# Blast furnace which utilize self repairing anti-corrosive coating material

# *SLAG LEAD SR*

【 Management Entity 】: Public Interest Incorporated Foundation, Kitakyushu foundation for the advancement of industry science and technology

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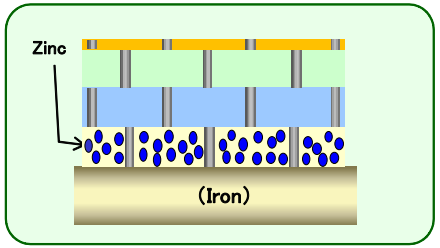
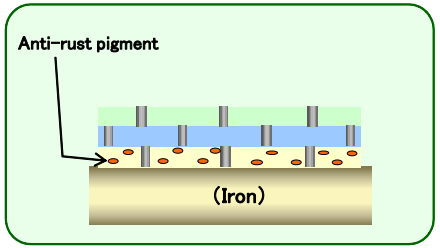
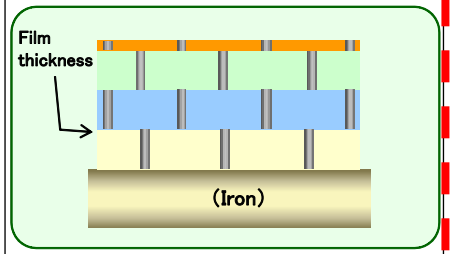
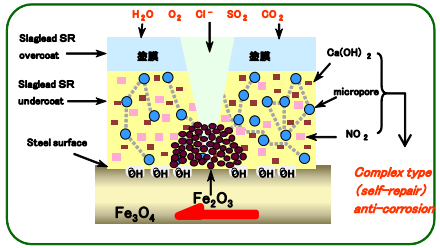
【Researcher】:

**DAIKI-KOGYO CO.,LTD**

**SL-TECH CO.,LTD**

# ① Topics and countermeasures in existing technology

| | Potential difference anti-corrosion method | Anti-rust pigment anti-corrosion method | Film thickness anti-corrosion method | Self repairing anti-corrosion method |
|---|---|---|---|---|
| anti-rust theory | Method that use electrode already has in metal<br>To protect iron from rust<br>・・・Zinc plating, Zinc rich paint | Method to make it harmless from water<br>・・・Pigment anticorrosion<br>Make water harmless with anti-rust pigment<br>Cannot fulfill film thickness. | Water blocking method.<br>・・・capsule anti-corrosion<br>Coat until no through pin hole.<br>(min at least 200 $\mu$ ) | Electrochemical effect Surface passivation (increase electric potential), prevent Fe ion flow out<br>・・Make passivated film under strong alkaline atmosphere<br>・・Make passivated film with special anti-rust agent ($NO_2^-$) |
| Coating film conceptual diagram |  |  |  |  |
| Characteristic | [Standard electrode potential of main metal<br>・・・(Hydrogen electrode basis)<br>(Gold) Au + 1.498<br>(Silver) Ag + 0.799<br>(Iron) Fe − 0.440<br>(Zinc) Zn − 0.763<br>(Aluminium) Al − 1.662<br>Ionizing trend<br>Use material with lower electrode than iron,<br>It will be sacrifice to protect corrosion for iron<br>①Ant-rust effect is different by surface preparation<br>②It's general heavy anticorrosion method | [Chemical effect]<br>React to water, generating alkali substance, and adsorb it into iron surface, making iron surface alkalinity<br>→(No iron rust under alkaline atmosphere)<br>$Pb_2O + H_2O \rightarrow Pb(OH)_2$Lead hydroxide will make alkalinity on moisture permeation<br>[Physical effect]<br>From reaction between zinc and oil, adhesive film will be formed and reduce water made<br>Pb + RCOOH → RCOOPb Zinc soap<br>①Need recoating to remove pin hole.<br>② Ant-rust effect is different by surface preparation . | [Merit]<br>①Can repeat coating with same material.<br>[Demerit]<br>①Need to repeat coating to remove pin hole.<br>② Ant-rust effect is different by surface preparation .<br>③It's general heavy anticorrosion method.<br>④Macrocell corrosion may occur. | [Merit]<br>①It's complex (self-repair) anti-corrosion<br>②Reinforced anti-rust by appropriate permeation of anti-rust agent.<br>③Chloride ion (Cl−) is passive film ($FE_2O3$) of chloride and dissolve iron which is metal (flow out as $Fe^{2+}$), but special anti-rust agent ($NO_2^-$) will react with $2Fe^{2+}$, making passive film.<br>$3Fe^{III}{}_2O_3$(red rust)+$NO_2^-$ ⇌ $2Fe^{III\,II}{}_3O_4$ (passive)+$NO_3^-$<br>[Demerit]<br>①Growth rate of overcoat material must be the same level as undercoat one, cannot use only overcoat material |
| Topic | Big initial cost | Short life time and corrosion will start from scratch of film<br>  | Long life time about 20 years then corrosion will start from scratch of film | ・Life time 30 years<br>・Prevent corrosion from coating scratch |

