

**ONTARIO HYDRO RESEARCH DIVISION'S PROGRAM
FOR TREATMENT OF SPENT ION-EXCHANGE RESINS**

by

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ABSTRACT

A brief review of the evolution of work programs for chemical treatment of spent ion-exchange resins in Ontario Hydro's Research Division, is presented. Attention has been focussed on pre-treatment processes for the treatment of the spent resins prior to encapsulation of the products in solid matrices. Spent Resin Regeneration and Acid Stripping processes were considered in some detail. Particular attention was paid to carbon-14 on spent resins, its determination in and removal from the spent resins (with the acid stripping technique). The use of separate cation and anion resin beds instead of mixed bed resins was examined with a view to reducing the volume of resin usage and consequently the volume of waste radioactive ion-exchange resin generated.

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1. INTRODUCTION

Large quantities of synthetic organic ion-exchange resins are used in the purification circuits of Ontario Hydro's nuclear generation stations, all of which use CANDU-PHW (Canada Deuterium Uranium-Pressurized Heavy Water) nuclear reactors. The major purification circuits, in terms of ion-exchange resin consumption are the moderator and the Primary Heat Transport (PHT) systems. Mixed bed resins, manufactured by Rohm and Haas Company, have been and are being used in all of Hydro's nuclear power stations. Amberlite IRN-154, L/C - a mixture of a strong acid cation resin in lithium form and a strong base anion resin in hydroxyl form, is used in the PHT circuit, the pH of which is maintained between 10.0 and 10.5 with lithium hydroxide. Amberlite IRN-150, L/C - a mixture of a strong acid cation resin in hydrogen form and a strong base anion resin in hydroxyl form, is used in the moderator circuit, primarily for boron removal. Low chloride (L/C) formulations of the above resins are used to minimize chloride ingress into the systems. Amberlite IRN-300, which is a mixture of a strong acid cation resin in hydrogen form and a weak base anion resin in free base form, is used for gadolinium removal (without removal of boron) in the Bruce "A" nuclear generating station.

2. STORAGE COSTS OF SPENT ION-EXCHANGE RESINS

In Ontario Hydro, spent ion-exchange resins from the moderator and the PHT systems (except at Pickering Nuclear Generation Station) are slurried into spent resin storage tanks after dedeuteration. The spent resins are transferred into 3 m³ liners, which are then transported to Bruce Nuclear Power Development (BNPD) Radioactive Waste Operations site for storage. The type of storage chosen for the liners depends on the radiation field on the resins. If the contact radiation field is greater than 15 R/h, the liners are stored in Quadricells at a storage cost of about \$15,000/m³. If the radiation field is less than 15 R/h, the liners are stored in trenches at a storage cost of about \$3000/m³. Because of the high storage costs, there exists a considerable economic incentive for volume reduction of the spent radioactive ion-exchange resins.

3. OVERVIEW OF RESEARCH PROGRAM

Figure 1 shows, in a condensed format, the evolution of work programs in Ontario Hydro's Research Division (primarily by the Water Research Unit) on treatment of spent ion-exchange resins for achieving radioactive waste volume reduction. The major steps in the work program are shown in the boxes. The arrows show the direction of flow of information. Boxes in dotted lines indicate work planned for the future.

