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# HYDROGEN PICKUP MODELS FOR ZIRCALOY-2, ZIRCALOY-4, M5™ AND ZIRLO™

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**Abstract:** The United States Nuclear Regulatory Commission (USNRC) is currently considering implementing hydrogen based regulations for several accident scenarios such as loss-of-coolant accident (LOCA) and reactivity initiated accident (RIA). Many vendor fuel performance codes do not contain an approved hydrogen pickup model. The NRC steady state fuel performance code, FRAPCON-3.4, currently contains hydrogen pickup models for Zircaloy-2 cladding under boiling water reactor (BWR) conditions and for Zircaloy-4, ZIRLO™, and M5™ cladding under pressurized water reactor (PWR) conditions.

In anticipation of the USNRC using the hydrogen pickup models in FRAPCON-3.4, the models were re-evaluated against current data and any modifications to these models are reported in this paper with standard deviations on the predictions. The BWR hydrogen pickup model is a function of burnup and can be applied in any fuel performance code. The PWR hydrogen pickup models are fractions of the released hydrogen that is picked up by the cladding and is therefore dependent on the corrosion models in FRAPCON-3.4. However, given best-estimate or conservative corrosion predictions, these pickup fractions should yield best-estimate or conservative hydrogen levels.

**Keywords**: hydrogen pickup; FRAPCON; Zircaloy; ZIRLO; M5

## 1. INTRODUCTION

FRAPCON-3.4 (Geelhood et al, 2011a) is the U.S. Nuclear Regulatory Commission (USNRC) steady-state fuel performance code. This code is used by the NRC as a tool to audit vendor fuel performance codes during the licensing of these codes. It is also used to assist USNRC staff in writing regulations, regulatory guides and standard review plans.

Recent assessments of FRAPCON-3.4 (Geelhood et al, 2011b and Geelhood et al, 2009) have concluded that FRAPCON-3.4 provides a best-estimate calculation of fuel performance, including temperature predictions, fission gas release predictions, void volume predictions, cladding corrosion predictions and predictions of cladding hoop strain during power ramps.

Historically, the FRAPCON-3.4 predictions of cladding hydrogen concentration had not been heavily scrutinized because vendor fuel performance codes did not use cladding hydrogen concentration in their comparison of code predictions to any specified acceptable fuel design limits. However, recent evidence has made it clear that hydrogen plays a key role in the embrittlement of zirconium-based cladding alloys and should therefore be well predicted by fuel performance codes in order to assess the condition of the fuel rods following various design basis accidents such as loss-of-coolant accident (LOCA) and reactivity initiated accident (RIA) where the cladding is expected to undergo significant strain.

In order to provide USNRC with best-estimate hydrogen pickup models based on the most recent publically available data, a literature search was conducted to find additional hydrogen concentration data to be combined with the data used to develop the current hydrogen pickup models. All these data will be used to reassess the applicability of the hydrogen pickup models for each cladding alloy in FRAPCON-3.4 and to recalculate the standard error of the code predictions relative to the data. If the data show that any of the current hydrogen pickup models are inadequate for predicting the full data set, then a new model will be proposed and included in the next release of FRAPCON-3.

FRAPCON-3.4 also includes features to evaluate the impact of uncertainty of various models and material properties on the code predictions. These features include pre-programmed values for the standard error for each selected model or material property. The revised standard errors calculated in this study for the hydrogen pickup models will be included in the next release of FRAPCON-3.

## 2. ORIGINAL FRAPCON-3 MODELS

The corrosion and hydrogen pickup models were recently assessed (Geelhood and Beyer, 2008) and updated models were included in FRAPCON-3.4. The hydrogen pickup models that are currently in FRAPCON-3.4 are described below.

For the pressurized water reactor (PWR) cladding, Zircaloy-4, ZIRLO™, and M5™, it was found that the hydrogen content in the cladding can be accurately modeled by using a constant pickup fraction. This fraction is defined as the fraction of the hydrogen that is liberated by the metal-water reaction given in Equation 1 that is absorbed by the cladding.

$$Zr + 2H_2O \rightarrow ZrO_2 + 2H_2 \quad (1)$$

FRAPCON-3.4 uses the following pickup fractions for PWR cladding alloys.

