

THE DEVELOPMENT OF DECONTAMINATION LIQUID WASTE TREATMENT SYSTEM FOR NUCLEAR POWER PLANT DECOMMISSIONING BEFORE DISMANTLING

T.Onozawa, S. Saishu, M. Saito and T. Yamanaka
Nuclear Power Engineering Corporation
Tokyo, Japan

T. Izumida
Hitachi Works, Hitachi Ltd.
Ibaraki, Japan

K.Funahashi, M. Kondo
Power & Industrial Systems R & D Division, Hitachi Ltd.
Ibaraki, Japan

Y. Furutani, K. Fujiwara and Y. Hashimoto
Research and Development, Hitachi Nuclear Engineering Co., Ltd.
5-2-2 Omika-cho, Hitachi-shi, Ibaraki-ken, 319-1221 Japan

ABSTRACT

We have studied liquid waste treatment from decontamination process before dismantling the nuclear power plant. We composed several treatment process from conventional treatment techniques about three developed decontamination reagents, which contained mainly 0.1%, 2%hydrochloric acid and 0.1%oxalic acid. Through the fundamental and the scale up test, these processes were evaluated, and the basic process of treating the decontamination liquid waste, which considered the character of liquid waste, was developed.

INTRODUCTION

Nuclear Power Engineering Corporation(NUPEC) has carried out "The Development on Decommissioning Technique for Commercial Nuclear Power Plants" which was sponsored by Ministry of International Trade and Industry (MITI). In this test, the development of liquid waste treatment techniques have been performed, too. This report presents the applicable liquid waste treatment system for the decontamination liquid waste of the dilute hydrochloric acid with reducing reagent, the Conc. hydrochloric acid with reducing reagent and the dilute oxalic acid with reducing reagent.

Elemental techniques for liquid waste treatment (decomposition of organic compounds, adsorption of organic compounds, neutralization, ion exchange, evaporating concentration and so on.) were studied and combined into several processes for each decontamination liquid waste. To evaluate those processes, at first, fundamental tests studying the capability of elemental techniques were performed on the small scale experiment (Beaker scale experiment) with simulated liquid waste. And then, scale-up tests (Ability of treatment rate 20L/h) were carried out by using the apparatus that was able to test those processes in series. By considering the results of these experiments, finally the most applicable process

for each liquid waste was selected and basic processes of Liquid waste treatment system were decided.

COMPONENTS OF DECONTAMINATION LIQUID WASTE AND THE PROBLEM FOR TREATING LIQUID WASTE

Supposed components of decontamination liquid wastes are showed in table1. The solved crud are assumed to be Fe, Co(radio activated) and so on.

Table 1. Supposed components of decontamination liquid waste.

Kinds of liquid waste	Components(wt%)	
Diluted hydrochloric acid with reducing reagent	Hydrochloric acid	0.1 %
	Vanadium chloride(III)	0.16 %
	Inhibitor	0.2 %
	Solved crud	0.03 %
Diluted oxalic acid with reducing reagent	Oxalic acid	0.1 %
	Vanadium(III) oxalate	0.1 %
	Solved crud	0.02 %
Conc. hydrochloric acid with reducing reagent	Hydrochloric acid	2 %
	Vanadium chloride(III)	0.16 %
	L-ascorbic acid	0.18 %
	Solved crud	0.04 %

Three decontamination liquid waste are separated into dilute liquid waste and conc. liquid waste.

It was supposed that the dilute liquid waste are treated with ion exchange resin and the other are neutralized and evaporated.

However, those decontamination liquid waste contain several characteristic components. For example, the organic inhibitor in the dilute hydrochloric acid with reducing reagent affects on cation ion exchanger resin. the inhibitor prevents the reaction of ion exchange and causes the amount of cation resin to increase in three times. The composition of oxalic acid in the dilute oxalic acid reduces the amount of secondary waste. It is clear that treating for the conc. hydrochloric acid with reducing reagent waste with ion exchanger resin increases the amount of the secondary waste, because hydrochloric acid concentration is 20 times as large as the dilute hydrochloric acid with reducing reagent.

COMPOSED OF LIQUID WASTE TREATMENT PROCESS

Considering the type of the decontamination liquid waste, treatment processes were composed from conventional techniques. Fig.1. shows supposed treatment processes.

