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Corrosion Resistant Steel Plate for Crude Oil Tanker (NSGP™)

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Abstract

NSGP™-1 and NSGP™-2, corrosion resistant steels, have been developed for cargo oil tanks of crude oil tankers. Steel plate for ship is usually required to have highly efficient weldability, however; corrosion resistant steel generally contains too much alloy to be good at highly efficient weldings. Nippon Steel & Sumitomo Metal Corporation has clarified the corrosion mechanism and developed low alloyed corrosion resistant steels that satisfy the requirement from the perspective of both corrosion test of IMO and high efficient weldability, the same as conventional steel for ships. These show excellent corrosion resistance on boards.

1. Introduction

In the 1990s, the marine pollution caused by crude oil spills from tankers was emerged as a matter of grave concern. The rules and regulations on tankers imposed by the International Maritime Organization (IMO) have become increasingly stringent. Representative examples thereby include the requirement of double hull construction as a structural improvement measure and the establishment of protection criteria for crude oil tanks (MSC. 288 (87)) as an anticorrosion measure.

As per the protection criteria for crude oil tanks of tanker ships implemented in 2013, the corrosion-resistant steel that had been proposed by Japan was approved for the first time in the ship industry as an anticorrosion measure that could be substituted for painting. This was because of the corrosion test method employed by Nippon Steel & Sumitomo Metal Corporation and the results of the company's experimental application of its corrosion-resistant steel to an actual vessel.

At the time of preparation of the above protection criteria, while the durability of the paint film was assumed to be 15 years, the target corrosion loss of the corrosion-resistant steel in 25 years was less than the design corrosion allowance specified in the rules and regulations for the classification of ships.

In the development of corrosion-resistant steels, clarifying the mechanism of corrosion is one of the important matters. Nippon Steel and Sumitomo Metal by itself clarified the mechanism of corrosion on the basis of the results of a corrosion investigation of more than 10 large-scale crude oil tankers by the 242nd Workshop (SR 242) of Japan Ship Technology Research Association. The investigation was conducted during 1999–2001 to cope with the problem of damage to the crude oil tank interiors of double hulled tankers.

The mode of occurrence of corrosion to the interior of a crude oil tank differs between the tank bottom and the tank top. The bottom is subject to hemisphere-like localized corrosion ("pit"), whereas the top is subject to general corrosion. In view of the difference of corrosion mechanism, Nippon Steel & Sumitomo Metal has newly developed two versions of corrosion-resistant steels, Nippon Steel & Sumitomo Metal's Green Protect (NSGP™)-1 and NSGP-2. Capitalizing on its technical expertise accumulated by more than 50 years of experience in the development of low-alloy corrosion-resistant steels, the company has succeeded in securing both good corrosion resistance and weldability with smaller amounts of alloying elements. Incidentally, NSGP-1 was co-developed with Nippon Yusen Kaisha (NYK).

Using the above steels for crude oil tankers, it is possible to cut the man-hours for painting the tanks, erecting scaffoldings for the painting work, etc. and to reduce the emissions of volatile organic compounds (VOC) from the paint during construction of the tankers. In addition, after construction, it should be possible to reduce the cost of repair and shorten the period of repair.

In this study, we shall describe the mechanisms of corrosion of steel plate for the crude oil tank bottom ("bottom plate") and top ("upper deck plate"), the corrosion resistance and mechanical properties of NSGP-1 and NSGP-2, and the results of application of those steels to actual tankers.

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2. Corrosion-Resistant Steel for Bottom Plate (NSGP-1)

2.1 Mechanism of corrosion of bottom plate [1–3]

The type of corrosion of the bottom plate of a crude oil tank is local pitting, which can reach a maximum of 10 mm in depth. **Figure 1** shows the mechanism of corrosion of bottom plates derived from the results of a field investigation and laboratory tests.

