

# Generation of surface degraded layer on austenitic stainless steel piping exposed to flowing sodium in a loop: intercomparison of long-term exposure data

S. Rajendran Pillai

*Corrosion Science and Technology Division, Materials Characterization Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603102, Tamil Nadu, India*

Received 14 November 2003; accepted 23 February 2004

## Abstract

Exposure of austenitic stainless steels to high temperature sodium causes leaching of the constituent elements. Different elements are leached to different extent on account of the difference in their solubility in sodium. Nickel is having the highest solubility and hence would be leached out preferentially. The leaching of nickel causes the destabilization of the austenite and promote the generation of ferrite phase. The layer containing ferrite is referred to as 'surface degraded layer'. This layer may have undergone the leaching of other elements like chromium also. The paper compares the thickness of surface degraded layer reported by different investigators. An ambiguity in the literature in explaining the observed corrosion behaviour and need to distinguish between complete metal loss and generation of degraded layer has been clarified in this paper.

© 2004 Elsevier B.V. All rights reserved.

## 1. Introduction

In general, the exposure of stainless steel to high temperature sodium brings about four modes of corrosion [1]. The consequences are considered to be the same for all the grades of austenitic stainless steel of comparable composition.

- (i) Thinning of the wall due to complete loss of material by leaching.
- (ii) Preferential leaching of the elements leading to the generation of surface modified layer of altered chemical composition and inferior mechanical strength.
- (iii) Formation of carburized/decarburized austenite layer, the depth of which depends on the duration of exposure, the temperature and the activity of carbon in sodium. Nitridation/denitridation would

also play a role if the steel exposed contains significant concentration of nitrogen (such as in the case of 316 LN SS).

- (iv) Precipitation of carbides in the matrix brought about by thermal effects. Nitrides also would form the corresponding precipitate if the steel contained nitrogen.

The dependence of oxygen on the corrosion of stainless steel exposed to sodium has been well studied. On the other hand, the exact role of carbon promoting or inhibiting material loss is not clearly documented. Carbon forms a carbide and try to form a role in the leaching kinetics. In all the austenitic grades of stainless steels, the main carbide former is chromium. In the case of molybdenum-containing alloy, the reduced rate of metal loss is attributed to the generation of corrosion resistant nodes [2].

This paper compares the data on thickness of degraded layer reported in the literature by different investigators.

*E-mail address:* [srp@igcar.ernet.in](mailto:srp@igcar.ernet.in) (S. Rajendran Pillai).

## 2. Analysis of data in the literature

### 2.1. Yoshida et al. [3]

In basic research, the test duration are in the range of 10 000–20 000 h. However, the operational life of a nuclear reactor is much higher. Hence the structural material of the experimental loop was analyzed to produce precious data about real long-term interaction of sodium and stainless steel. These authors analyzed pipe materials of 304 SS that were in operation in a loop for nearly 100 000 h. They have found that the thickness of the degraded layer ( $Y$ ) can be related to the temperature and duration of exposure ( $t$  is the time in h) by the following expressions:

$$873 \text{ K}; \quad Y = -112.5 + 32.5 \log_{10}(t), \quad (1)$$

$$823 \text{ K}; \quad Y = -97.1 + 25.8 \log_{10}(t), \quad (2)$$

$$773 \text{ K}; \quad Y = -64.7 + 17.2 \log_{10}(t). \quad (3)$$

The velocity of sodium in the loop was maximum of 1 m/s. Oxygen content of sodium was maintained to less than 10 ppm.

### 2.2. Ganesan et al. [4]

These authors analyzed specimens from a loop construction material. The material of construction was corresponding to the AISI equivalent of 304 SS. The loop has been operated for 80 000 h before deciding to dismantle. However, they have compared the thickness of the surface degraded layer with that obtained by employing equation suggested by Thorley and Tyzack [5]. The equation proposed by Thorley and Tyzack is given by,

$$\log_{10} S(\text{mil/a}) = 2.44 + 1.5 \log_{10} [\text{O}] - 75312/(2.3RT). \quad (4)$$

Here [O] is the concentration of oxygen in sodium in PPM;  $R$  the gas constant in  $\text{J K}^{-1} \text{mol}^{-1}$ ;  $T$  the temperature (K); 1 mil = 25  $\mu\text{m}$ .

This equation evaluates the complete loss of material and not the thickness of the retained 'surface degraded

layer'. As such Ganesan et al. have not measured the thickness of the layer lost. The corroded layer they have observed can only be compared with the surface degraded layer for which Eq. (4) cannot be employed. On the other hand the data obtained by Ganesan et al. [4] can be compared to similar data obtained by Yoshida et al. [3] based on the Eqs. (1)–(3) and given in Table 1.

