RADIOACTIVE SPENT RESIN TREATMENT SYSTEM UTILIZING A RADIONUCLIDE-RESIN SEPARATION TECHNIQUE

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ABSTRACT

In Japan, radioactive spent ion exchange resins which arise in nuclear power plants are mainly stored in exclusive tanks, now. This is not only because the quantity of the spent resins is relatively small and the tank storage has been sufficient to store them for a considerably long term but because the fact that the spent resins are organic materials with a relatively high activity makes it uneasy to produce a stable form by conventional solidification methods. However, recently, the plan and criteria for final storage/disposal of nuclear power plant waste are under development.

Considering these conditions, it is necessary in the near future to effectively convert the spent resins into a material of a stable form suitable for the final storage/disposal. Mitsubishi Heavy Industries, Ltd. is developing a spent resin treatment system utilizing a radionuclide-resin separation technique which is flexibly applicable to existing power plants and has obtained prospects of its practical use.

This paper places a focus on describing the developmental work on radionuclide-resin separation and related techniques, the key of the treatment system.

INTRODUCTION

As the spent resins are organic and exposed to high radiation for a long period of time, they may be chemically and physically damaged. Therefore, in view of long-term storage or disposal as radioactive waste, it is considered desirable to convert them into a stable inorganic material by a certain method. At the same time, it is desirable that they are reduced in volume as small as reasonably achievable.

Incineration is thought to be the most effective method for satisfying the above requirements, that is, the conversion of the spent resins into a stable form and sufficient volume reduction. Direct incineration, however, results in higher dose rate and harder maintenability of the incinerator. In addition, a higher purification efficiency for exhaust gas is required in order to minimize radioactive emissions. Accordingly, to adopt such method is not considered a good policy from both technical and economical viewpoints.

Therefore, we have adopted a radionuclide-resin separation method as a preprocessing in order to avoid a higher activity input to the incinerator.

System Concept

This separation method is the heart of the total system concept in which radionuclides are removed from the organic spent resins and then the inactivated resins are converted into inorganic materials by incineration, and the removed radionuclides are solidified in inorganic materials, too. Figure 1 shows the concept This method can be considered as one of the preprocessing systems when incinerator and solidification systems or other equipment are used for processing the resins and separated radionuclides. Hence it is expected that the scales of extended or newly constructed installations can be very small, when the system is back-fitted in an operating plant.

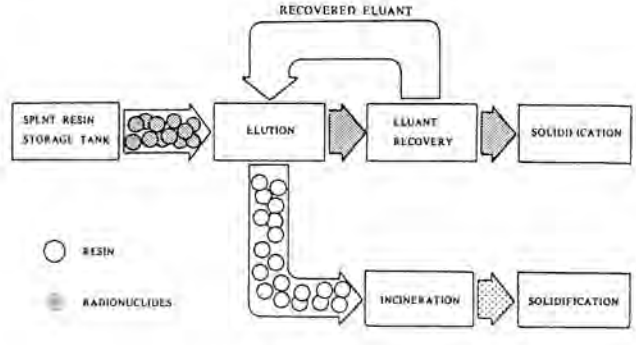

Fig. 1 System Concept

Basic Flow Description

Figure 2 shows the basic flow of the radioactive spent resin treatment system based on a radionuclide elution method employing a H_2SO_4 aqueous solution, which is an appropriate eluant as described later. The eluant of a H_2SO_4 aqueous solution is fed to the elution column charged with spent resins in order to remove radionuclides by eluting them from the resins. Radionuclide cations of Co^{2+}, Cs^{+}, etc. absorbed on

the spent resins are eluted into the solution after being exchanged with cations, such as H^+, of the eluant. The eluate (spent eluant) which contains eluted radionuclides is directed to a diffusion dialyzer. This diffusion dialyzer is equipped with an anion exchange membrane and is divided into two compartments by the membrane. In Fig. 2, the eluate is introduced to the left (dialyzate) compartment in an upward flow and pure (demineralized) water is fed to the right (diffusate) compartment in a downward flow. While, the eluate is passing through the compartment, SO_4^{2-} and H^+ move from the left compartment to the right compartment through the membrane. However, most radionuclides are cations and they flow out of the compartment without moving to the right compartment due to the characteristics of the anion exchange membrane. Thus H_2SO_4 is recovered from the eluate containing radionuclides. The recovered H_2SO_4 is recycled to the elution column.