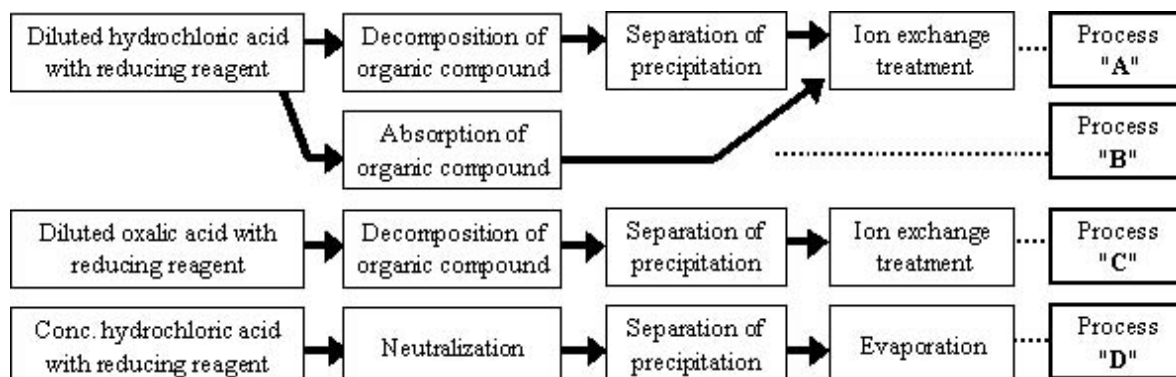


Fig.1. Supposed treatment process

The decomposition of organic compound and the absorption of organic compound for Process "A" and "B" are to remove the inhibitor. After the decomposition of organic compound, metal ion are oxidized and precipitated as hydroxide. The Separation of precipitation should follow. In Process "C", the decomposition of organic compound decomposes oxalic acid. As mentioned above, the separation of precipitation follows. In Process "D", the liquid waste are neutralized, separated from metal precipitate and concentrated by evaporation. Consequently liquid waste are concentrated waste and distilled liquid.

Then it was preliminarily investigated that how to decompose, to absorb and to separate. It was supposed that what oxidation reagents were used on the decomposition of organic compound and which active carbon or zeolite were good to treat liquid waste. Evaluation points were the amount of decomposition and absorption, the amount of secondary waste and the scale of treatment apparatus. Likewise, the separation of precipitation (filtration, sedimentation and centrifugation) were evaluated on the capability of separation, handling and the scale of treatment apparatus. Table 2 shows the results of preliminary investigation.

Table 2. The results of preliminary investigation

Method of treatment			Amount of decomposition and absorption	Amount of secondary waste	Scale of apparatus
Decomposition of organic compound	Oxidation	O ₃	⊙	⊙	△
		H ₂ O ₂	○	⊙	○
		KMnO ₄	○	△	○
Absorption of organic compound	Absorption	Activated carbon	○	○	○
		Zeolite	△	△	○
			Amount of removal	Handling	Scale of apparatus
Separation of precipitation	Filtration		○	○	○
	Sedimentation		○	○	○
	Centrifugation		○	△	△
⊙:excellent ○:good △:normal					

In the table 2, ozone is good in terms of the amount of decomposition and secondary waste. Because it's solubility is small, a large amount of ozone may be needed. Thus a reaction tank and a gas recovery device may be complex and large scale. Usage of potassium permanganate increased the amount of secondary wastes. Finally, hydrogen peroxide on the decomposition of organic compound was decided. In the choice of activated carbon or zeolite for the absorption of organic compound, the activated carbon was chosen because the adequate zeolite must be used, which has the same size hole as organic compound's diameter, otherwise the capability of absorbing organic compounds was very poor. And the activated carbon has the advantage of reduction of waste by burning it. The sedimentation and the filtration were chosen for each liquid waste.

Fundamental Test for Treatment Techniques

In order to observe the capability of treatment techniques in the each liquid waste treatment process. we performed the laboratory scale test using the beakers and so on. Table 3 shows the components of simulated liquid waste. Fe was substituted for dissolved crud.

