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Authors's reply to 'Generation of surface degraded layer on austenitic stainless steel piping exposed to flowing sodium in a loop: inter comparison of long term exposure data', by S. Rajendran Pillai

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Abstract

This is an elaborate author's reply to a comment 'Generation of surface degraded layer on austenitic steel piping exposed to flowing sodium in a loop: inter comparison of long term exposure data' by S. Rajendran Pillai appearing in this proceedings. The basic misunderstanding as seen in the above comment about the mass loss due to sodium exposure, which is reflected throughout the above comment, has been explained in detail in this reply for better understanding of the phenomenon. It is precisely mentioned and understood that Thorley and Tyzack model deals with complete mass loss and not mere degradation. The total mass loss corresponds to mass loss due to wall thinning and that due to degraded layer formation. Though Thorley and Tyzack model is the most pioneering model in the field of sodium corrosion, the inadequacies of this model for materials without molybdenum such as SS 304 with very long exposure in sodium is clearly brought out in this paper. This model has been successfully applied to calculate life of clad tubes, which have relatively short stay in reactor core. Yoshida models are highlighted and compared with our experimental results. Yoshida models are not valid below certain durations owing to the empirical nature of such expressions. Thorley and Tyzack model can be used for SS 316 LN as this alloy contains molybdenum and nitrogen both of which imparts corrosion resistance in sodium. What is required is that one needs to establish the extent to which this model can be applied for materials exposed to high temperatures and very long durations. The details are discussed in this reply.

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1. Introduction

There is a basic misunderstanding about the mass loss due to sodium exposure, which is reflected throughout the manuscript submitted by Pillai [1]. During steady state corrosion, in addition to wall thinning, there will always be some mass loss arising due to degraded layer. This mass loss depends on the degraded layer width. The corrosion rates of austenitic stainless steels, under otherwise identical conditions, are significantly influenced by the dissolved oxygen in liquid sodium. This can be seen from the expression derived by Thorley and Tyzack [2] relating the oxygen content in sodium to the corrosion rate of austenitic stainless steels under high velocity conditions. The expression is given below

$$\mathrm{Log}S = 2.44 + 1.5 \times \log(\mathrm{O}) - 18\,000/(2.3 \times RT),$$

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where S is the rate of metal loss (in./1000/yr), O is the oxygen concentration (ppm) and T is the temperature of sodium (K).

2. Our comments

It is precisely mentioned and understood that Thorley and Tyzack model [2] deals with complete mass loss and not mere degradation. The total mass loss corresponds to mass loss due to wall thinning and that due to degraded layer formation. Both chromium and nickel leach out from stainless steel. When nickel content is <5%, the degraded layer is called a 'ferrite layer'. There is preferential leaching of chromium owing to its solubility in sodium as well as oxygen enhanced leaching by forming $NaCrO_2$. In the case of nickel, since no ternary oxide is formed, corrosion is determined by elemental solubility and diffusion from the stainless steel matrix to sodium interface. For lower temperature and shorter duration of exposure, the wall thinning is predominant with negligible contribution from the degraded layer since the metal loss from the degraded layer is diffusion assisted. It is well known that the wall thinning is difficult to measure accurately (±1 μm). The calculated layer width represents not only the contribution due to wall thinning but that due to degraded layer also. However, the experimentally observed data [3] correspond only to the degraded layer. Hence, if one adds the wall thinning contribution also, the total layer width would be still higher than what is presented in Table 3 in Ref. [3]. This implies that the calculated layer width based on Thorley and Tyzack model, would still be much less than the total layer width (wall thinning + degraded layer). In the initial stages of corrosion, the degraded layer contribution to mass loss is less and during steady state corrosion (at higher temperature and longer durations) the contribution due to degraded layer would be substantial. This again further confirms our analysis that Thorley and Tyzack model underestimates the corrosion loss for higher duration of the order of 100 000 h or more, which is normally observed during the life of sodium systems. Since it is basic and simple understanding that the calculated layer width (calculated using Thorley and Tyzack model) corresponds to wall thinning and degraded layer, the same was not explicitly mentioned in our earlier paper [3]. Nevertheless, the inference drawn from the experimental results, goes further to support the inference that the observed layer widths are much larger compared to those calculated based on Thorley and Tyzack model.