Zircaloy-4 in PWR conditions – 15%
ZIRLO™ in PWR conditions – 12.5%
M5™ in PWR conditions – 10%

The standard errors for the hydrogen concentration in each of these alloys using the pickup fractions above are:

Zircaloy-4 in PWR conditions – 40 ppm
ZIRLO™ in PWR conditions – 162 ppm
M5™ in PWR conditions – 20 ppm

For boiling water reactor (BWR) conditions, a constant hydrogen pickup fraction does not fit the observed hydrogen concentration data. Therefore, FRAPCON-3.4 uses a burnup-dependent hydrogen concentration model. For Zircaloy-2 prior to 1998 (when the vendors did not have tight control over composition and second-phase precipitate particle size), the following equations are used.

$$H_{Tot} = 47.8\exp[-1.3/(1+BU)] + 0.316BU \quad \text{BU<50} \quad (2)$$

$$H_{Tot} = 28.9 + \exp[0.117(BU-20)] \quad \text{BU>50}$$

For modern Zircaloy-2 since 1998 (when the vendors have had tight control over composition and second phase precipitate particle size), the following equation is used

$$H_{Tot} = 22.8 + \exp[0.117(BU-20)] \quad (3)$$

Where:
$H_{Tot}$ = total hydrogen, ppm (wt)
BU = local axial burnup, GWd/MTU

For pre-1998 Zircaloy-2 cladding, the standard error is 10 ppm below 50 GWd/MTU. No data are available to calculate a standard error above 50 ppm. For post-1998 Zircaloy-2 cladding, the standard error is 11 ppm below 49 GWd/MTU and 61 ppm above 49 GWd/MTU.

## 3. DATA COMPARISONS AND MODEL UPDATES

A literature search was conducted to expand the database of hydrogen concentration data that will be used to assess the hydrogen pickup models in FRAPCON-3.4. The hydrogen data that is used in this database consists of measurements of hydrogen performed on a full cladding ring with an associated measurement of oxide thickness. The measurements of hydrogen concentration are made by hot vacuum extraction and as such include all the hydrogen in the cladding including that in the metal and in the oxide. The corresponding oxide thickness measurements are made by metallographic measurements on cladding cross sections or by eddy current measurements. The oxide thickness measurement is used to calculate the hydrogen liberated by the metal-water reaction (Eq. 1) and dividing the measured hydrogen concentration by this quantity results in a hydrogen pickup fraction for that sample.

The following sections describe the addition of new data to those data that had previously been available. The data that had previously been available are combined in this paper as a single data set and are referred to as "original data". These data are described by Geelhood and Beyer (2008).

BWR Zircaloy-2

There was not a large quantity of previously unused Zircaloy-2 data that was found. One previously unused source of Zirclaoy-2 data was from the pre-characterization of BWR Zircaloy-2 rods that were subjected to reactivity-initiated accident (RIA) testing at the NSRR reactor and summarized by Vitanza (2007). Eleven such rods consisting of old Zircaloy-2 (prior to 1998) were discovered and three rods consisting of modern Zircaloy-2 were discovered. In addition, another source of Zircaloy-2 hydrogen data was found (Shimada, 2006). These rods were all subjected to irradiation under controlled water chemistry in an attempt to reduce the hydrogen pickup. These data demonstrate that the use of controlled water chemistry was successful in reducing the hydrogen concentration in Zircaloy-2 relative to other Zircaloy-2 data available. Figure 2 shows these data are below the other modern Zircaloy-2 data.

Figures 1 and 2 show the pre-1998 Zircaloy-2 hydrogen data and the post-1998 Zircaloy-2 hydrogen data. It can be seen from these figures that the additional data lie within the data scatter of the original data used to develop the FRAPCON-3.4 correlations.