On the bottom plate of a crude oil tank, the residing of water, without which the bottom plate will not corrode during transportation of crude oil, is observed. The water is brine (neutral water) containing a high concentration of chloride, which is to have emerged from the crude oil during transportation. On the other hand, the crude oil tank interior is covered with a crude oil component called an oil coat. Similar to the paint film, the oil coat insulates the steel surface from the environment. Therefore, it is considered that corrosion occurs where the oil coat is defective.[1]

If corrosion occurs, the pH in the pit decreases as a result of hydrolysis. Since brine of high concentration (10 mass%) resides on the bottom plate, the corroded part can become a highly acidic environment. Therefore, it is considered that active dissolution takes place in the pit, resulting in semispherical corrosion. According to a study, the values of pH measured in actual pits were 1.5 or less. On the other hand, from the results of SR 242, it is considered that the pit stops developing after dock inspection.[1] Nippon Steel & Sumitomo Metal has developed NSGP-1 that dramatically lowers the rate of corrosion in the above environment.

2.2 Results of corrosion test

Figure 2 shows the result of NSGP-1 on the corrosion test of IMO.[3] For the purpose of comparison, the test result of conventional steel is also shown. The corrosion rate of NSGP-1 is approximately one-half that of the IMO criterion. **Photo 1** shows examples of the results of a corrosion test of NSGP-1 welded joints. According to the unified interpretation, UI SC258[4], of the International Association of Classification Societies (IACS), the difference in level between the base metal and the weld metal shall not exceed 30 μm, or shall be 50 μm or less assuming the boundary inclination is 15° or less. When a conventional welding material is used, a marked difference in level (approximately 60 μm) can be observed between the base metal and the weld metal. Conversely, when an exclusive welding material of Nippon Steel & Sumikin Welding Co., Ltd. is used, no difference in level is observed between the base metal and the weld metal.

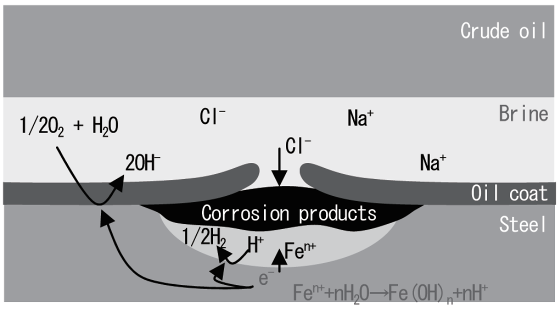

Fig. 1 Summarized process and mechanism of localized corrosion on COT bottom plate

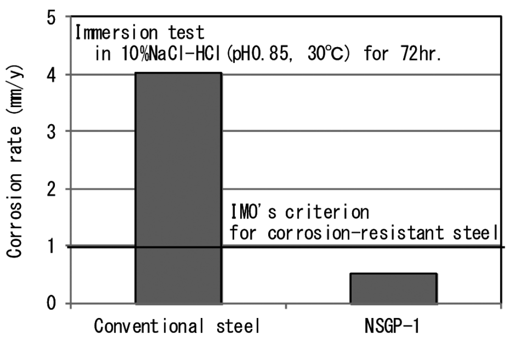

Fig. 2 Corrosion test results of NSGP-1 and conventional steel

2.3 Mechanical properties of NSGP-1

Table 1 shows the principal mechanical properties of NSGP-1. They are nearly the same as those of the conventional steel compared. Note that the chemical composition of NSGP-1 meets the W30 specification of the IACS unified regulation, UR, on the appropriate corrosion-resistant steels.

2.4 Weldability of NSGP-1

Table 2 shows the results of a y-groove weld crack test (JIS Z 3158). No weld cracks were observed, indicating that NSGP-1 has good weldability.