Suppose the wall thinning is measured accurately (say x μm), then this need to be added to the experimental degraded layer to get the total corrosion. As stated earlier, the metal loss contribution due to wall thinning will comparatively be higher than that due to degraded layer in the initial stages of corrosion. However, for long durations (as encountered during system life time), the metal loss due to degraded layer could be comparable to that due to wall thinning since we observe fairly thick degraded layer.

The data of Thorley and Tyzack is substantiated and supported by Borgstedt for laboratory experiments [4] and corresponds to materials with relatively shorter service in sodium. The results given in our earlier paper [3] are based on specimens taken from sodium loop after very long exposure of the order of 80 000 and 100 000 h and clearly indicate that the layer widths are much more than that calculated using this model.

The formation of corrosion resistant nodes and the role of molybdenum in corrosion resistance are already discussed in detail by Shiels et al. [5], Fukutomi et al. [6], and Kolster and Bos [7]. We further substantiated and supported their analysis and conclusions based on our results. According to Shiels et al. [5], alloys without molybdenum leach out faster as in such cases, corrosion resistant nodes are not formed and they develop porosities. Molybdenum plays an important role in forming corrosion resistant nodes. The metal loss is not same in all the stainless-steels. In the case of Mo containing alloy, there is reduced rate of metal loss due to corrosion resistant nodes formation. This is confirmed in our results too by the micorcavities formed in SS 304 due to prolonged exposure to sodium and thermal aging.

Table 1
Rate of metal loss in sodium, calculated using Thorley and Tyzack model

T (K)	Metal loss	Oxygen (ppm)				
		1	2	3	5	10
773	μm/1000 h	0.693×10^{-2}	1.992×10^{-2}	3.660×10^{-2}	7.870×10^{-2}	2.230×10^{-1}
	$g/(m^2\,h)$	0.054×10^{-3}	0.156×10^{-3}	0.286×10^{-3}	0.616×10^{-3}	1.743×10^{-3}
873	μm/1000 h	2.640×10^{-2}	7.555×10^{-2}	1.388×10^{-1}	2.986×10^{-1}	8.446×10^{-1}
	$g/(m^2\,h)$	0.206×10^{-3}	0.591×10^{-3}	1.086×10^{-3}	2.340×10^{-3}	6.610×10^{-3}
973	μm/1000 h	7.610×10^{-2}	2.218×10^{-1}	4.001×10^{-1}	8.610×10^{-1}	2.435
	$g/(m^2\,h)$	0.595×10^{-3}	1.710×10^{-3}	3.130×10^{-3}	6.739×10^{-3}	1.906×10^{-2}

Sodium velocity = 4–6 ms^{-1}.

Thus it is obvious that the comparison of corrosion data from materials such as SS 304 and SS 316, as presented in Table 1 of Pillai's paper [1] is incorrect.

3. Application of Thorley and Tyzack model to calculate the life of clad tubes

This model has successfully been applied to calculate the life of clad tubes [8], which have relatively short stay in reactor core. The rate of metal loss was calculated at temperatures 773, 873 and 973 K for various oxygen contents in sodium ranging from 1 to 10 ppm, using the corrosion model by Thorley and Tyzack as shown in Table 1. Since extrapolation and application of experimental results towards prediction of lifetime of nuclear components is the ultimate objective of these types of studies, an attempt was made to predict the lifetime of AISI type 316 SS and D9 alloy (modified austenitic stainless steel) using the generally accepted corrosion model. The Thorley and Tyzack model is found to be valid experimentally and is also recommended in literature as the most suitable model for extrapolation and application of experimental results to predict the lifetime of various components in nuclear power plants [4]. Using this model, theoretical predictions for lifetime of stainless steels AISI type 316 and D9 alloy clad tubes have been made for long term exposure in the temperature range from 773 to 973 K in dynamic sodium (4–6 ms^{-1} velocity) containing 2–10 ppm of oxygen. Wall thickness of 370 μm for stainless steel AISI type 316 SS and 430 μm for D9 alloy clad tubes have been used in the calculations. Allowing 10% loss (wall thinning + degraded zone) as maximum permissible for clad tubes, lifetime predictions were made and the results are presented in Table 2.