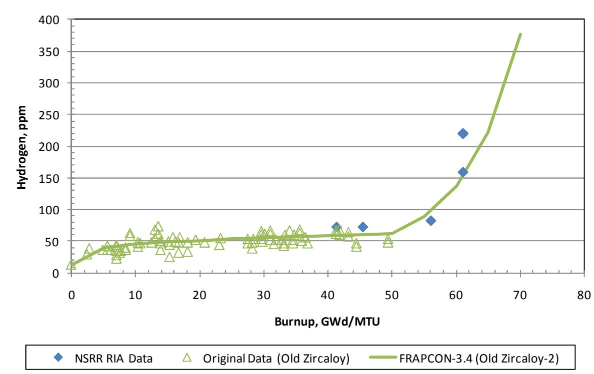


Fig. 1 Hydrogen concentration model and data for pre-1998 Zircaloy-2 cladding under BWR conditions

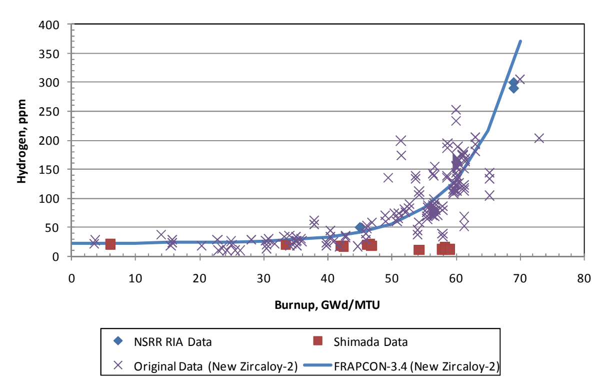


Fig. 2 Hydrogen concentration model and data for post-1998 Zircaloy-2 cladding under BWR conditions

The standard errors of the models relative to all the data are similar after the inclusion of the new data. For pre-1998 Zircaloy-2 cladding, the standard error is 10 ppm below 50 GWd/MTU and 54 ppm above 50 GWd/MTU.

For post-1998 Zircaloy-2 cladding, the standard error is 13 ppm below 49 GWd/MTU and 60 ppm above 49 GWd/MTU.

PWR Zircaloy-4

During the previous assessment of the Zircaloy-4 hydrogen pickup model, there was a significant set of data available that included a measurement of oxide thickness and hydrogen concentration. These data were used to select the hydrogen pickup fraction and calculate a standard error.

During this assessment, substantially more Zircaloy-4 data were found including oxide thickness and hydrogen concentration (Yagnik et al., 2005, Bossis et al., 2005, Lyon, 2005, Garde et al., 2009., Kitagawa et al., 2005, Billone, et al., 2008). Also included is data from the pre-characterization of PWR Zircaloy-4 rods that were subjected to RIA testing at the NSRR reactor and summarized by Vitanza (2007). These data include standard Zircaloy and low tin Zircaloy. Most of these data are from stress-relief annealed (SRA) samples, but there are some data from recrystallized annealed (RXA) samples. One source of data was found from rings with spalled oxide. (Desquines, 2007). These data are not included in this assessment as the hydrogen contained in these rings likely includes some hydrogen that diffused to the area of spallation and is not representative of the amount picked up from the metal water reaction. Hydrogen in cladding with spalled oxide is discussed later in this paper.

The pickup fractions calculated from these measurements are shown in Figure 3. The data below 10 microns of oxide thickness shows a larger scatter than the other data because a small uncertainty in oxide thickness or hydrogen concentration can lead to a larger change in pickup fraction than at a higher oxide thickness. The average of all the data above 10 microns was found to be 15.3%.

