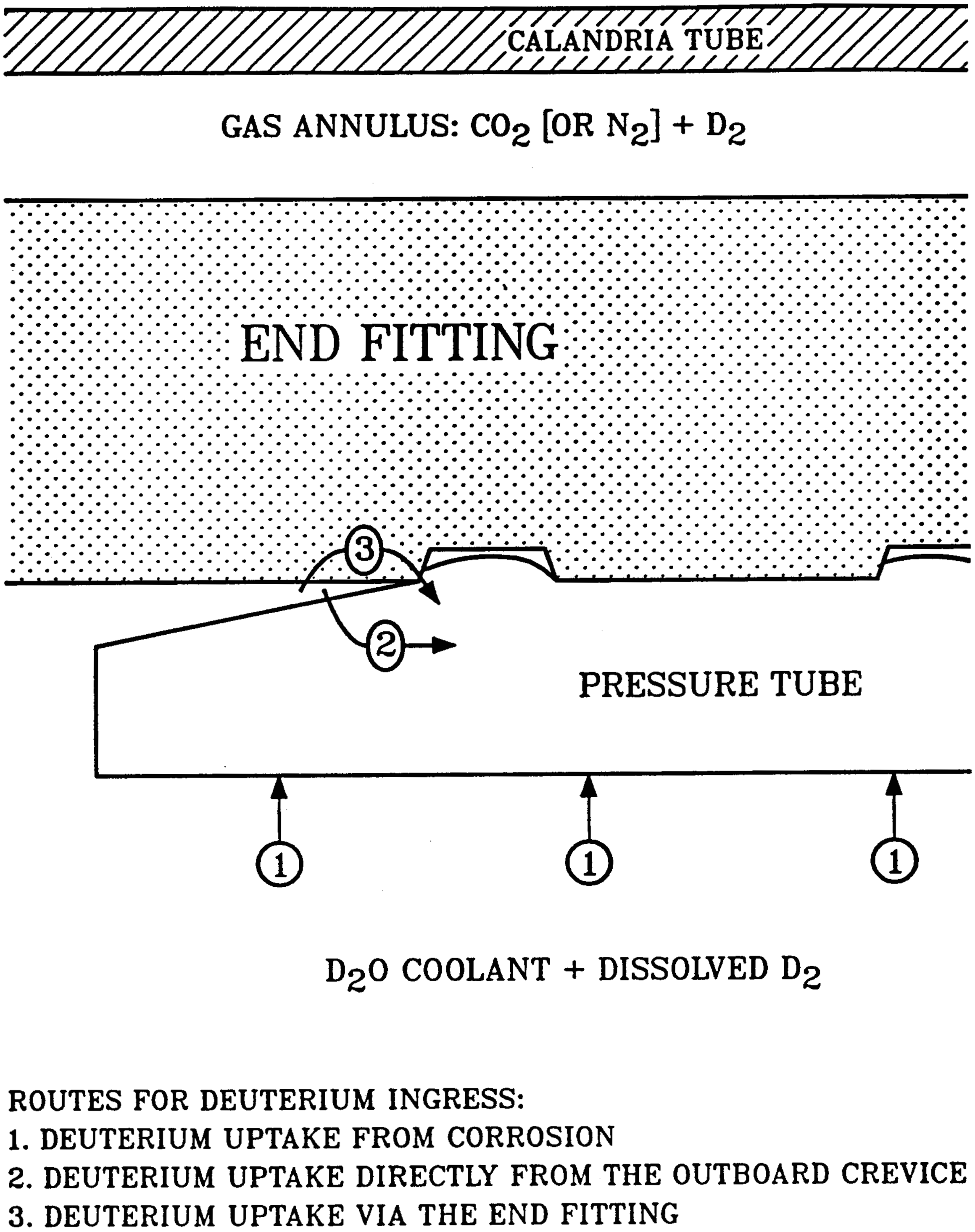
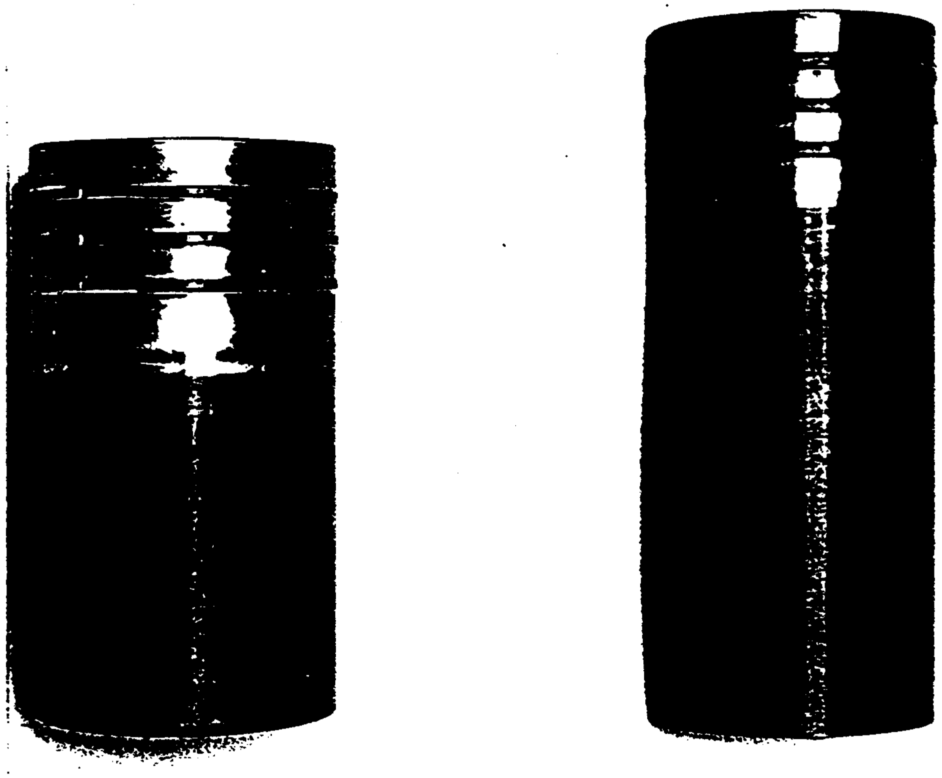


