

# Development of Surface Treatment Technique Promoting Protective-rust Formation

by

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## Synopsis

*Weathering steels develop a protective-rust layer during outdoor exposure. This layer acts as a barrier which slows further corrosion, thus enabling weathering steels to be used in structural applications without coating. However, there are some problems, for example, it is difficult to form the protective-rust in chloride environment in use of uncoated weathering steel.*

*Weather-Act method was developed as a new surface treatment technique for weathering steels, and enable to promote the growth of Cr-substituted goethite which was the final form of the protective-rust.*

*It is hoped that this technique will be applied widely, because it solves some problems of uncoated weathering steel.*

## 1. Introduction

Weathering steels are low alloyed steels which contain a small amount of alloying elements such as Cr, Cu, P and Ni which improve atmospheric corrosion resistance. The formation of protective and stable rust layer on the surface of steels leads to significant decrease of atmospheric corrosion.

Since weathering steels were adopted as a structural material for bridges at 1978 in Japan, about twenty years have passed and use of weathering steels have gradually increased to mitigate the maintenance cost. However several problems were encountered.

In order to solve the problems, on the basis of the ground that protective rust layer is composed of Cr-substituted Goethite, we have developed a weathering steel treated with new surface technique which promotes protective rust formation.

## 2. Problems of Weathering Steels without Coating

The application of weathering steels without coat-

ing leads to the problem of surface appearance such as the stain of concrete because of the formation of rust-laden water in early stage as well as ordinary steels.

Furthermore, weathering steels have not high corrosion resistance under chloride containing environments and protective rust layer does not form in such environments where the content of air-borne sea salt particles above 0.05 mdd (mg NaCl/dm<sup>2</sup>/day). **Figure 1** shows the safety region of the application of weathering steels without coating in Japan. Recently deicing salt has been sprayed at superhighways in winter, and it influences the corrosion behavior of weathering steels. These problems are summarized in **Table 1**.

## 3. Protective and Stable Rust of Weathering Steels and its Evaluation Method

Several kinds of iron rust compounds were formed by the corrosion of steels in atmospheric environments. Typical rust constituent compounds are shown in **Table 2**.

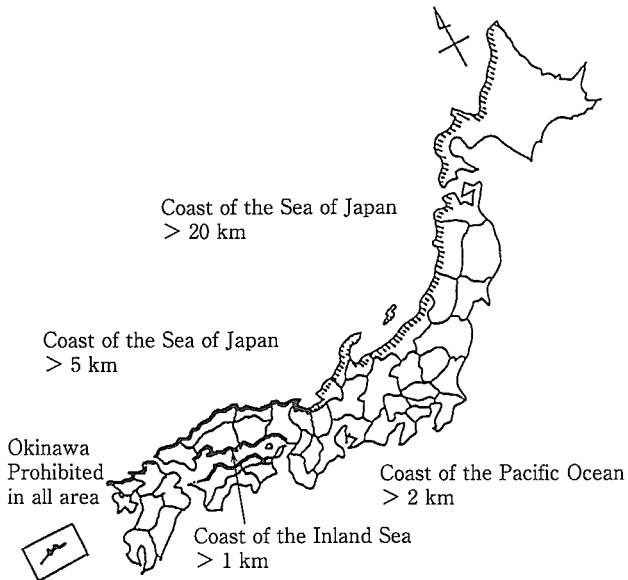


Fig. 1 Safety region where weathering steels are able to be used without coating in Japan

Table 1 Problems in the application of weathering steels without coating to bridges

1	Stain of concrete by rust-laden water at early stage. (Poor appearance)
2	Long term over 10 years until the formation of protective and stable rust layer. (Red rust)
3	Protective rust can not form under high chloride environments. Safety region : The content of air-borne sea salt particle 0.05 mdd (mg·NaCl/dm <sup>2</sup> /day)
4	Corrosion increase by a large amount of deicing salt spray owing to the inhibition of stud tire.