After the radionuclides are removed from the spent resins, the resultant inactivated resins are discharged to the incinerator. The unrecovered acid liquid containing the eluted radionuclides is solidified into an inorganic form after concentrating by an evaporator or the like.

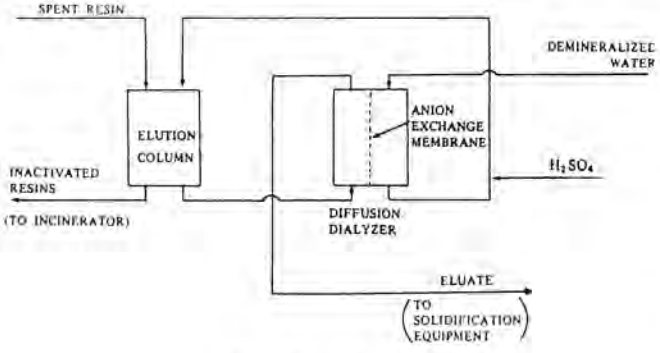

Fig. 2 Basic Flow

COMPONENT TEST

Purpose

Annual quantity and radioactive concentration of spent resins discharged from a PWR plant are generally about 10 m^3 and 35 to 350 Ci/m^3, respectively. Therefore the activity contained in the spent resins will be in the range of about 350 to 3500 Ci/a. On the other hand, the activity being actually disposed of in an incinerator is up to about 5 Ci/a. Therefore it is necessary to reduce the activity of the spent resins to the extent of that disposable activity down to about 10^{-2} to 10^{-3} of the initial activity in order to prevent the incinerator from being highly radioactivated. Accordingly, for this purpose the elution efficiency required for this system should be about 10^2 to 10^3 in terms of decontamination factor (DF), which is defined as:

$$DF = \frac{\text{activity of spent resins (before elution)}}{\text{activity of inactivated resins (after elution)}}.$$

From this point of view, the component tests first investigated whether the elution efficiency (E_{eff}) attained that value of DF or not. Secondly eluant recovery efficiency (R_{eff}) and radionuclide leakage (L) in the eluant recovery process with a diffusion dialysis were studied. Here, the above terms mean as follows:

$$E_{eff} = \frac{N_e}{N_r} \times 100\ (\%)$$

$$R_{eff} = \frac{C_{rec}}{C_e} \times 100\ (\%)$$

$$L = \frac{N_{rec}}{N_e} \times 100\ (\%)$$

Where:

N_r = quantity of specimen nuclides (or activity) in charged resins*/batch in mg or μCi

N_e = quantity of eluted specimen nuclides (or activity) in eluate/batch in mg or μCi

C_e = quantity of eluting chemical (H_2SO_4) in eluate/batch in mg

C_{rec} = quantity of eluting chemical (H_2SO_4) in recovered eluant/batch in mg

N_{rec} = quantity of permeated specimen nuclides (or activity) in recovered eluant /batch in mg or μCi

*Note:

For the cold test, the quantity of specimen nuclides in spent (simulated) resins can be calculated from the quantities of such nuclides before and after soaking in the soak used for the sample resin preparation.

For the hot test, the activity in charged spent resins can be determined as the sum of the activities in resultant eluate and inactivated resins after elution.

Cold Test Methods

Eluting capabilities of H_2SO_4 and Na_2SO_4 base eluants were examined utilizing simulated resins adsorbing nonradioactive nuclides of Co and Cs. Among conceivable eluants H_2SO_4 and Na_2SO_4 were selected as a typical strong acid and a neutral salt, respectively, considering their availability and ease of handling in the plants. And Co and Cs were selected as typical nuclides to be eluted, because Co and Cs isotopes comprise approximately 85 percent of total activity found in spent resins from the average PWR plant (See Fig. 3). Then, the recovery efficiency, in relation to Co and Cs leakages through the diffusion dialysis membrane, was measured for H_2SO_4, which had indicated the highest eluting capability in the elution test.

