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## Radiation induced change in the affinity of a plastic resin to chlorine contained in artificial tap water

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### Abstract

$\gamma$ -Radiation curing of a polyacetal resin was attempted in order to eliminate the unsuitable property for the joints of tap water pipes. In the case of non-irradiated resin, almost all available chlorine (AC) contained in usual tap water disappeared.

$\gamma$ -Irradiation of the resin showed an indirect effect on eliminating such a property; that is, a decrease in the amount of AC from artificial tap water (test solution) showed a decrease to JIS (Japan Industrial Standards) level of requirement at certain absorption doses.

However, it was also found that the decrease in the amount of AC from the test solution increased with time after  $\gamma$ -irradiation.

### Introduction

Radiation curing has been widely used for the modification of existing materials and the creation of entirely new material in many industries.<sup>1,2,3,4)</sup>

The present authors carried out  $\gamma$ -radiation curing of a polyacetal resin which was developed for use in joints of (tap) water pipes.

There are several requirements for materials used for the joints of tap water pipes, which have been regulated by JIS (Japan Industrial Standards). The resin was tested against the JIS requirements to determine the points of unsuitability for the joint of tap water pipes. The results showed that almost all available chlorine (AC) contained in usual tap water as a disinfectant disappears within 24 hours when the resin is immersed in tap water.

In order to eliminate this defect,  $\gamma$ -radiation curing was applied, and the change in the affinity of the irradiated resin to AC was investigated (dissolution test).

This paper shows the results of the dissolution test on resin samples  $\gamma$ -irradiated with various doses.

### Experimental

Resin sample: The resin sample used in this study was a poly-acetal copolymer prepared from trioxane as the main starting material.<sup>5,6,7,8)</sup> Some of the physical and

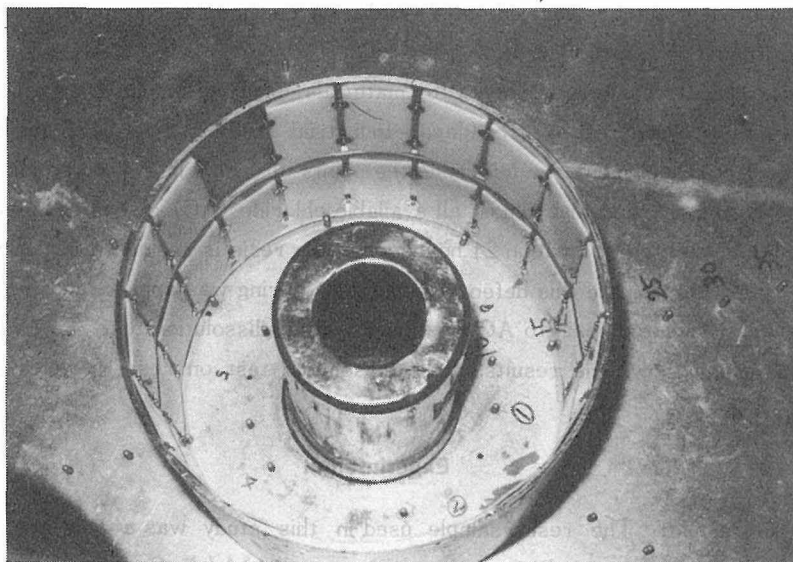
mechanical properties of the resin were tabulated in Table 1.<sup>8)</sup>

$\gamma$ -Irradiation of plastic resin sample: Irradiation of the poly-acetal resin sample was carried out by using  $^{60}\text{Co}$  (0.421 Mrad/h) as a radiation source. Absorption dose at all points on the sample holder was measured by means of Fricke dosimetry. Seven plates of the samples set on the sample holder were irradiated simultaneously (Photos 1 and 2). The sample holder was an iron drum coated with zinc. It was rotated during  $\gamma$ -irradiation.

