# Preliminary study on organic acid degradation of the corrosion protection coating layer

# Background and Objectives

## Background

- Recently, **degradation caused by organic acids** has been reported in places where **epoxy resin coating** is applied (e.g. building pits).
- WWTPs have facilities where the organic acids concentration can be high, such as  sludge treatment. So the “JS Corrosion Control Manual* 2017 edition" has newly established quality **standards for requiring organic acid resistance.**

※ Corrosion Control Manual for Sewerage Concrete Structures

- However, there is insufficient knowledge on the degradation of the organic acid coating layer and the physical property change caused by degradation.

## Objectives

- **Obtain knowledge on the degradation of the corrosion protection coating layer by organic acids:** Conduct an **acetic acid immersion test** in response to the quality standards of the JS corrosion control manual, using **organic acid resistant** coating materials and **organic acid intolerance** coating materials.

# Procedure and Materials (1): Used materials and test conditions

## Materials

- Used four types of epoxy resins marketed by two manufacturers of anti-corrosion coating materials. The main difference is the curing agent. The common type is an aliphatic amine. The organic acid-resistant type is an aromatic amine.

| Organic acid resistant | Manufacturer#1 | Manufacturer#2 |
|---|---|---|
| No (common type: Widely used at WWTPs for corrosion prevention) | N1 | N2 |
| Yes (used in building pit, etc.) | A1 | A2 |

## Conditions

- **6 conditions** , including the test conditions specified in the quality standard of the JS Corrosion Control Manual (in red bold letters in the table), **for each anti-corrosion coating material, 24 conditions in total**

| Item | Condition | |
|---|---|---|
| **Anti-corrosion coating material** | Regular epoxy resins: 2 types, organic acid resistant types: 2 types | 4 conditions |
| **Concentration of aqueous acetic acid solution** | 0%(underwater), **5%**, 10% | 3 |
| **Temperature** | **23±2℃**, 30±2℃ | 2 |
| **Days of immersion** | **60 days** | 1 |

# **Procedure and Materials (2):** Test procedure

## Preparation of specimen

- **Formed into a 70×70×2 mm plate.** After curing at 23°C for 14 days, used for testing.

## Immersion test

- Put 4.8L of immersion solution in a closed container (5L) made of anti-corrosion resin, and dipped 3 pieces of each anti-corrosion coating specimen, a total of 12 specimens lined up at intervals of about 1cm (see photo below).

- Wrap the entire container with aluminum foil to protect it from light, and place it in an incubator.

- Replace all of the soaking solution every seven days once in a 7 days, when removing the specimens for appearance confirmation.

- As a blank test, place two specimens of each anti-corrosion coating material in an incubator, shaded from light, and left in the incubator without soaking.

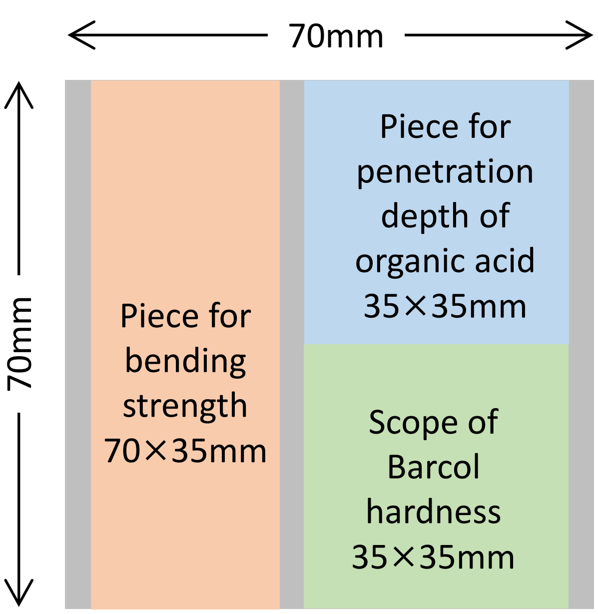
Set up condition of specimens

# Procedure and Materials (3): Measurement items and schemes ①

- Removed specimens from the immersion solution every 7 days or so, to confirm their appearance and to measure their external dimensions, thickness and weight.
- After 60 days of soaking, measured the Barcol hardness within the specified range of the test specimen, and cut out the test specimens for the measurement of bending strength and organic acid penetration depth (lower right).