Figure 5: Principal routes for deuterium ingress at rolled joints.



ROLLED

NOT EXPOSED

ROLLED

EXPOSED

(a)

(b)

Figure 6: Zr-2.5Nb pressure tubes removed from joints rolled with 403 stainless steel end fittings: (a) end fitting removed immediately after rolling, and (b) rolled joint assembly exposed in an out-reactor loop for 60 days at 260°C then end fitting removed.

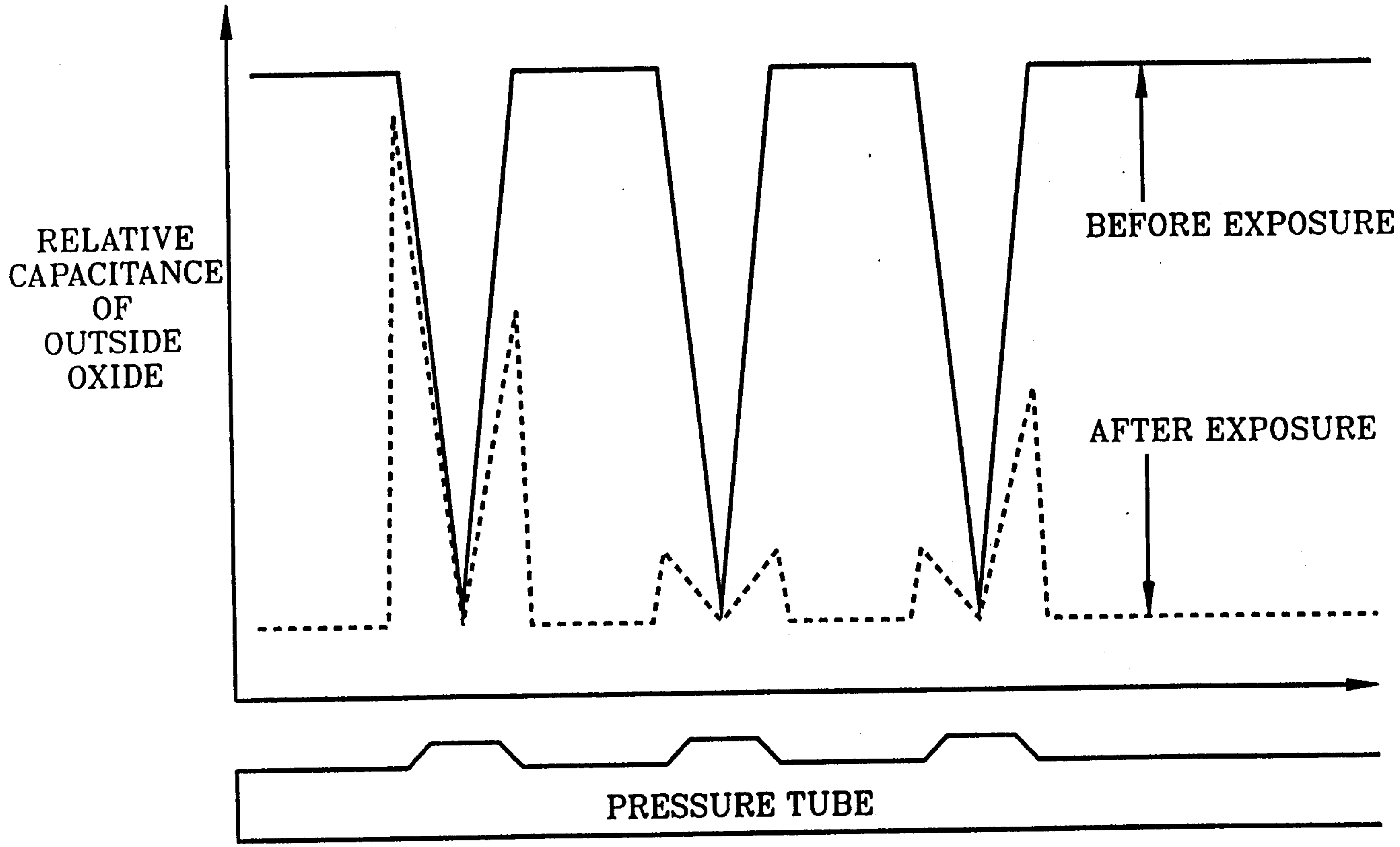