Table 3 shows the results of a Charpy impact test of a NSGP-1 welded joint. The joint was prepared by one-side submerged arc

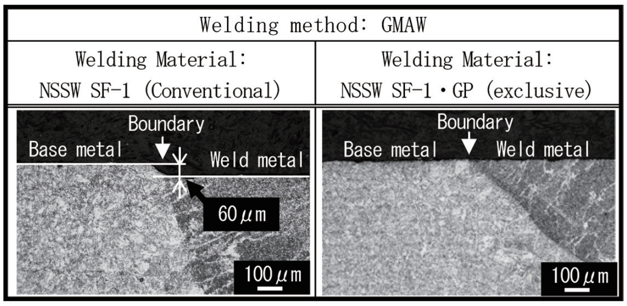

Photo 1 Cross section view of welded joints of NSGP-1 after corrosion test

Table 1 Mechanical properties of steel plate of NSGP-1 (plate thickness: 25 mm)

	Yield strength (N/mm²)	Tensile strength (N/mm²)	Elongation (%)	$vE_{-20°C}$ (J)
NSGP-1	462	554	22	273
D36 TM spec.	≧ 355	490–620	≧ 18	≧ 34

Table 2 Results of y-groove weld cracking test

Plate thickness	Temp. / Humidity	Preheat temp.	Crack ratio		
			Surface	Section	Root
20 mm	13°C / RH90%	0 °C	0 %	0 %	0 %
		25 °C	0 %	0 %	0 %

Table 3 Impact test results of welded joint (plate thickness: 20 mm)

Notch position	Weld metal	Fusion line	HAZ 1 mm	HAZ 3 mm	HAZ 5 mm
$vE_{0°C}$ (J)	117	103	103	193	208

HAZ: Heat affected zone

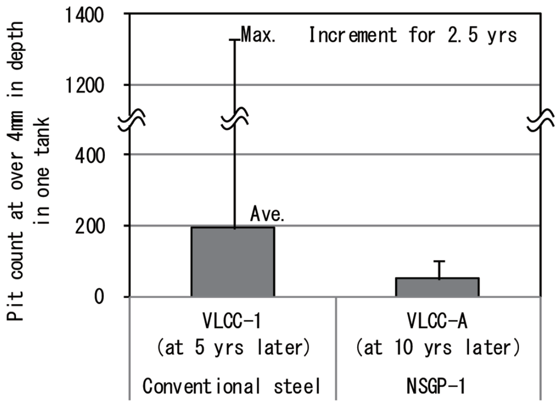

Fig. 3 Observed pit count for VLCC-1 using conventional steel upon 5-year and VLCC-A using NSGP-1 upon 10-year inspection

welding (FAB process), and the input heat was approximately 125 kJ/cm. Every part of the welded joint had the required toughness of 34 J or more, indicating that NSGP-1 has good weldability.

2.5 Results of application of NSGP-1 to tankers

NSGP-1 has already been applied to the crude oil tank bottom plates of some 10 very large crude oil carriers (VLCCs).

At first, NSGP-1 was applied in 2004 to a total of 15 tank bottom plates on a trial basis. Of the 15 tanks, six were unpainted. **Figure 3** shows the average and maximum numbers of pits requiring repair (i.e., pits 4 mm or more in depth) counted during the fourth dock inspection (after 10 years of use) for the six unpainted NSGP-1 tanks. In the figure, the numbers of pits counted by SR 242 during the second dock inspection (after 5 years of use) for conventional steel tanks are also shown as VLCC-1.[1] Both indicate the changes in numbers from the preceding dock inspection.

In the 5th-year inspection of conventional steel tanks, there was a tank, whose number of pits increased by more than 1 300, with the average number of pits being 200 per tank. Conversely, in the 10th-year inspection of the NSGP-1 tanks, the number of pits per tank was not more than 100, with the average being approximately 50 pits per tank. Thus, it could be confirmed that NSGP-1 used for the bottom plates of crude oil tanks had good resistance to pitting corrosion.