Table 2 Rust constituent compounds formed in atmospheric environment

Compound	Color	Density (g/cm <sup>3</sup> )	Crystal system	Remarks
Fe <sub>3</sub> O <sub>4</sub> (Magnetite)	Black	5.18	Cubic	Black rust Mill scale
γ-FeOOH (Goethite)	Brown or Yellow	4.26	Orthorhombic	Cr-substituted Goethite : (α-(Fe <sub>1-x</sub> Cr <sub>x</sub> )OOH) Fine particle (nano-size)
β-FeOOH (Akaganeite)	Brown or White	3.56	Tetragonal	Cl <sup>-</sup> contains. Formation only in chloride environments.
γ-FeOOH (Lepidocrocite)	Orange	4.09	Orthorhombic	Red rust

Other : Amorphous rust

As a result of the characterization on the rust layer of weathering steels which was exposed a quarter of century in industrial area, it was found that the final protective and stable rust layer was composed of not amorphous rust which had been recognized previously but densely packed nano-size Cr-substi-

tuted Goethite : α-(Fe<sub>1-x</sub>Cr<sub>x</sub>)OOH<sup>1)5)</sup>. Based on this, a new model of long-term growth of the protective and stable rust layer was proposed. Cr-substituted Goethite is very fine, and water, oxygen and corrosive substances are hard to permeate.

Furthermore, chloride ions are also difficult to pass because of the cation selective property of Cr-substituted Goethite membrane. **Figure 2** shows the change in transference number of Cl<sup>-</sup> as a function of the Cr content in the synthetic Cr-substituted Goethite membrane. It is found that the increase of Cr content changes anion selective property into cation selective property on the characteristic of membrane<sup>6)</sup>.

On the other hand, Lepidocrocite membrane pos-

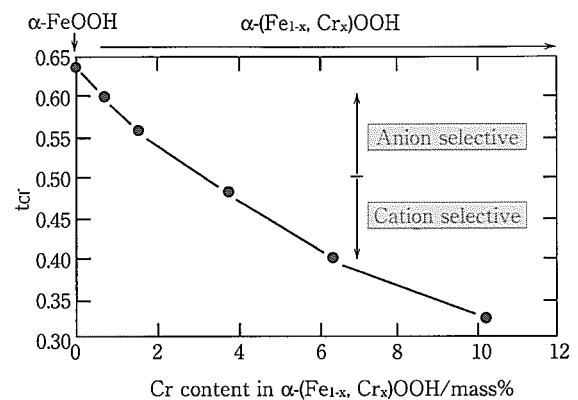


Fig. 2 Transference number of Cl<sup>-</sup>(t<sub>Cr</sub>) as a function of the Cr content in the synthetic Cr-substituted Goethite membrane

sesses anion selective property. The rust layer formed on weathering steel has double layer structure and protects steel from corrosion because the formation of bipolar membrane suppresses cathodic reaction. Its model is shown in **Figure 3**.

Thus, the formation of α-FeOOH in inner layer and γ-FeOOH in outer layer is important on the protection ability of rust. **Figure 4** shows that the ratio of α-FeOOH/γ-FeOOH in rust increase gradually as time passes. **Figure 5** shows the relationship between corrosion rate of weathering steel and the ratio of α-FeOOH/γ-FeOOH in the rust. Corrosion rate decreases to nearly zero when the ratio of α-FeOOH/γ-FeOOH in rust exceeds 1.4. The ratio of α-FeOOH/γ-FeOOH in rust can be recognized as rust stability index, that is, when this value exceeds 2, it can be said that rust layer is stable. This critical value was determined in the consideration of measurement error and safety.