Table 3. Components of simulated liquid waste

Kinds of simulated liquid waste	Components(wt%)	
Diluted hydrochloric acid with reducing reagent	Hydrochloric acid	0.1 %
	Vanadium chloride(III)	0.16 %
	Inhibitor	0.2 %
	Fe	0.03 %
Diluted oxalic acid with reducing reagent	Oxalic acid	0.1 %
	Vanadium(III) oxalate	0.1 %
	Fe	0.02 %
Conc. hydrochloric acid with reducing reagent	Hydrochloric acid	2 %
	Vanadium chloride(III)	0.16 %
	L-ascorbic acid	0.18 %
	Fe	0.04 %

(1) The test of the decomposition of organic compounds

The purpose was to observe the amount of decomposing the inhibitor and oxalic acid by hydrogen peroxide. Using beakers and hot stirrer, solution temperature was risen to 95℃ and then hydrogen peroxide was added. To see the amount of decomposition, the decomposition rate (%) was defined. It was calculated by measuring TOC concentrations. TOC is the concentration of total organic carbon. Equation 1 shows the decomposition rate (%).

$$\text{Eq.1 } \text{Decomposition rate(\%)} = (1 - \text{Processed waste's TOC} / \text{Original waste's TOC}) \times 100$$

(2) The test of the absorption of organic compound

The purpose of this test was to removal the inhibitor in its solution using activated carbon. The apparatus consisted of a roller pump and a activated carbon column(volume 250mL). The activated carbon was granular. The solution flow rate was 12mL/min and measured TOC concentrations at the point passed through column.

(3) The test of the separation of precipitation

The filtration and the sedimentation for each liquid waste was tested. Simulated liquid wastes were dilute liquid wastes that had been decomposed and the conc. liquid waste which had been adjusted to pH9. The filter with pore size 1.0μm were used. A time was measured when a given volume of solution was filtered.

In the sedimentation test, A time when the precipitate sank into the bottom of solution measured using measuring cylinder. From this result, the sedimentation method was evaluated in terms of the availability for the liquid waste. About the simulated conc. liquid waste, we used a strong anionic precipitant, but the precipitant was not available for dilute liquid waste because their pH were very low(1-2).

SCALE UP TEST

We studied the character of treatment techniques from fundamental tests. While the results of fundamental tests are described later, the filtration was adequate for dilute liquid wastes and the sedimentation for other. Parts of the separation in fig.1 were remade with reflecting those results. The purpose of scale up test is to observe combination between techniques in their process concerning a large volume of solution. Fig.2 shows the apparatus used on this test.