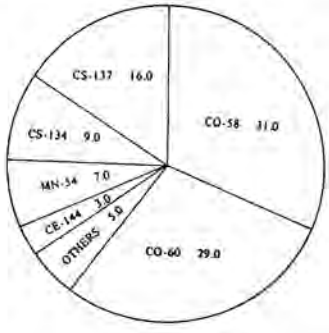

Fig. 3 Percentage of the Radionuclides in Spent Resins (average PWR plant)[1]

Table I shows the conditions of sample preparation for these tests. The same mixed bed resins as actually used in PWR plants were soaked in a boric acid solution (in simulation of primary coolant) containing the prescribed amounts of Co and Cs as shown in Table I (a) so that these nuclides could be adsorbed on the resins, thus sample resins were prepared. The remaining amounts of Co and Cs in the soak were measured for determining their amounts adsorbed on the sample resins. The elution tests were repeated three times using three different eluants as shown in Table I(b). In each of the tests, the sample resins of 100ml were charged in the elution column of the equipment as shown in Fig. 4, and the eluant was passed through the column by an amount of the column volumes (CV) of up to 50 (50 times of the volume of the charged resins) at a certain constant space velocity (SV) to elute the nuclides (See Table II). Then, the eluted nuclides were quantitatively analyzed.

For the eluant recovery test, a 2N-H_2SO_4 aqueous solution was prepared to contain nonradioactive nuclides of Co and Cs by 100mg/l each as shown in Table I(c). This simulated eluate and demineralized water were fed counter-currently into the dialyzate and diffusate compartments, respectively, of the diffusion dialyzer shown in Fig.5 at an identical flow rate. Then, the nuclides and H_2SO_4 permeated into the diffusate through the membrane were quantitatively analyzed.

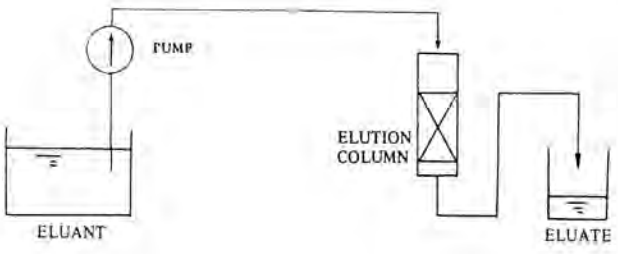

Fig. 4 Elution Test Equipment

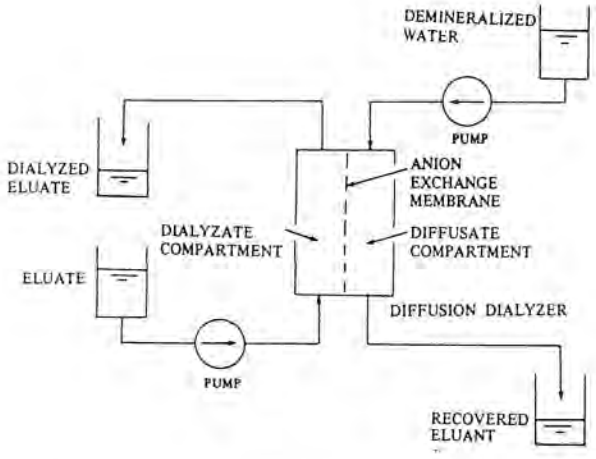

Fig. 5 Eluant Recovery Test Equipment

TABLE I Conditions of Sample Preparation

(a) Resin Preparation (Soaking) Conditions for Elution Tests (Cold)

Type of Resins	:	mixed bed (DIAION SMN-3^{TM*})
Volume of Resins	:	750 ml
Volume of Soak	:	90 l
Composition of Soak	:	Co 20 mg/l
		Cs 100 mg/l
		B 1000 mg/l
Soaking Time	:	abt. 24 h
Temperature	:	18 °C

* Mixture of cation and anion exchange resins of a crosslinked polystyrene matrix with exchange capacity ratio 1:1.

(b) Type and Concentration of Eluant

Cold	Hot
H_2SO_4 : 0.1N, 2N	H_2SO_4 : 1N, 2N
Na_2SO_4 : 2N	

(c) Composition of Eluate for Recovery Test

Cold	Hot
H_2SO_4 : 2N	(Eluate obtained from the elution test using 2N-H_2SO_4 solution)
Co : 100 mg/l	
Cs : 100 mg/l	

TABLE II Conditions of Tests

Items		Cold	Hot
Elution Test	Resin Bed Volume (Charge)	100 ml	3 ml
	Column Volumes (CV)	0 - 50	
	Space Velocity (SV)	const.	
	Temperature	18 °C	
Eluant Recovery Test	Flow Rate Ratio (FRR)	1.0	
	Temperature	18 °C	

$$CV = \frac{\text{(Volume of Eluant Passed)}}{\text{(Resin Bed Volume)}}$$

$$SV = \frac{\text{(Volume of Eluant Passed)}}{\text{(Resin Bed Volume)} \cdot \text{(Eluant Passing Time)}} (h^{-1})$$

$$FRR = \frac{\text{(Demineralized Water Flow Rate)}}{\text{(Eluate Flow Rate)}}$$

Cold Test Results

The elution test results are outlined as follows, and shown in Fig. 6.