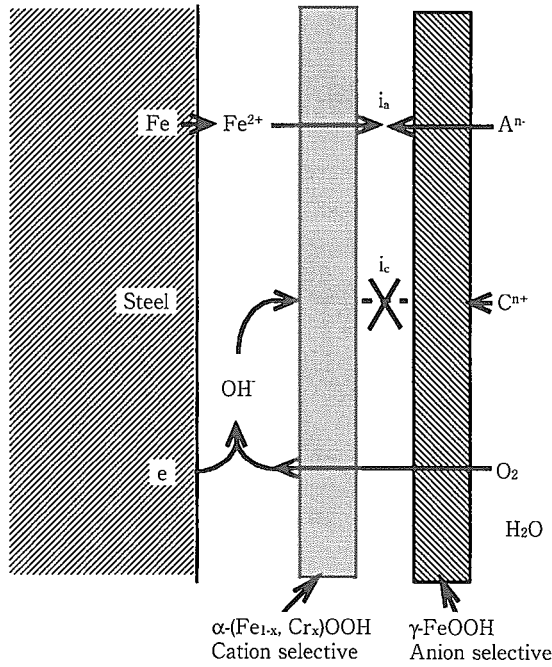


Fig. 3 Suppression model of cathodic reaction (oxygen reduction) by the bipolar membrane  
 (Anodic reaction : Possible)  
 (Cathodic reaction : Impossible)  
 (A<sup>-</sup> : Anion, C<sup>+</sup> : Cation)

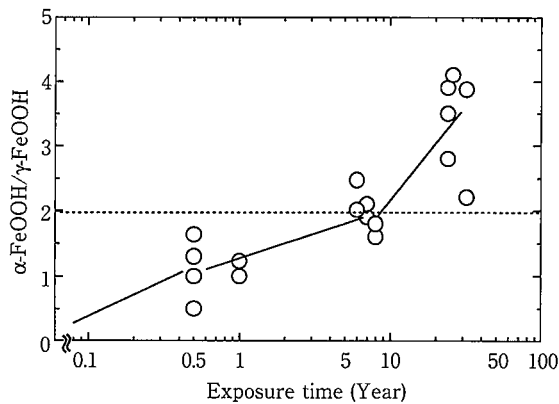


Fig. 4 Relationship between rust stability index ( $\alpha$ -FeOOH/ $\gamma$ -FeOOH) and exposure time at Amagasaki

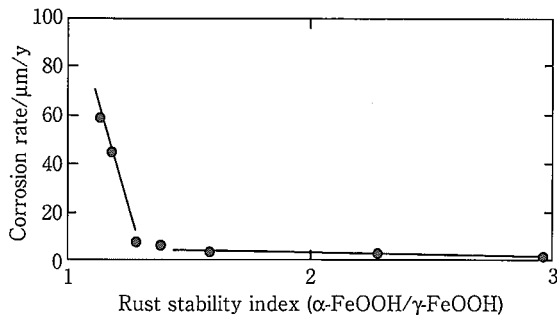


Fig. 5 The relationship between rust stability index ( $\alpha$ -FeOOH/ $\gamma$ -FeOOH) and the corrosion rate

## 4. Promoting Protective and Stable Rust Layer Formation Treatment of Weathering Steels (Weather-Act Treatment)

### 4.1 Promoting Protective and Stable Rust Formation

It was found that Cr-substituted Goethite was rapidly formed by the presence of Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution on weathering steels through the investigation on artificial reproduction method of Cr-substituted Goethite. Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> reacts with H<sub>2</sub>O to form SO<sub>4</sub><sup>2-</sup> and Cr<sup>3+</sup>. SO<sub>4</sub><sup>2-</sup> ions accelerate the dissolution of steel and promote the formation of Goethite. On the other hand, Cr<sup>3+</sup> ions form fine particles of Cr-substituted Goethite and improve the protection ability of rust layer. As a result, the protective rust layer is formed on the weathering steels.

Until the perfect formation of protective rust layer on all over the surface of the steels, it is necessary that Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> present uniformly on the steels. The mixture of vinyl-butyril resin and Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> was coated on the surface of the steel, whose thickness was about 17 micron. This technique has led to the protective and stable rust promoting formation of weathering steels in atmospheric environments. This is newly developed surface treatment technique of weathering steels : Weather-Act Treatment.

Figure 6 shows the formation process of protective rust layer on Weather-Act treated weathering steel. Under atmospheric environments, reaction is promoted at the interface treated film/steel and protective rust layer is formed on the surface of steels for several years. Resin fades out and only protective rust layer remains.

