Development of Anti-Corrosion Steel for Cargo Oil Tanks

Hiroshi Shiomi[1)], Michio Kaneko[2)], Kazuyuki Kashima[3)], Hiroki Imamura [4)]
and Tsutomu Komori [5)]

[1)] The Japan Iron and Steel Federation, Technical Committee of Steel Plates for Shipbuilding, (JFE Steel Corporation), Tokyo, Japan, E-mail:h-shiomi@jfe-steel.co.jp
[2)] Nippon Steel Corporation, Futtsu, Japan, E-mail:kaneko@re.nsc.co.jp
[3)] Sumitomo Metal Industries LTD., Amagasaki, Japan, E-mail:kashima-kzy@sumitomometals.co.jp
[4)] Kobe Steel LTD., Kakogawa, Japan, E-mail:Imamura.hiroki@steel.kobelco.co.jp
[5)] JFE Steel Corporation, Fukuyama, Japan, E-mail:t-komoti@jfe-steel.co.jp

Abstract

A 3-year study focusing on cargo oil tank (COT) corrosion of oil tanker had been carried out by the Panel SR242 committee of The Shipbuilding Research Association of Japan since 1999 to 2001. This panel was formed by so many organizations – research institutes, a class, ship owners, shipbuilders and steel makers – that the study was very extensive and practical. The study revealed corrosion condition of inside COT that had been unclear and the mechanism of initiation and progress of corrosion. Valuable information for the corrosion mechanism in COT was attained. The simulated corrosion test methods were also established by this study. Based on these results, some steel makers started the development of anti-corrosion steels in 2002 and some excellent anti-corrosion steels for COT were developed recently. Laboratory test results have revealed that these developed steels have high corrosion resistance compared with conventional steels under the corrosion environments of upper deck plate and/or inner bottom of COT.

These anti-corrosion steels have already applied to a number of crude oil tankers. Recently one of the evaluation results were obtained, on such steel that has been applied to actual inner bottom plates of COT in VLCC without protective coating. At the inspection after two years and three month service, this anti-corrosion steel showed corrosion prevention performance, which was expected from the laboratory corrosion test results. Then, there was no need of any painting repair or welding repair.

1 CORROSION MECANISMS OF COT

There are two types of corrosion in COT, the general corrosion of upper deck plate and the pitting corrosion of inner bottom plate. In COT, inert gas preventing explosion and H_2S gas originated from crude oil exist (Fig.1). Backside of upper deck is exposed to the wet and dry conditions cyclically because of temperature change during day and night. Condensation of water takes place. Moreover, elemental Sulfur would be generated by oxidation of H_2S with oxygen. And the general corrosion of the upper deck plate is enhanced by the condensate water (Fig.2). Key facts found by SR242 are as bellows.

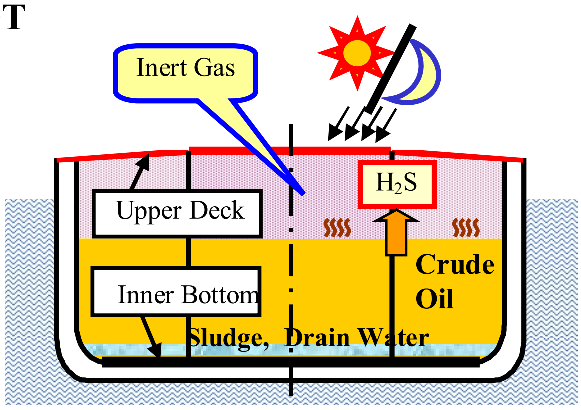

Fig.1 Corrosion environment of COT

(1) Gaseous composition in COT is very unique. H2S gas exists in high concentration and O2, H2O and CO2 are co-existing with H2S.

(2) The most of flaky products on upper deck is not corrosion product. About 60wt% of them is elemental S.
(3) So the corrosion rate of upper deck plate is not so high. In SR242 measurements, average rate is below 0.1mm/yeare.

