NIPPON STEEL TECHNICAL REPORT No. 90 JULY 2004

UDC 669 . 14 . 018 . 841 - 462

New S-TEN™1 Steel Tubes – Renewal of Sulfuric-acid-resistant Steel, S-TEN™1 –

Junichi OKAMOTO*1 Akira USAMI*2
Akio SOENO*3 Hiroyuki MIMURA*2
Tetsuo ISHITSUKA*2

Abstract

S-TEN™*1, a corrosion resistant steel for sulfuric acid dew, has been widely used in flue gas treating equipments such as air preheaters, smoke stucks and ducts as a countermeasure for low temperature corrosion caused by sulfur oxides. However recently, the steel also is required to corrosion resistance against hydrochloric acid dew corrosion resulting from lower-temperature waste gas at waste incinerating facilities. So, Nippon Steel Corporation has just developed "new S-TEN™1" steel having not only corrosion resistant for sulfuric acid, but also excellent corrosion resistant for hydrochloric acid. This paper explains qualitative characteristics of electric resistance welding tube made of new S-TEN™1 steel, combining the comparison new S-TEN™1 with S-TEN™1.

1. Historical Overview of Development of S-TEN™1 and New S-TEN™1 Steels

When a fuel containing sulfur (S) such as heavy oil, liquefied natural gas or coal is burned, sulfur oxides (SO_X) form, and SO_3 is one of those sulfur oxides. When the temperature of the exhaust gas falls to the dew point or below, or the gas contacts a cold wall surface, the SO_3 and H_2O in the gas combine to form a highly concentrated sulfuric acid which causes steel materials to corrode. This phenomenon is called sulfuric-acid dew-point corrosion. Under such a condition, quite different from the corrosion condition in normal atmosphere, heavy corrosion occurs not only to ordinary carbon steels but also to stainless steels.

That weathering steels containing Cu resisted corrosion in a sulfuric-acid dew-point environment was discovered in U.S.A. In Japan, on the other hand, the influence of alloying elements over the resistance to the sulfuric-acid dew-point corrosion was studied around 1960 on the basis of the similar effects in weathering steels, and as a result, steels having improved corrosion resistance were developed[1). Among those, S-TEN™1[2)] developed by Nippon Steel Corporation (then Fuji Iron and Steel Co., Ltd.) was one of the most resistant to such a corrosive environment of acid dew point owing to the facts that each of Cu and Sb contained in the steel inhibited anodic reactions and that these elements also formed a film of Cu_2Sb on the surface of steel materials to inhibit cathodic reactions as well. While S-TEN™1 has been widely used in the form of heavy plate and thin sheet products, it has come to be used also in the form of steel pipes since the 1980s.

In the meantime, under dioxin suppression regulations enacted in 2002, it became necessary to cool exhaust gas from waste incineration plants rapidly to low temperatures, and as a consequence, there emerged a new corrosive environment in which hydrochloric acid forming as a result of the combustion of food or plastic wastes was involved (see **Fig. 1**). In response to this new situation, new S-TEN™1 was developed and commercially launched into the market. New S-TEN™1 is a steel developed on the basis of S-TEN™1 and having significantly enhanced resistance to hydrochloric-acid dew-point corrosion. That steel has been commercially available in the