Figure 7: Relative contact capacitance typical of pressure tube outside oxides after rolling (before exposure) and after subsequent exposure of the rolled joint assembly to CANDU PHTS conditions.

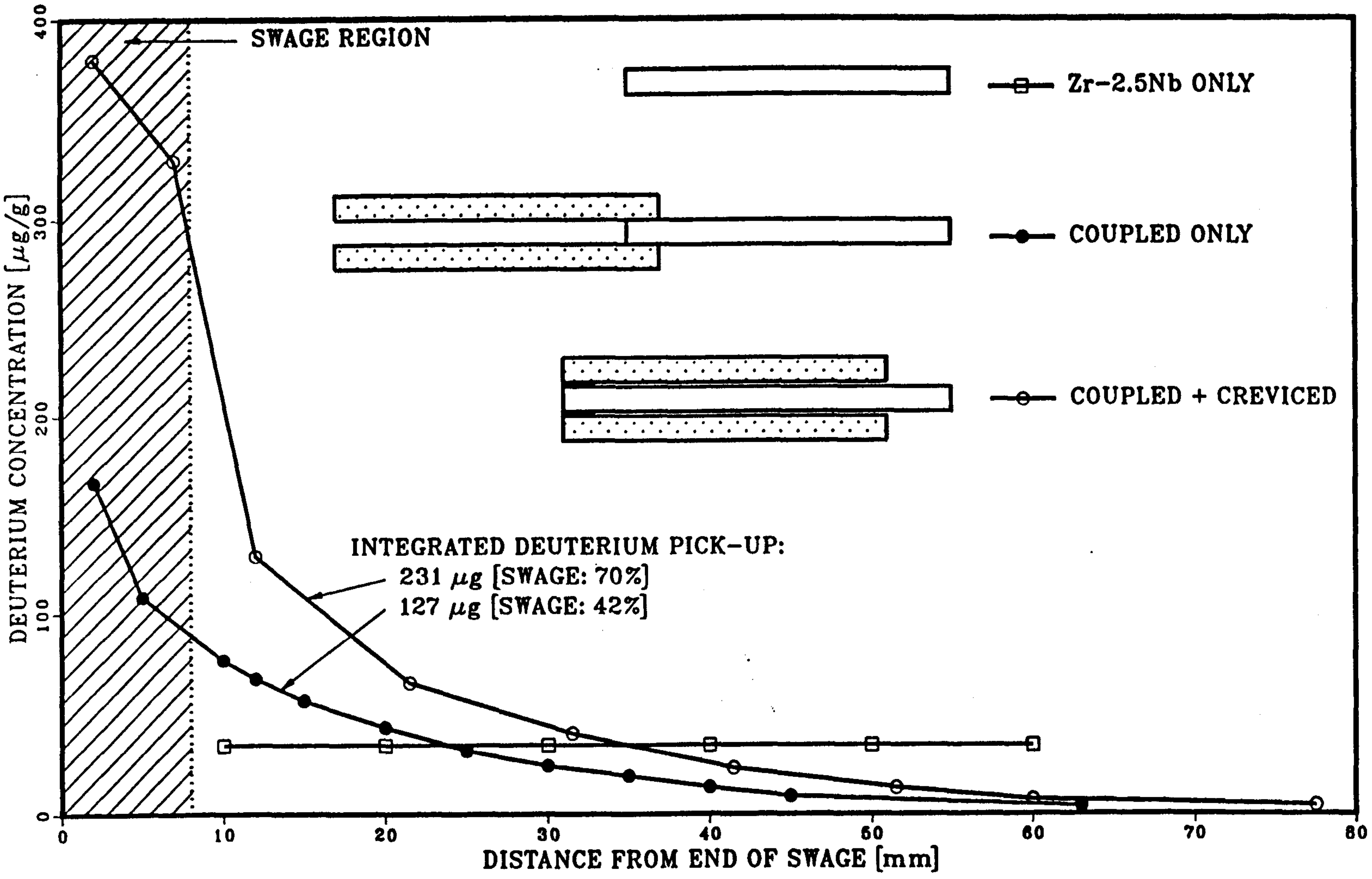


Figure 8: Comparison of the deuterium uptake profile for three bare Zr-2.5Nb rods: one swaged to a 410 stainless steel sleeve; one swaged within a 410 stainless steel sleeve so as to create a 25 μm crevice; and one corroded alone. Autoclave conditions: 66 days at 300°C in pD 10.3 (LiOD) D_2O, degassed.