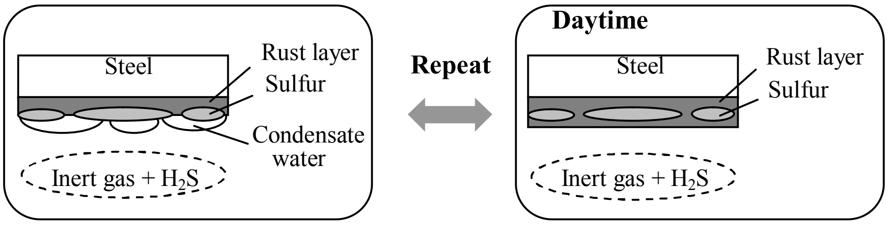

Fig.2 Corrosion mechanism at the upper deck of COT

The inner bottom plate is covered with oil coating layer containing sludge, drain water including highly concentrated chloride ions and H_2S originated from crude oil. In general, oil coating decreases corrosion rate. Partial defects of the oil coating, however, would be caused by crude oil washing. Then the inner bottom plate is exposed to severe corrosion environment with concentrated chloride ion and H_2S. This condition causes and enhances the pitting corrosion of the bottom plate at the defect of the oil coating. Key facts for inner bottom plate corrosion are as bellows.

(1) There is neutral brine (not sea water). It contains 10mass% NaCl.
(2) In oil coat, solid state S exists, and it's wt% is 2.0~7.5.
(3) At pit inside, pH of solution is lower than 1.5.

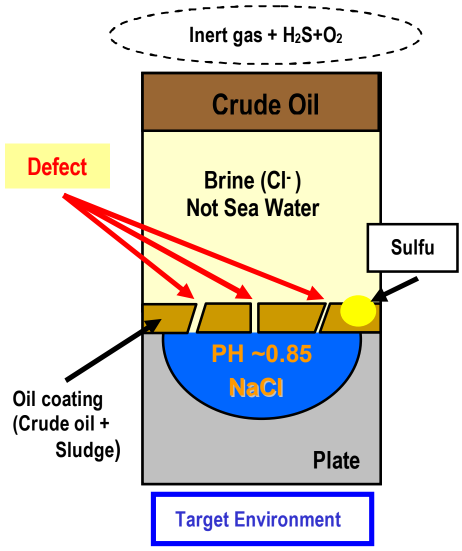

Fig.3 Corrosion mechanism at the inner bottom of COT

2 DEVELOPMENTS OF ANTI-CORROSION STEELS

Corrosion resistant steels against separated environments with SO_2, H_2S or Cl^- are being supplied already in commercial basis in many fields. As for ships, anti-corrosion steels for COT were developed by taking the improvement of these corrosion resistant steels, into account in the complex corrosion environment of COT, which found by SR242 researches. These anti-corrosion steels show excellent performance. Some examples of developed steels are shown below.

2.1 *Anti-Corrosion Steels for COT Bottom plates*

Two kinds of approaches had been done, for developing of anti-corrosion steel for COT bottom plates. The first approach was simulation of the local condition of inside the corrosion pits. In SR242 results, one of the important fact is that pH of pit inside is lower than 1.5. The developed steel (Steel-A) was selected from a point of this view. Fig.4 shows ratio of developed steel's corrosion rates to conventional steel's. In the extremely low pH solutions (pH=0.85), simulated COT bottom plate condition, corrosion rate of steel-A is less than 1/5 of conventional steel's. This steel-A has been applied actual vessels and good results were obtained.

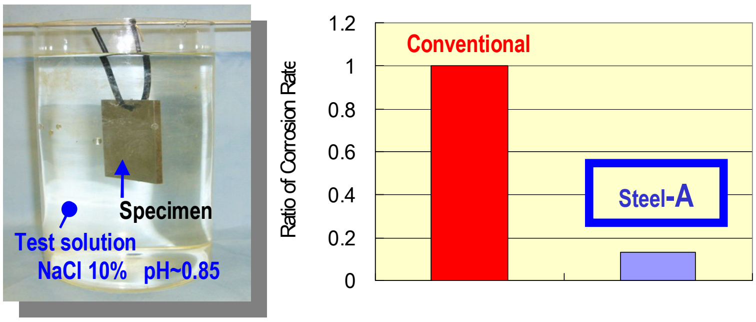

Fig.4 Simulated corrosion test and performance of the newly developed steel(Steel-A)

Another approach is to test steels in the chamber where the conditions of COT inner bottom area is well simulated. Fig.5 shows one of the test methods that are based on SR242 results. Corrosion appearance of the test plate is shown in Fig.6. It is very similar to actual pitting in COT. The simulated corrosion tests on the developed steel (steel-B) were carried out. Thickness of test plate is 16.5mm and this test plate is adjusted to DH36 grade steel plate for hull structure. Weldability and other mechanical properties are equivalent to the conventional DH36 hull structure steel. This steel gives full play to corrosion resistance in the environment of inner bottom plates of COT. Test results indicate that corrosion rate of this steel after 2.5 years would be less than 1/5 of the conventional steel's rate in inner bottom environment. See Fig.7.

