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1. Introduction
Fiber Reinforced Plastics (FRPs), which are composed of high strength fiber and synthetic resin, have excellent properties such as specific strength, impact resistance and chemical properties e.g. waterproofness and corrosion resistance. Since they have also good moldability, there is advantage of producing one-of-a-kind thing. Owing to these advantages, they have been used as storage tanks, pipes and ducts in chemical plant where there is corrosive process fluid: acid, base, organic solvent and others.

Although FRPs have high corrosion resistance, they degrade slowly over a few decades in severe environment. In addition to physical degradation e.g. crack, delamination and swelling, chemical degradation (corrosion) might be occurred. Process fluid reacts with resin and turns it into corroded product. Enough data for such corrosion reactivity has not been reported because there are many combinations of resin and fluid. Therefore it is not easy to predict their degradation based on prior incident. As a result, leakage of process fluid from apparatus might be occurred. For example, we have experience of the fatal accident that workers, who climbed onto the roof of chemical storage tank, fell into it because of FRP roof degradation. However, generally just visual examination is conducted at best. Non-Destructive Test (NDT), which effectiveness is confirmed, is required to check such degradation on FRP device.

1.1. Corrosion Forms of Organic material
Corrosion of thermosetting resin used as FRP-matrix in corrosive solution is mainly classified into 3 types (Fig.1, [1]): ‘Surface Reaction Type’, ‘Corrosion Layer Forming Type’, and ‘Penetration Type’. In the Surface Reaction Type, corrosion product dissolves into the solution from the surface of the resin, and the corrosion develops uniformly over entire surface. In the Corrosion Layer Forming Type, corrosion product is left as layer form on the surface. In the Penetration Type, solution penetrates into resin and strength declines suddenly after a long time. Especially this Penetration type is peculiar to organic materials; in spite of former two correspond to metal general corrosion.

As described below, Effectiveness of NDT method for FRP device should be different depending on these corrosion types. Therefore, effectiveness should be confirmed each corrosion type.

1.2. Ultrasonic Test as NDT
Ultrasonic test (UT, Fig.2) is one of the most general non-destructive tests and metal [2] and concrete structures [3] are inspected as practical use.
Ultrasonic reflects, refracts and scatters at the sound interface between different materials. Observing these signals informs its thickness, sound velocity and flaws such as crack and delamination. In organic materials, effectiveness of UT is confirmed as inspection method for Carbon fiber Reinforced Plastics (CFRPs) in aerospace field particularly [4]. Furthermore, Amadatsu and Kan et al. conducted UT for corrosion resistant FRP devises in chemical plant and showed that UT is useful to measure thickness of such a corrosion resistant FRP device [5, 6].

1.3. Thickness measurement principle by ultrasonic

A probe is attached one side of a plate-shape specimen with echo gel. A pulse wave is transmitted from the probe and reflected at the back side surface and refracted waves are received by the same probe (Fig.3). The received wave is taken in waveform by oscilloscope as shown in Fig.4 and saved on PC. Reflected echo peak from the other side of the specimen (bottom echo) provides Ultrasonic propagation time (time of flight) $t$ [s]. By substituting this value with substance-specific sound velocity into the equation (1), thickness of specimen can be obtained.

$$L = \frac{C \cdot t}{2} \quad (1)$$

1.4. Measurement error of UT

In general, when a value is obtained by using measurement instrument, it should contain a certain extent of measurement error. If the measurement is conducted over and over, distribution of frequency for this measurement will be as follows shown in Fig.5. The red line (A) in this figure indicates that the average of the distribution deviates from true mean value and this contributes to measurement error. On the other hand, the blue line (B) shows that the average is same as true value but distribution is wide. As seen above, distribution width also contribute to measurement error. The former is usually regarded as “accuracy”, the latter is regarded as “precision”. Effectiveness of NDT should be evaluated from these points of view, respectively.

When the thickness of FRP device in chemical plant is measured by UT, a decrease in the accuracy and the precision is caused by the following factors respectively from a viewpoint of corrosion form type and measurement principle.