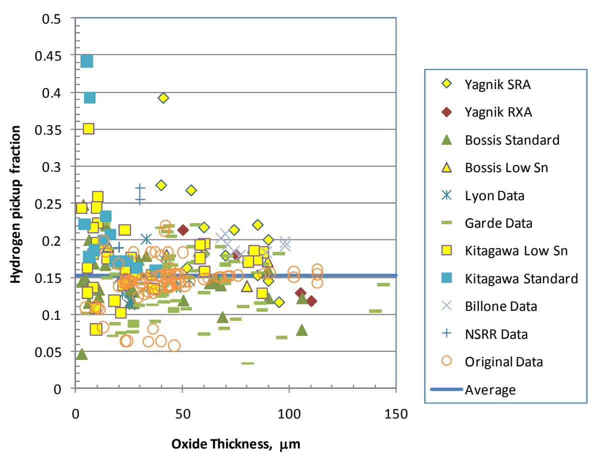


Fig. 3 Hydrogen pickup fraction data for Zircaloy-4 cladding under PWR conditions

Using a pickup fraction of 15.3%, the hydrogen concentration was predicted for each point and compared to the measured hydrogen concentration. A standard error of 94 ppm was calculated. Compared to the values in FRAPCON-3.4, the mean is similar (15% vs. 15.3%) and the standard deviation is greatly increased (40 ppm vs. 94 ppm). The increased standard error is likely due to differences in operation and fabrication. Figure 4 shows the predicted hydrogen using a 15.3% pickup fraction as a function of the measured hydrogen. Also shown is the 2-σ uncertainty bound on the model predictions. This pickup fraction is only applicable for Zircaloy-4 cladding without spalled oxide. However, it is applicable to both standard and low-Sn Zircaloy-4 cladding

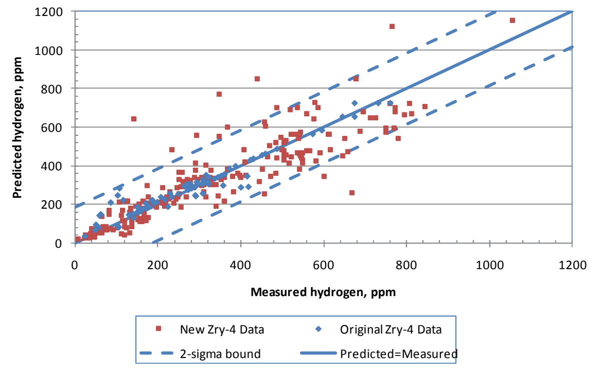


Fig. 4 Predicted Zircaloy-4 hydrogen concentration using a 15.3% pickup fraction as a function of measured hydrogen concentration

PWR ZIRLO™

During the previous assessment of the ZIRLO™ hydrogen pickup model, there was a very limited set of data available that included a measurement of oxide thickness and hydrogen concentration. These data were used to select the hydrogen pickup fraction and calculate a standard error, although the standard error was large, due to the scatter in the data and the small number of samples.

During this assessment, substantially more ZIRLO™ data were found including oxide thickness and hydrogen concentration (Garde et al. 2009, Desquines, 2007, Billone, et al., 2008). Also included is data from the pre-characterization of PWR ZIRLO™ rods that were subjected to RIA testing at the NSRR and Cabri reactors and summarized by Vitanza (2007). NRC also provided some hydrogen data from North Anna ZIRLO™ rods that was measured at Studsvik. These are similar to those rods analyzed by Billone et al. (2008). No oxide spallation was observed for any of these samples.

The pickup fractions calculated from these measurements are shown in Figure 5. The data below 10 microns of oxide thickness shows a larger scatter than the other data because a small uncertainty in oxide thickness or hydrogen concentration can lead to a larger change in pickup fraction than at a higher oxide thickness. The average of all the data above 10 microns was found to be 17.3%.

