

# A STUDY ON CORROSION MECHANISM OF FBR STRUCTURAL MATERIAL IN SMALL SODIUM LEAK UNDER INSULATOR

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## **ABSTRACT**

In order to clarify the corrosion mechanism of FBR structural material by small sodium leak under mineral wool insulator in the secondary or ancillary circuits of Fast Breeder Reactors, sodium leak test has been carried out in the FUTUNA loop at Cadarache (CEA). The mock-up was a 316L stainless steel pipe 12-inch in diameter covered with the insulator. The test lasted for 240 hours at a leak rate of 0.1cc/min at 793K in atmosphere.

The corrosion of the structural material has been extensively observed under the periphery of the massive leakage products. The corrosion mechanism has been estimated based on the results of material analyses and thermodynamic data. It was found that the main corrosion mechanism could be similar to that prevailing in  $\text{Na}_2\text{O}+\text{Na}$  environment, namely the 'NaFe double oxidization type corrosion'. Na-Si complex oxide, which was identified in the outer region of the corrosion product formed from the reaction between the main elements of the insulator and leakage sodium,

was thermodynamically stable, and no direct influence on the steel was observed.

Based on these results, a number of corrosion tests were further carried out at OEC (JNC) in order to obtain the corrosion behavior below the melting point (about 873K) of the main product,  $\text{Na}_4\text{FeO}_3$ . It was concluded that the weight loss at 873K or below could be predicted by the time dependence properties based on the diffusion law.

## **INTRODUCTION**

As a coolant of Fast Breeder Reactors (FBRs), sodium reacts with oxygen and moisture in air at elevated temperature. And it is known that structural material is damaged by its by-products. Therefore, it is essential to clarify the corrosion phenomena prevailing under the sodium leak condition to estimate the structure integrity.

Research on the corrosion mechanism of structural materials in leakage sodium has been actively carried out since 1980's. Newman [1], [2] has conducted corrosion tests

in various sodium compounds on the assumptions of the sodium-water reaction in the steam generator and of the sodium leak in the secondary circuits. In addition, corrosion formula has been proposed in the latter. Knights et al. [3] have performed experiments under corrosive environments generated by the sodium-water reaction, and suggested one corrosion mechanism. Aoto [4] has proposed two corrosion mechanisms based on thermodynamic study to explain the corrosion behavior observed in sodium leak tests corresponding to the secondary circuit condition and the sodium leak incident which occurred in Japanese prototype Fast Breeder Reactor 'Monju' in 1995. Two corrosion models based on the findings have been put forward [5], [6].

In order to describe the corrosion behavior of the structural materials under small sodium leak in the secondary or ancillary circuits of European FBRs, in connection with the leak before break (LBB) research, Commissariat à l'Energie Atomique (CEA) has conducted studies since 1989 [7]. Until now, it has been confirmed that leakage sodium reacts with the insulator directly covering the sodium pipe, and that sodium leak can continue in certain conditions to proceed as massive leakage product is formed. The corrosion of the structural material has been observed under the periphery of the products to a great extent. Based on the investigation, they have established electrochemical model for the phenomena.

In this paper, the corrosion mechanism of the materials under the insulator is proposed based on the results of more detailed observations and thermodynamic estimation. Subsequently, the corrosion formulas in the environment are presented.

This study has been carried out at CEA-Cadarache under the collaboration on FBRs

between Europe and Japan.

## EXPERIMENT

The testing mock-up is shown in figure 1. The material of the 12-inch diameter pipe was made of type 316L stainless steel. On the lower side of the orifice, the analyzing plate for X-ray examination which consisted of the same material, was fitted. The heater was installed inside the pipe. The insulator of 250 mm thickness was directly placed around the pipe corresponding to that of European FBRs. Its chemical composition is given in table 1. The mock-up was set up in a sodium leak test facility called FUTUNA-2 (figure 2). The test lasted for 240 hours at a leak rate of 0.1 cc/min at 793K in atmosphere (table 2).