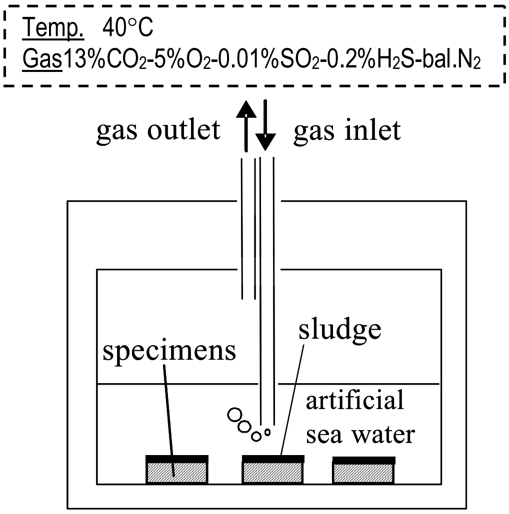

Fig.5 Simulation test method for COT inner bottom plates (Steel-B)

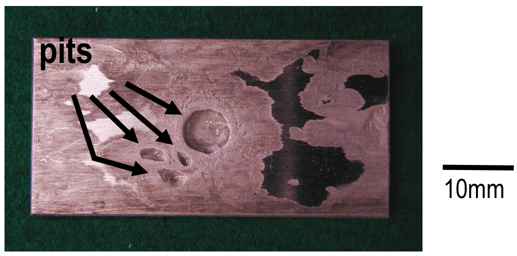

Fig.6 Simulated pit

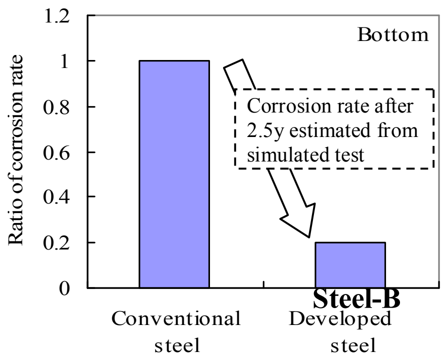

Fig.7 Performance of Steel-B

2.2 *Anti-Corrosion Steel for Upper Deck Corrosion*

Fig.8 shows one of the simulated corrosion test method for COT upper deck corrosion. This method was established based on the test results by SR242 committee too. This test method simulates the appearance and progress mode of corrosion in COT very well. Corrosion products on the upper deck analyzed by X-ray diffraction is shown in Table 1. Corrosion products and morphology are similar to those of actual COT. These results suggest that corrosion observed in actual COT is well reproduced. Fig.9 shows the test results for Steel-B, by this simulation method. Test results indicate that corrosion rate of Steel-B after 2.5 years would be less than 1/4 of the conventional steel's rate in upper deck environment.

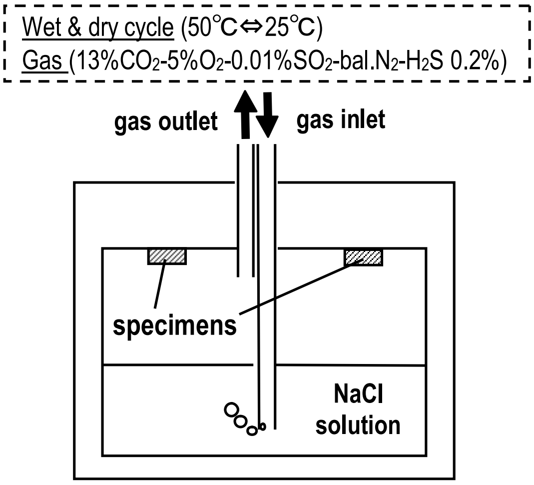

Fig.8 Simulation test method for COT inner bottom plates (Steel-B)

Table 1 Composition of corrosion products

			(mass%)
	FeOOH +Fe3O4	Elementa l S	Others
COT	45%	12%	43%
Simulated	41%	21%	38%

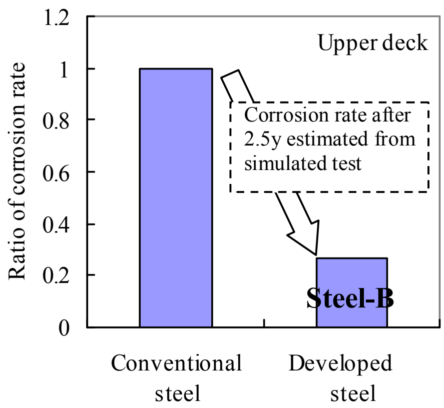

Fig.9 Performance of Steel-B

3 ONBOARD EVALUATION OF AN ANTI-CORROSION STEEL APPLIED TO COT INNER BOTTOM PLATES

These anti-corrosion steels have already applied to a number of crude oil tankers, for upper deck plates and/or inner bottom plates of COT. Recently one of the evaluation results were obtained, on such steel that has been applied to actual inner bottom plates of COT in VLCC without protective coating.

