

## **DEVELOPMENT OF RADIOACTIVE WASTE TREATMENT SYSTEM USING SUPERCRITICAL WATER**

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### **ABSTRACT**

In nuclear facilities, there is some organic waste containing radioactive material. In the future, it is desired that this waste will be decomposed to reduce the volume and become stable. Toshiba has developed a waste treatment system using supercritical water. First, supercritical water was applied to the decomposition of used ion exchange resin for water purification in a nuclear power plant. Actual plant size apparatus was constructed with a treatment capacity of 1 kg ion exchange resin an hour. A kinetic model that can predict the ion exchange resin decomposition yield was also developed, and treatment conditions were determined using this model. Test revealed that 99.9% or more ion-exchange resin was decomposed at 723K and 30MPa. This decomposition yield predicted by the kinetic model fitted with the observed ion exchange resin decomposition yield. Moreover, compact equipment with a treatment amount of 33g /h was developed for decomposing organic solvents such as the liquid scintillation counter cocktail that is used for analyzing radionuclides. Test revealed that 99.9% or more liquid scintillation counter cocktail was decomposed at 773K and 30MPa. The equipment dimensions are about 2mL×1mW×1mH. It can even be installed in the glove box in nuclear facilities. Various types of organic liquid waste, for example, tributyl phosphate, turbine oil, silicone oil, etc. can be treated with this equipment. One such type of equipment has already been installed in a nuclear facility in Japan to treat organic liquid waste such as the liquid scintillation counter cocktail and has been operating well.

### **INTRODUCTION**

Supercritical water whose temperature and pressure exceed 647K and 22MPa is an excellent solvent for organic compound decomposition, since oxygen and organic compounds can exist in a single homogeneous fluid phase. Organic compounds can be decomposed fast and completely using supercritical water and almost all reactants can be kept in the water during organic compound decomposition. Thus, utilizing supercritical water to treat organic waste is an attractive prospect.

The study on the organic compounds decomposition using supercritical water was started by Modell <sup>1)</sup> in 1980. Then, many researchers studied the organic compounds decomposition. Li

<sup>2)</sup> summarized a part of these studies. In Japan, the commercial plant for decomposing liquid waste containing organic chlorine compounds such as Trichloroethylene has been operating.

In nuclear facilities, there is some organic waste containing radioactive material. In the future, it is desired that this waste will be decomposed to reduce the volume and become stable. At Los Alamos National Laboratory, EDTA (ethylenediamine tetra acetic acid) decomposition using nitrite and nitrate were studied in supercritical water <sup>3)</sup>. Moreover, at CEA, the mixture of dodecane and Tributyl phosphate (TBP) was decomposed in supercritical water <sup>4)</sup>.

Toshiba has developed two types of radioactive waste treatment system using supercritical water. The first is the treatment system of an ion exchange resin for water purification in a nuclear power plant. The temperature and time process conditions were optimized to realize a treatment capacity of 1 kg ion exchange resin an hour and 99.9% or more decomposition of organic substances. The second is the treatment system of an organic solvent such as the liquid scintillation counter cocktail that is used for analyzing radionuclides. The temperature and time process conditions were optimized to realize a treatment capacity of 33g liquid scintillation counter cocktail an hour and 99.96% or more decomposition of organic substances.

This paper examines and reveals the decomposition and equipment characteristics of these two systems.

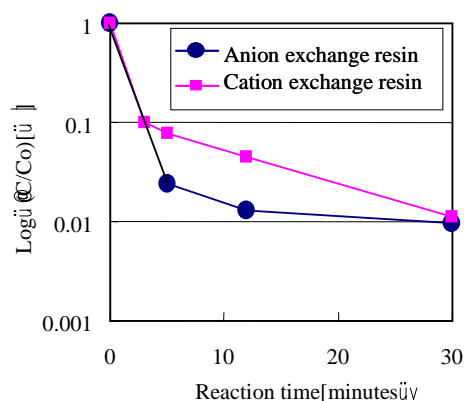
### **Ion Exchange Resin Decomposition**

First, supercritical water was applied to the decomposition of an ion exchange resin for water purification in a nuclear power plant.