Measurement items and schemes

| Frequency | Item | Scheme |
|---|---|---|
| Once in seven days | Appearance | Visual observation(photographing) |
| | External dimension | Measure the center of each side of the specimen with a caliper to the nearest 0.01mm |
| | Thickness | Measure the center of the specimen with a thickness gauge to the nearest 0.01mm |
| | Weight | Immediately after pulling out from the solution, wipe off the adhesive water and measure to the nearest 0.01g |
| After 60 days' immersion | Barcol hardness | Barcol hardness test for glass fiber reinforced plastics (JIS K 7060) |
| | Bending strength | Based on the determination of plastic bending properties (JIS K 7171) |
| | Penetration depth of organic acid | EDS analysis with marking alkaline |




Measurement after immersion and sampling image

# Procedure and Materials (4): Measurement items and schemes ②

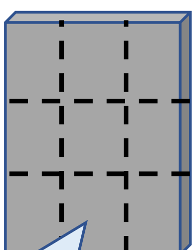
## Alkaline Marking

- Anti-corrosion coating materials (resins) contain many components (C, H, O) of organic acids, which makes direct analysis impossible. So the penetration depth of organic acids is measured by the alkaline marking.*

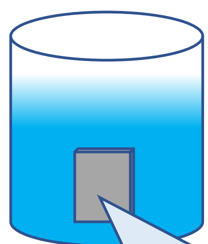
*Kubouchi et al. (2017) Evaluation procedure for the penetration depth of organic acid into epoxy lining material using alkaline pretreatment, Proceedings of the 55th Japan Annual Technical Conference on Sewerage

- In this study, the specimens were immersed in 20% potassium hydroxide solution, which is an alkaline solution, at 60°C for 10 hours.

**Specimen after immersion test** → **Immerse in alkaline solution** → **Measure the distribution of alkali elements**



Cutting out a cross-sectional sample



Alkali permeates the area where acid permeated (formation of potassium salt, etc.)

Scanning Electron Microscope with EDS

Measure the distribution of the desired alkali elements (K elements, etc.) by EDS analysis.* Indirectly evaluate the penetration depth of organic acids.

Outline of alkaline marking

*EDS: Energy Dispersive X-ray Spectroscopy

# **Immersion Test Results (1):** Change in appearance

- **Regardless of the material or test conditions, the general type resin showed appearance changes** including loss of surface gloss, roughness, and softening
- **The organic acid-resistant resin showed no change in appearance** even after 60 days of immersion.

<u>The transition of surface condition and appearance of specimens</u>

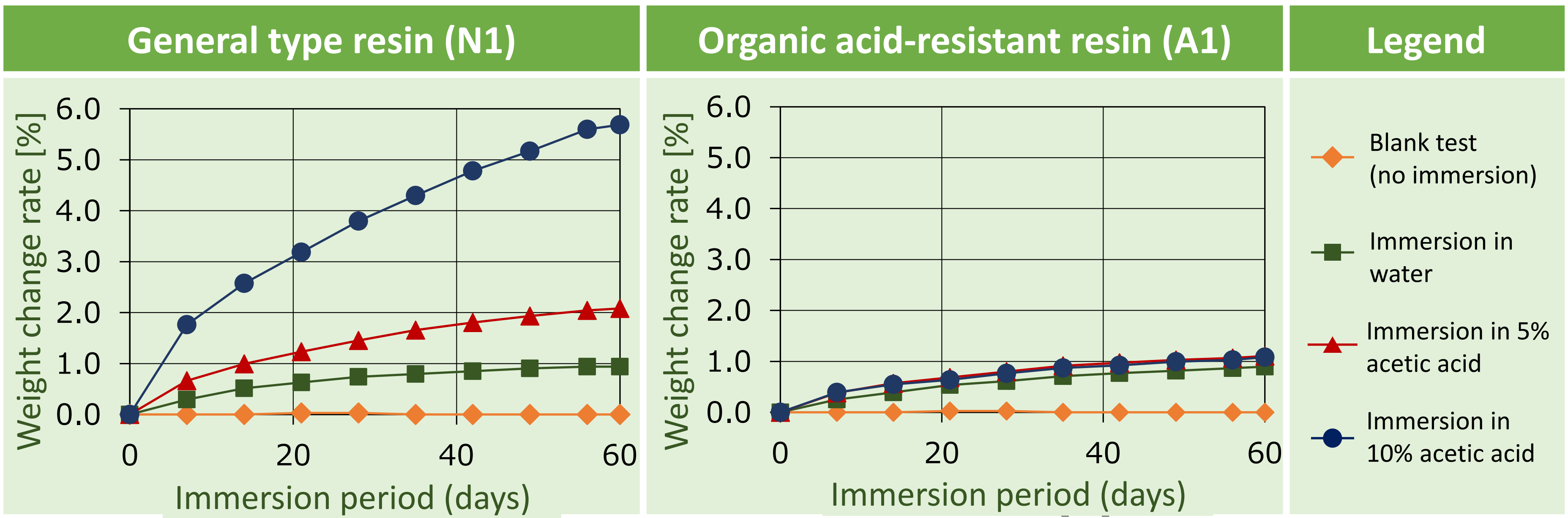
| Days of immersion | | General type resin | Organic acid-resistant resin |
|---|---|---|---|
| Surface condition | Seven days | Loss of gloss | Glossy, no change in appearance such as softening or roughness |
| | Around 20-30 days | Increased roughness and swelling | |
| | Around 30-40 days | Softening | |
| | After 60 days | | |
| **Example of the external appearance of specimens after 60 days***<br>**(Acetic acid 10%, 23℃)** | | <br>Anti-corrosion coating material: N1 | <br>Anti-corrosion coating material: A1 |