# ② Compare between existing technology and latest technology

## ◆Result comparison of anti-rust function

| Existing technology | Latest technology |
|---|---|

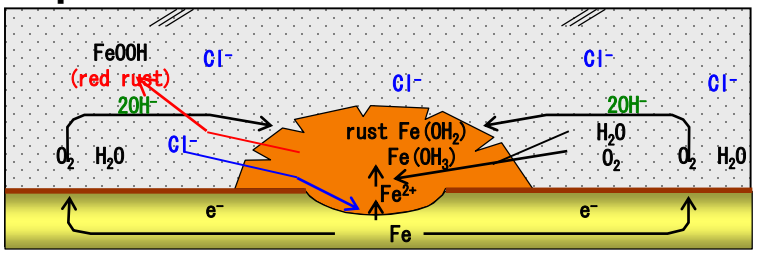


<CASS test condition>

Spray CASS solution of pH3 for 4Hr
↓
Drying 2Hr
（60℃・humidity 50%）
↓
Damp heat test 2Hr
（50℃・humidity 95%）

×200 times

【Principle of corrosion】




(1) $Fe \rightarrow Fe^{2+} + 2e^-$ (anodic reaction:corrosion part)

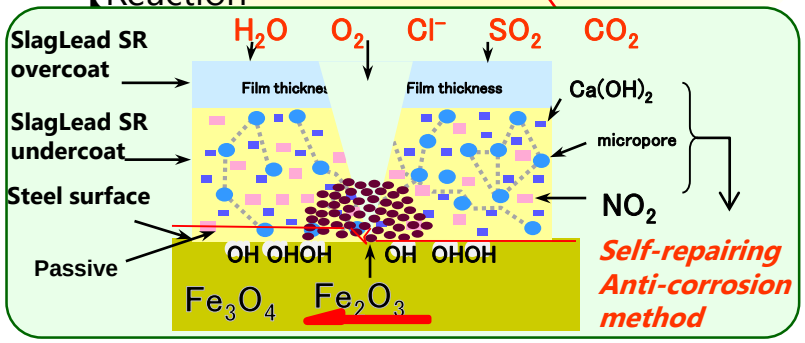
(2) $H_2O + 1/2\ O_2 + 2e^- \rightarrow 2OH^-$ (cathodic reaction:anti-corrosion part)

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \rightarrow Fe(OH)_3 \rightarrow FeOOH$

(Ferrous hydroxide) (Fhydroxide) (red rust)

$OH^-$ Herric $_2O$

【Reaction




$2Fe^{2+} + 2OH^- + 2NO_2^- \rightarrow Fe_2O_3 + H_2O + 2NO$

**$3Fe^{III}_2O_3$(red rust)$+NO_2$- ⇌**

**Some oxide of iron returned to nitrous acid, becoming safely oxidized passivity.**

**No rust although got scratch, target life time 30 years**

# ③ Explanation of technology seeds

※pH and electric potential (equivalent to electric anti-corrosion concept, different from existing technology)

**SlagLead SR**

**After kneading (paste form)**

(pH 13.20)

**SlagLead SR powder**

(pH 11.32)

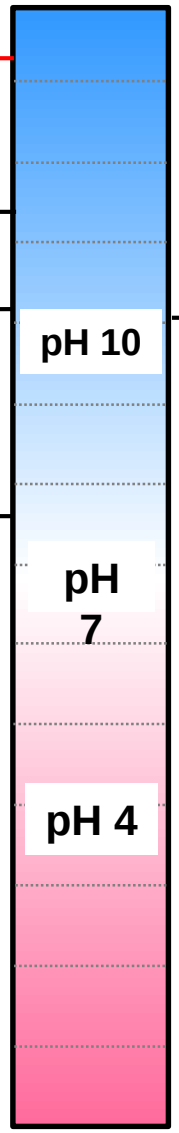
**Strong solvent epoxy hardener**

(pH 10.24)