### **Development of Kinetic Model of Resin Decomposition**

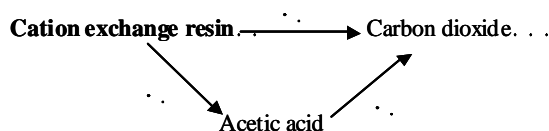
To investigate the applicability of SCWO to the ion exchange resin decomposition, we examined the influence of the experimental conditions such as reaction temperature and time on the complete decomposition of the ion exchange resin. Furthermore, a simple kinetic model was examined to estimate the resin decomposition yield.

Ion exchange resin is a gel-type ion exchange resin that introduces an ion exchange group into a copolymer of styrene and divinylbenzene. Using supercritical water, the ion exchange resin generated carbon dioxide, water, sulfuric acid and ammonia.

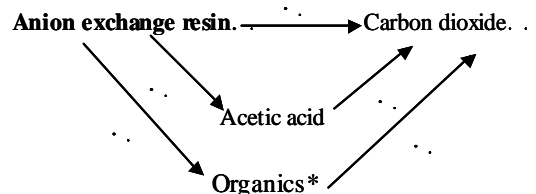


First-order plot of resin decomposition rate at 673K and 30MPa

(a) Cation exchange resin



(b) Anion exchange resin



\*Decomposition rate is almost equal to ethanol's.

Kinetic model of resin decomposition

**Fig. 1. Ion exchange resin decomposition using supercritical water**

Figure 1 shows the first order plot of the resin decomposition rate. Fifteen mg of ion exchange resin and 0.2g of hydrogen peroxide were put in a cylindrical reactor with material and volume type 316 SS and 5.6 cm<sup>3</sup>, respectively. The reactor was heated in a sand bath for a setting time. After the reaction, the reactor was removed from the sand bath and immersed in water at temperature of 293K. During the experiment, the temperature in the reactor, which was controlled by the sand bath temperature, was 673K. The pressure in the reactor, which was controlled by the weight of water added to the reactor, was 30MPa. The normalized carbon residual ratio is the ratio of the amount of organic carbon in decomposition liquid (C), and the amount of carbon in the ion exchange resin (Co). In the cation and anion exchange resin, the normalized carbon residual ratio decreased with the reaction time. At 30 minutes, 99% ion exchange resin was decomposed. As the first order plot of the resin decomposition rate was not on a straight line, the resin decomposition path was composed of two or more paths.

For the cation exchange resin, the organic material in the decomposition liquid was investigated in detail. A half of the total organic carbon (TOC) was acetic acid at 3 minutes and all TOC was acetic acid at 30 minutes or more. Judging from the results, the decomposition of acetic acid was the rate-controlling step in the resin decomposition.

A kinetic model of cation exchange resin decomposition is proposed in Figure 1<sup>5</sup>, where  $k_1$  is the rate constant of the decomposition of the resin to carbon dioxide,  $k_2$  the rate constant from resin to acetic acid, and  $k_3$  the rate constant from acetic acid to carbon dioxide. The total kinetic expression is given by

$$-(d[Rc]/dt) = (k_1 + k_2)[Rc] \quad (\text{Eq.1})$$

$$-(d[Ac]/dt) = k_3 [Ac] - k_2[Rc] \quad (\text{Eq.2})$$

[Rc]: TOC concentration of the resin

[Ac]: TOC concentration of acetic acid

The change of the TOC concentration in liquid, [Rc+Ac], is given by (Eq.3).

$$\frac{[Rc+Ac]}{[Rc+Ac]_0} = \frac{k_2}{(k_1 + k_2 - k_3)} \exp(-k_3 t) + \frac{k_1 - k_3}{(k_1 + k_2 - k_3)} \exp(-(k_1 + k_2) t) \quad (\text{Eq.3})$$

[Rc+Ac]<sub>0</sub>: Initial TOC concentration (Amount of carbon in the ion exchange resin)

[Rc+Ac]/[Rc+Ac]<sub>0</sub> is equal to the normalized residual carbon ratio. As  $t$  is 0, [Rc+Ac]/[Rc+Ac]<sub>0</sub> is equal to unity. By fitting the experimental data, the value of  $k_1/k_2$  was determined to be 7.7 and the value of  $k_3$  was determined to be 0.0013 s<sup>-1</sup> at 673K and 30MPa.