*The left end is a blank test specimen (not immersed) and the remaining three are immersion test specimens.

# Immersion Test Results (2-1): Weight change

- **The general type resin** showed **a more significant weight change rate as a higher concentration of acetic acid** in the immersion solution. It was **remarkable at 10%** acetic acid concentration.
- **The organic acid-resistant resin** showed the same change as that of immersion in water. There was **no effect of** acetic acid immersion on the **weight change**.
- There was little difference in the weight change rate depending on the manufacturer or water temperature.

Example of transition in weight change rate (water temperature 23°C)

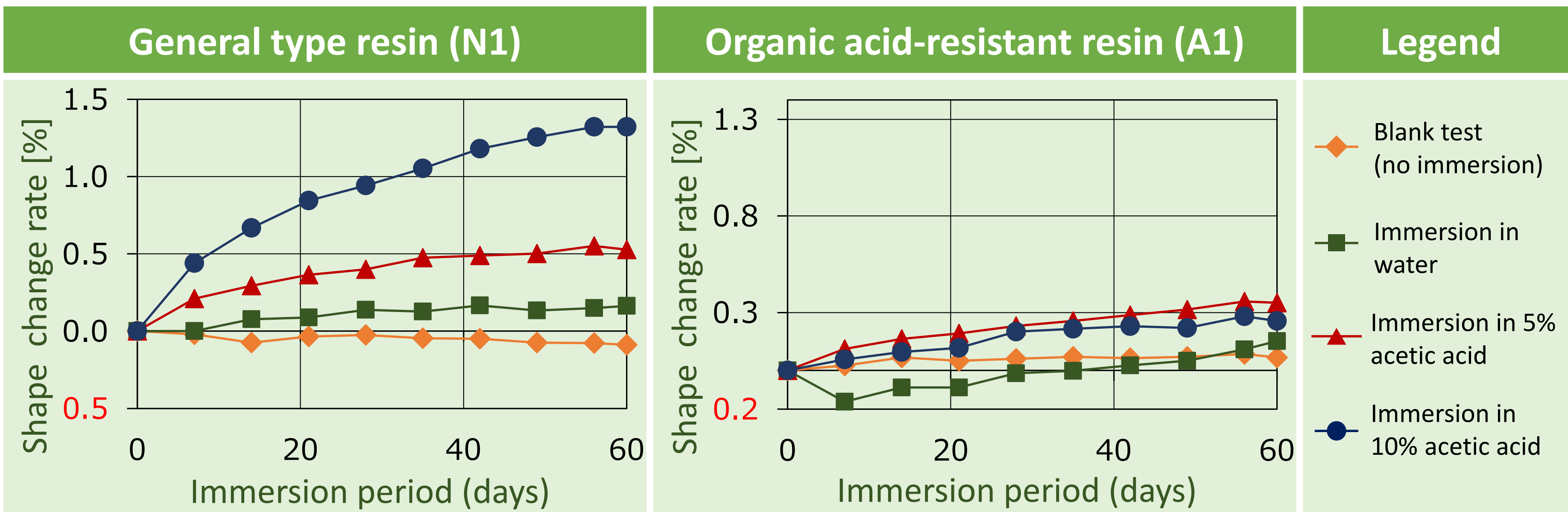