1. When aqueous solutions of 0.1N- and 2N- H_2SO_4 were used as the eluant, elution efficiency improved, with the higher concentration, up to more than 99.9% for both Co and Cs at a CV of 10.

2. In the case of a Na_2SO_4 aqueous solution, a concentration of 2N gave an elution efficiency nearly comparable to that given by 2N-H_2SO_4 for Cs, and however, only about 50% for Co even at a CV of 50.

The results indicate that H_2SO_4 is excellent as an eluant and its preferred concentration is about 2N or more.

The results of the eluant (H_2SO_4) recovery test are outlined as follows:

1. The leakage of the nuclides increased with the increase of H_2SO_4 recovery efficiency as shown in Fig. 7.

2. The H_2SO_4 recovery efficiency of 70 to 80%, which is thought to be acceptable in practical use, was obtained keeping the leakages of Co and Cs as low as reasonably possible in the range of 2 to 4% and 10 to 20%, respectively.

3. The leakage of Co was a fraction of that of Cs, and it was therefore found that Co was more readily prevented from permeating into the recovered H_2SO_4 than Cs.

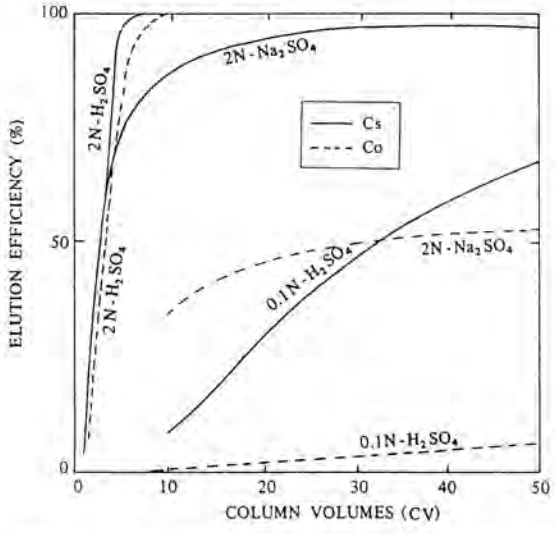

Fig. 6 Co and Cs Elutions vs Column Volumes

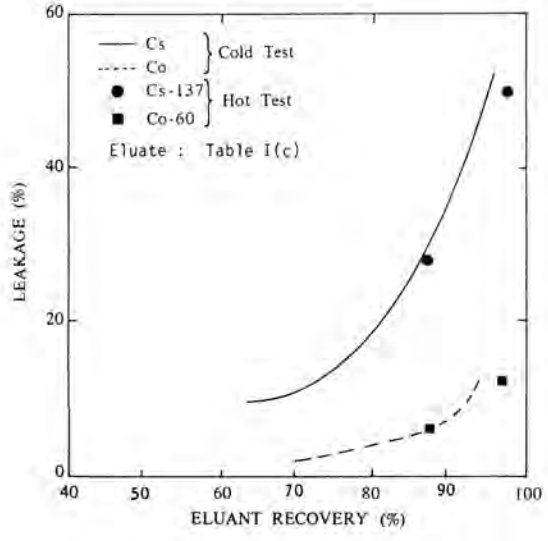

Fig. 7 Nuclide Leakage vs Eluant Recovery

Hot Test Methods

To confirm that the above cold test results would be applicable to actual spent resins, the following tests were carried out on the samples obtained from an operating PWR plant. Table I and Table II present their conditions.

One of the samples of actual spent resins was charged in the column of the equipment shown in Fig. 4. Then, the elution operation was performed by feeding a 1N-H_2SO_4 aqueous solution as much as a CV of up to 50 at the same constant SV in the cold tests, followed by activity measurements of the eluted Co-60 and Cs-137 in the eluate and those remaining on the inactivated resins, as well as H_2SO_4 concentration of the eluate. The operation was repeated on another sample using a 2N-H_2SO_4 aqueous solution.