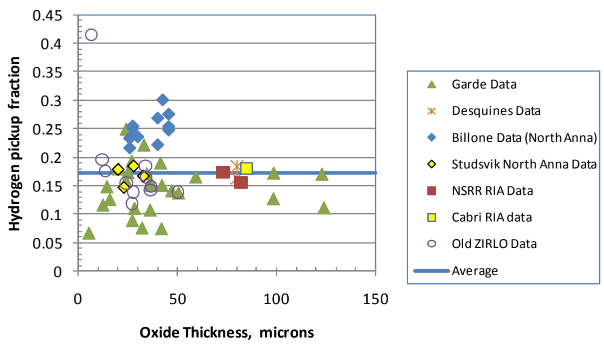


Fig. 5 Hydrogen pickup fraction data for ZIRLO™ cladding under PWR conditions

Using a pickup fraction of 17.3%, the hydrogen concentration was predicted for each point and compared to the measured hydrogen concentration. A standard error of 110 ppm was calculated. Compared to the values in FRAPCON-3.4, the mean is considerable higher (12.5% vs. 17.3%) and the standard deviation is considerably reduced (162 ppm vs. 110 ppm). The revised standard error is similar to that of the Zircaloy-4 data and therefore seems reasonable. Figure 6 shows the predicted hydrogen using a 17.3% pickup fraction as a function of the measured hydrogen. Also shown is the 2-σ uncertainty bound on the model predictions.

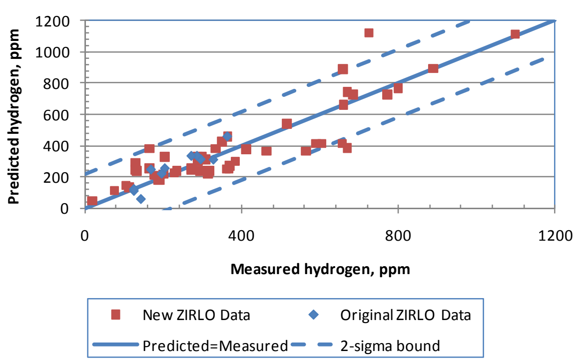


Fig. 6 Predicted ZIRLO™ hydrogen concentration using a 17.3% pickup fraction as a function of measured hydrogen concentration

<u>PWR M5™</u>

During the previous assessment of the M5™ hydrogen pickup model, there were no data available that included a measurement of oxide thickness and hydrogen concentration. Hydrogen data was only presented as a function of burnup. Therefore in order to compare to these data, typical cases were run with FRAPCON-3.4 and the measured and predicted data were compared.

During this assessment, M5™ data were found including oxide thickness and hydrogen concentration (Bossis et al., 2005, Billone, et al., 2008, Chuto et al., 2008). Also included is data from the pre-characterization of PWR M5™ rods that were subjected to RIA testing at the NSRR and Cabri reactors and summarized by Vitanza (2007).

The pickup fractions calculated from these measurements are shown in Figure 7. The data below 10 microns of oxide thickness shows a larger scatter than the other data because a small uncertainty in oxide thickness or hydrogen concentration can lead to a larger change in pickup fraction than at a higher oxide thickness. The average of all the data above 10 microns was found to be 10%.

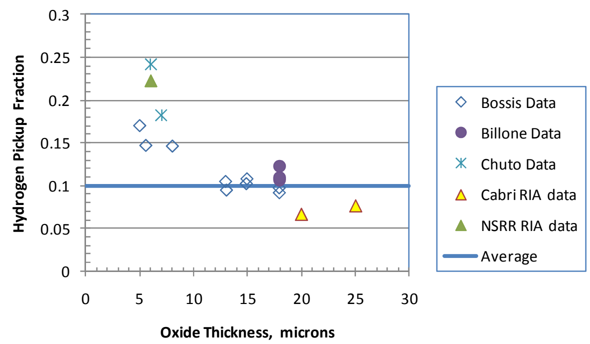


Fig. 7 Hydrogen pickup fraction data for M5™ cladding under PWR conditions

Using a pickup fraction of 10%, the hydrogen concentration was predicted for each point and compared to the measured hydrogen concentration. A standard error of 23ppm was calculated. These values are similar to what was estimated previously for M5™. Figure 8 shows the predicted hydrogen using a 10% pickup fraction as a function of the measured hydrogen. Also shown is the 2-σ uncertainty bound on the model predictions.