In early stages of reaction, a by-product of FeSO<sub>4</sub> may form on the steel surface, which does not influence the protection ability and cleans with rain in the future because of high solubility.

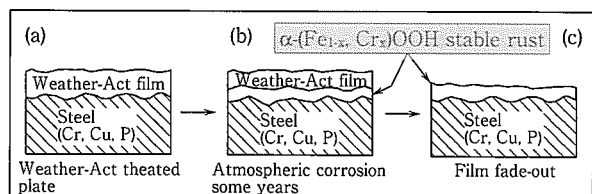


Fig. 6 A model of the formation process of protective and stable rust on Weather-Act treated plate

## 4.2 Treatment Process

Figure 7 shows the treatment process of Weather-Act method. Both plate treatment and products treatment are available. Furthermore the application of Weather-Act treatment for old existing weathering steel bridges is available. In that case, Weather-Act treatment is applied after removing the rust layer on the steel with power tool.

## 4.3 Protection Ability

Photo 1 shows the surface appearance of simulated structure which was made of a weathering steel and an ordinary steel with and without Weather-Act treatment. In order to find the formation of rust-laden water, lowest parts of the structure was coated with white paint. Apparently, even the untreated weathering steel as well as untreated ordinary steel brought poor appearance with the presence of a considerable amount of red rust. On the other hand, Weather-Act treated steels led to attractive appearance.

Figure 8 shows the exposure test result of Weather-Act treated weathering steels at Amagasaki (Industrial area) and Naoetsu (Coastal areas) for

4 years. Though, in general, it takes over 10 years to become the ratio of  $\alpha$ -FeOOH/ $\gamma$ -FeOOH in rust above 2, which suggests the formation of protective rust layer for weathering steels without coating, it was found that Weather-Act treatment accelerated the formation of protective rust for a relatively short time. Exposure site of Naoetsu is located 100m from seaside and the content of air-borne sea salt particles is about 0.4 mdd(mg-NaCl/dm<sup>2</sup>/day) which means very corrosive environment. Even in such a severe environment : Naoetsu, the formation of protective rust layer was observed in several years as well as in mild environment : Amagasaki.

Figure 9 shows the average corrosion loss in plate thickness vs. exposure time of weathering steels with and without Weather-Act treatment. Weather-Act treated steels have higher corrosion resistance than untreated steels, which may suggest that it is caused by the presence of resin which covers the steel surface. However, corrosion rate decreased with exposure time and protective ability improved with time. These phenomena are opposite to ordinary coating by paint, in which case protection ability is high at

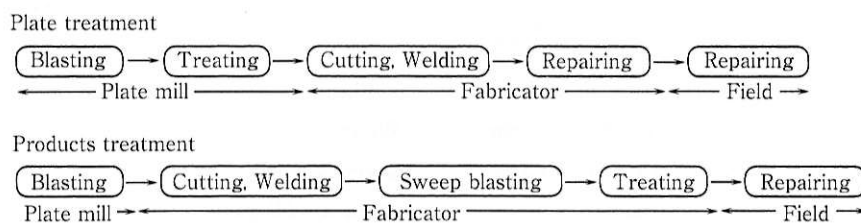
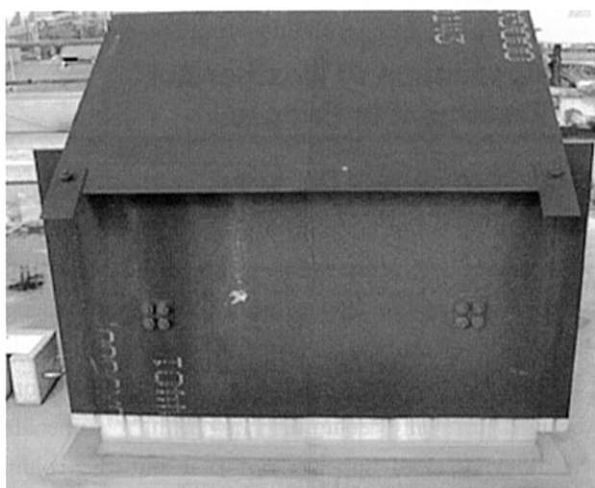
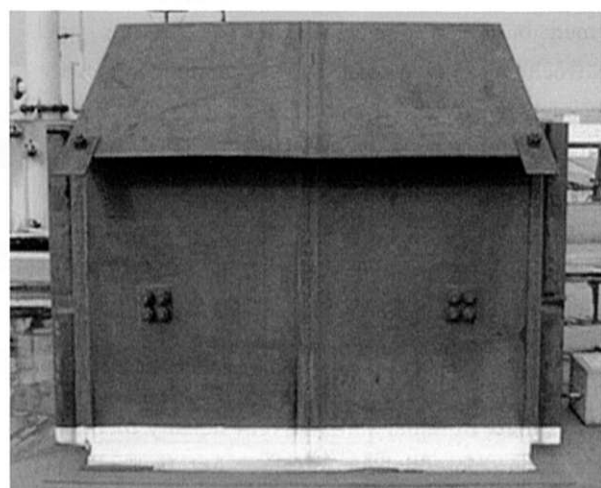


