KOBELCO

FERROCO TUBE

SHINKO METAL PRODUCTS CO.,LTD.

LLOYD'S REGISTER QUALITY ASSURANCE · ISO9001 · UKAS MANAGEMENT SYSTEMS 001

The corrosion resistance of the copper alloy tube used in heat exchangers is heavily dependent on the state of the protective film on the inside surface of the tubes. One effective method of forming this protective film is ferrous ion injection into the cooling water, but depending on the quality of the seawater used it may be difficult to form a sound protective film. In recent years there has been a trend against the injection of high concentrations of ferrous ions into seawater for environmental reasons.
We have developed a copper alloy tube manufactured with an iron oxyhydroxide protective film, identical to that created by ferrous ion injection. This tube has achieved widespread utilization in the industry under the trade name "Ferroco Tube."

1 Features

1. An iron oxyhydroxide protective film, identical to that created by ferrous ion injection, is in place before the usage, delivering superior corrosion protection effect even as an initial protective film.

2. There is none of the swelling of the film normally associated with cathodic protection. As a result, cathodic protection can be applied under exactly the same conditions as for aluminum-brass bare tube, with no special requirements for potential control.

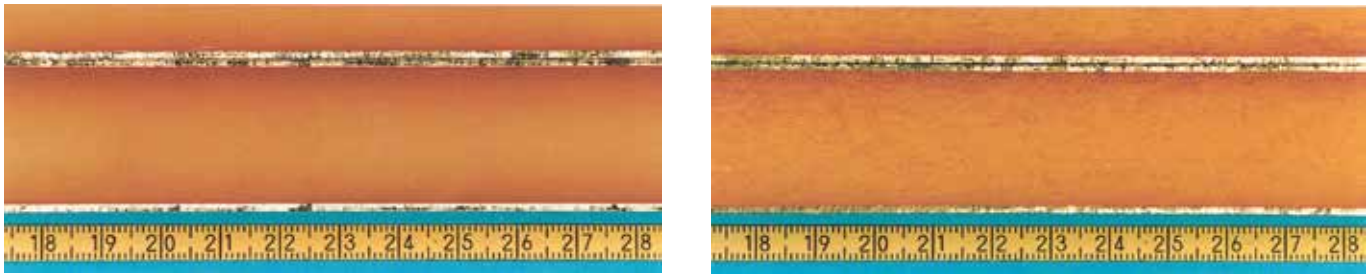
3. Maintenance tasks such as sponge ball cleaning, brush cleaning and eddy current inspection can be performed in exactly the same way as for aluminum-brass bare tube.

4. There is nc need of high density ferrous ion injection after partial replacement at the plant where ferrous ion injection is continuously performed.
Therefore the entire heat exchanger will enjoy improved heat transfer performance.

2 Protective Film Properties

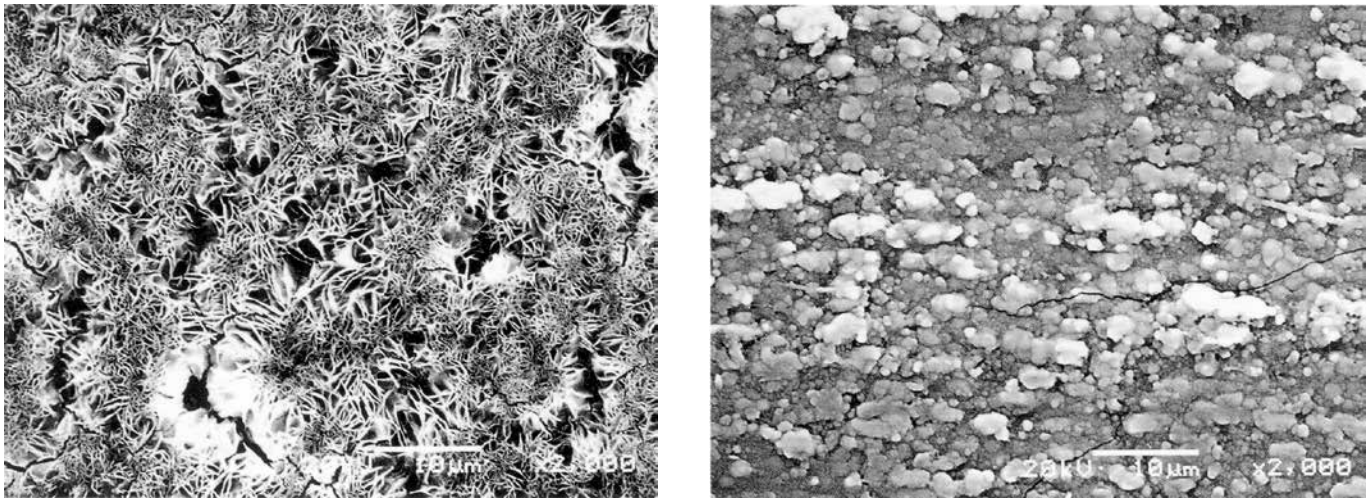
● Film surface state

The surface appearance of the film is quite similar to that formed through ferrous ion injection, but examination under an electron microscope reveals needle-like (acicular) crystals in the Ferroco tube film, indicating its superior crystallization.