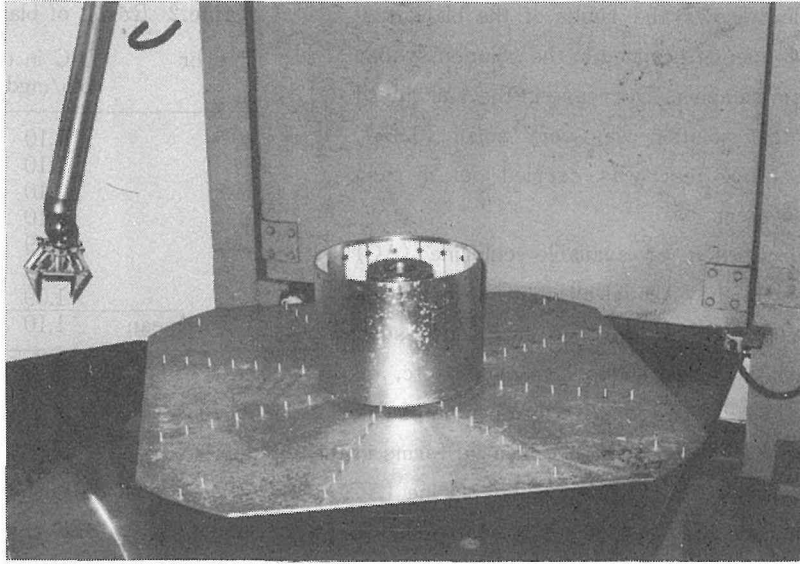
Dissolution test: Photo 3 shows a typical example of the present dissolution test. All experiments were carried out by using a reaction vessel (1 dm<sup>3</sup>) with a glass holder at 25°C. Seven plates of the plastic resin sample (10×5×0.2 cm) were digested into one test solution (600 cm<sup>3</sup>). The test solution was prepared as follows. Saturated lime water (70 cm<sup>3</sup>) was added to pure water to an equal 3.8 dm<sup>3</sup> in volume. A 0.1 % sodium hypochlorite solution (7 cm<sup>3</sup>) was added to the solution, and the pH was adjusted to 7.5 to 8.0 with carbon dioxide. After allowing the solution to stand for 24 hours, the pH and AC contents of the solution were adjusted to 7.0±0.2 and 1.0–1.2 mgCl<sub>2</sub>m<sup>-3</sup>, respectively, and then used for the test solution.

**Table.1** Some physical and mechanical properties of the resin sample

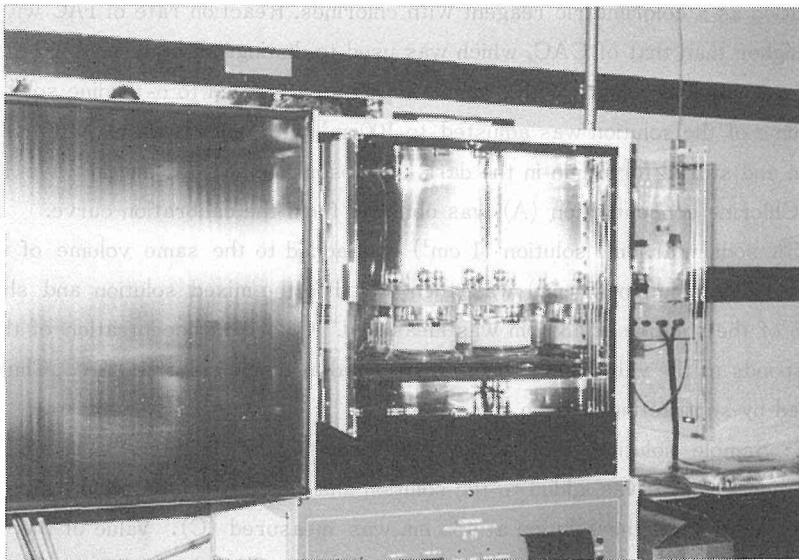
Density	1.410
Thermal deformation temp. (°C)	110
18.6 kgcm <sup>-2</sup>	158
4.6	
Linear expansion coefficient (cm/cm/°C)	10×10 <sup>-5</sup>
Burning rate (cm/min)	2.8
Melting point (°C)	165
Specific heat (Kcal/kg°C)	0.35