Fig. 7 Treatment process of Weather-Act method



Uncoated mild steel

Uncoated weathering steel



Weather-Act treated weathering steel

Photo 1 Surface appearance of simulated structure of Weather-Act treated weathering steel exposed at Amagasaki which located in industrial region for 3 years

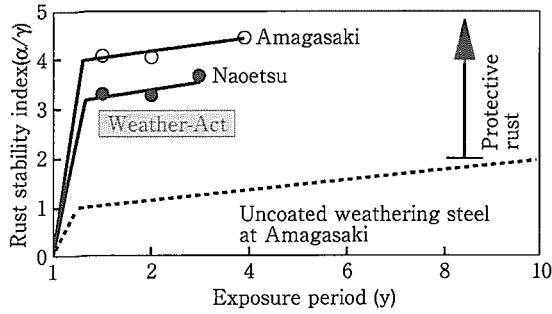


Fig. 8 Rust stability index ( $\alpha$ -FeOOH/ $\gamma$ -FeOOH) vs. exposure time curves

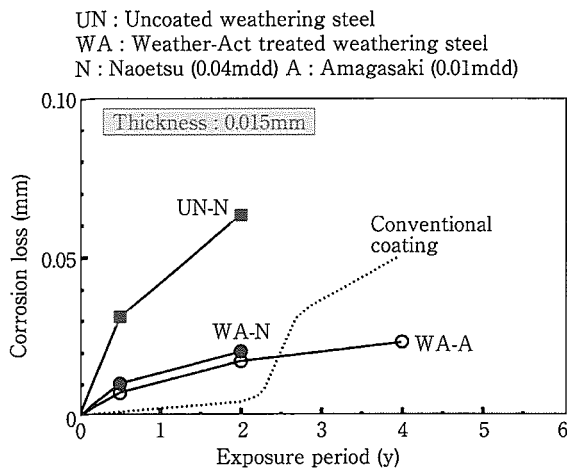


Fig. 9 Relationship between corrosion loss and exposure time

early stage but the gradual deterioration of coating bring the increase of corrosion rate. As for the Weather-Act treatment, corrosion rate decreased with time except for initial rapid corrosion by sulfuric acid. The protective and stable rust layer is able to form through these process.

In order to clear the protective ability of rust layer formed on Weather-Act treated weathering steel, electrochemical investigation was carried out on the specimen which was exposed at Naoetsu for 3 years by comparison with an uncoated weathering steel with protective rust layer exposed at Amagasaki for 30 years. **Figure 10** shows the anodic polarization curves. Current density is related to corrosion rate : the current density is smaller as corrosion resistance is higher. Low limiting current density in anodic polarization curves means that protective ability of rust layer is high. In initial state current density increased with raising potential for Weather-Act treated steel as well as uncoated weathering steel. But current increase was not observed on Weather-Act treated steel exposed for 3 years, which suggests that protec-

tive rust layer formed on the steel.