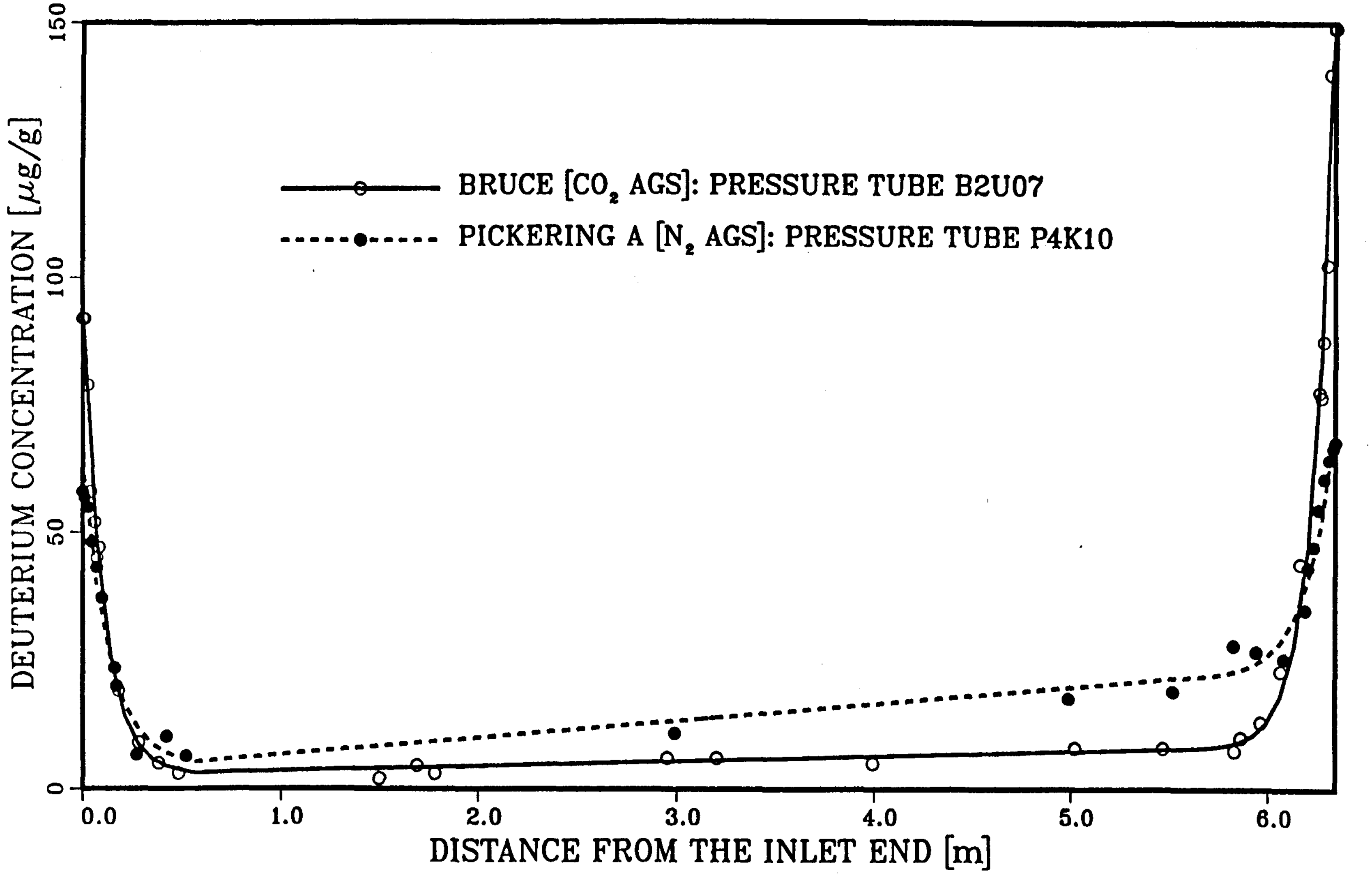


Figure 9: Deuterium concentration along CANDU pressure tubes showing the enhanced buildup at the rolled joints. The data shown are for fuel channel P4K10 from Pickering, which had a nitrogen annulus gas system (AGS), and B2U07 from Bruce with a CO_2 AGS. The tubes were removed after approximately 10 hot years.