Then, the kinetic model of the cation exchange resin decomposition was applied to temperatures of 723K and 773K, and the measured value was compared with the estimated value. The result is shown in Table I<sup>6</sup>. It assumes that  $k_1/k_2$  is constant on temperature change. The value of  $k_3$  was calculated by (Eq.4) formula. The value of  $E_a$  used is from the data by Lee<sup>2</sup>. The estimated value and measured value are about the same. Therefore, the cation exchange resin decomposition yield can be estimated using this model.

$$k_3 = A \exp(-E_a/RT) \quad (\text{Eq.4})$$

A: Pre-exponential factor  $1.2 \times 10^{10} [\text{s}^{-1}]$   
 Ea: Activation energy  $167.1 [\text{kJ/mol}]$   
 R: Gas constant  $8.314 [\text{J/mol K}]$   
 T: Temperature [K]

**Table I. Comparison of estimated normalized residual carbon ratio with measured value in the cation exchange resin decomposition**

| Temperature | $k_3$                  | Normalized residual carbon ratio |           |
|-------------|------------------------|----------------------------------|-----------|
|             |                        | Measured                         | Estimated |
| 723K        | $0.01 \text{ s}^{-1}$  | 0.011                            | 0.006     |
| 773K        | $0.063 \text{ s}^{-1}$ | <0.001                           | <0.001    |

Pressure: 30MPa, Time: 5 minutes,

Hydrogen peroxide: 7 times as large as the stoichiometric value

Moreover, for the anion exchange resin, the organic material in the decomposition liquid was investigated in detail. Acetic acid and another organic material whose decomposition rate is smaller than acetic acid remained in the decomposition liquid. The kinetic model of the anion exchange resin decomposition is proposed in Figure 1, where  $k_4$  is the rate constant from resin to organic material whose decomposition rate is smaller than acetic acid, and  $k_5$  is the rate constant from organic material to carbon dioxide. By fitting the experimental data, the value of  $k_1/k_4$  was determined to be 97, the value of  $k_2/k_4$  was 2, the value of  $k_3$  was  $0.0013 \text{ s}^{-1}$  and  $k_5$  was  $0.00001 \text{ s}^{-1}$  at 673K and 30MPa.

$$d[\text{Bc}]/dt = k_5[\text{Bc}] - k_4[\text{Rc}] \quad (\text{Eq.5})$$

[Bc]: TOC concentration of organic material whose decomposition rate is smaller than acetic acid

Alcohol like ethanol has a small decomposition rate compared with acetic acid. Thus, the organic material whose decomposition rate is smaller than acetic acid is assumed to be ethanol. The kinetic model of the anion exchange resin decomposition was applied to temperatures of 723K and 773K, and the measured value was compared with the estimated value. The result is shown in Table II<sup>5</sup>. It assumes that the value of  $k_1/k_4$  and  $k_2/k_4$  is constant on temperature change. The value of  $k_3$  was calculated by (Eq.4) formula. The value of  $k_5$  was calculated by the (Eq.6) formula determined by Helling<sup>7</sup>.

$$k_5 = A \exp(-Ea/RT) \quad (\text{Eq.6})$$

A: Pre-exponential factor  $6.5 \times 10^{21} [s^{-1}]$

Ea: Activation energy  $340 [kJ/mol]$

At 723K, the normalized residual carbon ratio was estimated using the value of  $k_5$  calculated by (Eq.6) formula. Consequently, the estimated value was 0.007, the measured value was 0.001 and the estimated and measured value differed slightly. Then, by fitting the experimental data, the value of Ea was assumed to be 320kJ/mol. The normalized residual carbon ratio was estimated using the value of  $k_5$  calculated by (Eq.7) formula. At 723K and 773K, the estimated value and measured value are about the same. Assuming that the value of  $k_5$  has almost the same decomposition rate as ethanol, the anion exchange resin decomposition yield can be estimated using this model.