Ferroco Tube　　Film formed by ferrous ion injection

Photo 1 Surface Appearance of Protective Film



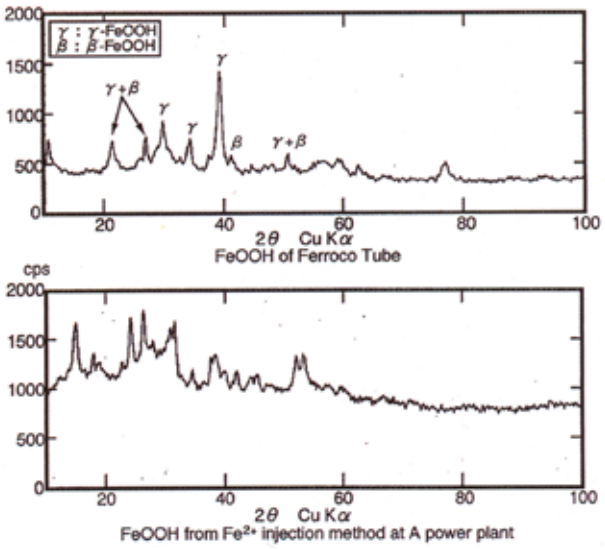
Ferroco Tube　　Film formed by ferrous ion injection

Photo 2 SEM Photomicrograph of Film Surface

X-ray diffraction analysis of film

The primary constituent of the film is iron oxyhydroxide (FeOOH). Compared to the protective film formed by ferrous ion injection, the Ferroco Tube film has a much sharper diffraction pattern, indicating its superior

Fig. 1 X-Ray Diffraction Analysis of



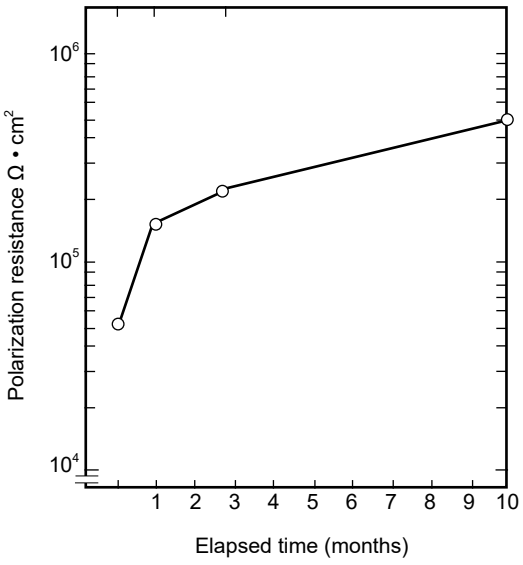
Ferroco Tube film

Film formed by ferrous ion injection

Electrochemical characteristics

The protective film of Ferroro Tube delivers sufficiently high polarization resistance in its as-manufactured state, and also the film will continue to mature over time as water flow continues.

Fig. 2 Change Over Time in Polarization Resistance (model condenser test results)



Test conditions
Seawater : Clean seawater
Fe^{2+} injection : 0.005ppm

Wear resistance

The protective film of Ferroco Tube offers superior wear resistance to that formed through ferrous ion injection, but wear is unavoidable when mechanical cleaning is used. For this reason, excessive cleaning should be

Table 1 Film Weight Loss to Sponge Ball Cleaning

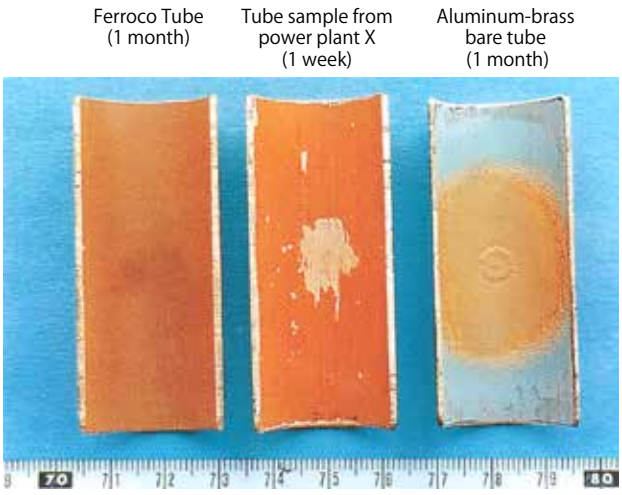
Sample tube	Sponge balls passed	
	1,000	3,000
Ferroco Tube	5%	24%
Tube sample from power plant X	35%	100%
Tube sample from power plant Y	18%	72%