*1 Pipe & Tube Division
*2 Steel Research Laboratories
*3 Kimitsu Works

* S-TEN is Nippon Steel Trademark

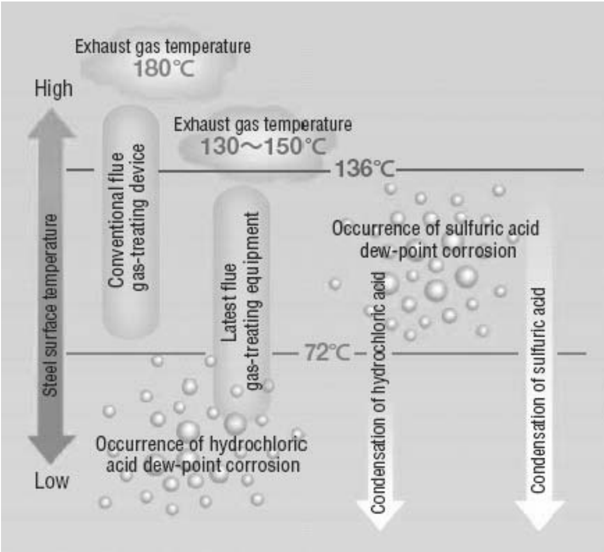


Fig. 1 Mechanism of sulfuric- and hydrochloric-acid dew-point corrosion occurring in flue-gas treating equipment at waste incineration plants (in the case of exhaust gas comprising SO_3: 6 ppm, HCl: 300 ppm, H_2O: 30%)

form of flat and tubular products since October, 2002.

Small diameter pipes of new S-TEN™1 formed by the electric resistance welding (ERW) method have been widely used, especially for the air preheaters of thermal power plant boilers, waste incineration boilers and various types of heating furnaces. The high quality ERW pipes of the new steel are produced under the same quality control system established for the steel pipes for power plant boiler applications. In order that the ERW pipes of the new steel could be applied not only to non-pressure steam pipes but also to pressure parts such as fuel economizer pipes, Nippon Steel obtained authorization for the general use of the product as a material in accordance with the technical standard for the materials for thermal power plant facilities in 2001. Further, in May, 2002, the product was included in the technical standard as a standard material (KA-STB 380J1 for thermal power plant applications).

This paper presents the quality and properties of ERW steel pipes of new S-TEN™1, comparing them with those of ERW steel pipes of conventional S-TEN™1.

2. Quality and Properties of New S-TEN™1 Steel Pipe

2.1 Chemical composition, mechanical properties and application test results

The chemical composition of new S-TEN™1 is shown in part (a) of **Table 1**. New S-TEN™1 has a lower C content and has a higher Mn content than those of conventional S-TEN™1 instead. In addition, its corrosion resistance is enhanced by means of combination of alloying elements added by small amounts.

The mechanical properties of an example of new S-TEN™1 steel pipes are shown in part (b) of Table 1. According to the product specification, the tensile strength of a new S-TEN™1 steel pipe is 380 N/mm^2 or higher, which is the same as that of conventional S-TEN™1 and intermediate between those of JIS STB 340 and STB 410; the actually measured tensile strength of new S-TEN™1 is substantially the same as that of conventional S-TEN™1.

The results of flattening, flaring and reverse flattening tests of new S-TEN™1 steel pipes, 89.1 mm in outer diameter and 5.0 mm in wall thickness, are shown in **Table 2** and **Photo 1**. No crack occurred at ERW seams at any of the tests, evidencing good workability of the product.

Table 1 (a) Chemical compositions of S-TEN™1 / new S-TEN™1 (ladle analysis) (mass%)

	C	Si	Mn	P	S	Cu	Sb	Ni
Specification	≤0.14	≤0.55	≤1.60	≤0.025	≤0.025	0.25-0.50	≤0.15	≤0.50
S-TEN1 example	0.096	0.19	0.35	0.009	0.006	0.26	0.096	0.18
New S-TEN1 example	0.029	0.21	0.89	0.010	0.006	0.32	0.097	0.21

Table 1 (b) Mechanical properties of S-TEN™1 / new S-TEN™1 tubes

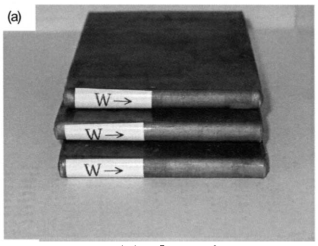
	Yield strength (N/mm^2)	Tensile strength (N/mm^2)	Elongation (%)	Hardness (HRB)
STB 340 specification	≥215	≥340	≥35	≤77
STB 410 specification	≥245	≥410	≥35	≤79
New S-TEN1 / S-TEN1 specification	≥230	≥380	≥35	–
S-TEN1 example	281	415	52	70
New S-TEN1 example	293	404	53	69