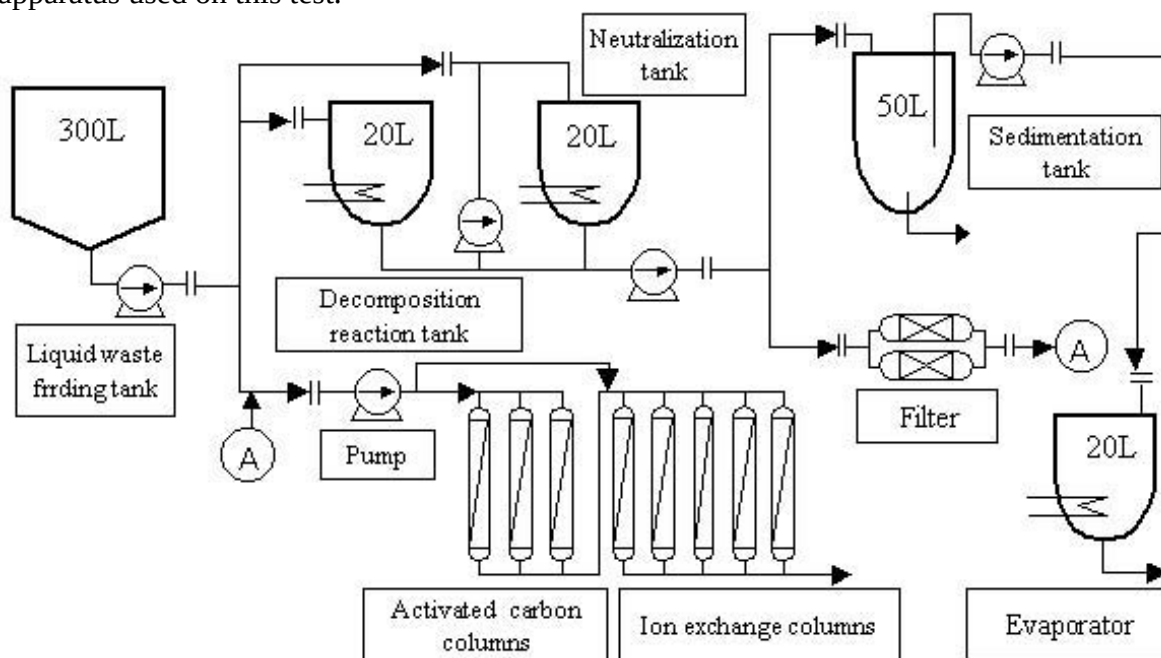


Fig. 2. The scale up test apparatus flow

Main components are a decomposing reaction tank, a neutralization tank (each volume 20L), the filter (the filter's area was 540cm^2), a sedimentation tank (volume 50L), a ion exchange column(volume $1\text{L}\times 5$), a activated carbon column(volume $1\text{L}\times 3$) and a evaporation tank(volume 20L). They are connected by pipe and placed as the liquid waste is brought along the each liquid waste treatment process. This apparatus has the capability of handling about 20L liquid waste per hour.

(1) the simulated dilute hydrochloric acid with reducing reagent waste

we tested two processes, which were process "A" (the decomposition · the filtration · the ion exchanger treatment) and process "B" (the absorption · the ion exchanger treatment).

Process "A" ; the decomposition treatment was performed at 95· and 0.075mol/L perhydrogen oxide was added. The flow rate through the filter was 1.2L/min , which was an upper limit flow of the filter. Kinds of the ion exchange resin were Amberlite IR-120B and IRA-400T. The space velocity (SV) of solution was 12.

Process "B" ; the same activated carbon as the fundamental test was used in the absorption treatment and the SV was 3.6. The ion exchange resin was same kinds of the

process "A" but the SV was defined 10.8 because of the ion exchange column following at the activated carbon ones in series.

(2) the simulated dilute oxalic acid with reducing reagent waste

The process was "the decomposition · the filtration · the ion exchanger treatment". The condition was same as the process "A".

(3) the simulated conc. hydrochloric acid with reducing reagent waste

The process was "the neutralization · the sedimentation · the evaporation". Sodium hydroxide was used on the neutralization and adjusted pH9. the strong anionic precipitant was used on the sedimentation. the evaporation was carried out under the atmospheric pressure (1 atm).

Results and Discussions

(1) The fundamental tests

Fig.3 shows comparison of the amount of perhydrogen oxide added and the decomposition rate.

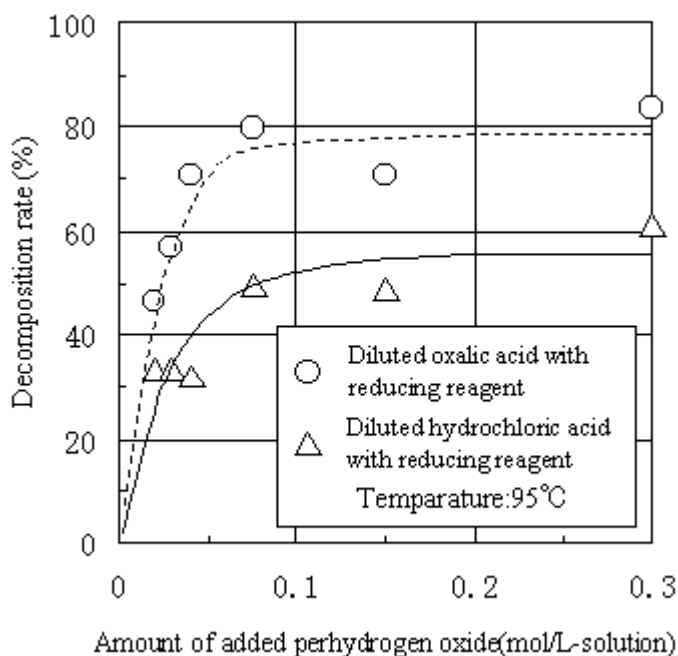


Fig. 3. Comparison of the amount of perhydrogen oxide added and the decomposition rate

Only by adding perhydrogen oxide, the decomposition rate was over 80% in the case of the simulated dilute oxalic acid with reducing reagent waste. This reason is assumed that metal ions (vanadium and iron) reacted perhydro oxide and produced OH radical, which has a strong potential of oxidation (ref.1). However crud concentration is low, the decomposition rate will be sufficiently high because of the decon. reagents containing metal ion (vanadium) in constant concentration. On the other hand the decomposition rate of the simulated dilute hydrochloric acid with reducing reagent waste was up to 50%. This is the reason why inhibitor is a kinds of surfactant and hardly decomposed so that it is a heterocyclic compound, which has a long side chain. The other factor is that oxidation

reagent can hardly contact with the inhibitor because of its low concentration (as TOC 70ppm). Although the decomposition rate was different in both cases, The adequate amount of perhydrogen oxide added was 0.075mol/L(volume of liquid waste) as the decomposition rate was saturated over this value.