At each dock, the depth of every pit is measured during periodical inspection of crude oil tanks starting from the initial dock inspection.[3] As shown in **Fig. 4**, the pit depths measured in the 10th-year inspection were almost the same as those measured in the 5th-year inspection, indicating that the pits had not increased in depth during that 5-year period. In addition, as a result of measurement of the bottom plate thicknesses, it was confirmed that the initial bottom plate thicknesses had remained the same, indicating that NSGP-1 was free from general corrosion.[3]

Next, NSGP-1 was applied unpainted to a total of 15 crude oil tank bottom plates. For six VLCCs running on different lines, the results of pit counts during the initial dock inspection (2.4 to 3.1 years after they were implemented) are described below.[5] **Figure 5** shows the average and maximum numbers of pits 4 mm or more in depth in the tanks of each of the six VLCCs. In the figure, the results of pit counts by SR 242 for conventional steel tanks are also shown as VLCC-2.[1] The conventional steel tanks had an average of approximately 100 pits, with the maximum number of pits being nearly 400 per tank. Conversely, for five NSGP-1 tankers, except for VLCC-C, the average number of pits was 1.6 per tank, with the

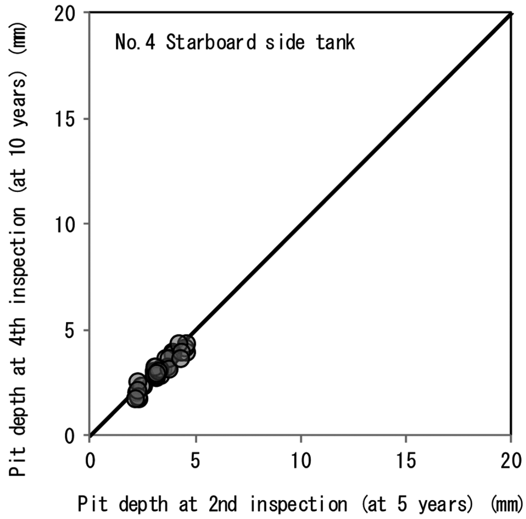

Fig. 4 Depth measurement result of the fifth year and the tenth year of the same pits

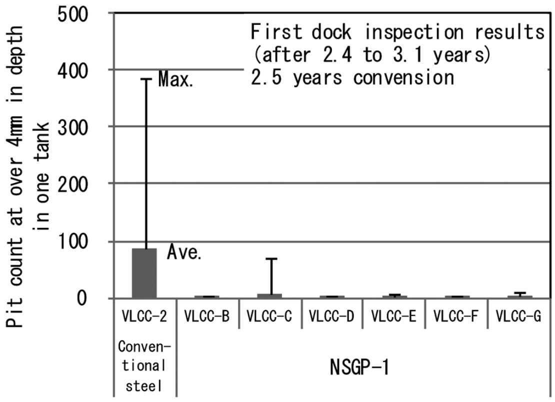

Fig. 5 Observed pit count of VLCC-2 using conventional steel and six VLCCs using NSGP-1

maximum number being less than 10 per tank. Thus, NSGP-1 significantly reduced the number of pits in the bottom plates of crude oil tanks. Although the occurrence of pits in those VLCCs is irregular, the results of a factor analysis suggest that the irregularity is due at least with respect to the mode of operation of each individual VLCC and we have found countermeasures for it.

3. Corrosion-Resistant Steel for Upper Deck Plate (NSGP-2)

3.1 Mechanism of corrosion of back of upper deck plate

The mode of corrosion at the back of the upper deck of a crude oil tank is so-called general corrosion, wherein the steel plate is corroded almost uniformly. It has been reported that the rate of corrosion is generally within 0.1 mm per year.[1] However, depending on the corrosion environment, the steel plate may be corroded at such a high rate that it cannot be used for the expected period of time. Although the steel plate can be painted for protection, the back of the upper deck plate, in particular, requires the initial painting and considerable cost of maintenance. Therefore, the development of new steel plates that can be used unpainted has been called for.