**Strong solvent epoxy main agent**

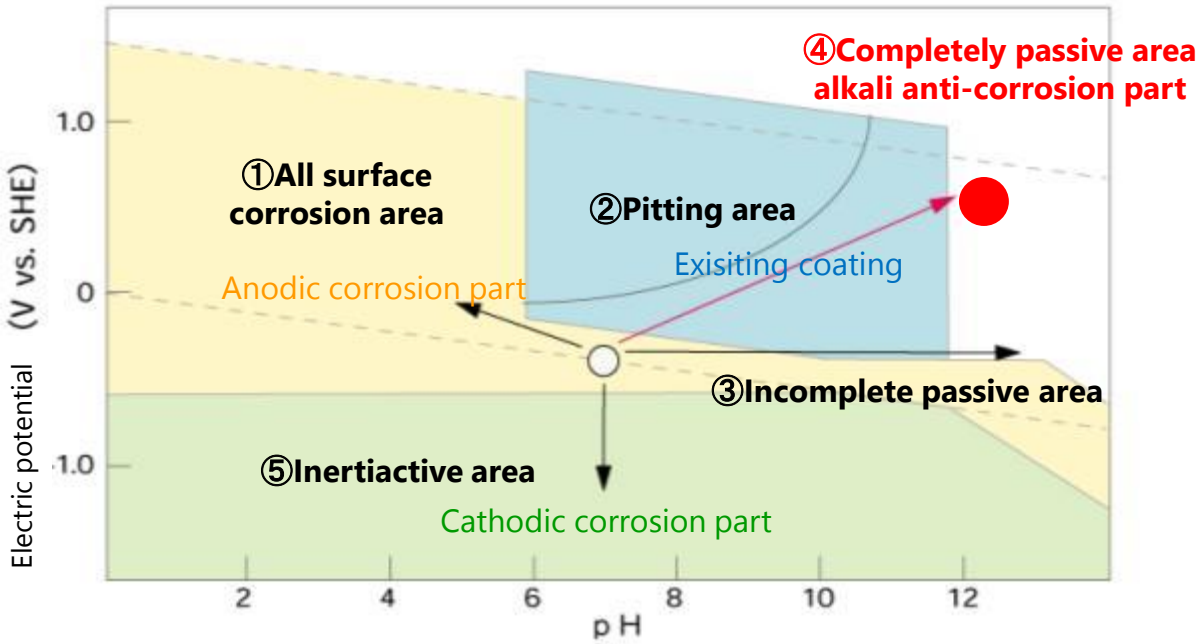
(pH 7.65)

**Strong solvent urethane main agent**




(pH 10.17)

**Strong solvent urethane hardener**



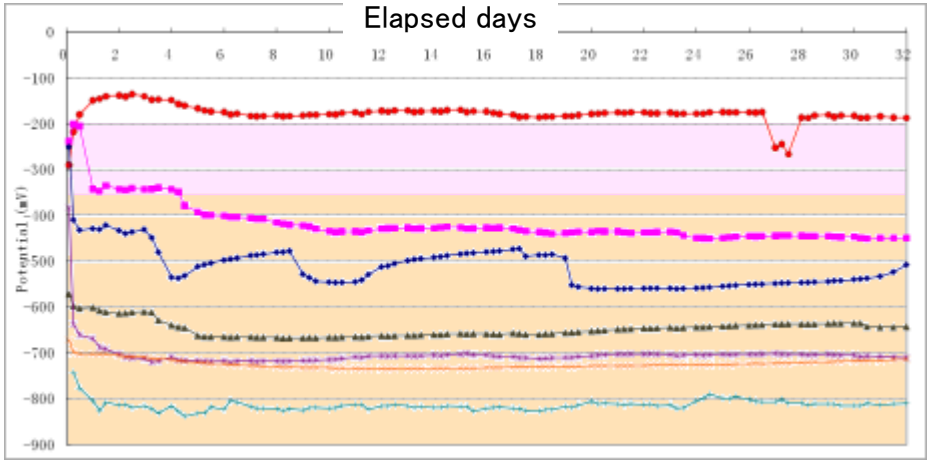

■Status of partial corrosion occurring in NaCl solution (0.01 molarity)

Practice of electrochemical for concrete structure 1998.2.

Kyushu Institute of Technology
Facility of applied chemistry
Professor Yuichi Shimizu

# ④ Anti-rust mechanism identification

## (1) Basic study about factor to contribute anti-rust results




◆ASTM standard (corrosion evaluation standard)

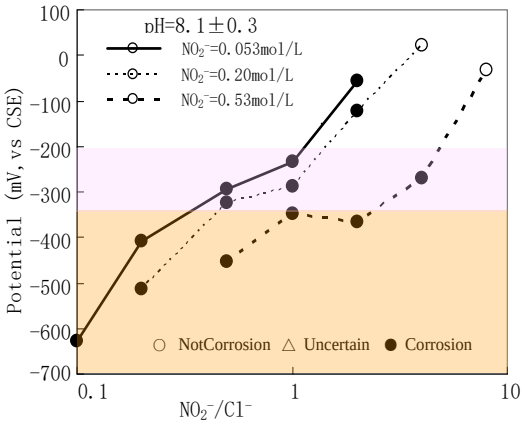
| | A | B | C |
|---|---|---|---|
| 1 | ○ | ○ | ○ |
| 2 | ○few | ○ | ○ |
| 3 | ○few | | ○ |
| 4 | | ○ | ○ |
| 5 | Current goods (epoxy resin coating) | | |
| 6 | | | ○ |
| 7 | Tested steel plate (no coating) | | |

| |
|---|
| No corrosion |
| -200～-350mV corrosion without area fixing |
| -350mV, or lower Corrosion area |

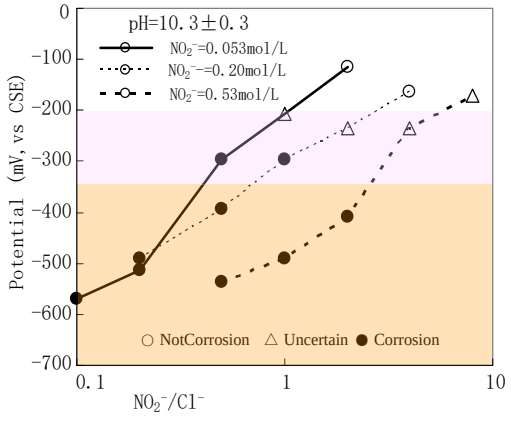
・Confirmed superiority of anti-rust results of developed goods with natural current measurement.