With increase in oxygen content from 1 to 10 ppm, at 773 K, the life of stainless steel AISI type 316 clad tubes decreases from 610 to 19 years and that of D9 alloy clad tubes decreases from 708 to 22 years. Similarly at 973 K, the lifetime decreases with increase in oxygen content from 1 to 10 ppm in sodium, from 56 to 1.7 years for SS 316 clad tubes and from 65 to 2 years for D9 alloy clad tubes.

4. Comparison with Yoshida et al. results

Yoshida et al. [9] have come out with empirical relations, based on their experimental results, between degraded layer width in SS 304 and duration of exposure in sodium for three different temperatures (773, 823 and 873 K for durations ranging from 10 000 h to 90 000 h). In Table 3 (Table 1 in Pillai's manuscript [1]), experimental degraded layer widths of Vaidehi Ganesan et al. and Pillai et al. are compared with results reported by Yoshida. It is well known that corrosion of materials by sodium depends on the nature of material being tested, sodium temperature, time of exposure, velocity of sodium and oxygen content. However, it is to be noted that the conditions of testing in all the three cases are different as shown in the Table above. Thus direct comparison of corrosion results for different materials under different experimental conditions, as indicated by Pillai [1], is not valid.

Oxygen content in sodium plays a major role in determining metal loss due to sodium exposure. This is also evident from Thorley and Tyzack model. The

Table 2
Lifetime of clad tubes predicted using Thorley and Tyzack model

T (K)	Specimen	Life time (years)				
		Oxygen (ppm)				
		1	2	3	5	10
773	SS 316L FBTR	609.5	212.0	115.4	53.6	19.0
	D9 PFBR	708.3	246.6	134.1	62.3	22.0
873	SS 316L FBTR	160.0	55.9	32.8	14.5	5.0
	D9 PFBR	185.9	65.0	35.4	16.4	5.8
973	SS 316L FBTR	55.5	19.4	10.6	4.9	1.7
	D9 PFBR	64.5	22.5	12.3	5.7	2.0

Table 3
The experimental conditions of corrosion experiments reported

	Material	Oxygen content (ppm)	Na velocity (ms^{-1})
Yoshida et al. [9]	SS 304	<10	0.3–1
Pillai et al. [1]	SS 316	2	5
Vaidehi Ganesan et al. [3]	SS 304	1–2	4

observed lower value for the degraded layer due to sodium exposure compared to that of Yoshida et al. is mainly due to the low oxygen content (1–2 ppm) in our studies [3]. But in Pillai's study [1], the material is SS 316 with sodium velocity of 5 ms^{-1} and oxygen content of <2 ppm. If the same logic holds good namely, oxygen in sodium plays a major role in deciding the metal loss and subsequent degraded layer and molybdenum present in the alloy (as in SS 316) is responsible for the reduced metal loss owing to the formation of corrosion resistant nodes, Pillai's results should show lesser degraded layer width compared to Yoshida, though in Pillai's experiments, the velocity is high.