① Accuracy
  - How to set substance-specific sound velocity
  - Variation of sound velocity in FRPs (Corrosion Layer Forming, Penetration)

② Precision
  - Limitations of measurement
  - Whether the tank/pipe is empty or not
  - Asperity of inside/outside surface (Surface Reaction Type, UV degradation)

A decrease of accuracy is affected by sound velocity. Sound velocity of thermoset resin can roughly range from 2000 to 2700 m/s. Moreover, glass fibers and voids in FRP also affect the sound velocity. It is difficult to set sound velocity correctly. Variation of sound velocity along depth direction, in the Corrosion Layer Forming Type and the Penetration Type, makes it all the more difficult to measure
accurately. To avoid inaccuracy, conducting another measurement of sound velocity is needed. Precision is affected by heterogeneous property of FRP such as fiber interface and void in matrix. Inside/outside surface asperity of FRP, as Surface Reaction Type and UV degradation, also influences precision. When the tank/pipe is full of liquid fluid, since ultrasonic transfer into fluid easier the echo reflected at the FRPs and fluid interface. This mechanism attenuates the signal and wrong another peak might be recognized as bottom echo. This can cause error.

![Fig. 5 Accuracy and precision](image)

### 1.5. Inspection Effectiveness in RBI

Many chemical plants in Japan were constructed in high economic growth period (1970's) and still have been working even though designed life of equipment is over. Periodic and predictive maintenances have been conducted, but in recent years, the number of accidents estimated as a result of aged degradation has been increasing. Risk Based Maintenance (RBM) and Risk Based Inspection (RBI) have been introduced to petrochemical and power plants. It has been reported that API (USA) [7] and RIMAP (EU) [8] have achieved some positive results. From these results, chemical companies in Japan also are starting new standard for maintenance based on risk.

In RBM and RBI, risk of each device is evaluated in perspective of consequence of failure and frequency of failure (Fig.6). Maintenance and inspection are conducted in high-risk devices prior to low-risk ones and maintenance and inspection cost for low risk devices can be leaved out. As a result, total risk of chemical plant can be decrease in limited maintenance cost.

However, these standards are mainly applied for equipment made of metal materials but not for those made of organic materials. For this reason, maintenance method of polymeric materials based on risk is necessary, and NDT method used in inspection also should be evaluated based on risk of organic material devices.

![Fig. 6 Risk Matrix](image)

In this research, thickness of three degraded FRP tanks and fresh FRP samples was measured by using UT and compared with the thickness by micrometer to make sure of its precision. After that, these data were discussed with relation to degradation analysis and corrosion form type.

### 2. Experiments

#### 2.1. Ultrasonic Test

Ultrasonic test measurement was conducted using instruments as illustrated in Fig. 2. A probe was mounted on one side of a specimen with echo gel. The diameter of the probe is 40 mm and its frequency is 1 MHz. This UT sensing device was driven by pulsar receiver (SQUARE WAVE PULSER RECEIVER MODEL 5077PR; Olympus). Pulse wave was transmitted from the probe, reflected at the other side surface and received by the same probe. The received wave was shown as waveform on oscilloscope (PDS5022T; OWON) and saved on PC.

#### 2.2. Evaluation of precision

To evaluate error of measurement value, the true value, is necessary. Thus thickness was measured by micrometer besides UT. Because micrometer is capable of measuring thickness much more precise than UT, the measured thickness can be recognized as true value. The measurement error of UT is defined as follow equation.

\[
\text{Error} = \text{UT Thickness} - \text{Micrometer Thickness} \quad (2)
\]

Few dozens of points per a sample were measured by UT and micrometer and then standard deviation was calculated.
2.3. FRP samples

UT measured degraded and virgin FRP tanks: NaClO aq. storage FRP tank (Surface Reaction Type), HCl aq. storage tank (Penetration Type), NaCl aq. storage tank (UV degradation) and virgin FRP sample. To study degradation and to confirm their corrosion form type, they were analyzed by SEM, EDS, FT-IR and bending strength.

2.3.1. NaClO aq. storage FRP tank

An FRP tank, which had stored 3 ~ 10 mass % sodium hypochlorite solution for 14 years at ambient temperature, was measured (Fig.7). Used matrix resin was vinyl ester. UT measurement was conducted twice, during operation (the tank was full of the solution) and under maintenance (the tank was empty) in 85 points of the tank’s wall and ceiling. After UT measurement, the tank was cut as samples and the points same as UT measurement were measured by micrometer.

As shown in Fig. 8, glass fiber is obviously exposed and yellow corroded resin was remained. This means that corrosion product dissolved into solution and remained glass fiber is appeared on the surface. This is why the corrosion type was classified as “Surface Reaction Type”. The other results of SEM, EDS and FT-IR also indicate features of this degradation form type.