Kyushu Institute of Technology
Facility of engineering
Associate Professor
Makoto Hibino

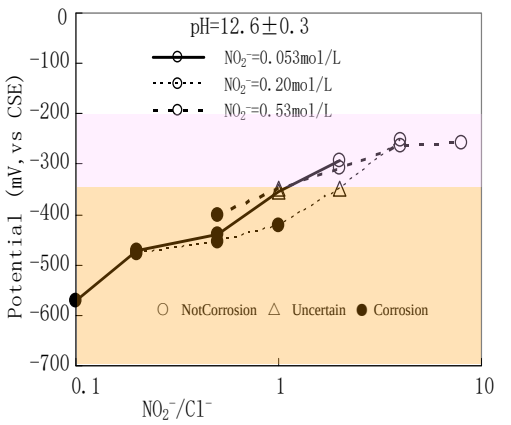
## (2) Effect from mole fraction of $NO_2^-/Cl^-$ and pH




(a)pH8.1




(b)pH10.3



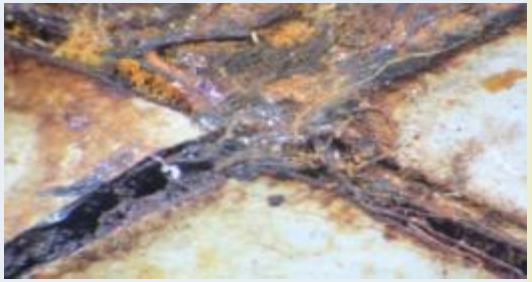
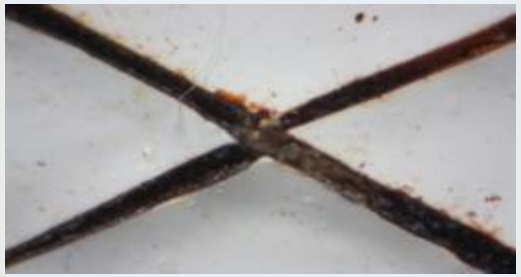

(c)pH12.6

・Anti-rust result of special anti-rust agent is, highest when strong alkali (pH≧10) and $NO_2^-/Cl^-$ ≧1

# ⑤ Anti-rust result verification of anti-rust agent

**200 cycles = 1600 hours past**

**JIS H8502 plating corrosion resistance test (neutral salt spray cycle test)**
**Salt spray (5% NaCl, 35℃,2h) → dry (60℃, 25% RH, 4h) → humid (50℃, 98% RH, 2h)**

| | Hard anti-corrosion coating (modified epoxy) | Complex self repairing coating (SlagLead SR) | Complex self repairing coating (without anti-rust agent) |
|---|---|---|---|
| Before test (40 times) |  |  |  |
| After test |  |  |  |
| After test (40 times) |  |  |  |

**Anti-rust agent contributes to corrosion resistance of SlagLead SR.**

# ⑥ Corrosion resistance due to difference of surface preparation

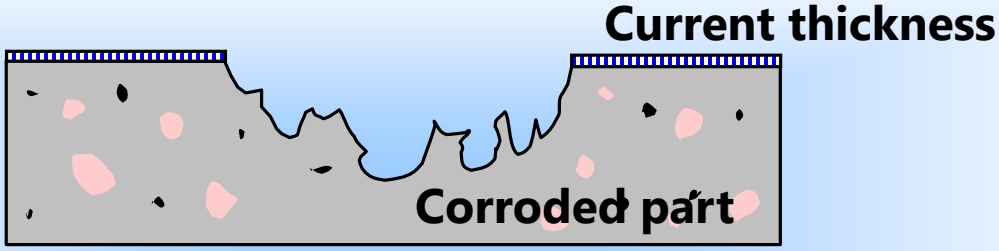
| Surface preparation | Used steel plate | Surface preparation method |
|---|---|---|
| (1) Sand blast | Steel plate | Blast (Sa2･1/2) |
| (2) Clean type 3 | Rusty steel plate | disk sander |
| | (3)Steel plate with casting | Degreasing only |