Pillai et al. [1] analyzed the generation of degraded layer by optical and scanning electron microscopy on specimens of 316 SS exposed to sodium at 823 K for 16 000 h. In this loop the velocity of sodium was 5 m/s and the oxygen content was maintained to less than 2 ppm by cold trapping. The data obtained is in fair agreement with that estimated by employing the equation of Yoshida et al. [3] and also compared in Table 1 above.

The above comparison of data in Table 1 should be considered as reasonably agreeing when one takes into account the factors that influence sodium corrosion. Factors influencing corrosion by sodium are;

- (i) flow rate;
- (ii) area ratio of hot and cold zones;
- (iii) maximum temperature of the loop, and
- (iv) contents of non-metals such as oxygen and carbon in sodium.

Ganesan et al. [4] have obtained the thickness of the surface degraded layer. As evident from Table 1, the thickness of the layer is 2–3 times lesser than that obtained by employing the equation of Yoshida et al. This variation could be attributed to possible difference in the chemistry of sodium and the operational parameters of the loop, especially for a very long duration.

However, Ganesan et al. [4] have compared the data on thickness of the 'surface degraded layer' with that of complete material loss proposed by Thorley and Tyzack [5] (Eq. (4)). This comparison is not relevant as Eq. (4) refers only to complete loss of material and should not be used for estimation of surface degraded layer. The difference obtained was 4–5 times higher (Table 3 in Ref. [4]) which is the result of wrong comparison.

In the original work of Thorley and Tyzack [5] it was stated that Eq. (4) is valid for oxygen content in the range of 5–100 ppm. Borgstedt [6], based on experiments in a sodium loop has proposed the validity of this

Table 1  
Comparison of thickness of surface degraded layer on stainless steel exposed to sodium in the loop

Duration and temperature	Thickness of surface degraded layer ( $\mu\text{m}$ )		
	Yoshida et al. [3]	Ganesan et al. [4]	Pillai et al. [1]
80 000 h at 823 K	29.4	12–15	–
80 000 h at 823 K + 20 000 h at 873 K	56.7	18–20	–
16 000 h at 823 K	11.4		10–15

equation to be sustained in the oxygen content range 2–9 ppm. In the study reported by Ganesan et al. the oxygen content was in the range of 1–2 ppm and as such forms yet another reason why the comparison and criticism of Thorley and Tyzack equation is not relevant. In fact, Eq. (4) is widely employed in estimating the complete loss of material when austenitic steels are exposed to sodium.

### 3. Conclusion

- (i) Thorley and Tyzack model provides still the most relevant expression to estimate the loss in thickness due to exposure to sodium.
- (ii) The surface degraded layer is predominantly a contribution of selective leaching of nickel and to some extent chromium. By analyzing sodium pipes of loops we get only this data and not the data on complete loss in thickness.
- (iii) For new austenitic alloys such as AISI 316 LN SS, rigorous experimental programme are required to arrive at an equation in the same line as Thorley and Tyzack's experiment. If such an effort is not forthcoming we still have to depend on the equation

proposed by Thorley and Tyzack which is pioneering and still the most reliable contribution in the aspect of corrosion.

### References

- [1] S.R. Pillai, H.S. Khatak, J.B. Gnanamoorthy, *Mater. Trans. JIM* 39 (1998) 370.
- [2] C.B. Shiels, A.R. Keeton, R.E. Witkowski, R.P. Anantamula, in: J.M. Dahlke (Ed.), *Proceedings of Second International Conference on Liquid Metal Technology in Energy Production*, CONF-8004001-P1, Richland, Washington, 1980, p. 7.
- [3] E. Yoshida, S. Kato, Y. Wada, in: H.U. Borgstedt (Ed.), *Proceedings of LMS-II*, Forshunszentrum, Karlsruhe, Plenum, New York, 1993, p. 55.
- [4] V. Ganesan, V. Ganesan, H.U. Borgstedt, *J. Nucl. Mater.* 312 (2003) 174.
- [5] A.W. Thorley, C. Tyzack in: *Proceedings of Liquid Alkali Metals*, BNES, London, 1973, p. 257.
- [6] H.U. Borgstedt, in: J.M. Dahlke (Ed.), *Proceedings of Second International Conference on Liquid Metal Technology in Energy Production*, Richland, Washington, American Nuclear Society, 1980, p. 7.