**Photo.1** Sample holder with resin samples



**Photo.2**  $\gamma$ -Irradiation of resin samples



**Photo.3** Reaction vessels with resin samples in a thermostated container

Relative surface area of the resin sample per one liter of the test solution was adjusted to  $0.12 \text{ (m}^2/1)$ . Samples were washed with purified distilled water for an hour at a flow rate of about  $30 \text{ (m/min)}$ , and then rinsed with the test solution prior to the dissolution test. Available chlorine (AC) in the test solution was determined at the initial run and 24

hours after each run.

Table 2 shows the results of the blank test in which AC was determined in the solution system without resin samples. Decrease in the amount of AC in the test solution was very small (0.9%). The above blank test was carried out in each dissolution system.

Determination of available chlorine (AC) in the test solution: Almost all chlorine in natural water is in the form of nitrogen compounds such as ammonium chlorides and chloroamines, etc, or it exists as hypochlorite ions. Determination of chlorine in aqueous solution is thus desirable in order to take into account the chemical forms in the solution.

According to the JIS, available chlorine (AC) is classified into three forms, i. e., free available chlorine (FAC), combined available chlorine (CAC) and total available chlorine (TAC). FAC contains chlorine molecules ( $\text{Cl}_2$ ) and hypochlorite ions ( $\text{ClO}^-$ ) in the solution. CAC is a chlorine species that combines ammonia or oxidizable nitrogen compounds. TAC is the sum of FAC and CAC.

In the present study AC in the solution was determined spectroscopically by using o-tolidine solution as a colorimetric reagent with chlorines. Reaction rate of FAC with o-tolidine was much higher than that of CAC, which was used to distinguish between FAC and CAC.

TAC: A suitable volume of the sample solution was added to o-tolidine solution ( $5 \text{ cm}^3$ ), and the volume of the solution was adjusted to  $100 \text{ cm}^3$  with pure water. After the solution was shaken and stored for 5 min in the dark, its absorbance at 435 nm in wave length was measured. Chlorine concentration (A) was obtained from the calibration curve.

A 0.5% sodium arsenic solution ( $1 \text{ cm}^3$ ) was added to the same volume of the sample solution. o-Tolidine solution ( $5 \text{ cm}^3$ ) was then added to the mixed solution and shaken well. Absorbance of the solution at 435 nm was measured. Chlorine concentration of the solution (B) corresponds to the value of the blank test. Total available chlorine (TAC,  $\text{Clmgdm}^{-3}$ ) was thus obtained by subtracting B from A.

FAC: Sample solution was added to o-tolidine solution ( $5 \text{ cm}^3$ ), and 0.5% sodium arsenic solution ( $1 \text{ cm}^3$ ) was added to the solution and mixed well. After left standing for 5 minutes, absorbance of the solution at 435 nm was measured (C). Value of the blank test (D) was obtained by the same procedure as that shown in TAC determination. Free available chlorine (FAC,  $\text{Clmgdm}^{-3}$ ) was obtained by subtracting D from C.

CAC: Combined available chlorine (CAC,  $\text{Clmgdm}^{-3}$ ) was obtained according to the following equation:  $\text{CAC} (\text{Clmgdm}^{-3}) = (A - B) - (C - D)$

Working range of the calibration curve was obtained from 0.1 to  $1.0 \text{ mgCl} \text{ dm}^{-3}$ . Experimental error for AC determination was in the range of  $\pm 0.02 \text{ mgCl} \text{ dm}^{-3}$ .

**Table.2** Result of blank test

Time/hr	TAC in the test soln/ $\text{mgdm}^{-3}$
0	1.10
24	1.10
	1.10
	1.10
	1.09
	1.09
	1.09
mean	1.10

### Results and Discussion

A dissolution experiment was carried out on non-irradiated original samples prior to  $\gamma$ -irradiation. As shown in Table 3, almost all of the TAC contained in the test solution disappeared during the test (within 24 hours at 25°C). The original sample did not pass the standard of the dissolution test set forth by JIS, which has it that the decrease in the amount of TAC from the test solution must be less than 0.7 mgCl<sub>2</sub>dm<sup>-3</sup>.