After the test, measurement of the pipe thickness, X-ray analyses of the leakage products and microstructural observations of the pipe were performed.

## RESULTS

### TEMPERATURE BEHAVIOR

The temperature behaviors in the vicinity of the orifice throughout the test period are illustrated in figure 3.

According to the output of the thermocouple set up in the orifice, the temperature rise which was apparently resulted from the interaction between sodium and oxygen, had been observed starting from leak initiation ( $T_0$ )

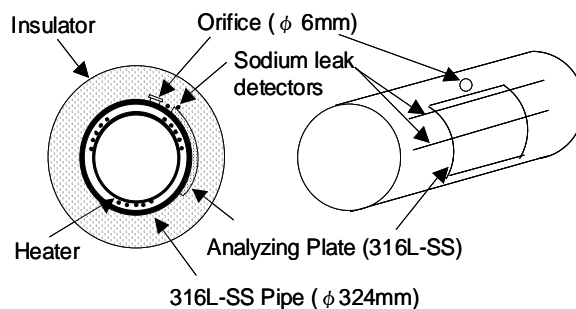


Fig. 1 Apparatus of testing mock-up

Table 1 Chemical Composition of Insulator (mass%)

SiO <sub>2</sub>	CaO	Al <sub>2</sub> O <sub>3</sub>	MgO
42%	37%	10.7	4%

Table 2 Test Condition

Temperature	793K
Leak Rate	0.1cc/min
Leak Time	240h

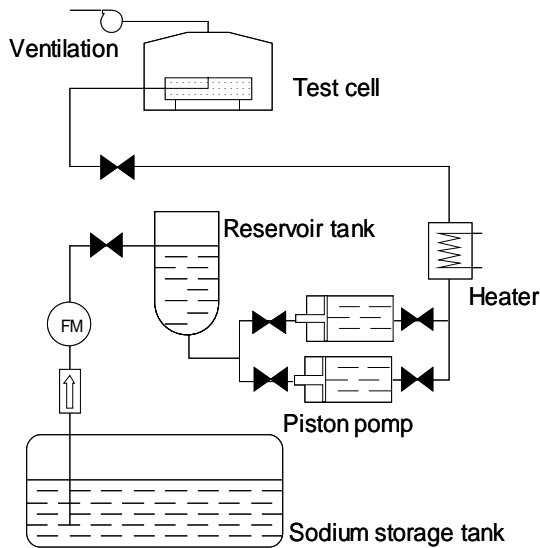


Fig. 2 Overview of the test facility

for 14 hours. The temperature eventually kept at 818K.

The temperatures of the three thermocouples mounted on the pipe at a distance of 50 mm from the orifice, sharply fluctuated in the range between 793K and 973K before these thermocouples failed. In this region, grooving corrosion with luster was observed (ref. next chapter). The temperatures of other thermocouples installed on the pipe were maintained at approximately 818K during the test period, excluding  $T_0+38$  hours to  $T_0+40$  hours. Based on the data from the thermocouple placed in the insulator, the temperature fluctuation, which seemed to be due to the chemical reaction between leakage so-

dium and the insulator, was seen from  $T_0+38$  hours to  $T_0+40$  hours.

## POST-TEST OBSERVATION

The photographs of the pipe after the test are shown in figure 4. Although discoloration owing to high temperature heating was observed on the surface of the insulator, leakage sodium was not observed (figure 4(a)). Green product was deposited on the pipe removed from the insulator, with a dimension of about 400 mm wide and 90 mm high (figure 4(b)). From this finding, it was considered that most of the leakage sodium was held within the product. The cross-section of the product is shown in figure 4(C). Semi-lustrous white product was observed inside the green product, and black one at the interface of the white layer and the pipe.