Test specimen : JIS Z 2201 No.11 or No.12B

Table 2 Formability test of S-TEN™1 / new S-TEN™1 tubes

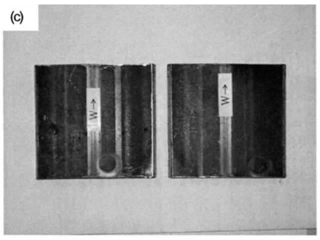
	Flattening*[1]	Flaring	Reverse flattening
Specification	No evidence of cracks to flattening height H $H = \frac{(1+e)\,t}{e+t/D}$ $e = 0.09$	1.2 times of outside diameter	No evidence of cracks
S-TEN1 example	No crack	No crack	No crack
New S-TEN1 example	No crack*[2]	No crack*[2]	No crack*[2]

*[1] H: distance between flattening plates (mm)
D: specified outside diameter of the tube (mm), t : specified wall thicness of the tube (mm)
*[2] See photograph 1



(a) Flattening

(b) Flaring



(c) Reverse flattening

Photo 1 Formability test result of new S-TEN™1 tubes

2.2 High temperature strength and creep properties

Fig. 2 shows the tensile test results of S-TEN™1 and new S-TEN™1 steel pipes at room temperature to 500°C. The strengths of both the steels are substantially the same. The minimum tensile and yield strengths of S-TEN™1 at different temperatures were calculated in accordance with the technical standard for thermal power plant facilities, and they are shown in the graph for reference purposes.

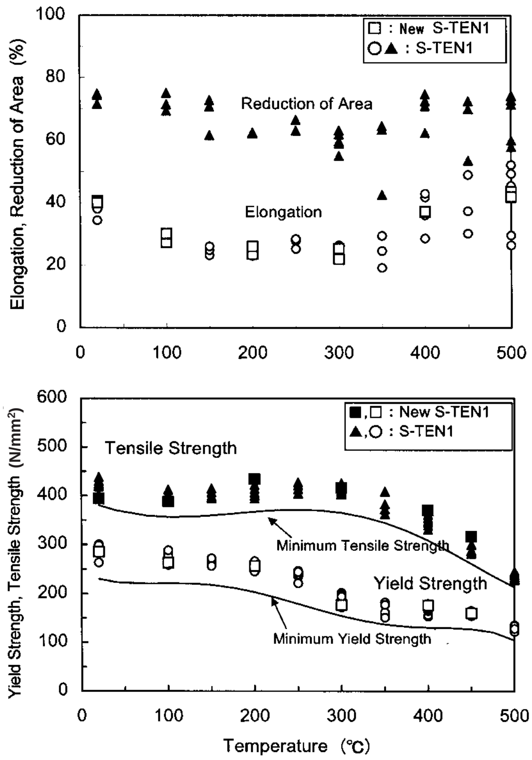


Fig. 2 Tensile properties at elevated temperatures for S-TEN™1 / new S-TEN™1 tubes

With respect to the creep rupture strength of new S-TEN™1 steel pipes, **Fig. 3** shows the relationship between load stress and the time to rupture. A maximum creep rupture time of approximately 9,000 h was recorded in a temperature range from 400 to 550°C. The average creep rupture strengths of conventional S-TEN™1 at different temperatures are shown in the graph with solid lines. Here, it is clear that both the steels are of the same level in terms of creep rupture strength.

It should be noted, however, that the maximum allowable tensile strength of the developed steel within the temperature range of its use (425°C or below) is determined not by creep rupture strength but by high temperature tensile strength. This means that even the maximum temperature of use of new S-TEN™1 is within the non-creep temperature range.

The maximum allowable stress (according to the technical standard for the materials for thermal power plant facilities) of S-TEN™1 and new S-TEN™1 steel pipes was calculated from the results of the high temperature tensile and creep rupture strength tests, and is plotted in **Fig. 4**. In the temperature range up to the highest temperature of use (425°C), the maximum allowable tensile stress of new S-TEN™1 is determined by the tensile strength at room temperature or the tensile or yield strength at high temperature. Since the creep rupture strength of new S-TEN™1 is high enough in this temperature range, it does not affect the value of the maximum allowable tensile stress.