Samples were then  $\gamma$ -irradiated for varying lengths of time, which corresponded to the absorption dose, ranging from 1 to 10 Mrad. More than half of the samples were broken by irradiation of more than 10 Mrad. Longer irradiation caused a change in the appearance of the samples: , that is, they changed in color from white to brown and became stiff in texture.

Table 4 shows the results of elementary analyses of non- and irradiated (4.5 Mrad) resin samples.

Figures 1 and 2 show the results of IR and UV spectra of non- and irradiated samples, respectively. These results indicate that cross linking and breaking of C—C bonds may occur simultaneously in irradiated samples.

Figure 3 shows the results of the dissolution test on  $\gamma$ -irradiated samples.  $\gamma$ -Irradiation of the samples did not have any direct effects on the decrease in the amount of TAC from the test solution into which samples were immersed immediately after  $\gamma$ -irradiation.

We then investigated the influence of cooling time after  $\gamma$ -irradiation on the decrease in the amount of TAC from the test solution. As also shown in Fig. 3, decreases in the amount of TAC from the test solution were the same independent of the cooling time.

$\gamma$ -Irradiated samples once used for the dissolution test were rinsed with pure water and immersed again into a new test solution for 24 hours at 25°C. The results are shown in Fig. 4. Degree of decrease in the amount of TAC from the test solution apparently decreased in all cases of irradiation. A minimum decrease in the amount of TAC from the test solution (0.64 mgCl<sub>2</sub>dm<sup>-3</sup>) appeared at the absorption dose of 6 Mrad. The samples themselves were further used for the dissolution tests after 360 and 816 hours of  $\gamma$ -irradiation. Decrease in the amount of TAC from the test solution was 0.64 mgCl<sub>2</sub>dm<sup>-3</sup> in both cases.

Figure 5 shows the decrease in the amount of TAC from the test solution for  $\gamma$ -irra

**Table.3** Dissolution test on non-irradiated samples

Time/hr	TAC in the test soln/mgdm <sup>-3</sup>	
0		1.11
24	1.	0.18
	2.	0.20
	3.	0.19
	4.	0.19
	5.	0.20
	Blank	1.09
Mean TAC decrease		0.90

**Table.4** Elementary analyses of non- and irradiated resin samples

	Weight /mg	C (%)	H (%)
Non-irradiated	2.257	40.38	6.92
Irradiated (4.5 Mrad)	2.222	40.53	6.90

-diated samples (absorption dose; 3.3 Mrad). Difference among five analytical values obtained in one experiment are in a range of  $ca \pm 0.02 \text{ mgdm}^{-3}$ . Each value of TAC decrease obtained in the initial dissolution test correlated well with that of the same sample obtained after a suitable cooling time. The tendency shown in Fig.5 appeared in all other cases examined, and it probably corresponds to variation of the absorption dose in one run.

$\gamma$ -Irradiation was further carried out in an aqueous solution with different pH into which resin samples were immersed. After irradiation, samples were washed with pure water, rinsed with test solution and used for the dissolution test. Figure 6 shows the results of the dissolution test on  $\gamma$ -irradiated samples which were previously immersed in 4% hypochlorite solution during irradiation. The appearance of the surface of the irradiated samples was remarkably changed with longer irradiation time (more than 90 hours). The decrease in the amount of TAC from the test solution was smallest in the samples irradiated for 18 hours. These samples were rinsed with pure water and used for other dissolution tests. As shown in Fig. 6, the mean decrease in the amount of TAC from the test solution was  $0.81 \text{ mgdm}^{-3}$  in the second dissolution test.  $\gamma$ -Irradiation of the samples had some effect (not directly) on the decrease in the amount of TAC from the test solution, but only when the samples were irradiated for 18 hours. This, however, did not meet the JIS requirement for tap water pipe joints.