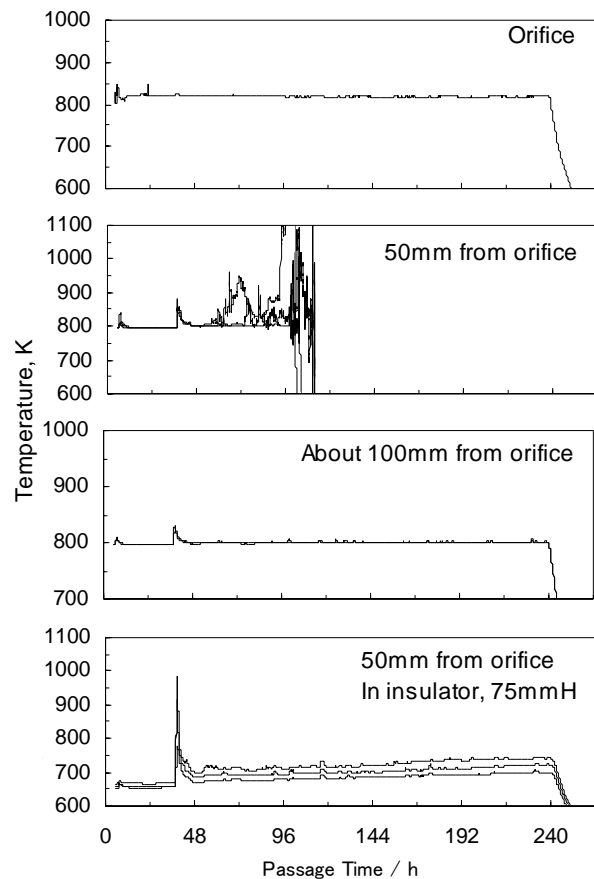


Fig.3 Temperature behavior

Table 3 X-ray Results

Sampling Positions	XRD Results
Green product near surface	Na <sub>4</sub> SiO <sub>4</sub> , NaAlO <sub>2</sub>
Black product on surface	NaFeO <sub>2</sub> , NaOH
White product near surface	Na <sub>2</sub> O <sub>2</sub> , Na <sub>2</sub> O, NaOH, (SiO <sub>2</sub> )