Using the kinetic model of the cation and anion exchange resin decomposition above, the decomposition yield could be determined.

$$k_5 = A \exp(-Ea/RT) \quad (Eq.7)$$

A: Pre-exponential factor  $6.5 \times 10^{21} [s^{-1}]$

Ea: Activation energy  $320 [kJ/mol]$

**Table II. Comparison of estimated normalized residual carbon ratio with measured value in anion exchange resin decomposition**

| Temperature | k               | $k_5$                       |                             | Normalized residual carbon ratio |                       |                       |
|-------------|-----------------|-----------------------------|-----------------------------|----------------------------------|-----------------------|-----------------------|
|             |                 | (Eq.6)                      | (Eq.7)                      | Measured                         | Estimated             |                       |
|             |                 |                             |                             |                                  | $k_5$<br>using (Eq.6) | $k_5$<br>using (Eq.7) |
| 673K        | $0.0013 s^{-1}$ | $2.6 \times 10^{-5} s^{-1}$ | $9.4 \times 10^{-4} s^{-1}$ | 0.024                            | 0.023                 | 0.021                 |
| 723K        | $0.01 s^{-1}$   | $1.8 \times 10^{-3} s^{-1}$ | $4.9 \times 10^{-2} s^{-1}$ | <0.001                           | 0.007                 | 0.001                 |
| 773K        | $0.063 s^{-1}$  | $6.8 \times 10^{-2} s^{-1}$ | $1.5 s^{-1}$                | <0.001                           | $1.8 \times 10^{-10}$ | $1.7 \times 10^{-10}$ |

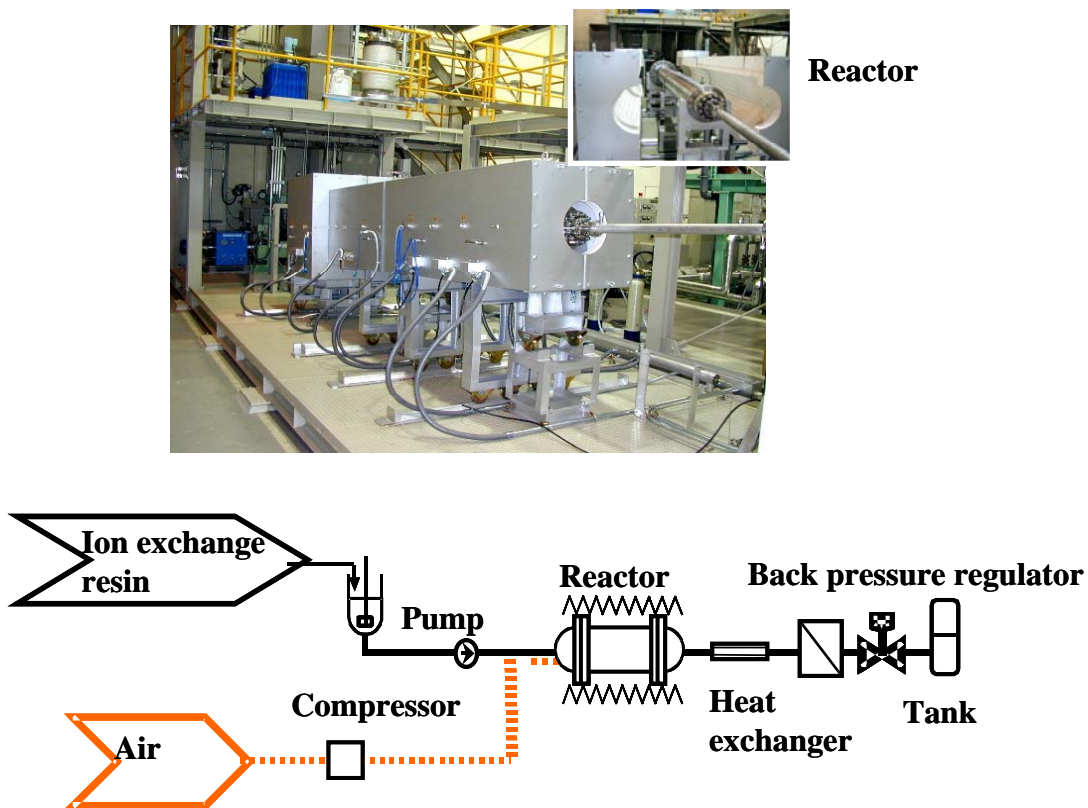
Pressure: 30MPa, Time: 5 minutes,

Hydrogen peroxide: 7 times as large as the stoichiometric value

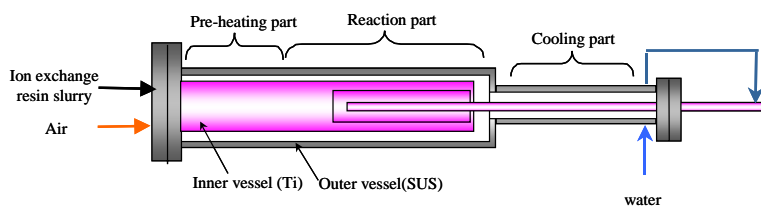
### Ion Exchange Resin Decomposition Test

The apparatus with the commercial scale reactor was designed using the kinetic model of resin decomposition and the apparatus performance was investigated.