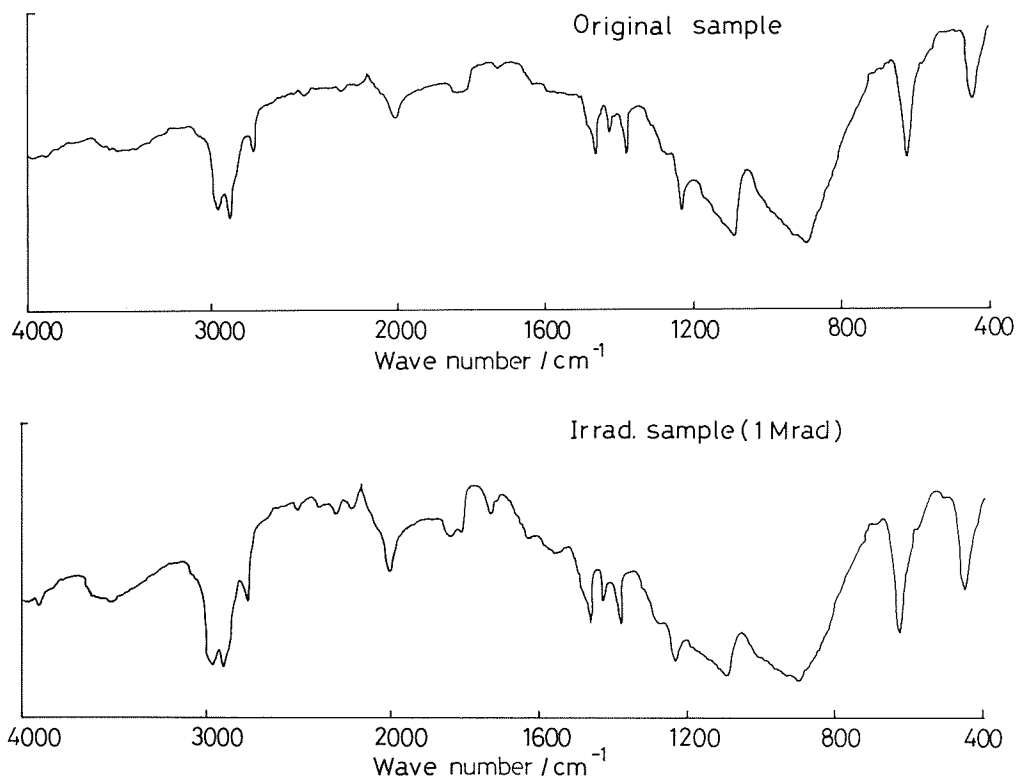


Fig.1 IR spectra of non- and irradiated resin samples

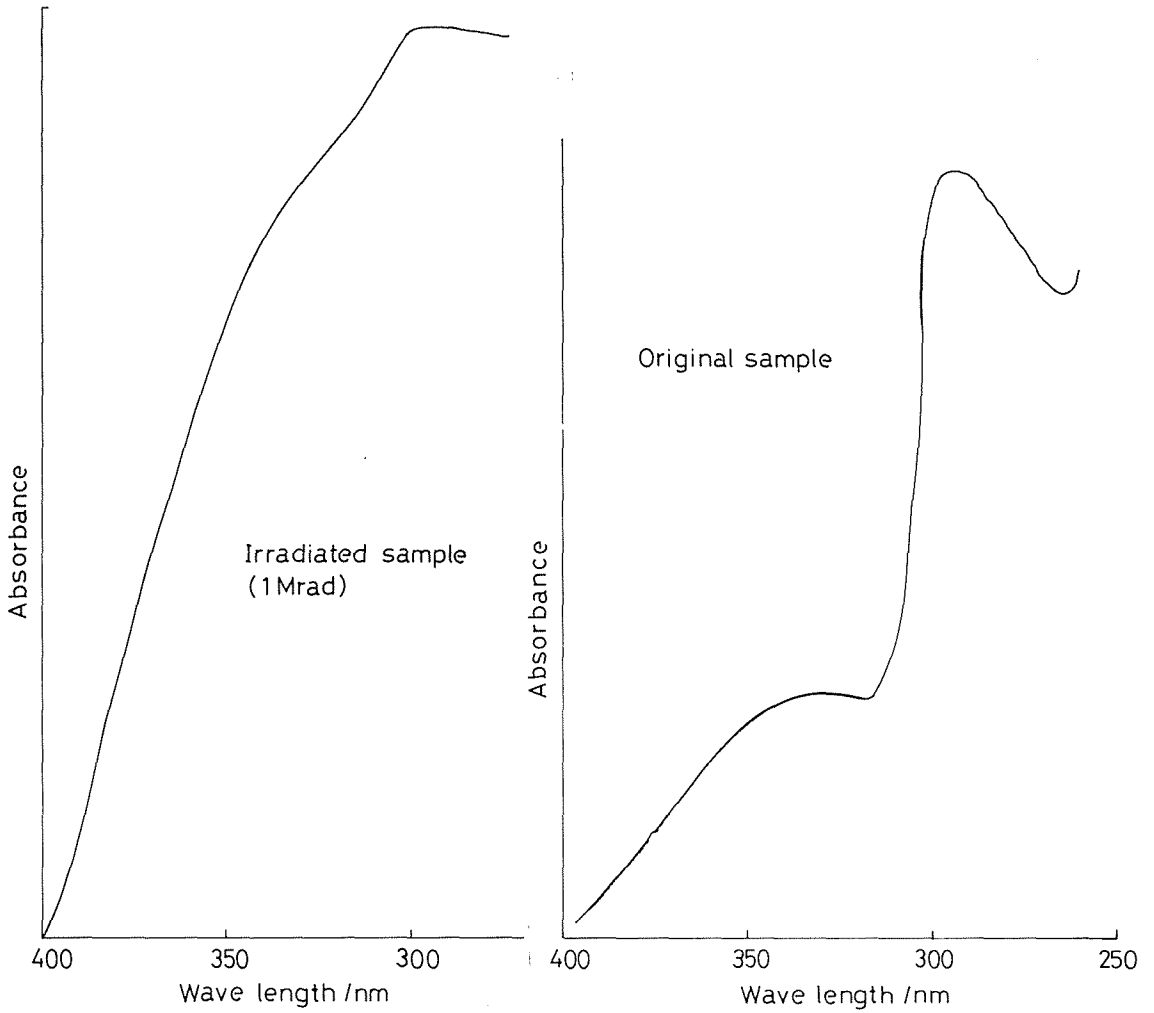


Fig.2 UV spectra of non- and irradiated resin samples

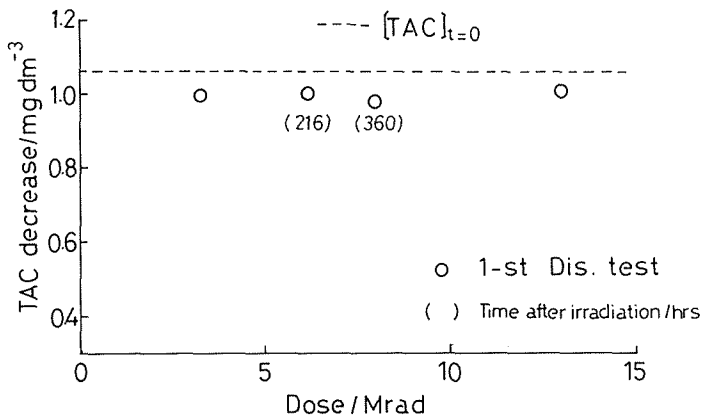


Fig.3 Result of first dissolution test on  $\gamma$ -irradiated resin samples



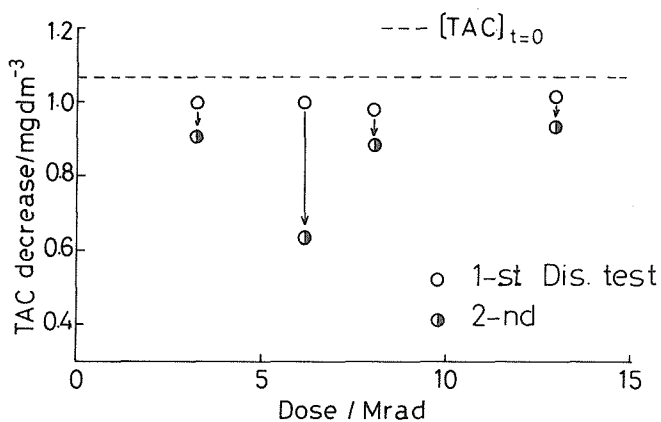


Fig.4 Result of second dissolution test on  $\gamma$ -irradiated resin sample

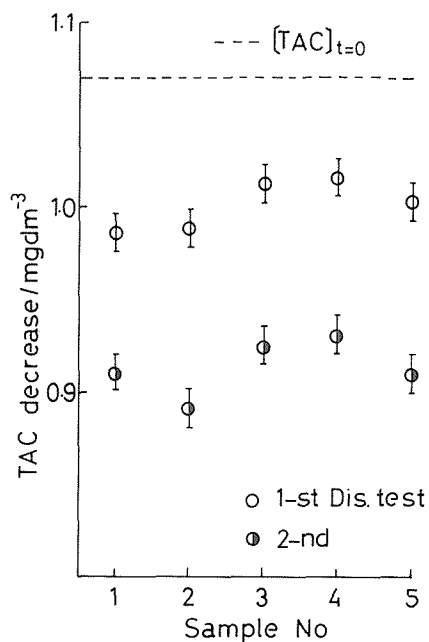