In the absorption treatment, to represent the results of the absorption test, the inhibitor's removal rate was defined, which was introduced by dividing TOC of processed solution by original TOC. Table 4 shows comparison of the amount of processed liquid waste and the inhibitor's removal rate.

Table 4. Comparison of the amount of processed liquid waste and the inhibitor's removal rate

Volume of treatment(mL)	1000	1500	2000	3000	4000	5000	6000
Inhibitor's removal rate(%)	96	94	92	86	80	78	71

The weight of activated carbon was 50g (0.5g/cm^2). Table 4 shows that the inhibitor was absorbed into the activated carbon. This method was available for the simulated dilute hydrochloric acid with reducing reagent waste. From this results, it is thought that 70-80%inhibitor can be removed when the large volume of liquid waste 60 times the volume of activated carbon was treated. And the extra mass of generated ion exchange resin will be reduced 30%. If this rate was 50% (TOC 35ppm in liquid), the extra mass increased 50%. Table 4 also shows rate to be liner change. To depress more extra amount, we need to reduce the amount of liquid waste per the unit of activated carbon. Though the activated carbon must be increased, it may be burned and reduced its volume. Thus the amount of the activated carbon which was used in this treatment don't contribute to the amount of secondary waste.

In the separation treatment, the amount and character of precipitation influences the filtration. Table 5 shows relation between the amount of liquid waste through a filter and the filtration time.

Table 5. Relation between the amount of liquid waste through a filter and the filtration time

Volume of filtration(mL)	Filtration time(s)		
	Diluted hydrochloric acid with reducing reagent	Diluted oxalic acid with reducing reagent	Conc. hydrochloric acid with reducing reagent
100	24	19	269
200	42	27	1098
300	61	35	
400	87	43	

Because the simulated conc. hydrochloric acid with reducing reagent waste was adjusted to high pH and much precipitate were generated, though it has 0.04%metal ion at most, the filtration was very hard. The result of the sedimentation is represented by calculation the

precipitation rate(%), which was defined by dividing the measured precipitate volume by original solution volume. Table 6 shows relation between the precipitation rate and the observation time.

Table 6. Relation between the precipitation rate and the observation time

Diluted hydrochloric acid with reducing reagent		Conc. hydrochloric acid with reducing reagent		Diluted oxalic acid with reducing reagent	
time(s)	Volume of the precipitation(%)	time(s)	Volume of the precipitation(%)	time(s)	Volume of the precipitation(%)
20	68	0	100	0	100
45	59	1800	96	300	98
90	56	2700	96	3600	90
780	54	3600	96		

Because the simulated dilute liquid waste's pH was low and the precipitant was able to be used, the precipitation hardly sedimented. But the simulated conc. liquid waste's precipitation rapidly sedimented.

Two results of the filtration and sedimentation show that the filtration was available for the dilute liquid waste and the sedimentation other.