**≪salt spray 2000Hr≫　left: modified epoxy　right: SlagLead SR**

**(1)Sand blasted steel plate**　**(2)Rusty clean type 3**　**(3)Steel with casting**

**Remarkable corrosion resistance regardless of surface preparation (can use with casted steel plate)**

# ⑦ Necessary coating thickness when recoat




**5μ ～ 10μ**

Power tool treatment on clean iron plate

**30μ ～ 50μ**

Blast treatment

**230μ**

Power tool treatment on rusty iron plate

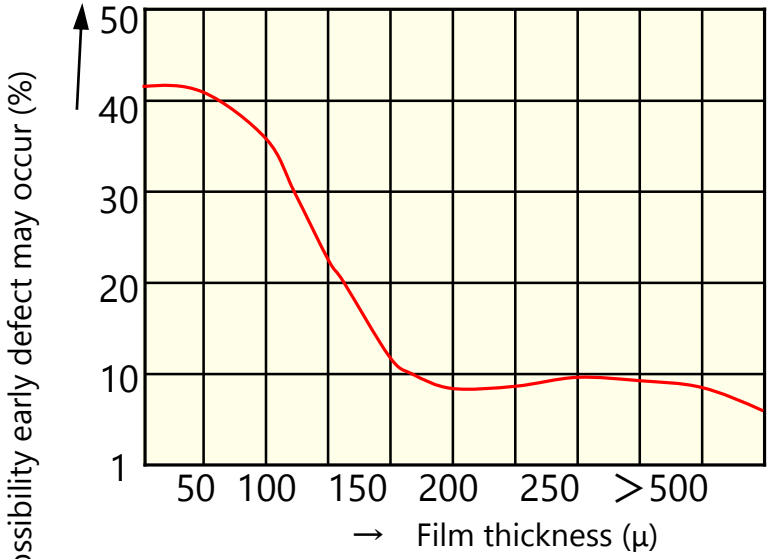
▼ Film thickness should be 200μ for resistance

▼ 200μ can live 80 months in coastal environment = (6.5 years) -> fall about 0.1% by rust

▼Need to consider about surface roughness

▼Necessary film thickness for 80 months with 0.1% of rusting ratio

**200μ ＋ surface roughness is necessary film thickness**




Relation between film thickness and early coating defect
(R.P.Pierce.Corrosion.8〔5〕.178(1952)

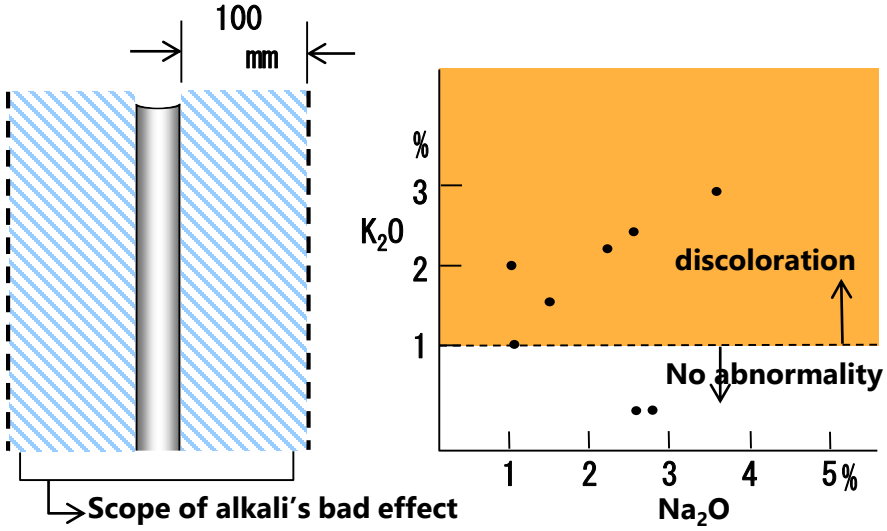
# ⑧ Alkali resistance of welded part

## ▼ Problem in welded part

a)Coating melting, exfoliation, color change due to alkaline
b)Film swelling due to hydrogen

## ▼ Bad effect of alkali to film thickness of welded part

a)Alkaline's shedding level==not over 100mm from welded part
b)Coating color change==$K_2O$ will change film color at least 1% in flux of welding rods
c)Low hydrogen typed welding rods has more alkalinity comparing with ilminite