2.3.2. HCl aq. storage FRP tank

An FRP tank, which had stored hydrochloric acid solution for 11 years at ambient temperature, was cut as sample and its 60 points were measured by UT. In this case, unfortunately measurement under operation was not conducted. The resin used for matrix resin of anti-corrosion layer is also vinyl ester. As shown in Figs. 9 and 10, the FRP is turned into green from outside, but black from inside. Cross-section of the sample shown in Fig.11 suggested black and green layers are formed in laminate from inside.

EDS analysis for Cl element on the cross-section shown in Fig.12 indicates chlorine penetrated into the black/green layer, however FT-IR results shows that chemical construction of these layers is the same as outside surface of the FRP tank. These phenomena indicate the corrosion type is classified as “Penetration Type.”
From surface observation, the vessel inside surface shows no color change and still has gloss like a fresh resin sample. EDS and FT-IR analysis does not indicate any degradation evidence. On the other hand, as shown in Fig.13, glass fibers are appeared on outside. It was estimated that this outside degradation was caused by sunshine ultraviolet.

2.3.4. Fresh FRP samples

Four fresh samples made of vinyl ester and/or polyester resin were prepared. As shown in Fig.14, these fresh samples were different in top coat. 15 points each sample were measured by UT and micrometer as same manner used in former degraded samples.

2.3.3. NaCl aq. storage FRP tank

An FRP tank, which had stored 25.5 mass % sodium chloride solution for 16 years at ambient temperature, was cut as sample and its 80 points were measured by UT and micrometer. Resin used in this equipment was also vinyl ester.
3. Result & discussion

3.1. Fresh FRP samples

At first the virgin samples were measured their thickness by UT and measurement values were compared with one of micrometer. Fig.15 shows thickness comparison by UT with that by micrometer for the virgin test samples of all four kinds. From this result, UT thickness didn’t exactly coincide with the true value. As you can see in Fig.16, measurement error was normally distributed and its standard deviation was 0.21 mm. This means that UT measurement contains to this extent even fresh FRP and this is the limitation of precision in UT measurement.

![Fig.15 Thickness with UT against micrometer](image)

![Fig.16 Error distribution](image)

3.2. Degraded FRP tanks

Standard deviations of the other tanks are also evaluated and the results are listed in table 1. The standard deviation of the NaClO tank is larger than that of the HCl/NaCl tank. When the waveform of the NaClO tank (Fig.4) is compared with that of the fresh tank (Fig.17 upper), amplitude of the bottom echo peak is so small that it is slightly difficult to recognize it distinctly. Therefore, some measurement thickness might be wrong owing to recognizing another peak as the bottom echo peak.

For the case of NaClO tank, as mentioned above, inside surface of its wall is rough. As shown in Fig.18, corroded resin, which changed its color and got brittle, partly remained on the surface and makes it rough. This may lead to scatter the ultrasonic measurement and attenuated the bottom echo in this type of samples. To confirm this phenomenon, inside surface was polished by sand paper (Fig.19) and the same point was measured by UT again. Compared with the waveform before polish, the bottom echo peak after polish became lager (Fig.17). This experimental fact proves the assumption to be right that roughness of inside surface attenuated the ultrasonic and UT measurement for surface reaction type can be less precise.

![Fig.17 Waveform of surface reaction type FRP sample (upper) and after polished (lower)](image)

For the same reason, UT measurement for UV degradation contains the error because glass fiber exposure on the outside surface makes the subject surface to be rough. However, UT measurement of the Penetration Type has less error because its surface where signal reflected is flat as you can see Figs. 10 and 11.
3.3. Whether the tank is full or empty

To confirm how the solution in the tank affects the precision of the UT thickness, standard deviation of the error was compared when the tank was full and empty by its content. The standard deviation of the empty tank was 0.69 mm, by contrast, that of the full tank was 0.79. Generally speaking, reflected signal at the interface between FRP and solution gets lower than that between FRP and atmosphere (empty case) because sound impedance of liquid process solution is closer to that of FRPs than ambient atmosphere as ultrasonic penetrates into solution. S/N ratio, the value that signal amplitude divided by noise, was calculated. The S/N ratio of the empty tank was about 2.1 [-] and the full tank was 1.5 [-] in average. This result also indicates that the bottom echo peak is more attenuated when the tank is full of solution. This means that if the more precise thickness is needed, the tank should be empty. In other words, measurement should be conducted when the chemical plant is under maintenance.