# Immersion Test Results (2-2): Shape change

- The general type of resin showed a tendency of larger change in dimension (length and width) and thickness with higher acetic acid concentration in the immersion solution and higher temperature
- Compared to the general resin, the organic acid-resistant resin showed less change in shape by immersion in acetic acid
- As the thickness was as small as 2 mm compared to the length and width of 70 mm, the change rate of thickness was larger than that of dimensions

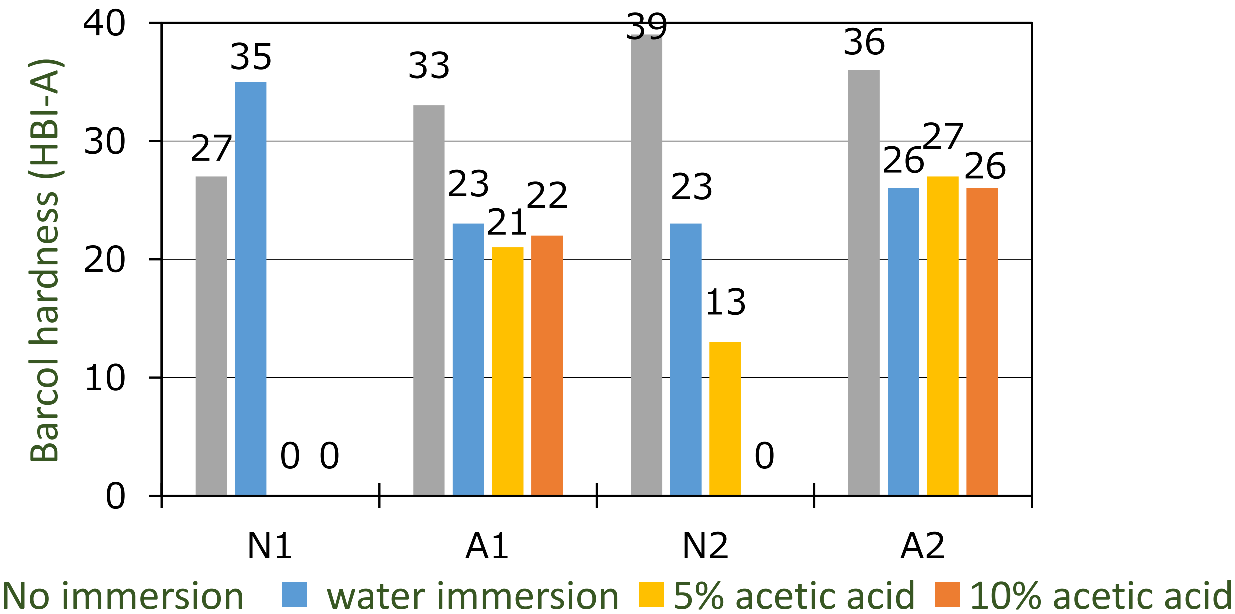
Example of immersion in N1, 23°C, 10% acetic acid for 60 days: dimensional change 1.3%, thickness change 4.1%

The transition of shape change rate (dimensional change, water temperature 23°C)