In the air gap at the back of the upper deck plate, there are corrosive gases, such as CO_2, O_2, and SO_2, since the engine exhaust called inert gas is let into the tank to prevent it from exploding. In addition, relatively high concentration of H_2S emerges from crude oil. **Table 4** shows the results of an analysis of the gases in the vapor-phase space at the back of the upper deck plate.[6] In the natural world, the coexistence of O_2 and H_2S as shown here can never be found. The implication is that the corrosion environment at the back of the upper deck plate is very unusual. Besides, the back of the upper deck plate is subject to repetitions of wetting with dew during nighttime and drying with warm air during daytime because of the difference in temperature between night and day. In the presence of CO_2 and SO_2, the pH of dew decreases from 2 to 4. The above corrosion environment is characteristic in that the products of corrosion include not only iron rust but also a relatively large amount of solid sulfur (S) as the product of oxidation of H_2S. The layer of corrosion products appears similar to a sandwich construction of rust and S. **Figure 6** illustrates the mechanism of corrosion. It is considered that the corrosion at the back of the upper deck plate progresses as the cycle of wetting and drying is repeated by weak acidic water in the presence of inert gas and H_2S.

3.2 Corrosion test procedure

We established a simulative corrosion test method considering the corrosion environment described above. **Figure 7** shows the schematic test apparatus. A simulated inert gas and H_2S were injected into distilled water in a sealed container to simulate the environment of the interior of a crude oil tank. The test piece fitted to the back of the container top was subjected to a temperature cycle of 25°C and 50°C to simulate the cycle of wetting with dew and drying with warm air.

Table 5 shows the composition of corrosion product formed on the test piece after the simulative corrosion test. The corrosion product composition was similar to that observed on an actual crude oil tank, and solid sulfur, which is characteristic of the product of corrosion in the actual environment, was also detected. As shown in **Fig. 8**, the presence of layers of solid sulfur was confirmed by an analysis of a cross-section of the corrosion product. Thus, it was confirmed that the laminar structure of rust and S observed in the

Table 4 Analysis results of gas concentration in vapor space of COT

Tank	3S	4C	4S	5C
Crude oil	A	B	C	D
H_2S	2790	1330	498	817
H_2O	4.9	3.9	5.3	2.5
O_2	1.7	2.5	1.8	3.9
CO_2	3.7	4.0	2.2	10.9
SO_x	1.3	3.9	1.6	2.7
N_2	32.9	45.0	25.7	62.0
C_xH_y	54.9	42.4	62.2	15.0

H_2S, SO_2: vol.ppm, Others: vol.%

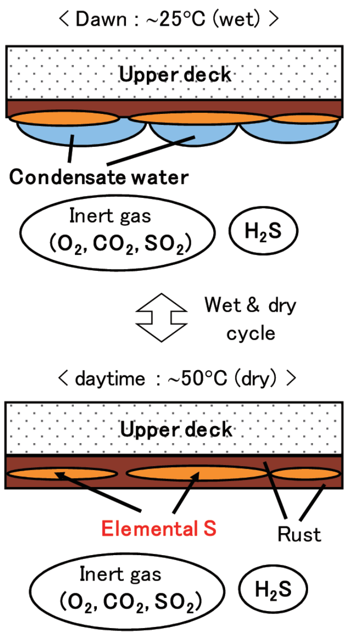

Fig. 6 Corrosion mechanism at COT upper deck plate

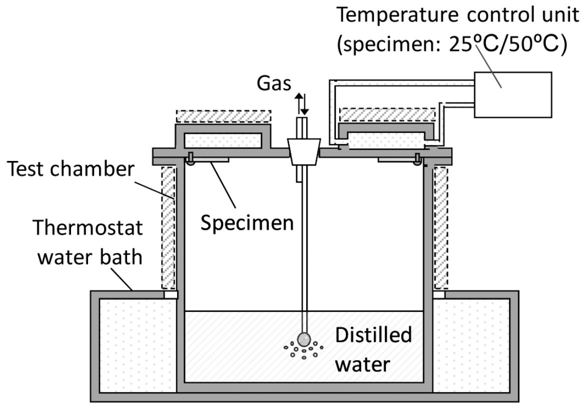

Fig. 7 Simulated corrosion test apparatus for upper deck of COT

Table 5 Compositions of corrosion products on simulated test specimen and upper deck plate of COT analyzed by X-ray diffraction method (mass %)