2.3 Workability[3)]

Like conventional S-TEN™1, new S-TEN™1 does not contain

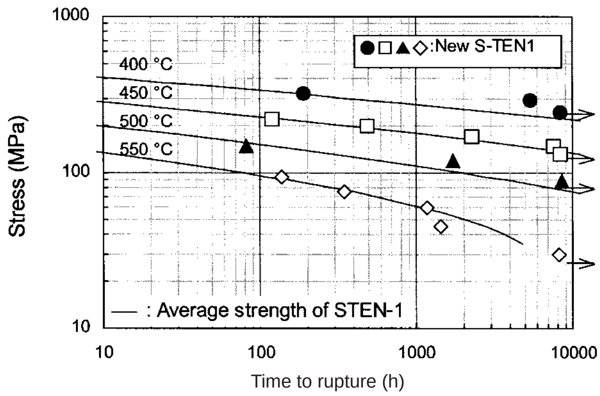


Fig. 3 Stress-rupture plot for new S-TEN™1 tubes

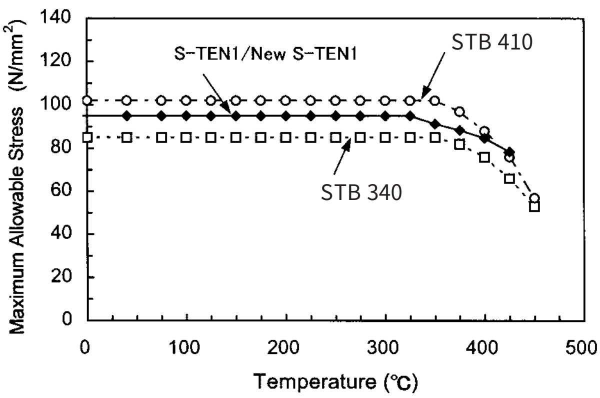


Fig. 4 Comparison of maximum allowable stress values for different steels

alloying elements such as Cr, and its C content is low. For this reason, the steel can be welded under the same condition as that applicable to ordinary carbon steels of the same strength level. **Fig. 5** shows the results of tensile tests of welded joints between new S-TEN™1 steel pipes. All the specimens ruptured at the base metal, which means that the strength of the welded joints was the same as that of the base metal and that good strength was achieved in the welded joints. For reference, in consideration of the corrosion resistance of the welded joints, the filler wire used for the test was FGC-55 (for weathering steels) of Nippon Steel Sumitomo Welding Industry. Filler wires resistant to hydrochloric-acid corrosion have been developed recently, and Nippon Steel recommends use of this type of welding material depending on the environmental condition of use.

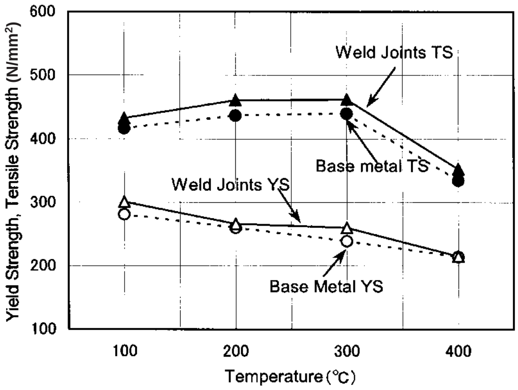


Fig. 5 Tensile properties at elevated temperatures for weld joints of new S-TEN™1 tubes

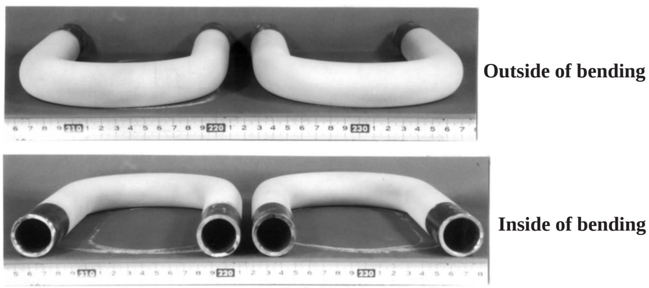


Photo 2 Cold bend test (bend radius: 65R(2.0D), after liquid penetrant testing)

Photo 2 shows specimens of new S-TEN™1 steel pipes, 31.8 mm in outer diameter and 2.9 mm in wall thickness, that underwent a cold bend test at a bend radius of 2.0D (R = 65 mm). No cracking was observed at a liquid penetrant test after the bending, and a smooth surface free of creases was obtained. Thanks to normalizing heat treatment applied to the entire pipes, bendability was good regardless of the position of ERW seams.