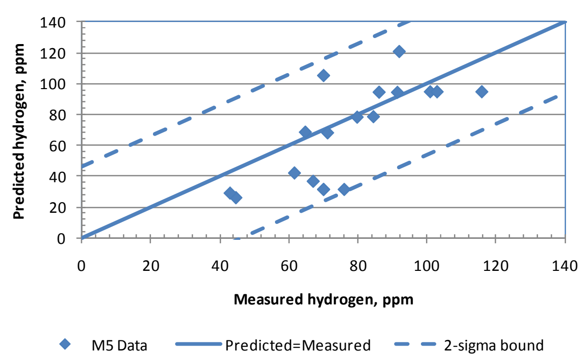


Fig. 8 Predicted M5™ hydrogen concentration using a 10% pickup fraction as a function of measured hydrogen concentration

## 4. DISCUSSION

During the data analysis of the hydrogen data shown in the preceding section, several interesting items were discovered. The first relates to the modeling of hydrogen concentration in cladding with spalled oxide. The second relates to the large localized data scatter observed in ZIRLO™ cladding. Each of these items are discussed in more detail in the following section.

<u>Hydrogen in Zircaloy-4 cladding with spalled oxide or oxide blisters</u>

As mentioned in Section 3, the hydrogen pickup models described in this paper are valid for cladding without spalled oxide. In Zircaloy-4, there have been some observations of oxide spallation when the oxide thickness is between 75 to 110 µm thick. When this occurs, there is often a very dense hydride rim observed in the cladding under the areas where the oxide has spalled. This is attributed to the cladding being slightly cooler in this location and the tendency of hydrogen to diffuse to cooler areas.

As a result of this, very high local hydrogen concentrations are measured in Zircaloy-4 cladding with spalled oxide in the area of spallation. This high hydrogen concentration is not due to higher hydrogen pickup but rather due to diffusion from other axial or radial locations to the cooler area where the oxide has spalled.

Because this process is a diffusion controlled process, there is some kinetic behavior, and it is difficult to predict the local hydrogen concentration without knowing how long the oxide had been spalled off in-reactor.

There was some data sets that contained spalled and non-spalled data (Yagnik et al., 2005, Desquines, 2007)and it was examined to determine if an enhancement in apparent hydrogen pickup fraction could be seen in those samples with spalled oxide and those without. The Yagnik (2005) data used previously in Section 3 had hydrogen concentration taken at axial locations away from the spalled oxide. The data shown here uses the hydrogen concentration at the location of spallation.

The Desquines (2007) data show an enhancement in the hydrogen with and without oxide spallation, but the Yagnik (2005) data do not. No clear trend between these data sets could be determined for calculating hydrogen concentration in samples with spalled oxide, but it is noted to be greater than the 15.3% pickup fraction calculated for Zircaloy-4 without oxide spallation.

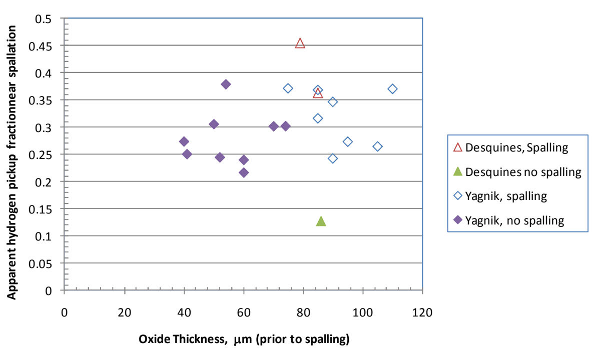


Fig. 9 Apparent hydrogen pickup fraction at location of spalling compared to rods with no spalling from same Zircaloy-4 data set

Hydrogen scatter in ZIRLO™ cladding

In the original FRAPCON-3.4 hydrogen pickup models, the ZIRLO™ model had a much greater standard error than the other PWR alloys (162 ppm for ZIRLO™ compared to 40 ppm for Zircaloy-4 and 20 ppm for M5™). This was originally attributed to the small number of ZIRLO™ data (11 ZIRLO™ data points vs. 92 Zircaloy-4 data points). Increasing the number of ZIRLO™ data resulted in considerably reducing the uncertainty such that with 61 ZIRLO™ data points and 295 Zircaloy-4 data points, the standard errors of the models are closer (110 ppm for ZIRLO™ and 94 ppm for Zircaloy-4).