Figure 2 shows the apparatus with the commercial plant scale reactor. The treatment capacity of the apparatus is 1kg ion exchange resin an hour and 99.9% or more ion exchange resin was decomposed. The apparatus consists of a reactor, a high-pressure pump that supplies resin



Commercial plant scale test equipment



Structure of the reactor

**Fig. 2. Apparatus with commercial plant scale reactor**

slurry to the reactor, a compressor which supplies air to the reactor, a gas-liquid separator, back pressure regulator and tanks.

Figure 2 shows the structure of the reactor where the pre-heating part, the reaction part and the cooling part are unified. The features of the reactor are shown below.

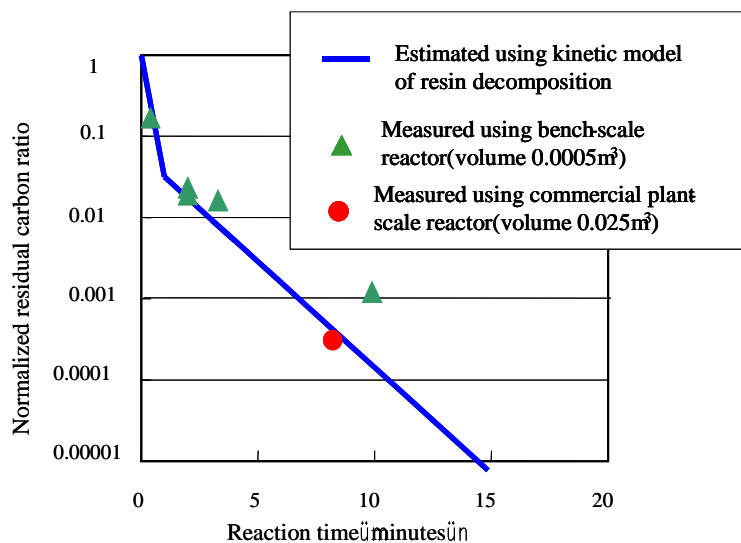
- Double vessel equipped with corrosion resistance and intensity  
The reactor consists of an outer vessel and an inner vessel. The crevice between the outer vessel and the inner vessel and the inside of the inner vessel are connected, and water is added here. By this method, the pressure of the inside of the inner vessel and outside becomes almost equal. When resin decomposes, sulfuric acid is generated. Therefore, the inner vessel is made of titanium that has strong anti-corrosion properties against sulfuric acid<sup>9</sup>.
- Two-step reactor in which a solid can be decomposed continuously  
The first step reactor is a vessel type reactor. This reactor has the function of mixing organic solid waste, such as resin, with oxygen. Then, organic solid waste is converted using water-soluble organic materials such as acetic acid. The second step reactor is a tube type reactor that is hard to mix in the direction of the flow. This reactor has the function of completely decomposing water-soluble organic materials into carbon dioxide.
- Compactability  
The reactor unifies the pre-heater part, the reaction part and the cooling part, thereby, allowing utmost minimization of the space in the high temperature part within the apparatus.

Using the commercial plant scale reactor with a reaction part capacity of 0.025m<sup>3</sup>, ion exchange resin decomposed continuously. Figure 3 shows the effect of the resin decomposition yield on the reaction time at 723K and 30MPa. The reaction time was changed from 0.5 to 10 minutes. Furthermore, the measured value using a bench scale reactor with a reaction part capacity of 0.0005m<sup>3</sup> and the estimated value using the kinetic model of the resin decomposition are shown in Figure 3<sup>5</sup>.

The normalized residual carbon ratio decreased with the reaction time. The measured value of the normalized residual carbon ratio was almost the same as the estimated value. In reaction time for one minute or more, organics such as acetic acid whose decomposition rate is small remains. The estimated value shows a straight line for one minute or more, because of only acetic acid decomposition. Tests revealed that 99.9% or more ion-exchange resin was decomposed at 723K, 30MPa and less than 10 minutes. Thus, it was confirmed that 99.9% of the resin decomposition yield was obtained with a commercial-scale apparatus.