3.1 Applied Area of Anti-Corrosion Steel

Anti-corrosion Steel (Steel-A) has been applied to inner bottom plates of COTs of a VLCC without coating as shown in Fig.10. Dock inspection was carried out at a dock after two years and three months service. At the dock, corrosion behavior of these COTs being built on the anti-corrosion steel has been investigated and evaluated quantitatively.

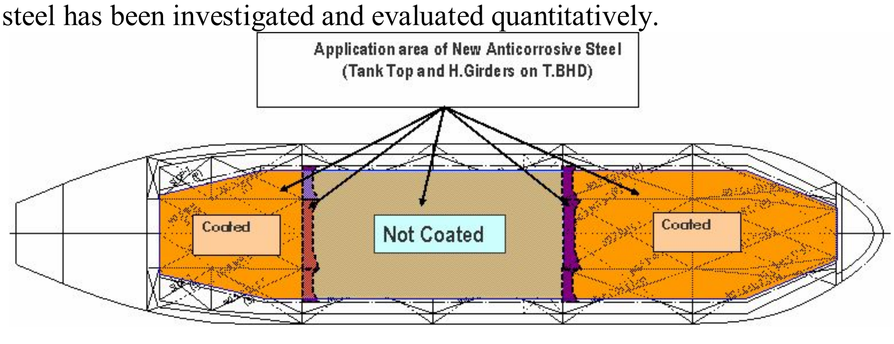

Fig.10 Applied area of the newly developed anti-corrosion steel without coating

3.2 Results on Pitting Frequency and Max Pit Depth on the Anti-Corrosion steel

As for pitting corrosion frequency on the anti-corrosion steel, no pit over 4mm in depth was observed. On the other hand, average frequency of pits over 4mm depth on conventional steels investigated in the past was about 140 counts per COT as shown in Fig.11. Hence, applying the anti-corrosion steel largely decreased pitting corrosion frequency.
As for observed maximum pit depth on the anti-corrosion steel onboard, it was less than 3mm as shown in Figure 12. On the other hand, maximum pit depth on conventional steels was from 7 to 11 mm. Hence, applying the anti-corrosion steel to the bottom of COTs largely decreased maximum pitting corrosion depth.
According to the results described above, the ship owner and the class judged that there was no need to repair, such as by coating, welding, and replacement, the inner bottom plate of COT.

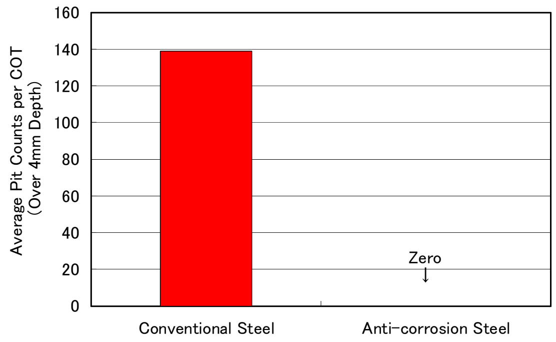

Fig.11 Average frequency of pits over 4mm depth per COTs

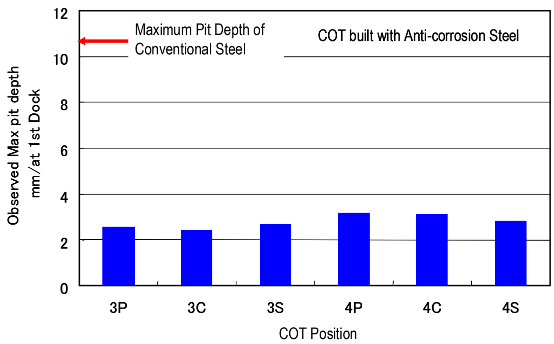

Fig.12 Maximum pit depth on conventional steel and anti-corrosion steel onboard

3.3 Physical Properties of the Anti-Corrosion steel

As well known, IACS standard for steel has been established and is in use to ensure physical property of steel, which is acceptable to shipbuilding and ship structure. The chemical composition of the Anti-Corrosion steel (Steel-A) that meets the IACS standard is shown in table 2. This Anti-Corrosion steel provides the same physical properties to the grade AH32 conventional hull structured steels. The shipbuilder who built the VLCC confirmed the physical properties by physical tests and experienced the same workability through its construction.