However, even after reducing the uncertainty by adding more data, it appears that ZIRLO™ has a larger variation in hydrogen concentration than the other PWR alloys. For example, Figure 5 shows hydrogen pickup fractions on samples from North Anna rods taken from the same lead test assembly (LTA) (diamond symbols) measured at Argonne National Lab (Billone et al., 2008) and at Studsvik. Figure 10 shows that the hydrogen pickup fraction can vary between 15% to 30% in rods from the same assembly.

Figure 10 shows the hydrogen pickup fraction from the North Anna rods measured by Billone et al. (2008) and those measured at Studsvik as a function of axial elevation. The hydrogen measured by Billone et al. (2008) was taken by cutting a cladding ring into four quarters and performing a hydrogen measurement on each quarter. The value reported is the average of four measurements and a plus/minus value representing the maximum and minimum measurements for the quarters is reported. This is an indication of the circumferential variation in hydrogen. The error bars in Figure 10 represent these maxima and minima. Circumferential variation is not available for the Studsvik North Anna data.

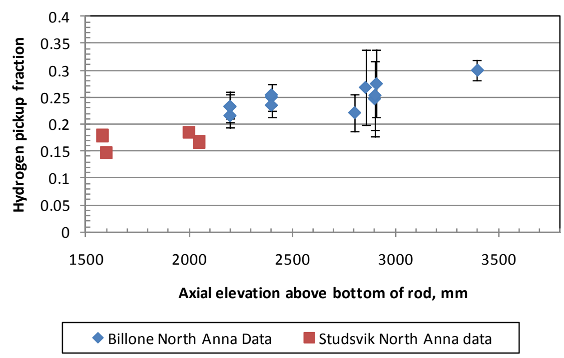


Fig. 10 Hydrogen pickup fraction as a function of axial elevation for ZIRLO™ North Anna rods. Error bars represent circumferential variation within each sample.

Figure 10 indicates that the average pickup fraction of ZIRLO™ increases with increasing elevation for the North Anna LTA rods. However, the circumferential variation in these rods is about the same magnitude as observed increase with axial elevation. None of these measurements were made on cladding under a grid spacer, so there should be no circumferential temperature gradient from the spacer.

If hydrogen pickup was found to be dependent on axial elevation, it would indicate that there is a temperature effect on the hydrogen pickup fraction since the coolant temperature increases with increasing elevation. Unfortunately, the other ZIRLO™ data in Figure 5 is not correlated to axial elevation and as seen in Figure 5, the Billone (2008) data seems biased higher than the rest of the ZIRLO™ data. Nevertheless, these data indicate that the hydrogen concentration in ZIRLO™ is more sensitive to local variations than Zircaloy-4.

## 5. SUMMARY

Table 1 shows a summary of the hydrogen models that are in FRAPCON-3.4 and the updates that have been made based on the expanded data comparison. The new models and uncertainties will be included in the next version of FRAPCON-3.

Table 1 Hydrogen models in FRAPCON-3.4 and new model

| Alloy | FRAPCON-3.4 | | New Model | |
|---|---|---|---|---|
| | Model | Std. dev. | Model | Std. dev. |
| **BWR** | | | | |
| Zry-2 pre 1998 | Eq. 2 | 10 ppm[1]<br>NA[2] | Eq. 2 | 10 ppm[1]<br>54 ppm[2] |
| Zry-2 post 1998 | Eq. 3 | 11 ppm[1]<br>61 ppm[2] | Eq. 3 | 13 ppm[1]<br>60 ppm[2] |
| **PWR** | | | | |
| Zry-4 | 15%[3] | 40 ppm | 15.3%[3] | 94 ppm |
| ZIRLO™ | 12.5%[3] | 162 ppm | 17.3%[3] | 110 ppm |
| M5™ | 10%[3] | 20 ppm | 10%[3] | 23 ppm |