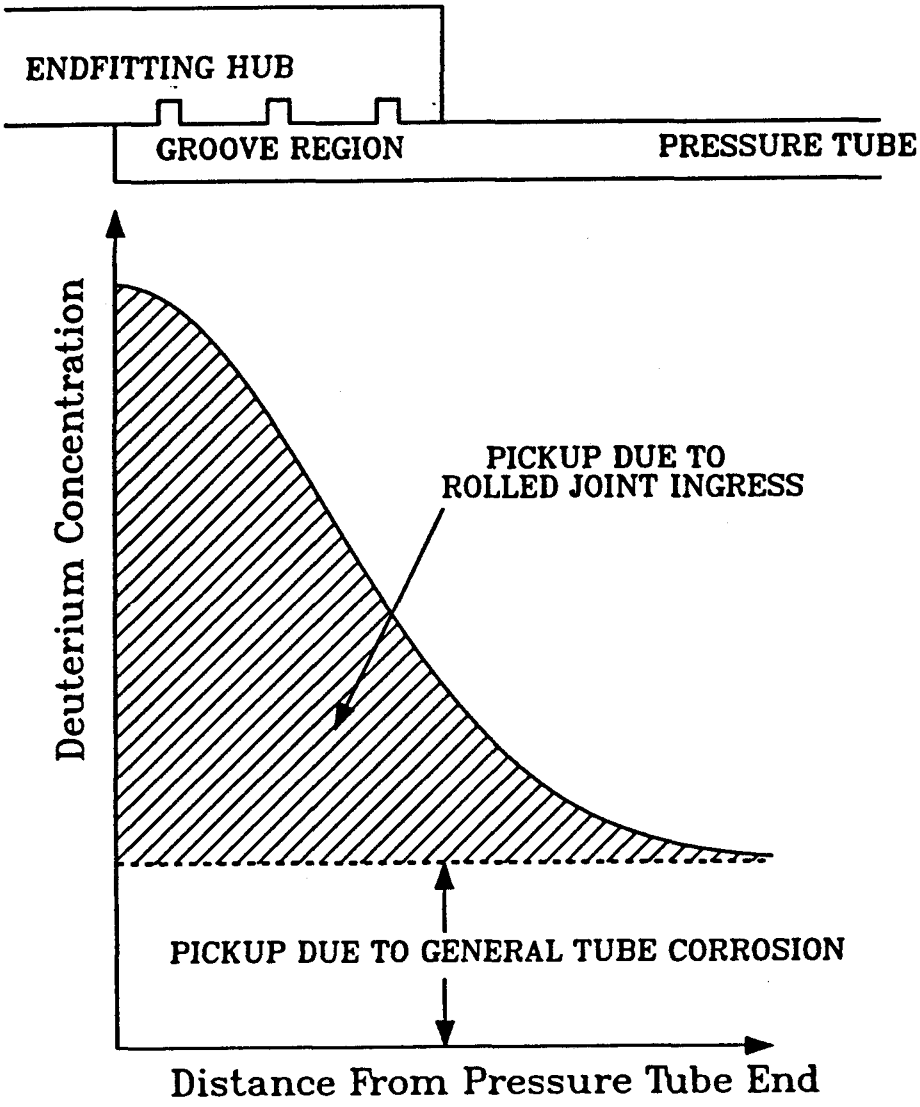


Figure 10: A schematic diagram of the deuterium concentration profile at the end of the pressure tube showing the contribution from deuterium ingress at the rolled joint and pickup due to corrosion along the pressure tube.