It is interesting to find that comparison of our results [3] with that of Pillai (velocity is comparable, oxygen is same, only the material is different) shows higher degraded layer (10–15 μm) for SS 316 for 823 K for relatively shorter exposure of 16 000 h compared to 12–15 μm reported by Vaidehi Ganesan et al. for material exposed at 823 K for 80 000 h as given in Table 1 in Ref. [1]. According to Table 1 in Pillai's paper [1], when the materials are different (SS 304 and SS 316), sodium velocity is different (1 and 5 ms^{-1}) and oxygen content is different (<10 and <2 ppm), the degraded layer widths of Yoshida et al. and Pillai et al. are comparable. This is to be explained. In Yoshida's paper [9], empirical relations, based on their experimental observation, between surface degraded layer and sodium exposure time for type 304 SS are reported. According to these relations, for materials exposed to sodium at 823 K, below 5800 h, the degraded layer is to be taken as zero while in actual experimental results, it is not so. These relations are valid only above certain durations (5800 h). Actually in our experiments we have observed for D9 alloy exposed to sodium at 773 K for 500 to 1000 h durations, the degraded layer width is 1.5–2.5 μm as reported in Table 5 of our earlier paper [3] although as per Yoshida's data for 773 K, below 5775 h no degraded layer should be formed. This only indicates the empirical nature of such expressions, which should not be considered for rigorous comparison of results.

If the (wall thinning + degraded layer), due to Na exposure is more than 10% of the original dimension of the thickness of the components, then we can assume, the life of the component is nearing to an end and it is not advisable to use the component for service further. If the Thorley and Tyzack model, as stated by Pillai, does not take mass loss due to degraded layer at all into consideration, then it is not advisable to use the model for life prediction. But Borgstedt has reported Thorley and Tyzack model (for oxygen content 2–9 ppm) as the best model in agreement with their experimental results in fast flowing sodium (tests at 873 and 973 K, up to 10 000 h, velocity 5 ms^{-1}, oxygen level 3.5–8.9 ppm) and recommended this model for extrapolation of steady state corrosion to long durations [4]. Steady state corrosion means there is definite degraded layer and also associated mass loss due to the same.

As mentioned earlier, during sodium corrosion, both nickel and chromium are depleted. Pillai [1] has mentioned that the surface degraded layer is predominantly a contribution of selective leaching of nickel and to some extent chromium. This is incorrect as chromium leaching is assisted by oxygen present in sodium. The degraded layer is due to the depletion of nickel and chromium [10]. The surface composition of a stainless steel specimen exposed to high velocity sodium at 1028 K for 2500 h is Fe = 96%, Cr = 3.5% and Ni = 0.5% [10].

5. Conclusions

It is necessary to add the loss in wall thickness due to sodium exposure to the experimentally observed degraded layer to arrive at total loss for materials exposed to long duration. Since such data are not available and is difficult to determine, the available experimentally observed degraded layer width was compared with the calculated layer width. Even in the absence of data on loss in wall thickness, it was possible to clearly bring out the inadequacies of Thorley and Tyzack model for materials without molybdenum such as SS 304 with very long exposure in sodium. This model can still be applied to all austenitic stainless steels exposed to sodium for relatively shorter duration. The applicability of this model for austenitic stainless steels containing molybdenum (SS 316, D9 alloy, etc.) for longer duration and higher temperatures in sodium systems needs to be established experimentally. The effect of molybdenum on corrosion resistance is brought out based on experimentally observed results, which is in-line with the findings cited in the literature. In Pillai's paper [1] the results are compared with the empirical relationship reported by Yoshida et al. [9]. It is observed that the empirical relationships for materials exposed at 773, 823 and 873 K are not valid for durations less than 5775, 5800 and 2895 h, respectively.

We do not anticipate any problem in applying Thorley and Tyzack model for SS 316 LN as this alloy contains molybdenum and nitrogen both of which give corrosion resistance in sodium. We do agree that Thorley and Tyzack model is the most pioneering and still the most reliable model for predicting corrosion of austenitic steels containing molybdenum. However, it is necessary to establish the applicability of this model experimentally for longer durations and higher temperatures. If, as stated by Pillai, the Thorley and Tyzack model does not take into account mass loss due to degraded layer at all, then again it is not advisable to use the model for prolonged exposure at high temperatures and life prediction. But the model is recommended for life prediction analysis. What is required is that one needs to establish the extent to which this model can be applied for materials exposed to high temperatures and very long durations.

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