For the eluant recovery test, the eluate obtained from the above elution test with a 2N-H_2SO_4 solution and demineralized water were fed into the diffusion dialyzer (Fig. 5) at a flow rate identical to each other and to that of the cold test. Then, the radionuclides (Co-60, Cs-137) and H_2SO_4 permeated into the diffusate were quantitatively measured.

Hot Test Results

The elution test results for the actual spent resins are shown in Fig. 8 and outlined as follows:

1. The elution efficiencies of more than 99.9%, which corresponds to a DF of 10^3 or more, were obtained for both Co-60 and Cs-137 at a CV of 10 - 15 when a 2N-H_2SO_4 aqueous solution was used as the eluant. The results shown in Fig. 8 are quite repetitive in camparison with those of the cold tests as shown in Fig. 6.

The results of the eluant recovery test are shown in Fig. 7 and outlined as follows:

1. The relation between the H_2SO_4 recovery efficiency and the radionuclide leakage of Co-60 and Cs-137 was in good agreement with that in the cold test.

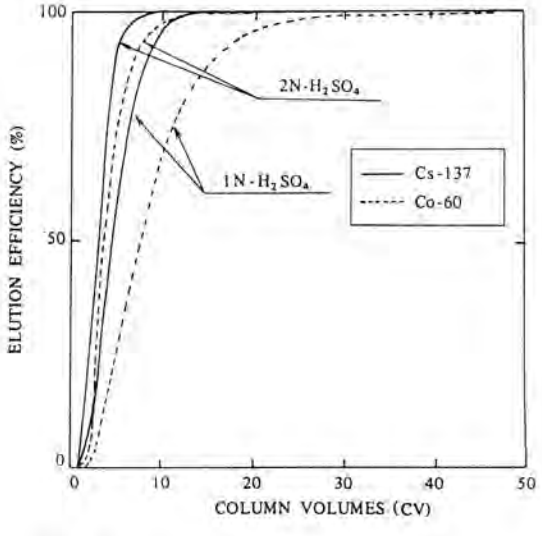

Fig. 8 Co-60 and Cs-137 Elutions Vs Column Volumes

Test Summary

The results of the cold and hot component tests are summarized as follows:

- Of the eluants tested, a 2N-H_2SO_4 aqueous solution was excellent, and proved to give the expected elution efficiency of more than 99.9% for both Co-60 and Cs-137.
- Though the higher the H_2SO_4 recovery efficiency, the more the nuclides leaked, it was confirmed that a high H_2SO_4 recovery efficiency of about 80% could be obtained keeping the leakages of radionuclides as low as reasonably possible in view of practical use.
- The conformity between the cold and hot test results justified that cold test results could be used maximally for designing a practical system.

OUTLINE OF PRACTICAL USE SYSTEM

Flow Planning

Figure 9 shows an example flow chart of the resin treatment system planned for practical use. Here, as a major piece of equipment for the elution process, a simple gravity charge type elution column proven in chemical and nuclear industries is employed for easy and ensured operation. In the eluant (H_2SO_4) recovery process, two diffusion dialyzers are used in series in order to reduce the quantity of waste (dialyzed eluate) as far as reasonably possible by additionally recovering the eluant from the first dialyzer tailing. Furthermore, a concentrator (e.g. evaporator) is installed before the second dialyzer, making the dialyzer smaller.

The whole of this system for disposing of both the stocks and arisings of spent resins in an average PWR plant can be installed within a space of $7^W \times 4\,\ell \times 7^h$ (m), except for the incinerator which may already exist.

Volume Reduction Effect

An example of a volume reduction effect to be derived from operating this system is shown in Fig. 10. The system can reduce the spent resins into solidified ash and eluate products having 1/5 of initial resin volume, shifting 99.9% or more of the resins' activity into a small volume of safe and easily manageable eluate products.