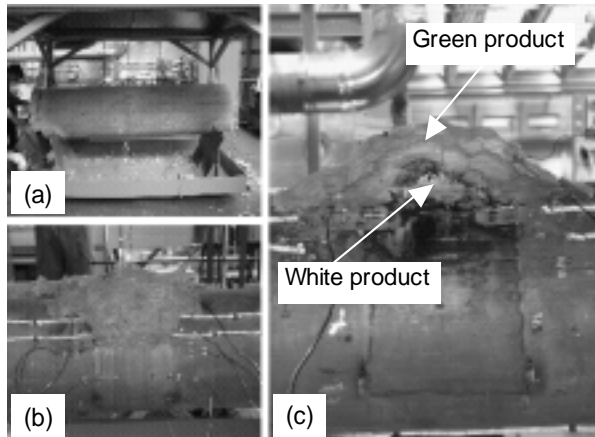


Fig. 4 The photograph of the mock-up

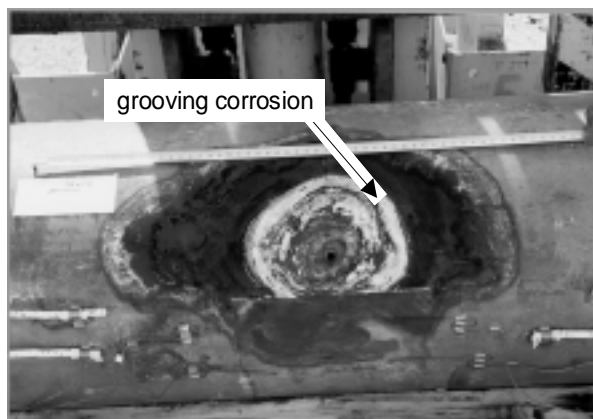


Fig. 5 The appearance of the pipe after water cleaning

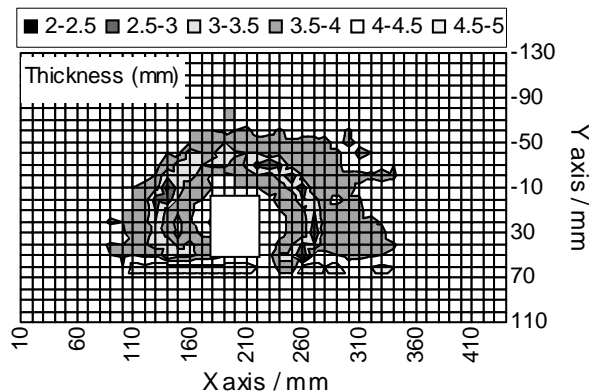
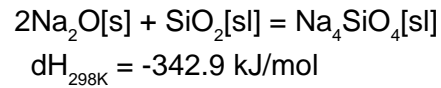


Fig. 6 Corrosion profile of the pipe

The result of X-ray analyses is summarized in table 3.

The green product was identified mainly as Na<sub>4</sub>SiO<sub>4</sub>, which was formed by chemical reaction between leakage sodium and the main element (SiO<sub>2</sub>) of the insulator.



The white product consisted of Na<sub>2</sub>O, which existed at low oxygen pressure, and stable compounds (Na<sub>2</sub>O<sub>2</sub> and NaOH) at atmospheric pressure. However, Na-Si-O complex oxide was not identified here. It seemed that Na<sub>2</sub>O<sub>2</sub> and NaOH were formed during storage because the sample was kept in the glove box in the presence of approximately 200ppm oxygen for 10 days.

Photographs of the pipe following water cleaning and of the pipe thickness are shown in figure 5 and 6. Three differential phenomena prevailed on the surface. The color of the inner region located under the white product was brown with partial gray, and the corrosion depth was less than 0.7 mm. The outer region located under the green product was blackish brown, and the depth was the same as that of the inner region. Concentric grooving corrosion of maximum depth 2.1 mm was observed between the two regions. The width was about 20mm, and the appearance was silver metallic with luster. There was an insignificant amount of corrosion product on the spot. Only NaFeO<sub>2</sub> and NaOH were identified in the product by X-ray analysis. In short, it was considered that the chemical reaction in Na-Fe-O system occurred in the area.

The results of optical microscopy of the cross section and scanning electron microscopy of the surface are shown in figure 7 and 8. It was proven that although oxide was found

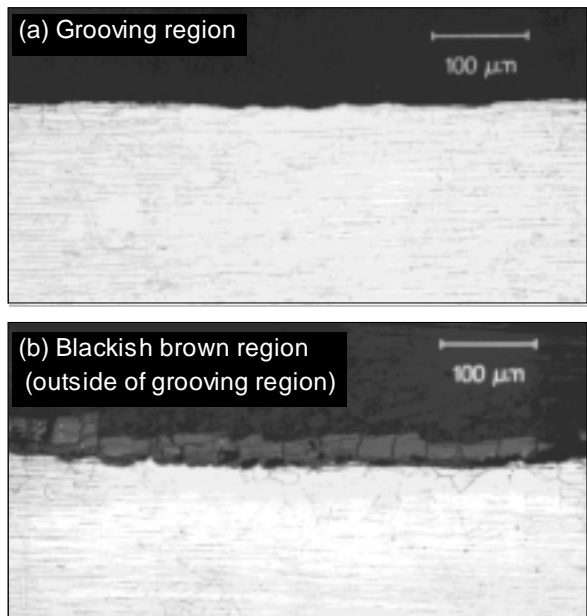


Fig. 7 Observation results of the pipe

in the outer region, none was observed in the grooving region. Furthermore, general corrosion prevailed without ruggedness.

## DISCUSSION

### CORROSION MECHANISM

The feature of the corrosion mechanism was understood based on the results of X-ray and microstructure analyses.

The main compound in the green product,  $\text{Na}_4\text{SiO}_4$ , is thermodynamically stable, and hence it is not possible for the compound to oxidize the steel (Fe). Therefore, the material located under the compound was slightly corroded. The compound hindered oxygen inward diffusion. In the mean time, sodium was continuously supplied from the orifice. As a result, the region containing the white product was kept at low oxygen potential during the test.