## ▼ Treatment methods for alkaline

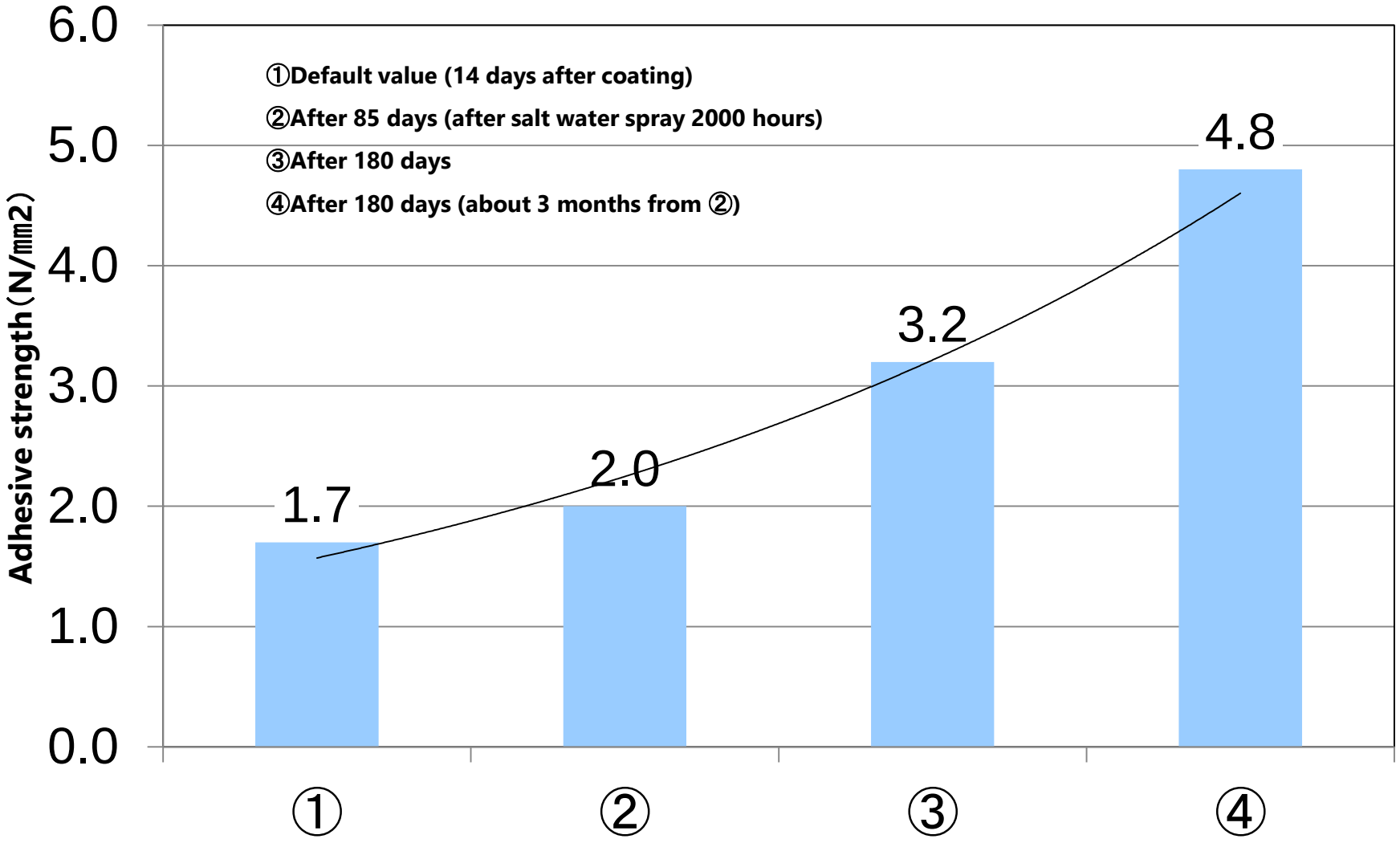
a)Blast treatment==mechanically remove
b)Use phosphoric acid, etc. for neutralization
c)Leave until red rust was generated

## ▼Emission period of hydrogen

| Type of welding rods | In case of spontaneous emission | | In case emit by heating |
|---|---|---|---|
| | Not oil-based coat | Oil-based coat | (Beat side heating) |
| Low hydrogen type (contains simultaneously welding) | 70 hours or upper | 20 hours or upper | 300℃ for 15 minutes |
| Ilmenite type | 200 hours or upper | 100 hours or upper | 300℃ for 15 minutes |

**No film deterioration at welded part due to alkali resistance.**

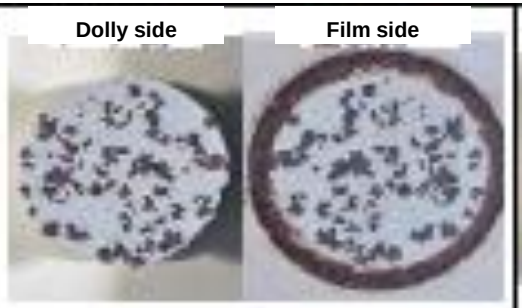
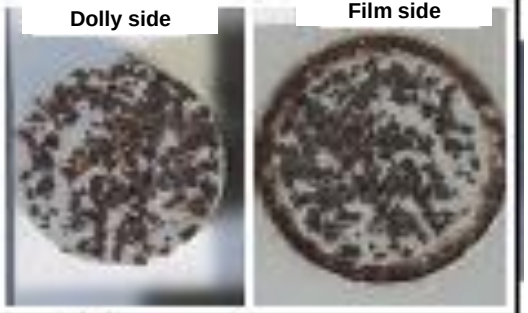
# ⑨ Aging of adhesive strength




**Adhesive strength will increase after time past**

# ⑩ Adhesion of steel plate surface

**◆Modified epoxy**
**Default value: 2.73MPa after SST: 2.47MPa**

| | | |
|---|---|---|
| Measure initial adhesion |   | |
| Adhesion | 3.4 MPa | |
| Measure adhesion After SST 2000 hrs |   | |
| Adhesion | 1.6 MPa | |