3.4. Accuracy of the UT measurement

As mentioned in 1.3 and 1.4, in order to measure thickness, substance-specific sound velocity is necessary and affects accuracy of UT measurement. Sound velocity of FRP might depend on their resin curing degree, glass fiber distribution, void size and content and corrosion type. Especially corroded FRP, classified as Corrosion Layer Type and Penetration Type, its sound velocity is lower than fresh. In this paper, to discuss precision without accuracy, the sound velocity was defined to conform the average of thickness evaluated by UT to the average of thickness by micrometer. That is to say, the average of error equal to zero.

If UT is actually conducted for the FRP device in chemical plant to measure the thickness, another correct measurement for sound velocity is necessary. For example, a part, where thickness can be measured by micrometer directly without destruction e.g. nozzle, manhole and nameplate, is used for measuring sound velocity by UT. Besides this, one of the ultrasonic methods using surface wave is developing and can measure sound velocity of sample just attaching to its one side [9]. This method might be able to measure sound velocity of sample from outside of the full tank.

However, these methods could not inform variation of velocity along the thickness of the plate sample in corroded FRP. Hence, another NDT method is required.

3.5. Discussion about Inspection Effectiveness in RBI

<table>
<thead>
<tr>
<th>Degradation Type</th>
<th>Fluid</th>
<th>Period of Use [year]</th>
<th>Average thickness [mm]</th>
<th>SD of UT Error [mm]</th>
<th>Sound Velocity [m/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Reaction</td>
<td>NaClO</td>
<td>14</td>
<td>9.82</td>
<td>0.69</td>
<td>3000</td>
</tr>
<tr>
<td>UV</td>
<td>NaCl</td>
<td>16</td>
<td>7.34</td>
<td>0.38</td>
<td>2650</td>
</tr>
<tr>
<td>Penetration</td>
<td>HCl</td>
<td>11</td>
<td>7.32</td>
<td>0.32</td>
<td>2350</td>
</tr>
<tr>
<td>Reference</td>
<td>-</td>
<td>-</td>
<td>10.47</td>
<td>0.21</td>
<td>2450-2700</td>
</tr>
</tbody>
</table>

Table 1 FRP data and Standard Deviation of UT error.
In API 581[10], one of maintenance standards based on risk, how a non-destructive testing method informs deterioration correctly is defined as “Inspection Effectiveness” and it categorized as 5 levels, from A (most effective) to E (equal to doing nothing). This standard mainly describes metal material device and organic material device is hardly explained.

Precision of UT for FRP, as described above, is convenient and reliable bases to define Inspection Effectiveness for each corrosion type. Table 1 also represent accuracy of UT and one of the values related to effectiveness as NDT. Effectiveness of UT is roughly classified into three categories based on these SD values, (1) A: less than 0.3 mm, (2) B: at least 0.3 mm and less than 0.6 mm, and (3) C: at least 0.6 mm. That’s why Inspection Effectiveness of UT is classified each degradation type as shown in Table 2.

<table>
<thead>
<tr>
<th>Degradation Type</th>
<th>Inspection Effectiveness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Reaction</td>
<td>C</td>
</tr>
<tr>
<td>UV</td>
<td>B</td>
</tr>
<tr>
<td>Penetration</td>
<td>B</td>
</tr>
<tr>
<td>Reference</td>
<td>A</td>
</tr>
</tbody>
</table>

4. Conclusion

In this research, the standard deviation of error in measuring thickness of FRP by UT is calculated to compare UT thickness with micrometer thickness in terms of precision.

Even fresh FRP sample standard deviation of UT in fresh sample was 0.21 and this was limit of UT for FRP device. The standard deviation in surface reaction type, the NaClO aq. Storage tank, was larger than the other degraded tank because the corroded inside surface scattered ultrasonic and the bottom echo attenuated. The standard deviation in Penetration type, the HCl aq. storage tank, is small because its surface is flat even though Cl penetrated into resin.

Solution in the tank also makes ultrasonic wave attenuated because ultrasonic easily penetrate into solution at FRP/solution interface and is less reflected than FRP/atmosphere interface.

Precision of UT for FRP, as described above, is useful to define Inspection Effectiveness for each corrosion type in perspective of Risk Based Inspection.

Reference