Grooving corrosion was observed between the two regions. On the surface, Na-Fe complex oxide was noted but none of iron oxide. The reason can be explained by the comparison of the standard free energy of iron oxide

formation with that of other oxides as shown in figure 9. Although  $\text{Na}_2\text{O}$  does not oxidize the steel (iron), it is possible for oxidation to occur through the formation of Na-Fe complex oxide. In brief, the chemical reaction of  $\text{Na}_2\text{O}$  and Fe might have prevailed in this area. Aoto et al. [5] has reported the same phenomenon with regard to the corrosion test in Na+ $\text{Na}_2\text{O}$  environment, and named it the 'NaFe double oxidation type corrosion'. In short, Na and  $\text{Na}_2\text{O}$  were considered to form in the region.

The width of the grooving corrosion was greater than that of other cases which were reported by Bertrand et al. It was considered that the width might have a relationship with

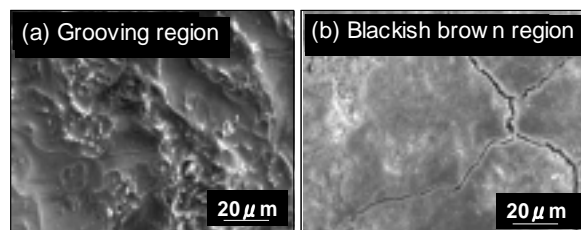


Fig. 8 Observation results of the surface

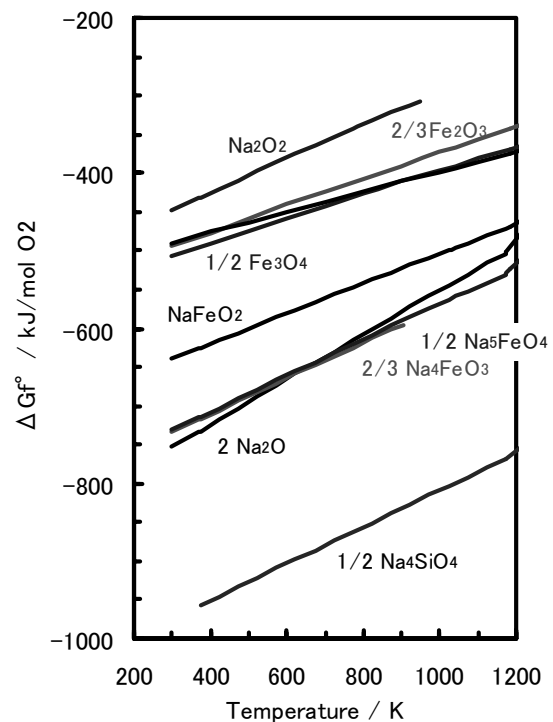


Fig. 9 Comparison of the standard free energy of iron oxide formation

the sodium leak ratio. Since this corrosion took place at  $\text{Na}_2\text{O}$  highest activity, the moving rate was based on the leak rate (figure 10).

### CORROSION FORMULA

The chemical diagram of Na-Fe-O system is shown in figure 11.  $\text{Na}_4\text{FeO}_3$  is formed in  $\text{Na}_2\text{O}$  and Na environment. It has been confirmed that the compound melted at about 923K [8]. Moreover, the corrosion rate in  $\text{Na}+\text{Na}_2\text{O}$  at temperature less than 923K was lower than the value of the average line based on the results over 973K [5]. In other words, the corrosion rate was limited by the diffusion step through layer of  $\text{Na}_4\text{FeO}_3$ , which was present in solid state below the melting point (about 923K).

The temperature of the surface was fluctuating between 793K and 973K before failure. Therefore, it is necessary to determine the metal loss prior to sodium leak detection for LBB estimation. For this reason, time dependence tests were carried out at temperature lower than the melting point of  $\text{Na}_4\text{FeO}_3$  in  $\text{Na}+\text{Na}_2\text{O}$ .