After the test, the existence of a pinhole was checked. Nitrogen gas put in the inner vessel shown in Fig. 2. The pressure of the inner vessel is regular for 30 minutes. So, there is no pinhole of the inner vessel.





**Fig. 3. Effect of resin decomposition yield on reaction time at 723K and 30MPa**

### Organic Liquid Waste Decomposition

Radioactive organic liquid waste exists in nuclear facilities. Using supercritical water, this organic liquid waste can be decomposed. Especially, compact equipment with a treatment amount of 33g/h was studied for decomposing organic solvents such as the liquid scintillation counter cocktail that is used for analyzing radionuclides.

Table III shows the result of the oxidative decomposition of organic liquid waste in supercritical water at 673K and 30 minutes. Silicone oil was examined at a pressure of 27 MPa and other waste was examined at a pressure of 30MPa. The main components of the liquid scintillation counter cocktail are phenol and a surface-active agent. Ninety-three percent of the liquid scintillation counter cocktail, 99% of turbine oil, TBP and 99.9% of the silicone oil changed to carbon dioxide. The liquid scintillation counter cocktail is the most difficult to decompose in the various types of organic liquid waste. Therefore, compact equipment that can decompose the liquid scintillation counter cocktail was developed.

The specification of the compact organic liquid waste treatment equipment with oxidative decomposition in supercritical water is shown in Table IV<sup>10</sup>. The treatment capacity of the equipment is 33g liquid scintillation counter cocktail an hour and 99.96% or more liquid scintillation counter cocktail was decomposed. Equipment consists of a reactor, a high-pressure pump which supplies the liquid scintillation counter cocktail to the reactor, a high-pressure pump which supplies hydrogen peroxide as the oxidizing agent to the reactor, a gas-liquid separator, back pressure regulator and tanks. The structure of the reactor is the same

as that of the resin decomposition reactor. The equipment dimensions are about 2mL×1mW×1mH. It can even be installed in the glove box in nuclear facilities

**Table III. Oxidative decomposition of organic liquid waste in supercritical water**

| Organic waste                         | Pressure | Decomposition yield |
|---------------------------------------|----------|---------------------|
| Liquid scintillation counter cocktail | 30MPa    | 93%                 |
| Tributyl phosphate (TBP)              | 30MPa    | 99%                 |
| Turbine oil                           | 30MPa    | 99%                 |
| Silicone oil                          | 27MPa    | 99.9%               |

Temperature: 673K, Time: 30 minutes

Using Toshiba's compact equipment, the liquid scintillation counter cocktail was decomposed continuously at 773K, 30MPa and 3.8 minutes. Figure 4 shows the change in the reactor temperature and TOC in effluent during decomposition. The TOC concentration in the decomposition liquid is 10 ppm or less, and was stable. The decomposition yield of the liquid scintillation counter cocktail is calculated at 99.96%.