Power plant X — *Fe^{2+} injection: 0.5 ppm x 2hr/2days*
Sponge ball cleaning: None
Period in operation: 1 year

Power plant Y — *Fe^{2+} injection: 0.02 ppm continuous*
Sponge ball cleaning: Yes
Period in operation: 7 years

Durability to water flow

BNF water jet testing was used to evaluate durability to water flow, and demonstrated that protective film of Ferroco Tube offers superior wear resistance to that formed through ferrous ion injection.



Test conditions
Test fluid : Clean seawater
Nozzle diameter : 2mm
Velocity : 9m/s

Photo 3 Film States After Water Jet Test

Heat transfer performance (heat transfer resistance of the film)

The heat transfer resistance of the Ferroco film is about 1.5 x $10^{-5}m^2$ k/W, which is equivalent to a 5% reduction in the coefficient of heat transfer for a condenser using new aluminum-brass tubing. This is an outstanding value for an initial protective film.

3 Corrosion resistance

Table 2 indicates the water flow test results in a model condenser. To better observe the corrosion dynamics where localized peeling of the film has occurred for some reason, the film was scratched prior to testing.

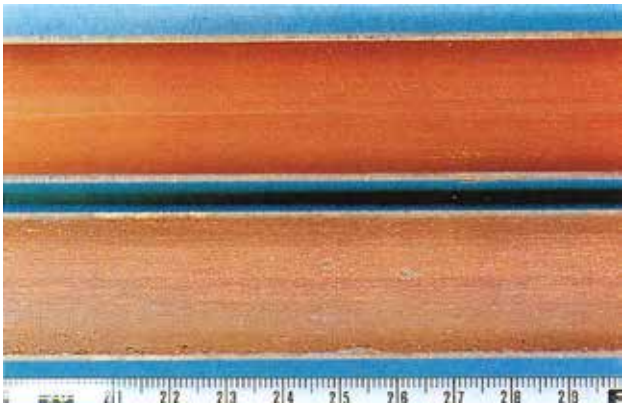
Table 2 Water Flow Test Results

Seawater	Corrosion depth (Unit : mm) Values in parentheses are for scratched regions	
	Ferroco Tube	Aluminum-brass bare tube
Clean seawater *Sponge ball cleaning: 10 balls/week*	None (0.02 to 0.05)	0.05 to 0.07
Chlorinated seawater *Residual chlorine: 0.2 ppm* *Sponge ball cleaning: None*	None (0.08 to 0.14)	0.17 to 0.25
Polluted seawater *S^{2-}: 0.1 ppm x 3 hr/day* *Sponge ball cleaning: 10 balls/week*	None (0.13 to 0.20)	0.26 to 0.34

Note: Flow rate: 2.0 m/s
Test duration: 2 years

The Ferroco Tube showed no corrosion in regions protected by the film. Corrosion in the pre-scratched regions was less than that observed in aluminum-brass bare tube. This fact indicates that even is the film should suffer minor damage during system operation, the high polarization resistance of the surrounding regions will rather act to minimize resulting corrosion