Table 2. A typical chemical analysis of the anti-corrosion steel (mass%)

	C	Si	Mn	P	S	Ceq
Anti-Corrosion Steel*1	0.124	0.26	0.96	0.014	0.007	0.331
Conventional Steel (AH32)	0.140	0.20	1.09	0.018	0.006	0.322
IACS Standard (AH32)	0.18	0.5	0.9 ~ 1.6	0.035	0.035	0.36

*1:A very small quantity of corrosion resistant elements is added.

3.4 Summary of the Onboard Evaluation of the Anti-Corrosion Steel

(1) Anti-corrosion steel has been applied to inner bottom plates of COT of oil tankers without coating.
(2) The validity of the anti-corrosion steel was confirmed onboard at its dock inspection. Maximum pit depth was less than 3mm, which required no repair.
(3) These onboard evaluation results were in good conformity with laboratory corrosion test results.
(4) It has been confirmed that the anti-corrosion steel provides the same physical properties and same workability to conventional steels.

4 BENEFIT OF THE ANTI-CORROSION STEELS

4.1 Pit Growth Stops at Dock Inspection

Intensive investigations were carried out on pitting corrosion phenomena on inner bottom plates of COT of VLCCs constructed by conventional steel. The fact reported was that pits that had been observed at dock inspections did not show further growth at the next dock inspections. This fact is explained as follow. At a dock, COT is cleaned and dried for inspection. After inspection, tanks will be filled with crude oil and oil coating, which prevents corrosion, will be formed on the surface of the bottom plates between corrosive substances. It is considered that, since the thickness of the oil coating at the already developed pits are thicker than that of the normal surface, the isolation effect of the steel surface from corrosive environment is higher than surrounding normal surface, as illustrated in Fig.13. Thus, the pitting corrosion growth stops at a COT cleaning and drying process, and it is a phenomenon common to the anti-corrosion steel.

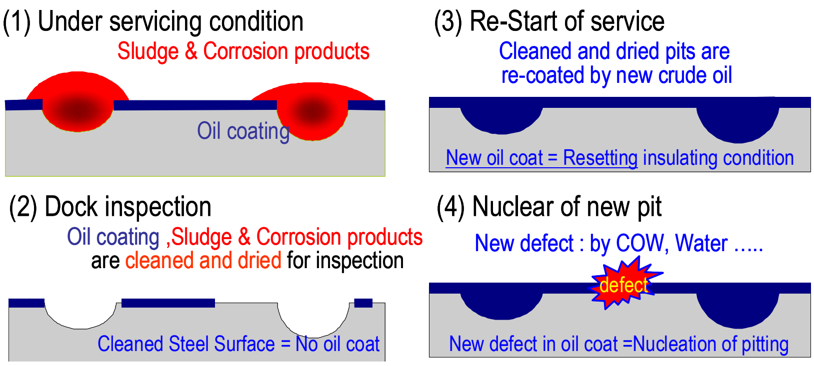

Fig.13 . Mechanism of pit growth termination at a dock

4.2 Potential Ability of Repair Free During Whole Ship Life

Considering the facts that i) maximum pit depth is shallow, ii) the growth stops at a COT cleaning and drying process after dock inspection, and iii) the number of the pits are very few, the anti-corrosion steel used for COT provides potential ability for repair-free throughout the life of the ship. Fig.14 illustrates the cycle that the maximum pit depth would not exceed diminution allowance and its growth stops at the dock inspection, while conventional steel would need repairs.

4.3 Lowering Risk for Perforation of Inner Bottom Plates by Anti-Corrosion Steel

Coating is one of the well-known corrosion prevention methods. Coating isolates steel surface from corrosion environments. On the other hand, anti-corrosion steel provides chemically inert property when the surface is being exposed to corrosion environment. So the primary corrosion preventive mechanism is completely different between anti-corrosion steels and coating. If the coating were applied completely, the isolation effect would be perfect. However, complete coating work with no defect from initial surface preparation to the final coating would be very difficult. In general very tiny defects exist in the coating layer, and moreover when the coating on conventional steels is broken, steel surface would be exposed to corrosion environment. The growth of pitting corrosion would start at high rate and the risk to perforate bottom plate and to spill crude oil out of COT would be substantial. On the contrary, as described before, anti-corrosion steel provides chemically inert property resulting low corrosion rate at corrosion environment. COT built with anti-corrosion steel keeps the above mentioned risk very low. See Fig.15.