# Immersion Test Results (2-3): Barcol hardness

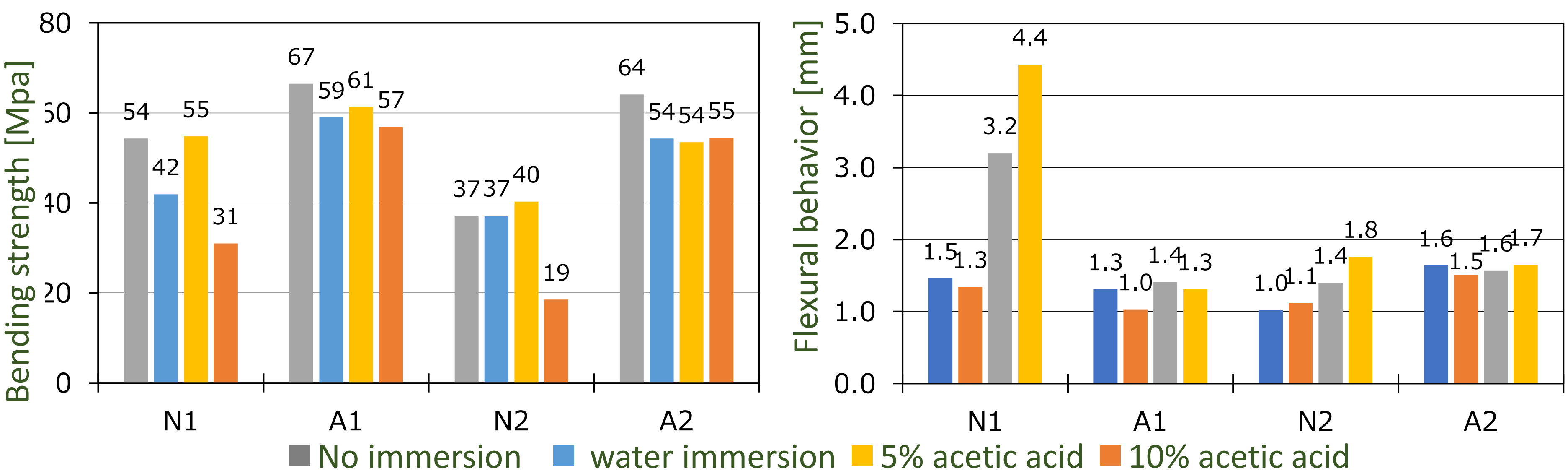
- The general type resins showed more loss of strength with acetic acid immersion than with water immersion. Both materials showed a significant decrease in hardness at 10% acetic acid immersion.
- The organic acid-resistant resins showed similar Barcol hardness between immersion in water and acetic acid. No effect of acetic acid immersion was observed.
- Under the same conditions, there was a tendency for the strength reduction to be slightly more significant at higher temperatures.




Example of Barcol hardness measurement results (temperature 23°C)

# Immersion Test Results (2-4): Bending strength, Flexural behavior

- The general type resin showed no decrease in bending strength after 5% acetic acid immersion. But, flexural behavior increased, and the tendency of resin softening was confirmed. 10% acetic acid immersion decreased bending strength while increasing flexural behavior and the tendency of resin softening was remarkable.
- The organic acid-resistant resin showed the equivalent level of bending strength/flexural behavior to that of immersion in water, and there was no effect of immersion in acetic acid.

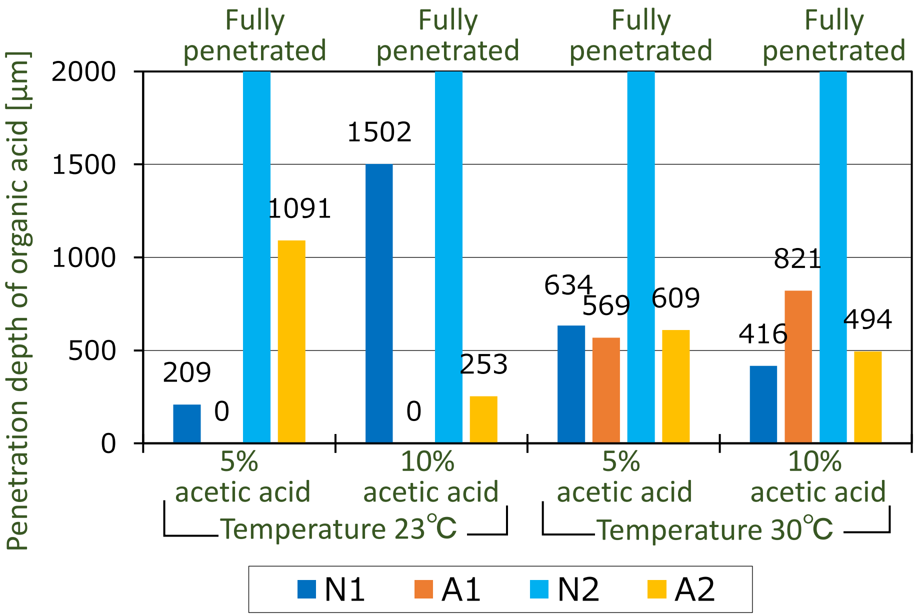



Example of bending strength test result (temperature: 23°C)