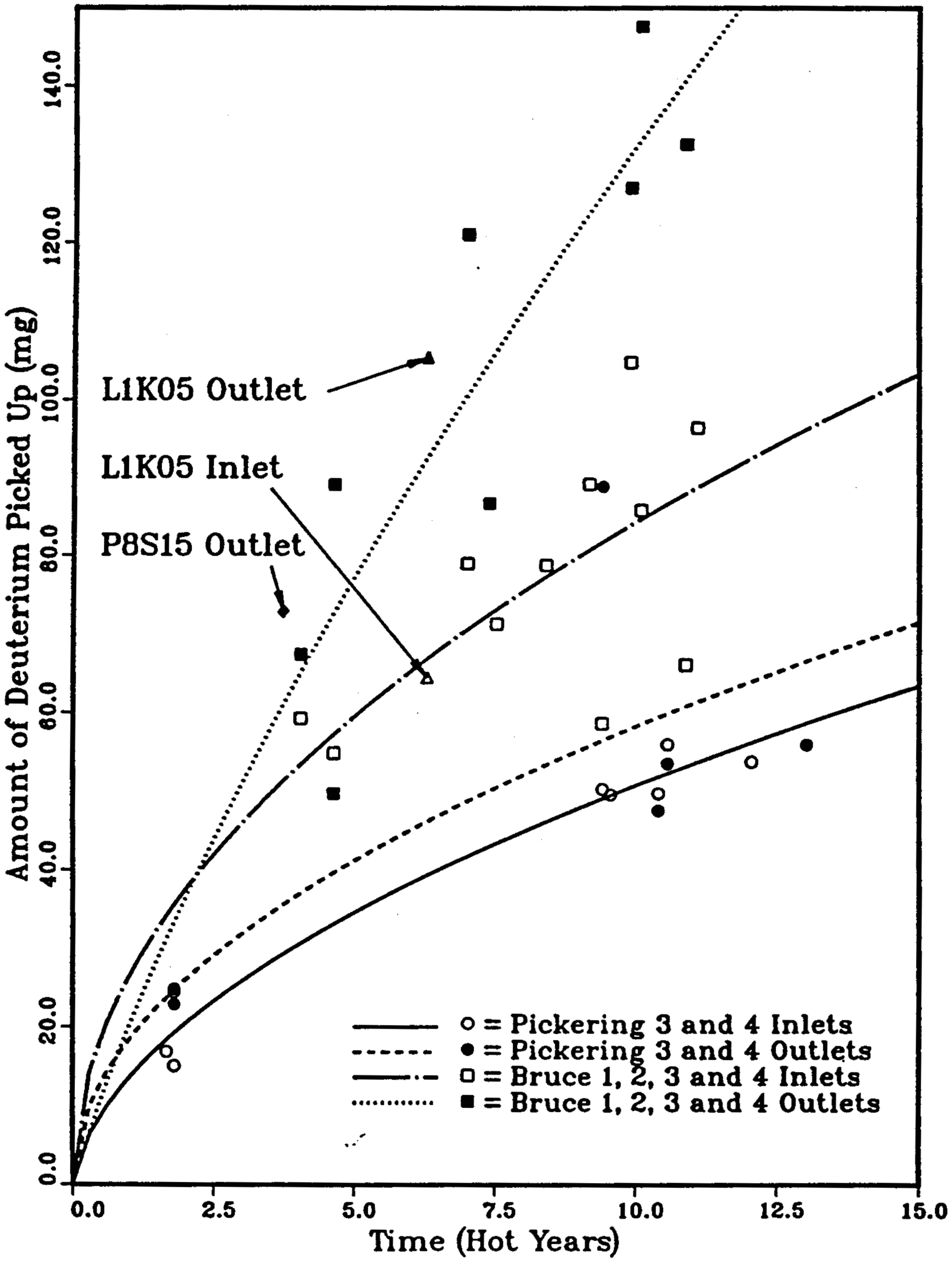


Figure 11: Amount of deuterium picked up via rolled joint ingress as a function of time. Symbols represent measured data while the curves are the best fits assuming a declining ingress rate.