**Interfacial failure**

**◆SlagLead SR**
**Default value: 0.83MPa after SST: 1.07MPa**

| | | |
|---|---|---|
| Measure initial adhesion |   | |
| Adhesion | 0.8 MPa | |
| Measure adhesion After SST 2000 hrs |   | |
| Adhesion | 1.0 MPa | |

**Failure inside coating**

**SlagLead SR will be destroyed inside film,**
**so it will protect corrosion of steel plate surface**

# ⑪ Effect of remaining salt and special anti-rust agent to steel material

**Attached table－Ⅱ.1.2 Effect of sticking salt removal, separated by treatment**

| Sticking salt volume before washing by water | Wash by water | | Power tool | | Use both power tool and waste | |
|---|---|---|---|---|---|---|
| | Sticking salt after treatment | Removal ratio (%) | Sticking salt after treatment | Removal ratio (%) | Sticking salt after treatment | Removal ratio (%) |
| (NaClmg/m$^2$) | (NaClmg/m$^2$) | | (NaClmg/m$^2$) | | (NaClmg/m$^2$) | |
| 218 | 20 | 90% | 110 | 49% | 52 | 76% |

Refer sticking salt volume by treatment method from Steel Highway Painting and Anti-corrosion manual issued by (corporate juridical person) Japan Road Association (issued by printing on 10 March 2010) P-Ⅱ122

◆ **Calculation**

Need chlorine ion ($Cl^-$) mole quantity included in sticking salt before washing by water

$$(Cl^-)\ \text{mole QTY} = 0.218 \times \frac{35.5}{58.5} \times \frac{1}{35.5} = 0.00373$$

NaCl＝ 58.5 (1gram-molecular weight)
$(Cl^-)$＝ 35.5 (1gram-ion weight)

Need nitrite ion ($NO_2$) mole quantity included in SlagLead SR standard specification

Coating volume of SlagLead SR is 500g/㎡(undercoating 1 layer standard coating volume 500g/m$^2$), containing special anti-rust agent 4% of total molecular weight (calculated by ingredient)

Therefore 500×0.04＝20(g) of special anti-rust agent is included

$$(NO_2^-)\ \text{mole QTY} = 20 \times \frac{92}{132} \times \frac{1}{92} \times 2 = 0.30303$$

Special anti-rust agent ＝ 132 (1gram - molecular weight)
$(NO_2)_2^-$＝ 92 (1gram - ion weight)×2

$$\frac{(NO_2^-)\ \text{mole QTY}}{Cl^-\ \text{mole QTY}} = \frac{0.30303}{0.00373} = 81.2 \geqq 1 \quad \cdots \text{OK}$$

Because special anti-rust agent 1 molecule contains 2 mole of nitrate ion, it's needed to add ($Cl^-$) method

Inbound salt volume able to prevent rust＝(0.30303-0.00373)×58.5＝17.50(NaClg/㎡)＝17500(NaClmg/㎡)