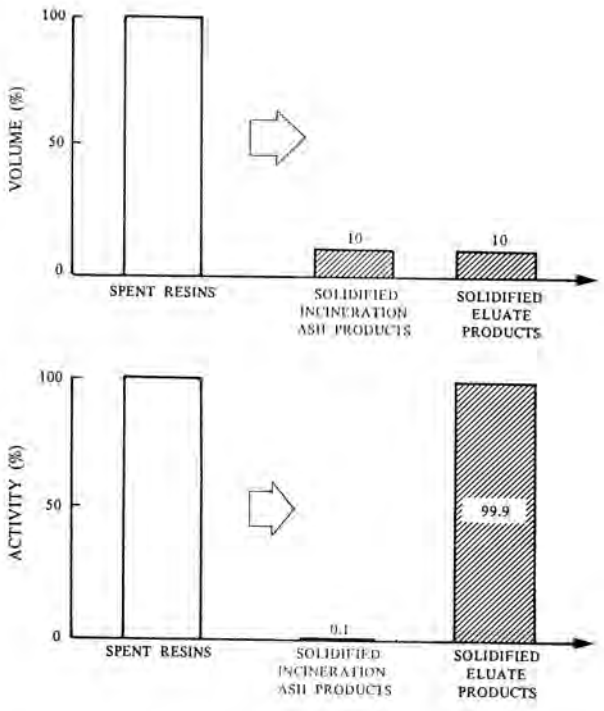

Fig. 10 Volume Reduction Effect of the Treatment System.

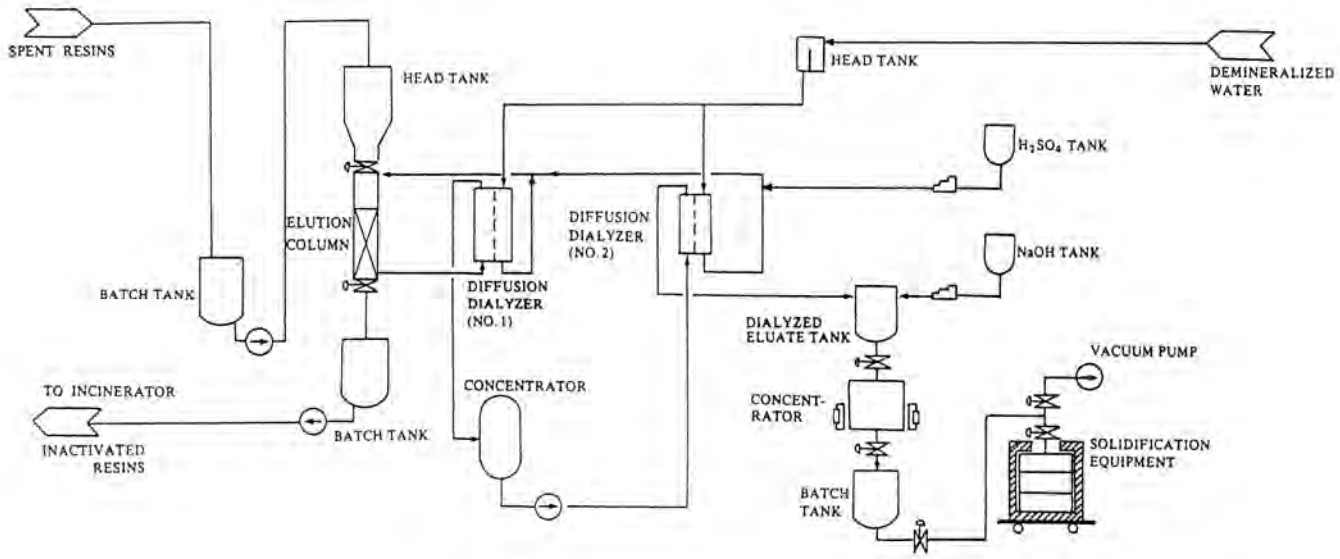

Fig. 9 Flow Chart of the Treatment System (Japanese Patents pend.)

CONCLUSIONS

Based on the results of the component tests using simulated and actual spent resins, the spent resin treatment system employing a technique of radionuclide elution coupled with a eluant (H_2SO_4 solution) recovery by diffusion dialysis has proved promissing for practical use. The system offers the following advantages.

- Final products are inorganic materials which provide superior long-term physicochemical stabilities.
- Principal processes are operable at normal temperature and pressure.
- System scale is compact.
- Operation and maintenance are easy. The system has few pieces of dynamic equipment, making its startup/shutdown easy.
- Running cost is low.
- Recovery of acid by diffusion dialysis is a proven technique.
- Amount of secondary waste is minimum.

Presently, a demonstration test is being planned in order to clarify the operating conditions and other specifics with a view to putting this resin treatment system into practical use.

REFERENCE

1. Electric Power Research Institute, "Identification of Radwaste Sources and Reduction Techniques", EPRI NP-3370, Vol. 2 (1984).