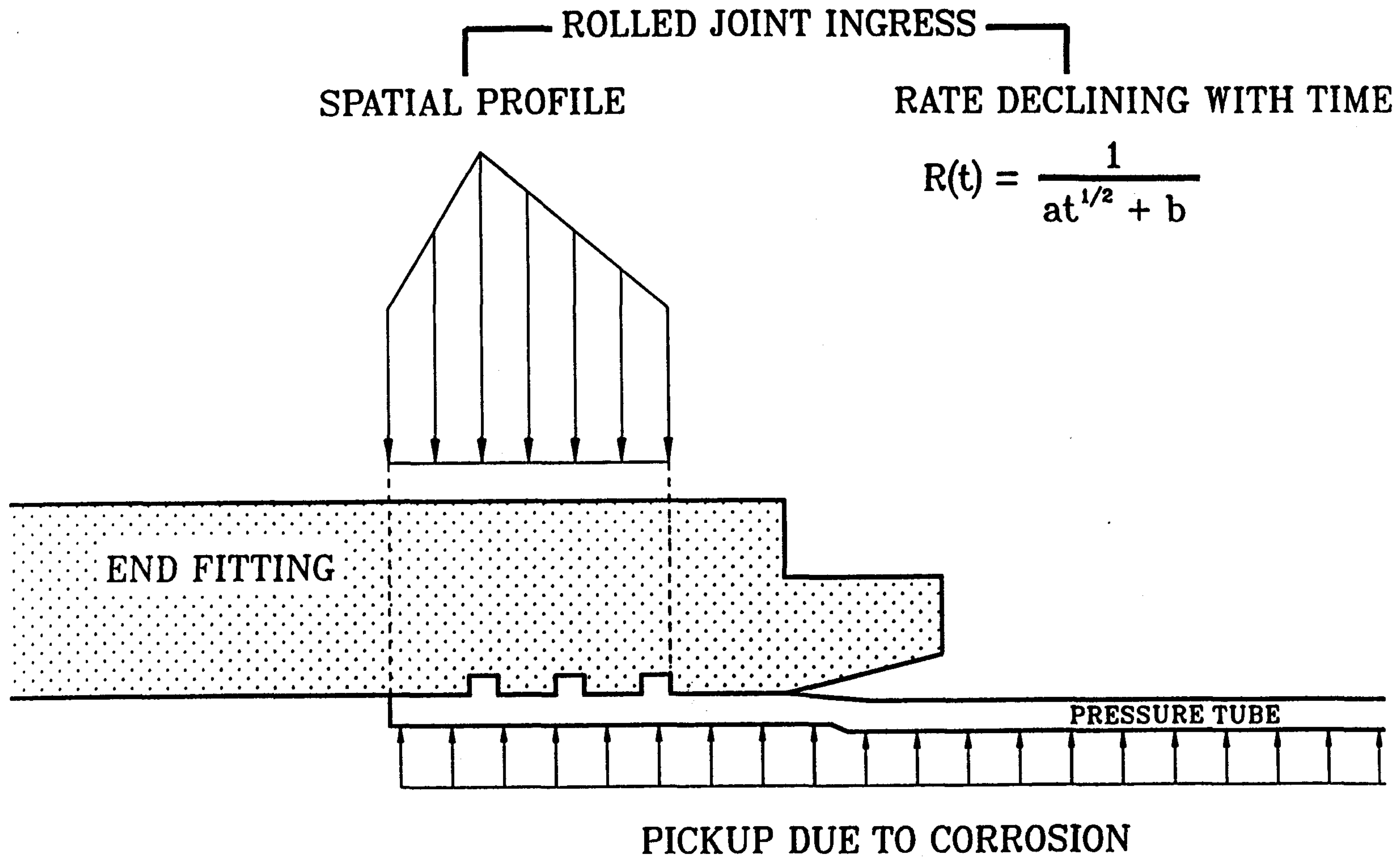


Figure 12: A schematic diagram of the rolled joint showing how deuterium ingress into the pressure tube is modelled.