Protective rust formed on Weather-Act treated steel exposed at Naoetsu for 3 years shows property likely passive state as same as that of no coated weathering steel exposed at Amagasaki for 30 years.

So, it is suggested that Weather-Act treatment forms protective rust in a short time even in salt surroundings.

WA : Weather-Act treated weathering steel exposed at Naoetsu for 3 years  
 UN : Uncoated weathering steel exposed at Amagasaki for 30 years  
 S : Side faced the sky E : Side faced the earth

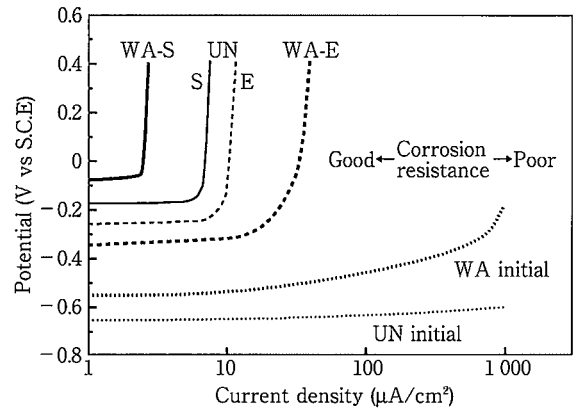


Fig. 10 Anodic polarization behavior of the protective rust layer formed by Weather-Act treatment (Compared with uncoated weathering steel)

**Photo 2** shows TEM image of the rusts on a Weather-Act treated steel exposed at Naoetsu for 3 years and an uncoated weathering steel at Amagasaki for 30 years. Both rusts are fine and compact, and it is sure that the promotively formed protective rust is equivalent to naturally formed protective rust for a long time.

### 5. Application of Weather-Act Treatment to Bridges

Weather-Act treatment has been already applied to 15 bridges for test and order. **Photo 3** shows the test bridge which passed over 1 year after construction. This bridge is located at mountain area in Tochigi Prefecture, and uncoated weathering steel is applied for the beam, and Weather-Act treatment is applied for only column. The beam of uncoated weathering steel appears red rust but the column of Weather-Act treated weathering steel shows good appearance. **Figure 11** shows the test results of repairing by Weather-Act technique on an existing

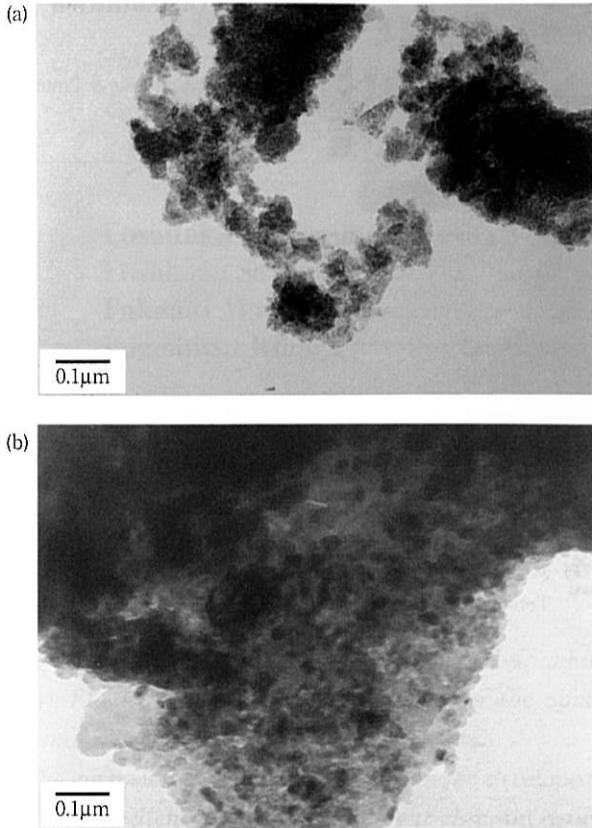


Photo 2 TEM image of the rust for outdoor exposure test  
 (a) Weather-Act treated steel exposed at Naetsu for 3 years  
 (b) Uncoated weathering steel exposed at Amagasaki for 30 years

weathering steel bridge in Miyazaki Prefecture. It is difficult to form protective rust for the bridge because the bridge is near the sea shore and the content of air-born sea salt particles exceed 0.4 mdd. Actually flaky rust layer was observed on uncoated weathering steel of this bridge which has been used for 7 years. It is found through the analysis of this rust that  $\beta$ -FeOOH, which is able to form only under