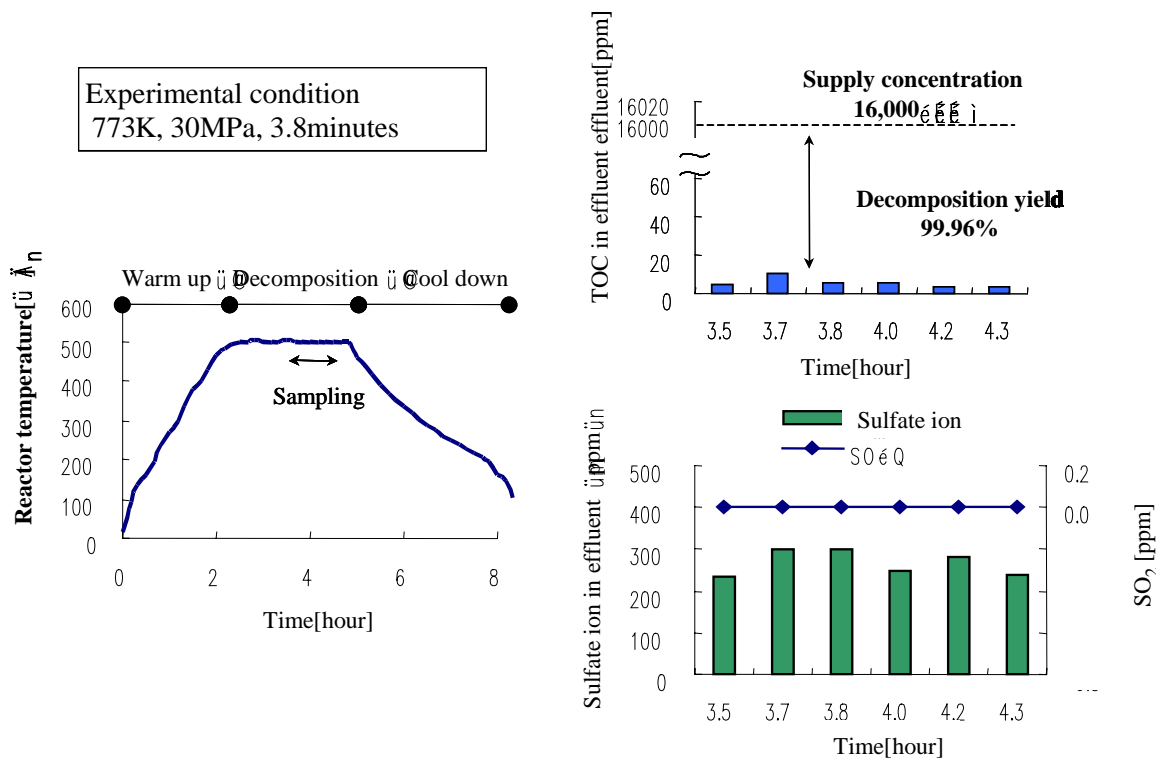
**Table IV. Specification of compact organic liquid waste treatment equipment with oxidative decomposition in supercritical water**

|                                   |                   |                                      |
|-----------------------------------|-------------------|--------------------------------------|
| Reactor                           | Material          | Outer: SUS Inner: Ti                 |
|                                   | Volume            | 0.0005m <sup>3</sup> (reaction part) |
| Space                             | 2mL × 1mW × 1mH   |                                      |
| Oxidizing agent                   | Hydrogen peroxide |                                      |
| Treatment amount <sup>*)</sup>    | 33g/hour          |                                      |
| Decomposition yield <sup>*)</sup> | Above 99.96%      |                                      |

<sup>\*)</sup> Liquid scintillation counter cocktail

Furthermore, the behavior of the sulfur in the liquid scintillation counter cocktail during decomposition was investigated. Figure 4<sup>10</sup> shows the change in the sulfate ion concentration and SO<sub>2</sub> concentration in effluent during decomposition. The SO<sub>2</sub> concentration is 0 ppm below the detection limit. On the other hand, the sulfate ion concentration in effluent was about 250 ppm. The recovery yield of sulfur was calculated using the sulfate ion concentration and is about 100%. The entire quantity of the sulfur was recovered in the water. Using supercritical water, almost all reactants, such as SO<sub>x</sub>, can be kept in the water. So, the exhaust gas is clean and exhaust gas processing equipment is unnecessary.

Test revealed that 99.9% or more liquid scintillation counter cocktail was decomposed at 773K and 30MPa. Furthermore, various types of organic liquid waste, for example, TBP, turbine oil, silicone oil, etc. can be treated with this equipment.



**Fig. 4. Behavior of carbon and sulfur in the liquid scintillation counter cocktail during decomposition**

## CONCLUSION

In nuclear facilities, there is some organic waste containing radioactive material. In the future, it is desired that this waste will be decomposed to reduce the volume and become stable. Toshiba has developed a waste treatment system using supercritical water.

First, supercritical water was applied to the decomposition of used ion exchange resin for water purification in the nuclear power plant. Actual plant size apparatus was constructed with a treatment capacity 1kg ion exchange resin an hour. Tests revealed that 99.9% or more ion-exchange resin was decomposed at 723K and 30MPa.

Moreover, compact equipment with a treatment amount of 33g/h was developed for decomposing organic solvents such as the liquid scintillation counter cocktail that is used for analyzing radionuclides. Tests revealed that 99.9% or more liquid scintillation counter cocktail

was decomposed at 773K and 30MPa. One set of equipment has already been installed in a nuclear facility in Japan to treat organic liquid waste such as the liquid scintillation counter cocktail and has been operating well.

It is expected that the application of supercritical water to waste treatment will progress in the nuclear field from now on, since the features of the supercritical water are regarded as fitting for radioactive waste treatment.

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