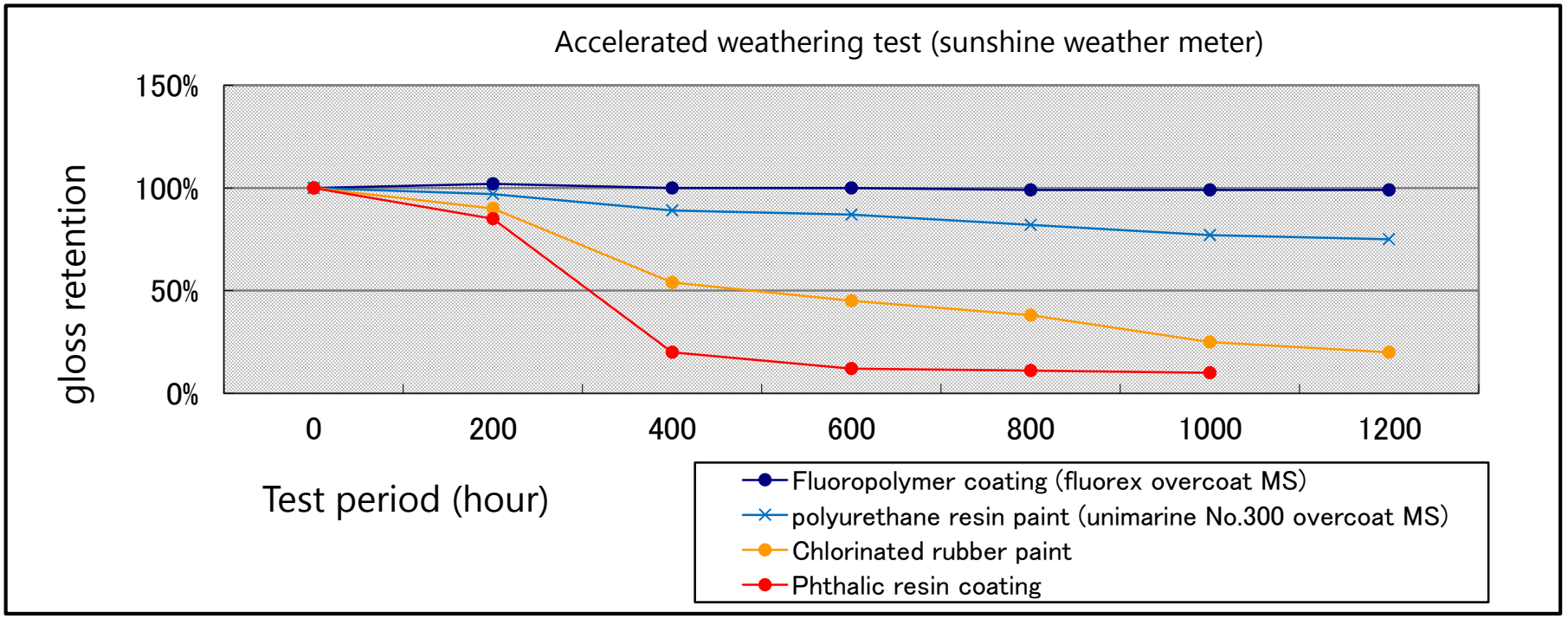
◆ **Summary**

## ④ Elucidation of anti-rust mechanism

・Anti-rust effect of special anti-rust agent is best in strong alkali (pH≧10) and $NO_2^-/Cl^-$ ≧1

**From investigation result comparing sticking salt in steel material with mole of special anti-rust agent, special anti-rust agent included in film is 80-350 times higher, and can expect for long life anti-rust.**

# ⑫ Life time of coating film (estimated from film depletion speed)




| Type of film | Fluoropolymer coating film | Hard polyurathane resin coating film | Soft polyurathane resin coating film | Epoxy resin resin coating film |
|---|---|---|---|---|
| Film depletion/ per year | 0.33-0.43 μm/year | 2 μm/year | 4 μm/year | 10 μm/year |

【Reference】**Selection from anti-rust control Vol.32, Honshu-Shikoku technical review Vol.16** (S46/7～S56/8, 10 years, exposure test result by Omaezaki)

SlagLead SR fluorex overcoat MS film thickness : **25μm**

**SlagLead SR estimated life=25μ/( 0.5μ/year)＝about 50 years**

# ⑬ Outdoor exposure test

## 2/Apr/2008～8/Aug/2009（281 days）after 1 year

Modified epoxy

Alkali coating

SlagLead SR 1 fine

SlagLead SR 2 fine

SlagLead SR 3 fine

## 2/Apr/2008～12/Jan/2012（1379 days）after 3.8 years

Modified epoxy

Alkali coating

SlagLead SR 1 deterioration

SlagLead SR 2 deterioration

SlagLead SR 3 deterioration

**SlagLead SR has anti-corrosion even if in sulfur gas atmosphere.**

# ⑭ Life time of Modified epoxy coating film (real machine chimney)

◆Status of modified epoxy coating on real machine
（20 years from recoating, 60μ×3 layers+30μ×2 layers)

If defect part occurs, corrosion will be faster, and film thickness will be peeled off


Notable corrosion at welding corner due to accumulation of splash and rain

・Protection coating is corroded from scratch, and that rust will expand on surface of coating and iron shell, peeling coating film off.








# Construction Experiences

**NYB outdoor exhaust equipment before construction**

**Cement silo before construction**


**Chemical factory before construction**

**NYB outdoor exhaust equipment 3 years after construction**

**Cement silo after construction**

**Chemical factory after construction**

# Construction Experiences

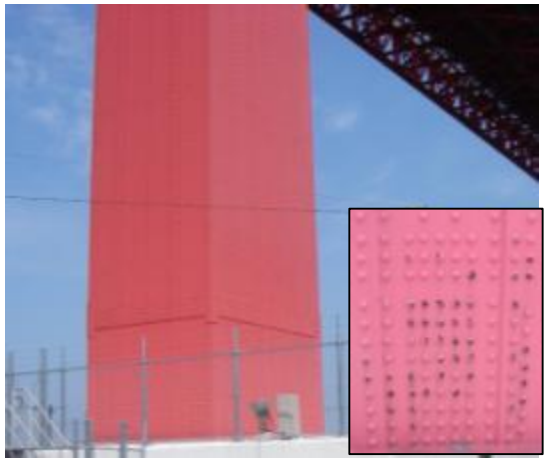
## Monorail & movable bearing part

Before construction

After overcoat

## Wakato great bridge & piers

Before construction



After construction

## Kita-Kyushu airport tent square

Right after construction

2 years after construction

# Construction Experiences

| | Ship's cargo | Concrete wall surface | 20t dump truck under chassis | Base of beverage tank |
|---|---|---|---|---|
| Before construction |  |  |  |  |
| After construction |  |  |  |  |
| Before construction |  |  |  |  |
| After construction |  |  |  |  |

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