3. Corrosion Resistance of New S-TEN™1 Steel Pipe

3.1 Resistance to sulfuric-acid dew-point corrosion[4)]

Test pieces of different steels were subjected to a 6-h immersion test in a 50%-solution of sulfuric acid at 70°C, the severest of corrosion test conditions under sulfuric acid/vapor equilibrium. The results are shown in **Fig. 6**. In this environment, even stainless steels (JIS SUS 304 and SUS 316L) suffered heavy corrosion, but new S-TEN™1 as well as conventional S-TEN™1 proved to have excellent corrosion resistance.

A steel-pipe type air preheater for a heavy oil-burning boiler is one of the typical facilities to which sulfuric-acid dew-point corrosion occurs[5)]. Generally speaking, corrosion occurs more intensively on the low temperature side of a preheater. Steel pipes (60.3 mm in outer diameter, 3.2 mm in wall thickness and 6,080 mm in length) of S-TEN™1 and an ordinary carbon steel, JIS STB 340-EG, were used in the front line of the reheater section of a steel-pipe type air preheater, and after use of the equipment for 1 year, some of the pipes were dismantled to investigate the state of their corrosion. The results are

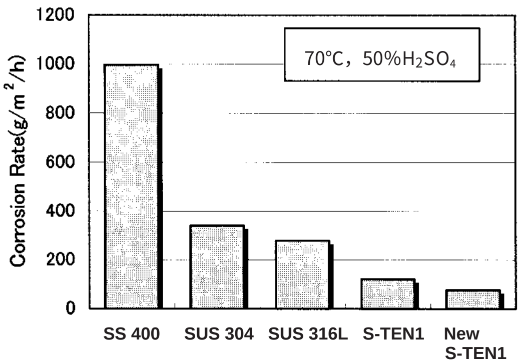


Fig. 6 Sulfuric acid immersion test results for different steels

Table 3 Field test results of S-TEN™1 tubes

Test location	Tube type air preheater at heavy oil-fired boiler of power plant A				
Test specimen attachment	Air preheater tubes of low-temperature side at front line				
Test condition	Flue gas temperature	124-130°C	Gas composition	SO_x	360 ppm
	Estimated dew point of flue gas	130°C		H_2O	About 10%
	Test specimen temperature	70-80°C	Test duration		4,808 h
			Times of interval		35 times
Test results		Measure corrosion mass (mm/4,808 h)		Estimated annual corrosion mass (one side) (mm/y)	
	Grade	Maximum	Average		
	S-TEN1	0.12	0.02	0.04-0.22	
	STB 340	0.62	0.25	0.46-1.13	

shown in **Table 3**. The structure of the reheater was such that the inner surfaces of the pipes were in contact with combustion exhaust gas, and the outer surfaces with air to be preheated. The estimated annual corrosion loss of the S-TEN™1 steel pipes was 0.04 to 0.22 mm, about one-fifth of that of ordinary carbon steel pipes, 0.46 to 1.13 mm. The corrosion product on the inner surfaces consisted mainly of $FeSO_4 \cdot H_2O$ and $FeSO_4 \cdot 4H_2O$, the typical corrosion product of sulfuric-acid dew-point corrosion; based on this, the environment to which the inner surfaces of the specimen pipes were exposed was presumed to be the one of sulfuric-acid dew-point corrosion. It is clear from the above results that S-TEN™1 steel pipes are excellent in the resistance to sulfuric-acid dew-point corrosion also in actual application.