	α-FeOOH	β-FeOOH	γ-FeOOH	Fe_3O_4	S	Others
Simulated test	30	0	3	8	21	38
COT	37	0	8	0	12	43

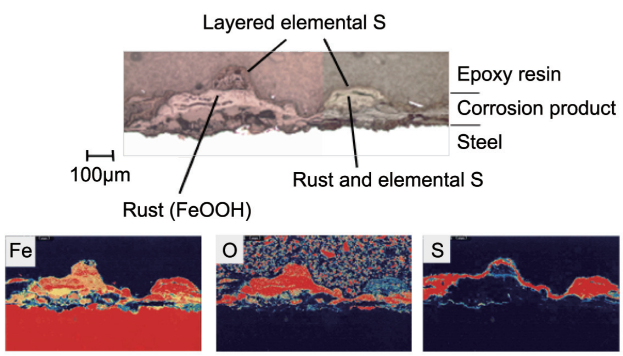

Fig. 8 Cross sectional morphology and distribution of elements by electron prove micro analyzer (EPMA) in corrosion product of specimen after simulated corrosion test for upper deck

actual environment can be reproduced by the present test.[7] Incidentally, the IMO's test method for evaluating corrosion products is based on the present test method.

3.3 Corrosion test results

Using the above simulative test method, we studied the effects of various alloying elements on the corrosion resistance of steel. On the basis of the study results, NSGP-2 was developed.[8] Because of the addition of trace alloying elements, NSGP-2 has much better corrosion resistance than conventional steel. **Table 6** shows the result of IMO evaluation of NSGP-2. The corrosion loss of plate in 25 years estimated by the present corrosion test was 1.53 mm, proving that the NSGP-2 meets the IMO specification. **Figure 9** shows the results of an electrochemical study of the mechanism of corrosion. In a weak acidic environment, the anode reaction of NSGP-2 is restrained before and after the corrosion test. Therefore, it is considered that both base metal and corrosion product restrain the matrix from dissolving, thus markedly improving the corrosion resistance of the steel.

3.4 Mechanical properties

Besides the corrosion resistance, the principal mechanical properties of NSGP-2 are shown in **Table 7**. In addition, the results of a y-groove weld crack test are shown in **Table 8**, and the results of a Charpy impact test are shown in **Table 9**. The toughness test pieces were prepared by submerged arc welding (3-electrode FCuB method) with the heat input of approximately 108 kJ/cm. The mechanical properties of NSGP-2 meet the specifications of the International Association of Classification Societies (IACS W30). In addition, it has been confirmed that NSGP-2 has good weldability and welded joint toughness. Therefore, similar to conventional steel, NSGP-2 can be applied to crude oil tanks.

3.5 Results of test application of NSGP-2 to tanker

NSGP-2 has been used for the upper deck plate of an aframax tanker on an experimental basis for approximately eight years. We evaluated the long-term corrosion resistance of the upper deck plate in the actual environment by means of plate thickness measurement at the time of each dock inspection. **Figure 10** shows the results of a corrosion test of NSGP-2 and the corrosion loss of the upper deck plate in 25 years estimated from the corrosion test results. The corrosion loss of NSGP-2 is much smaller than that of the conventional steel, proving that it displays good corrosion resistance in the actual environment. While the estimated corrosion loss of the conventional