Example of flexural behavior test result (temperature: 23°C)

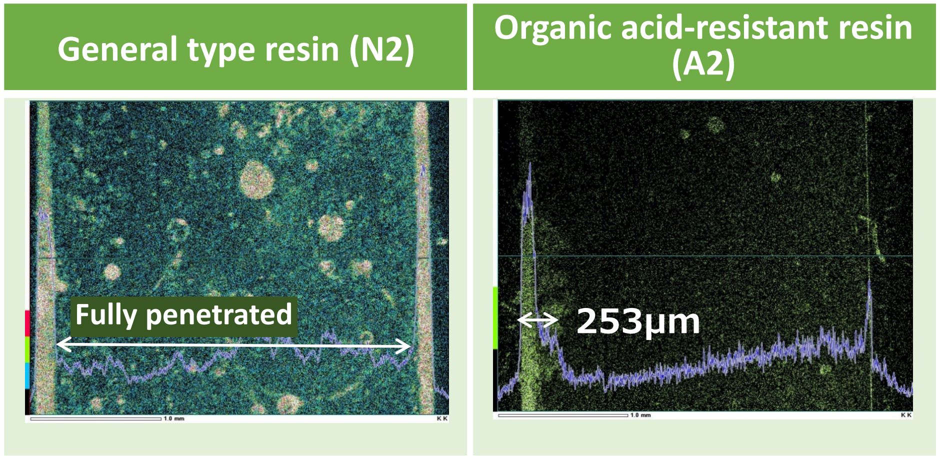
# Immersion Test Results (4): Immersion depth of organic acid

- The general type of resin showed acetic acid penetration in all test conditions. Material N2 showed acetic acid penetration throughout.
- At a temperature of 23°C, the organic acid-resistant resin had a smaller penetration depth than the general type resin. In particular, no acetic acid penetration was observed for Material A1.
- The effects of acetic acid concentration and water temperature on the penetration depth of organic acids differed depending on the anti-corrosion coating material. ⇒ There are still some issues to be solved for the quantitative evaluation scheme of penetration depth.




Measurement results of organic acid penetration depth

Example of EDS analysis image (10% acetic acid, 23°C)



# Summary of Immersion Test Results

- Degradation Phenomena of the Anticorrosion Coating Layer: As a result of acetic acid immersion tests using anti-corrosion coating materials (epoxy resins) with different organic acid resistance, the following findings were obtained.
  - The organic acid-resistant resin does not change in appearance by acetic acid immersion, and is less affected by acetic acid than the general type resin in terms of weight change, shape change, and physical property change such as hardness and bending strength.
  - In measuring the penetration depth of organic acids using the alkali marking method, acetic acid penetration was observed in all test conditions for the general type resins. On the other hand, the acetic acid penetration of the organic acid-resistant resin showed less acetic acid penetration than the general type resin.

- The test results show that the acetic acid immersion test specified as a quality standard in the JS Anti-corrosion Manual can evaluate the anti-corrosion coating layer's organic acid resistance.

# Future Issues

- The evaluation items for organic acid resistance in the JS anticorrosion manual (see table below) are for appearance only.

| Evaluation item | Quality standards |
| --- | --- |
| Appearance after immersion | There shall be no blistering, cracking, softening, or dissolution of the coating after immersion in a 5% acetic acid solution (23°C±2°C) for 60 days. However, the concentration of the acetic acid solution may be higher than 5%. |

- The results of this acetic acid immersion test provided the following findings.
  - Under the current test conditions, the appearance changes specified in the quality standard, such as blistering, are slight, and the evaluation may differ depending on the operator conducting the test.
  - The 10% acetic acid immersion had a more pronounced effect than the 5% acetic acid immersion.
  - The physical property measurements clearly showed the effect of organic acids on the general type resins. In particular, the Barcol test is simple and useful for the evaluation of organic acid resistance.

- To evaluate the effect of organic acids on the anti-corrosion coating layer, further knowledge accumulation through acetic acid immersion tests, etc., is expected to be reflected in the quality standard.

# Thank you for your attention

We appreciate the cooperation of Prof. Masatoshi Kubouchi of Tokyo Institute of Technology and other related parties for the measurement and evaluation of the penetration depth of organic acids.