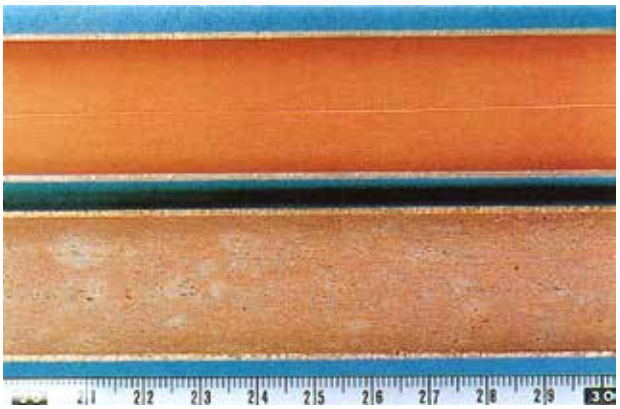
● Clean seawater



Ferroco Tube

Aluminum-brass bare tube

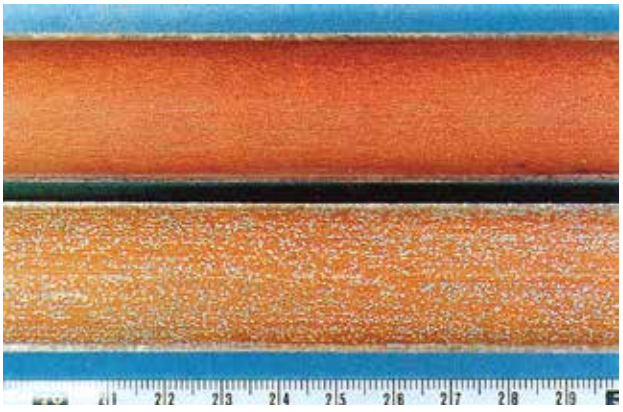
● Chlorinated seawater



Ferroco Tube

Aluminum-brass bare tube

● Polluted seawater



Ferroco Tube

Aluminum-brass bare tube

Photo 4 Tube Inner surface appearance After Water Flow Test

4 In-Service Performance

● Application in Condenser at Power Plant R

Table 3 Eddy Current Inspection Results

Period of operation	Tube type	Tubes tested	Corroded tubes	Corroded tube ratio
1989 to 1991	Old tubes	13,228	3,543	26,8%
	New tubes (bare tubes)	5.374	3,094	57.6%
1993 to 1994	Old tubes	12,866	3,037	23.6%
	New tubes (Ferroco Tubes)	3,509	32	0.9%

Note 1: Tube types
Old tubes: Tubes which have protective film on inner surface, formed through long periods of use.
New tubes: Tubes replaced in prior inspection
Note 2: Corroded tubes
Wall thickness decreased by at least 20% from prior inspection.

Summary of results

Bare tubes were used as replacements in the 1989 inspection, and the eddy current inspection performed in 1991 showed that corrosion was significantly more rapid in the replaced tubes than the old ones.
Ferroco Tubes were used as replacements in 1993, and the inspection the following year showed that corrosion in the replaced tubes was dramatically lower.

Table 4 Eddy Current Inspection Results

Estimate Wall Thickness Reduction	Machine A	Machine B	Total
80% or more	2	0	2
60 to 79%	1	0	1
40 to 59%	22	2	24
20 to 39%	0	0	0
0 to 19%	0	0	0
N.A.	1	2	3
Defect-free	1,930	1,952	3,882
Total	1,956	1,956	3,912

Note: Period of operation: January 1993 to December 1995 (approx. 3 years)

Tube sampling inspection results

All tube samples showed deposit attack due to accumulation of foreign matter. 0.3% sulphide was detected from scale, indicating a high level of sea water pollution.

Summary

Even though the site was utilizing polluted seawater, eddy current inspection after about three years of operation showed that 3,882 of 3,912 tubes (99.2%) were defect-free, demonstrating the efficacy of the initial protective

5 Usage of Ferroco Tubes

Handling

Transport, storage and installation of the Ferroco Tubes is handled in the same way as standard aluminum-brass tubes. The protective film will not peel even under normal flexing during installation, as long as the region is not subject to plastic deformation.

Tube expanding

From the viewpoint of tube expanding workability, in principle tubes with both ends are delivered without protective film for about the last 50 mm. The end regions are amply protected by cathodic protection, and in addition, high polarization resistance works cathedic protection so effective, there should be no worries of corrosion even when used without protective film. Please use them as delivered.

Cathodic protection

Use under the same conditions as aluminum-brass bare tubes. In cases where potential distribution may be non-uniform due to partial replacement, set the potential for the most noble region to -500 mV SCE. Localized drops in potential will not have an adverse effect on the film.

Tube internal cleaning

Sponge balls during system operation, or nylon brushes while the system is halted, are appropriate for cleaning foreign deposits from the interior of the tubes in the same fashion as for aluminum-brass bare tubes. When returning the system to normal operation after cleaning and recovering the protective film, the same procedure should be followed as for aluminum-brass bare tubes.

Eddy current inspection

The film has no effect on the inspection process, and the parameters are therefore the same as for tubes with no coating.

Ferrous ion implantation

When all tubes in the system are Ferroco Tubes, corrosion prevention effectiveness will be excellent even without ferrous ion implantation. If only some tubes are replaced and ferrous ion implantation is being used to minimize corrosion on other tubes, continue that implantation normally. The entire system will achieve improved heat transfer performance because, compared to uncoated tubes, it will not require as high an implantation concentration to create the initial film.

Prevention of foreign matter influx

Sharp foreign objects inside the tube may damage the protective film, and so the same measures used for aluminum-brass bare tubes should be taken to prevent influx.

6 Supported specifications

Type of film:	Iron oxyhydroxide
Film thickness:	5 to 15 µm avg.
Tube expanding:	No coating on expanding ends
Material:	Copper alloy (Alloy C44300, C68700, C70600, C71500, C71640 etc.)
Dimensions:	OD: 16 to 38 mm (ID 13 mm min.) Length: 25,000 mm max.

FERROCO TUBE

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