(2) Scale up test

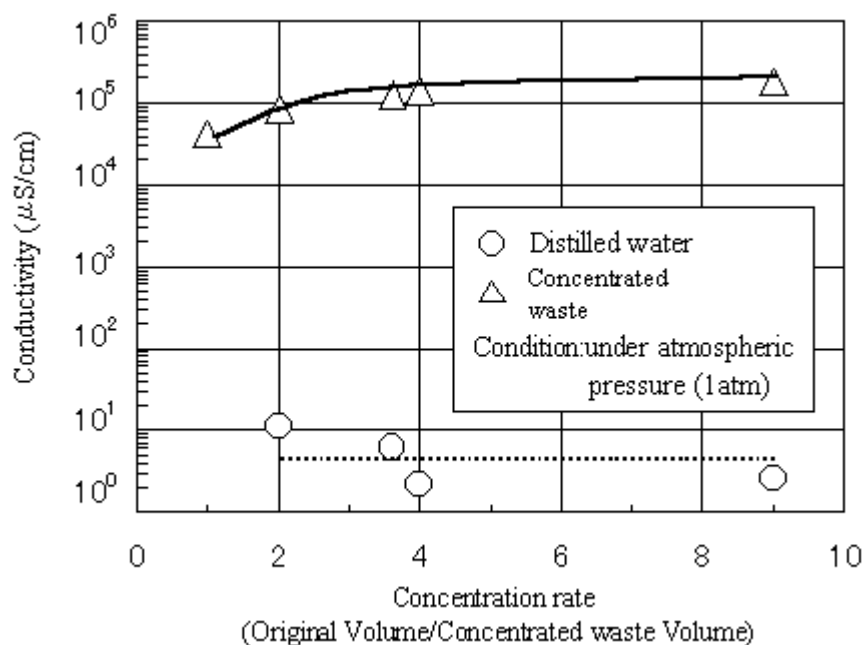
In process "A", the result of the decomposition treatment was same for the fundamental test. The amount of perhydrogen oxide was the adequate amount which was decided by the fundamental test. But in the filtration treatment, pressure inside the filter became very high immediately. The cause is assumed that the precipitate was very fine because hydrochloric acid was regenerated and pH became low (about over $2 \cdot 1.4$) by metal ions being oxidized and precipitated. It was calculated that the area of filter needs 1100cm^2 to treat 20L liquid waste at least. If a large amount of liquid waste (100m^3) is generated, the scale of a filter component may be very large.

To treat large volume of the dilute hydrochloric acid with reducing reagent waste, The filtration was not available. About process "C", the result of the decomposition test (80% decomposition rate) was same as the fundamental test without influence of scale up. The filtration treatment was easily handled. The area of the filter needed 133cm^2 (6.5cm diameter) in 1 batch. The precipitation was not fine and able to be treated with small filter. Two simulated dilute liquid waste was decomposed and absorbed to depress and to reduce the amount of generated ion exchange resin. Table 7 shows that how the amount of the ion exchange resin waste was depress and reduced.

Table 7. Effect of treatment techniques on the difference of the amount of the ion exchanger resin

Treatment technique		Volume of ion exchange resin generated from treatment process(mL)	
		Diluted hydrochloric acid with reducing reagent	Diluted oxalic acid with reducing reagent
Absorption of organic compound	Processed	72.3	
	Not processed	131.9	
Decomposition of organic compound	Processed		35.8
	Not processed		69.4

This result of the simulated diluted hydrochloric acid with reducing reagent waste was the result of process "B" because of the filtration in process "A" being hard. From table 7, it was clear that there was a large difference of the amount of generated ion exchange resin waste whether adsorption or decomposition organic compound was adopted or not. Process "B" and "C" are available. Process "D" was different from the dilute one. The result of the neutralization and the sedimentation test was same as the fundamental test. the precipitate was separated rapidly same as the fundamental test. The evaporation treatment follows. Conductivity of distilled water and concentrated waste was measured to observe the transport of metal opm amd solved compound from concentrated waste to distilled water. Fig.4 shows that relation between the increasing concentration rate, conductivity of distilled water and concentrated waste.

**Fig. 4.** Relation between the increasing concentration rate and conductivity of distilled water and concentrated waste

Conductivity of distilled water was low constantly. It shows that metal, chloric ion weren't transported to distilled water. Thus this process is effective in treating the concentrated hydrochloric acid with reducing reagent waste.

CONCLUSION

Through the fundamental and the scale up test, we appreciated the possibility of four treatment processes, which was composed from ordinary techniques, for developed decontamination reagents. following processes have been effective.

- (1) The dilute hydrochloric acid with reducing reagent waste ;
the absorption · the ion exchanger treatment.
- (2) The dilute oxalic acid with reducing reagent waste ;
the decomposition of organic compounds · the filtration · the ion exchanger treatment.
- (3) The concentrated hydrochloric acid with reducing reagent waste ;
the neutralization · the sedimentation · the evaporation

At the first step toward developing the liquid waste treatment system, Liquid waste treatment process was developed with ordinary techniques.

In the other study, the reuse system of chemical reagent in liquid waste from decontamination process using hydrochloric acid has been developed in other department. This system's main principle is the regeneration by electrolysis. From a simulated liquid waste (2%hydrochloric acid, 0.16%vanadium chloride and 300ppmCo²⁺), this system has recovered 90%hydrochloric acid.

At the second step for completing system, we continue to study liquid waste treatment processes with combining such techniques.

ACKNOWLEDGMENTS

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