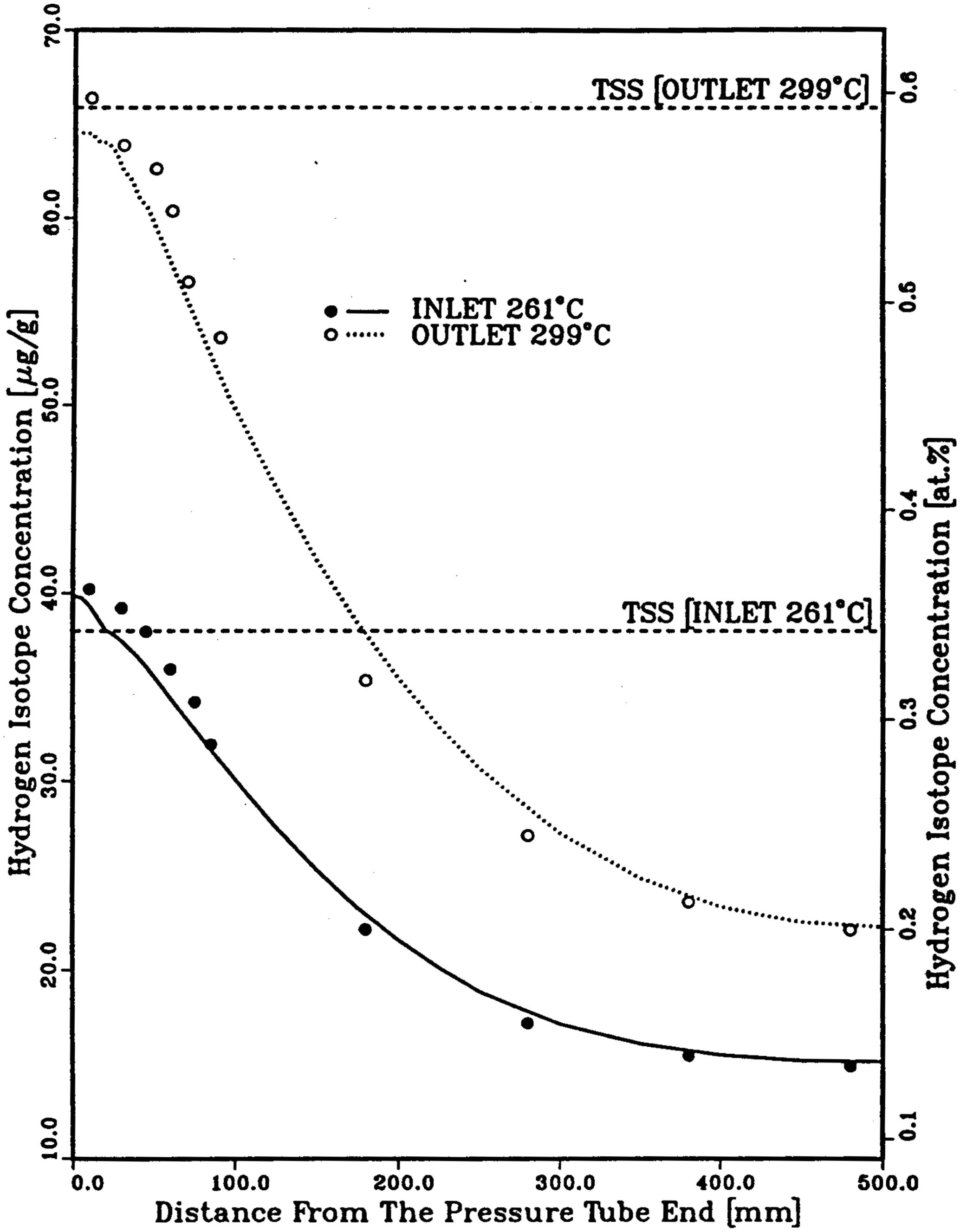


Figure 13: Hydrogen isotope concentration for the inlet and outlet ends of the pressure tube B2K03 showing measured data (symbols) compared to the results of model calculations (curves).

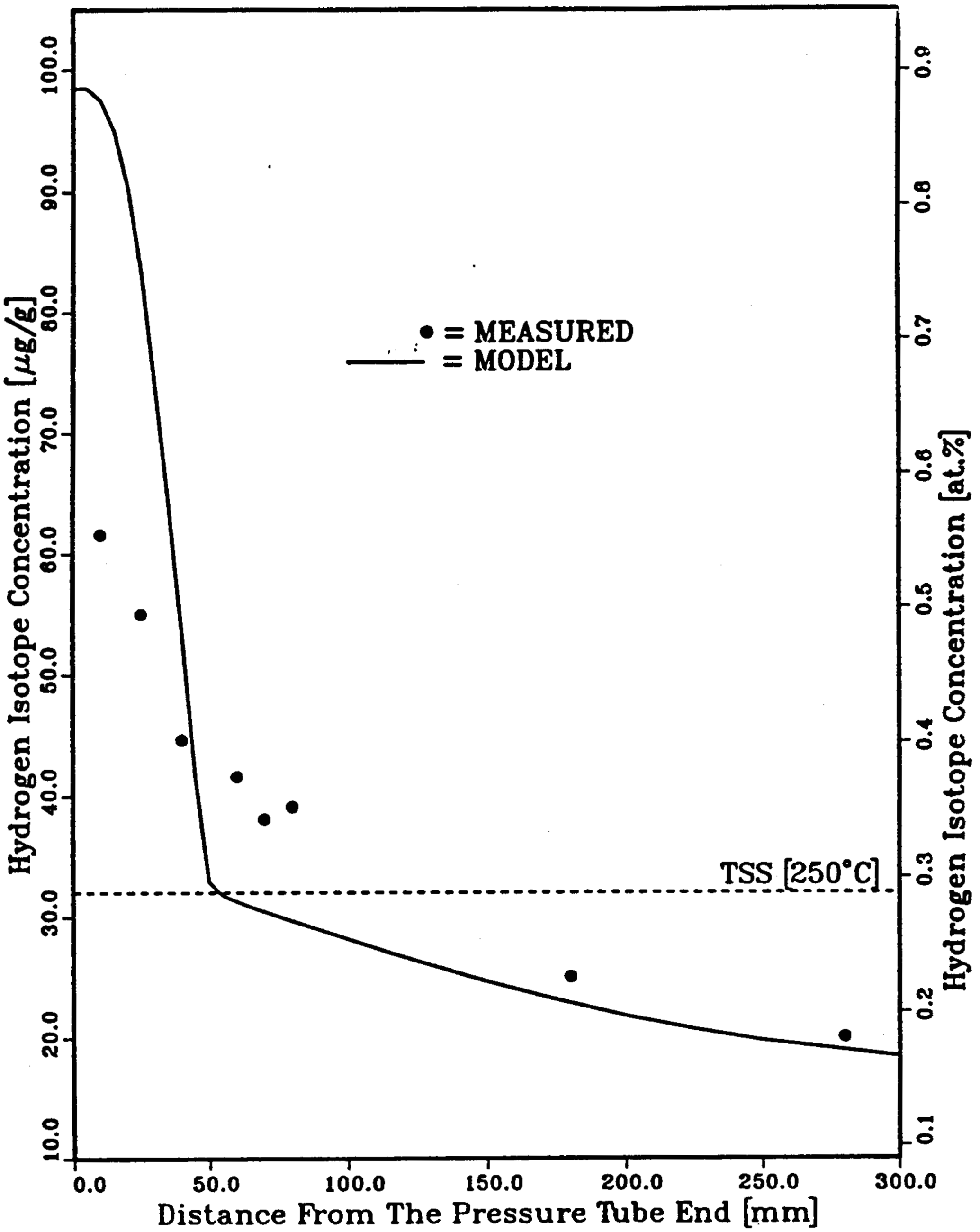


Figure 14: Hydrogen isotope concentration for the inlet end of the pressure tube B2U07 showing measured data (symbols) compared to the results of model calculations (curve).