Fig.5 Difference among five analytical values obtained in one irradiation (3.3 Mrad)

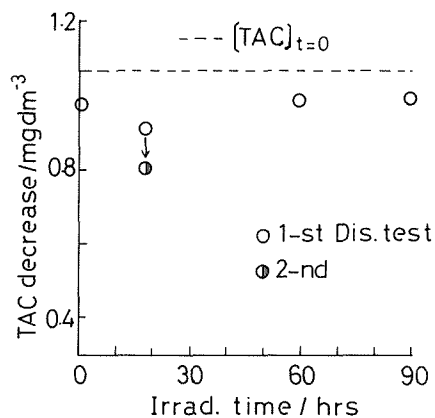


Fig.6 Result of dissolution test on  $\gamma$ -irradiated samples immersed in 4% hypochlorite solution during irradiation

The change in the AC that decreased with time was further investigated on samples that had passed the JIS requirement (Figure 4). As shown in Fig. 7, the decrease in the amount of AC from the test solution changed with time; it increased to  $0.87 \text{ mgCl dm}^{-3}$  after 5 months of  $\gamma$ -irradiation.

From the results obtained, it was concluded that  $\gamma$ -irradiation of the present resin samples alone was inadequate to improve the strong affinity for AC in tap water.

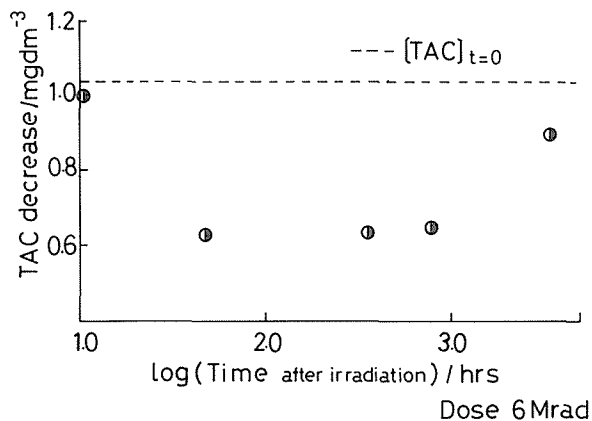


Fig.7 Change in AC decrease for  $\gamma$ -irradiated samples (6 Mrad) with time

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