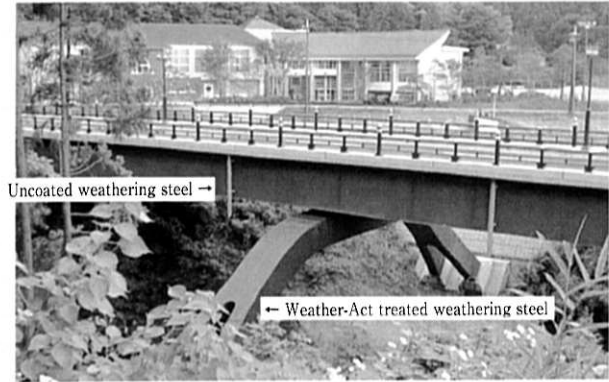


Photo 3 No.2 Sanwa bridge in Tochigi prefecture passed 1.5 years

chloride environments, formed in high ratio.

After removing the rust layer on the steel of this bridge with power tool, Weather-Act treatment with paint brushing was applied. The formation of  $\alpha$ -FeOOH was observed after 6 months exposure without forming  $\beta$ -FeOOH on the web, the upper and the lower side at flange. The application results of Weather-Act treatment to actual bridges of weathering steel revealed that Weather-Act treatment had good resistance to chloride containing environments.

### 6. Conclusion

The outline of protective rust formation mechanism and Weather-Act treatment which promotes protective rust growth for weathering steels was explained. Weathering steel has been taken interest in as a self-made corrosion prevention steel which forms protective and stable rust layer on its surface, but there are some problems in use of uncoating.

Weather-Act treatment, which is able to prevent

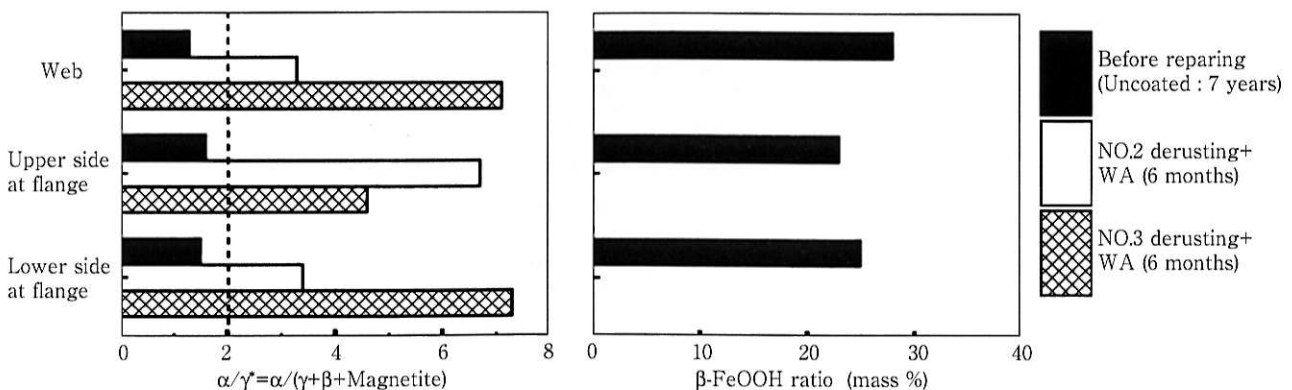


Fig. 11 Rust characterization before and after weather-act treatment at K bridge in Miyazaki prefecture (0.4mg·NaCl/day/dm<sup>2</sup>)

the part of concrete for bridges from staining with rust-laden water and to promote protective rust growth under chloride environments, is hoped to be applied widely because it solves the problems of uncoated weathering steel.



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