3.2 Resistance to hydrochloric-acid dew-point corrosion[6)]

The dew point of hydrochloric acid is considered to be 72°C or below, lower than that of sulfuric acid. After modifications of waste incineration plants to cope with the dioxin suppression regulations mentioned earlier, the temperature of exhaust gas became lower, and as a result, hydrochloric-acid dew-point corrosion began to occur to the exhaust gas system of some of the plants which had experienced only sulfuric-acid dew-point corrosion before (see Fig. 1).

Specimen pipes of various steels were subjected to a 6-h immersion test in a 10.5%-solution of hydrochloric acid at 80°C, a condition which corresponds to the environment of hydrochloric-acid dew-point corrosion. The results are shown in the upper part of **Fig. 7**. Like in the sulfuric-acid dew-point corrosion environment, new S-TEN™1 exhibited better corrosion resistance than stainless steels did. Thereafter, the specimens were immersed in the same solution for a longer period of time. The final results are shown in **Photo 3**. Whereas the wall thickness of the ordinary carbon steel specimen decreased to nearly one-tenth the original thickness and pitting corrosion occurred intensively to stainless steel specimens, the new S-TEN™1 specimen suffered little corrosion.

As one of the new characteristics of new S-TEN™1, it has been confirmed that the steel exhibits good corrosion resistance also in a dilute solution of hydrochloric acid having a pH of 1 or so, as shown in the lower part of Fig. 7. Although conventional S-TEN™1 does not exhibit good corrosion resistance in an environment of dilute hydrochloric acid, new S-TEN™1 is as corrosion-resistant as stainless steels.

On the other hand, in the flue gas treatment system of a waste incineration plant or the like in operation, ash containing chlorides of metal elements sticks to the surfaces of steel materials, and condensation of sulfuric acid takes place on the surfaces. These may lead to corrosion caused by sulfuric acid containing dissolved chloride ions (Cl^-). In consideration of this situation, specimens of different steels were subjected to a corrosion test in a sulfuric acid environment containing chloride ions. The results are shown in **Fig. 8**. The corrosion resistance of new S-TEN™1 was by far the best also in this environment; the steel is expected to show excellent corrosion resistance in the environment of actual application as well. While austenitic stainless steels are prone to stress corrosion crack (SCC) in an environment containing hydrochloric acid or chloride ions, one of the significant advantages of new S-TEN™1 is that it is free from SCC because it is a ferritic steel.

As an evaluation test in an environment of real use, test pieces of ordinary carbon steel, S-TEN™1 and New S-TEN™1 were set inside a dust collector duct of a coke oven plant. **Fig. 9** shows the measurement results of corrosion loss after exposure for about 6 months. In this relation, it has to be noted that, at a coal yard, which is usually located near the sea, seawater is sprayed on the stacks of coal, which is the raw material of coke, in order to prevent scattering of coal fine, and as a consequence, chlorides originating from the seawater are included in the exhaust gas from a coke oven plant, in

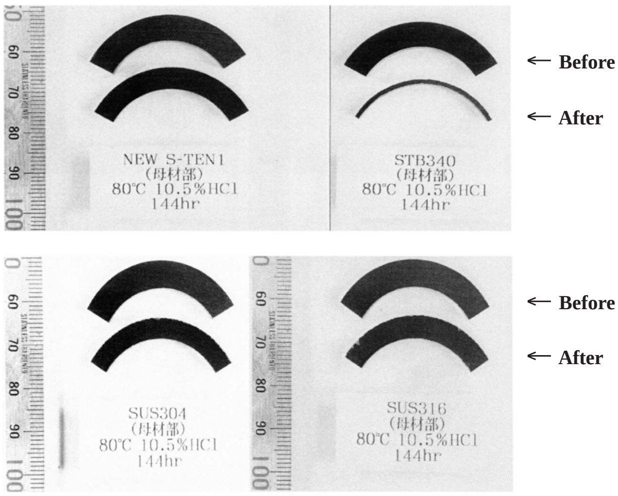


Photo 3 Hydrochloric acid (80°C, 10.5%) immersion test results for different tubes