Table 6 Simulated corrosion test results

	Test results
NSGP-2	1.53 mm
IMO spec.	≦ 2 mm

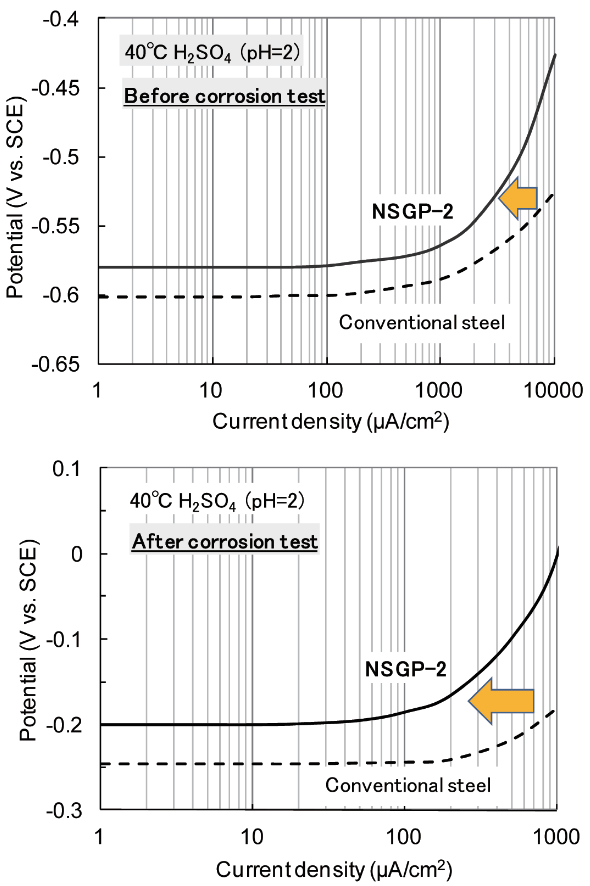

Fig. 9 Anodic polarization curves of conventional steel and NSGP-2

Table 7 Mechanical properties of NSGP-2 (plate thickness: 16.5 mm)

	YP (N/mm²)	TS (N/mm²)	EL (%)	$vE_{-20°C}$ (J)
NSGP-2	432	504	24	258
D36 TM spec.	≧ 355	490–620	≧ 20	≧ 34

Table 8 Results of y-groove weld cracking test

Plate thickness	Temperature / Humidity	Surface crack ratio	Section crack ratio
30 mm	20°C / 60%RH	0 %	0 %

Table 9 Impact test results of welded joint (plate thickness: 16.5 mm)

Notch position	WM	FL	HAZ 1 mm	HAZ 3 mm	HAZ 5 mm
$vE_{0°C}$ (J)	174	132	172	224	250

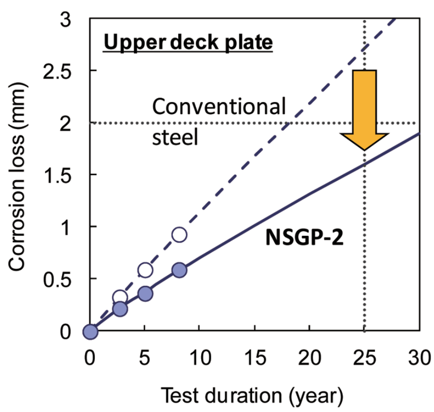

Fig. 10 Onboard test results of NSGP-2 and estimated corrosion loss after 25 years

steel plate in 25 years is approximately 2.7 mm, which exceeds the specified limit of 2 mm, that of NSGP-2 is 1.6 mm. Thus, it is possible to use the NSGP-2 upper deck plate unpainted for an extended period of time.

4. Conclusion

So far, we have discussed the mechanism of corrosion of crude oil tanks and described the corrosion resistance, mechanical properties, and application of NSGP-1/NSGP-2—corrosion-resistant steels for bottom and upper deck plates of crude oil tankers. By clarifying the corrosion mechanism for ourselves and imparting good corrosion resistance to steels by the addition of very slight amounts of alloying elements, we could develop new steel products having excellent corrosion resistance and weldability that can be handled in the same way as conventional steels. From the results of a long-term evaluation test on an actual crude oil tanker, it was confirmed that the newly developed steels have excellent corrosion resistance. As a result, NSGP-1 and NSGP-2 have secured certification of the Classification Society as the world's first corrosion-resistant steels that satisfy the IMO resolution MSC.288 (87). Now they can be applied unpainted to crude oil tankers. The exclusive welding materials developed for the new steels have also been approved by the Classification Society. It is expected that NSGP-1 and NSGP-2 will make it possible to significantly reduce the costs of construction and maintenance of crude oil tankers, reduce the emissions of VOCs, and shorten the period of repair.

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