[1] standard deviation below 50 GWd/MTU
[2] standard deviation above 50 GWd/MTU
[3] pickup fraction

## 6. CONCLUSIONS

Recent evidence has made it clear that hydrogen plays a key role in the embrittlement of zirconium-based cladding alloys and should therefore be well predicted by fuel performance codes in order to assess the condition of the fuel rods following various design basis accidents such as LOCA and RIA where the cladding is expected to undergo significant strain. In order to provide NRC with best estimate hydrogen pickup models based on the most recent publically available data, a literature search was conducted to find hydrogen concentration data to be combined with the data used to develop the current hydrogen pickup models. All these data were used to reassess the applicability of the hydrogen pickup models for each cladding alloy in FRAPCON-3.4 and to recalculate the standard error of the code predictions relative to the data.

The data showed a need to increase the hydrogen pickup model for ZIRLO™ cladding from 12.5% to 17.3%. The models for the other cladding alloys were acceptable. In addition the standard error for the Zircaloy-4 hydrogen predictions was increased from 40 ppm to 94 ppm and the standard error for the ZIRLO™ hydrogen predictions was decreased from 162 ppm to 110 ppm. The previous standard errors for the other cladding alloy models were similar to those previously calculated.

These hydrogen pickup models are not acceptable for predicting hydrogen concentration in cladding with spalled oxide.

## REFERENCES


[1] Billone, M., et al., 2008, *Cladding Embrittlement During Loss-of-Coolant Accidents*, NUREG/CR-6967, ANL-07/04.

[2] Bossis, P., et al., 2005, ASTM-STP 1467, pp. 494-525.

[3] Chuto et al., 2008, Nuclear Engineering and Technology, Vol. 41, No. 2, pp 163-170.

[4] Desquines, J., et al., 2007, *Release of the PROMETRA V2.5 material database (Zircaloy-4, ZIRLO, M5)* IRSN 2007-95.

[5] Garde, A.M., el al., 2009, *Hydrogen Pick-Up Fraction for ZIRLO™ Cladding Corrosion and Resulting Impact on the Cladding Integrity*, Proceedings of Top Fuel 2009, Paris, France, September 6-10, 2009.

[6] Geelhood, K.J., et al., 2011a, *FRAPCON-3.4: A Computer Code for the Calculation of Steady-State, Thermal-Mechanical Behavior of Oxide Fuel Rods for High Burnup*, NUREG/CR-7022, Vol. 1, PNNL-19418, Vol. 1.

[7]. Geelhood, K.J., et al., 2011b, *FRAPCON-3.4: Integral Assessment*, NUREG/CR-7022, Vol. 2, PNNL-19418, Vol. 2.

[8] Geelhood, K.J., et al., 2009, *Predictive Bias and Sensitivity in NRC Fuel Performance Codes*, NUREG/CR-7001, PNNL-17644.

[9] Geelhood, K.J. and C.E. Beyer, 2008, *Corrosion and Hydrogen Pickup Modeling in Zirconium Based Alloys*, 2008 Water Reactor Fuel Performance Meeting, October 19~23, 2008, Seoul, Korea.

[10] Kitaguawa, K., et al., 2005, *Post Irradiation Examination of Fuel Rods in 55GWd/t Lead Use Assembly*, Proceedings of 2005 Water Reactor Fuel Performance Meeting, October 2-6, Kyoto, Japan.

[11] Lyon, W.F., 2005. *US-PWR 16x16 LTA Extended Burnup Demonstration Program*, NEA-1738/01.

[12] Shimada, S. et al., 2006, J. of Nuclear Science and Technology, Vol. 43, No. 9, pp. 1021-1030.

[13] Vitanza, C., 2007. Nuclear Engineering and Technology, Vol. 39, No. 5, pp. 591-602.

[14] Yagnik S.K., et al., 2005, ASTM-STP 1467, pp. 604-631.