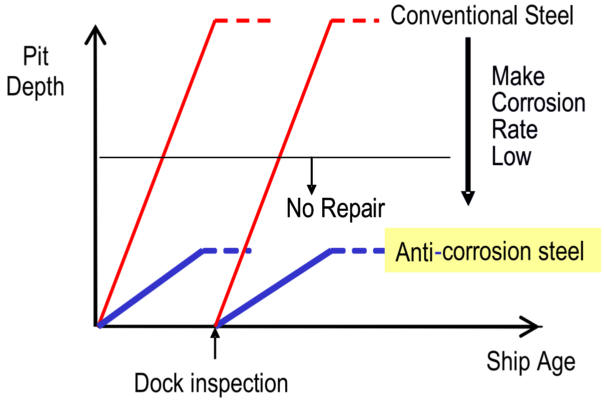

Fig.14 Repair free schematics for COTs built with anti-corrosion steel

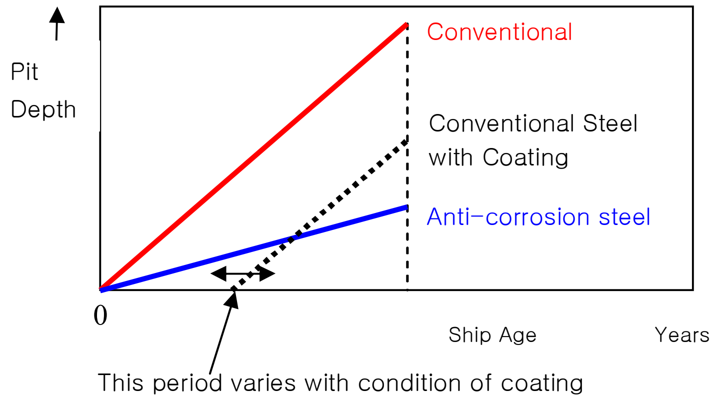

Fig.15 Risks for perforation of Anti-Corrosion Steel and conventional steel with coating

5 Conclusion

(1) Anti-corrosion steels will be an effective countermeasure against Oil Tanker Corrosion.
(2) These anti-corrosion steels provide the same physical properties to the conventional hull structured steels.
(3) Corrosion tests for COT inner bottom and upper deck plates have been developed.
(4) Validity of anti-corrosion steels was confirmed based on laboratory tests and actual vessel result.
(5) Potential ability for repair free for whole ship life is recognized.
(6) Anti-corrosion steels provide sophisticated solution for Oil Tanker Safety Problem.

References

Inohara, Y. Komori, T. Kyono, K. Ueda, K. Suzuki, S. and Shiomi, H. (2007) Developent of Corrosion Resistant Steel for Bottom Plate of COT, ISST2007, Osaka,

Inoue, K. Oshima, T. Yonezawa, M. Imai, S. Katoh, K. and Usami, A.. (2004), , TECHNO MARINE, No.878, pp.81-84.

Katoh, K. Imai, S. Yasunaga, T. Miyuki, H. Yamane, Y. Ohyabu, H. Kobayashi,Y. Yoshikawa, M. and Tomita, Y. (2003) Study on Localized Corrosion on Cargo Oil Tank Bottom Plate of Oil Tanker, World Maritime Technology Conference, San Francisco

Sakashita, S. Tatsumi, A. Imamura, H. and Ikeda, H. (2007) Development of Anti-Corrosion Steel for Bottom Plates of Cargo Oil Tanks, ISST2007, Osaka,

Tanino, Y. Kudo, S. Inami, A. Kashima, K. and Miyuki, H. (2006) Development of Corrosion Resistant Steel for Cargo Oil Tanks, Asia Steel International Conference, Fukuoka, 10D-7

Yasunaga, D.T. Katoh, K. Imai, S. Miyuki, H. Yamane, Y. Ohyabu, H. Saito, M. Yoshikawa, M. Kobayashi,Y. and Tomita, Y. (2003) Study on Cargo Oil Tank Upper Deck Corrosion of Oil Tanker, World Maritime Technology Conference, San Francisco