To obtain direct comparison with the results reported in the paper [5], the tests conducted in JNC took into account the followings:

- (1) The ratio of  $\text{Na}/\text{Na}_2\text{O}$  was 70mass%/30mass%. This ratio was chosen because in this case the mixture was liquid and the corrosion rate was very high.
- (2) The material used was carbon steel for comparison with reference [5].
- (3) The tests were performed in argon employing the test equipment as described in reference [5].

The results are indicated in figure 12: the average lines were based on parabolic law (see equations in the figure). It is clearly shown that metal loss could be predicted

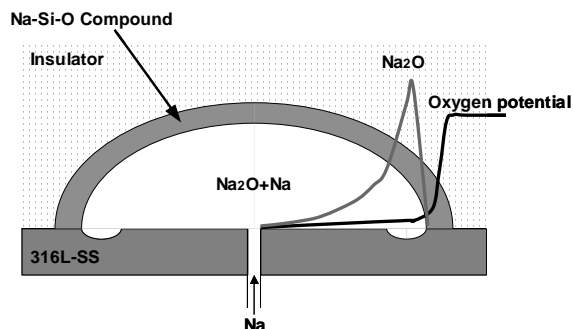


Fig. 10 Reaction phenomenon under insulator

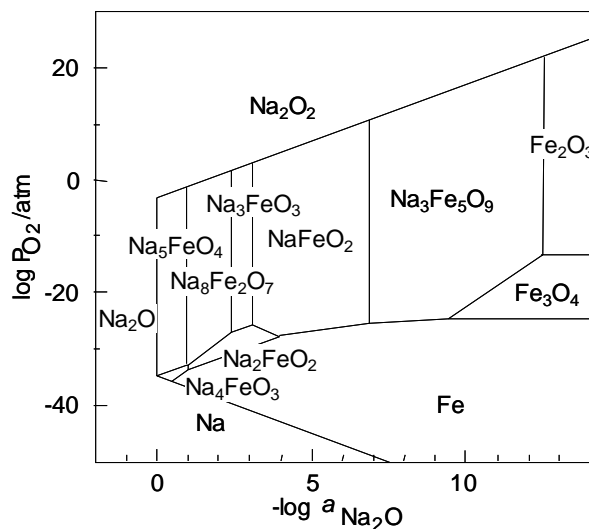


Fig. 11 Chemical diagram in Na-Fe-O system at 873K

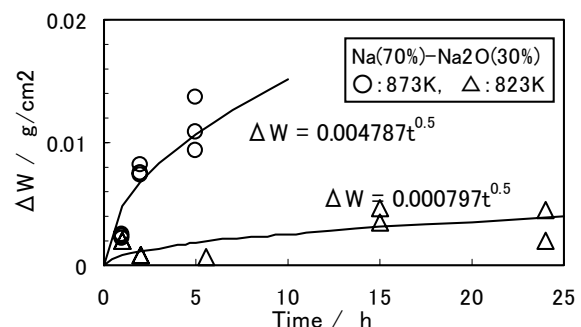


Fig. 12 Corrosion test results in  $\text{Na}+\text{Na}_2\text{O}$

based on the time dependence and that the rate was limited by the diffusion law.

### CONCLUSIONS

- (1) In order to obtain a better understanding of the corrosion mechanism of the structural material by small sodium leak in the secondary or ancillary circuits of FBRs, sodium leak

test was carried out together with material analyses. According to the results, it was clarified that the corrosion prevailed occurred in  $\text{Na}+\text{Na}_2\text{O}$ .

(2) It was proven that  $\text{Na}_4\text{SiO}_4$ , which was the main product of the reaction between leakage sodium and the main compounds of the insulator, was formed on the surface, and that it decreased the oxygen potential in the product.

(3) Based on these results, a number of corrosion tests were carried out in  $\text{Na}+\text{Na}_2\text{O}$  at 823K and 873K in laboratory scale in order to identify the time dependence of the corrosion rate: it was shown that metal loss at 873K or less could be predicted by the time dependence properties based on the diffusion law.

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