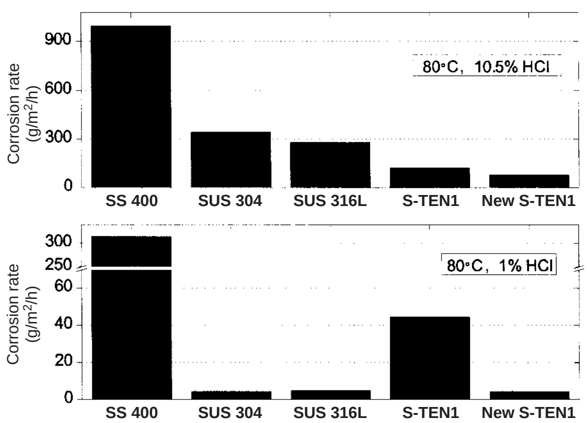


Fig. 7 Hydrochloric acid immersion test results for different steels

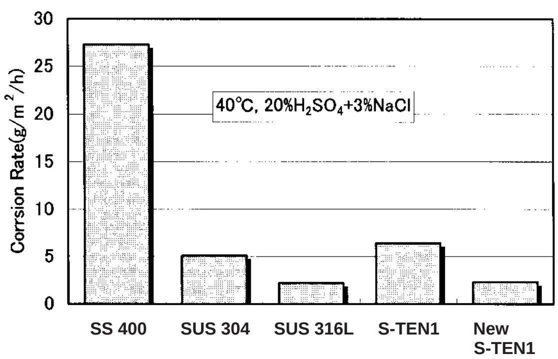


Fig. 8 Sulfuric acid with NaCl immersion test results for different steels

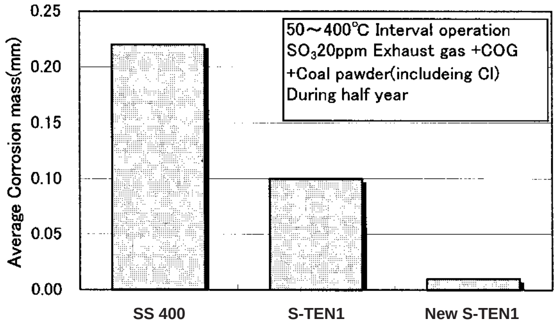


Fig. 9 Field test results of new S-TEN™1 under sulfuric-acid dew-point with chloride during half year

addition to usual sulfur oxides. In the above test in an actual environment of sulfuric-acid dew-point corrosion containing chlorides, new S-TEN™1 proved to have by far better corrosion resistance than the other steels, just like in the laboratory test.

4. Closing

As explained above, an electric-resistance-welded (ERW) steel pipe of new S-TEN™1 is an economical product owing to the fact that it is made of a low carbon steel containing only small amounts of alloying elements and nevertheless, is excellent in corrosion resistance as well as mechanical properties and workability. Since the launch of the product into the market in October 2002, it has been successfully used for various applications such as the air preheater for a waste incineration plant and that for a waste incineration boiler of a biomass power generation plant. In fiscal year 2003, the chemical composition of new S-TEN™1 was included in the technical standard for the materials for thermal power plant facilities, and thus conditions for wider application of the new steel to pressure parts have been provided.

Fin tubes are often used for a heat exchanger in order to increase the heat transfer surface area. For this application, Nippon Steel offers S-TEN™1-EX, a product excellent in workability specially designed for the use as the fins of a very small-diameter spiral fin tube.

As seen above, the economical new steel, new S-TEN™1, which is useful for environmental protection measures, is being continuously improved to respond to new requirements, and the steel is expected to expand its applications in the form either of tubular or flat product.

References

1) Matsushima: Trend of Iron and Steel Technologies. Iron and Steel Institute of Japan, 1995, p.1-7, 139
2) Teramae et al.: Fuji Iron and Steel Technical Report. 17, 103(1968)
3) The weld and bend tests were carried out by Nagasaki Shipyard of Mitsubishi Heavy Industries.
4) Okamoto et al.: Shinnittetsu Giho. (377), 42(2002)
5) Iijima et al.: Journal of Japan Petroleum Association. 8, 610(1965)
6) Okamoto et al.: Piping Technology. 45, (11), 602(2003)