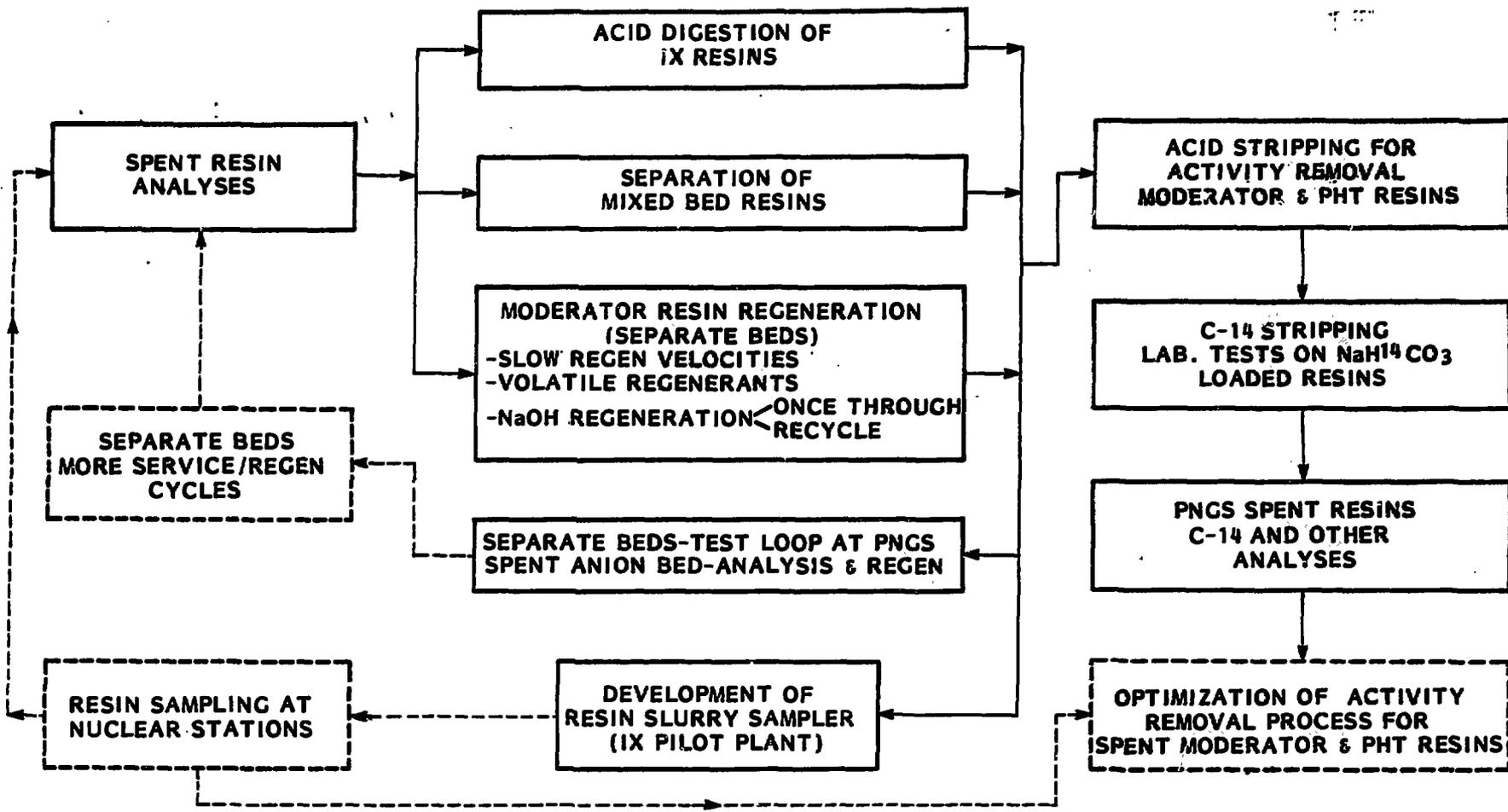


FIGURE 1

MAJOR AREAS OF RESEARCH INTO CHEMICAL MEANS OF TREATING SPENT ION EXCHANGE RESINS

We shall now proceed to describe the major areas of work in some detail.

Developmental work on solidification and immobilization of concentrated residues from the various pre-treatment processes is carried out by the Organic Materials Research Unit of the Research Division and will not be covered in this report.

4. SPENT RESIN ANALYSIS

Beginning in 1975, samples of spent ion-exchange resin from the moderator and the PHT circuits of Ontario Hydro's Pickering nuclear generating station (PNGS) were analyzed by Research Division (1,2,3,4) to determine the chemical and radiochemical composition of the spent resins. The radionuclide composition of a typical sample of spent PNGS moderator resin is shown in Table 1. Co-60 and C-14 are the major radionuclides of importance on the moderator resin. Cr-51, while present in high concentrations, is not of major significance from the radioactive waste storage point of view because of its relatively short half-life. Gamma radiation fields on the spent moderator resin samples were less than 1 R/h on contact. Analysis of the gamma spectrum revealed Co-60 to be the source of about 94 per cent of the gamma field from the resin. Boron is the major non-radioactive species of consequence.

Analysis of a sample of spent PHT resin is presented in Table 2. Cs-137 and Cs-134 which are radioactive by-products of the fission process are the radionuclides of major importance. Gamma radiation fields on the spent resins were about 20 R/h on contact, with Cs-137 and Cs-134 accounting for about 95 per cent of the radiation field. Carbon-14 activities were generally lower, by a factor of about 10, than in the moderator resins.

5. ACID DIGESTION PROCESS

This process was initially developed at the Hanford Engineering Development Laboratory (5) for treatment of low level wastes for plutonium recovery. Some developmental work on application of the technique to spent ion-exchange resins was performed by the Process Chemistry Unit of Ontario Hydro's Research Division (6). A simplified flow sheet of the acid digestion process is shown in Figure 2. The spent resin is added into a reactor containing concentrated sulphuric acid at 270°C. Sulphuric acid effects the carbonization of the resin and provides the high temperature medium for the oxidation of carbon. Nitric acid is then slowly added below the surface of the liquid. Nitric acid serves as an oxidizing agent and the carbonized resin is converted to carbon monoxide and carbon dioxide. The radioactivity remains primarily in the carbonaceous residue in the digester and has to be solidified for storage. The acids can be recovered for reuse.

TABLE 1

SPENT PNGS MODERATOR RESIN ANALYSIS (1977)

Radionuclide	Half-Life	Activity (Ci/m ³)
Co-60	5.3 y	3.5
Cr-51	27.8 d	1.9
Fe-59	45.1 d	0.03
Zn-65	243.6 d	0.19
Mn-54	303.0 d	0.03
Zr-95	65.0 d	0.03
Nb-95	35.1 d	ND
La-140	40.2 h	ND
I-131	8.1 d	ND
C-14	5730.0 y	47.0

y = years, d = days, h = hours, ND = Not Detected

TABLE 2

SPENT PNGS PHT RESIN ANALYSIS (1977)

Radionuclide	Half-Life	Activity (Ci/m ³)
Cs-137	30.2 y	14.0
Cs-134	2.0 y	4.5
Ce-144	285.0 d	1.7
Fe-59	45.1 d	0.007
Co-60	5.3 y	0.81
Zn-65	243.6 d	0.30
Ru-106	367.0 d	1.7
Ru-103	39.6 d	0.05
Mn-54	303.0 d	0.22
Zr-95	65.0 d	0.19
I-131	8.1 d	0.004
Cr-51	27.8 d	0.03
Nb-95	35.1 d	0.40
La-140	40.2 h	0.005
C-14	5730.0 y	5.6

y = years, d = days, h = hours

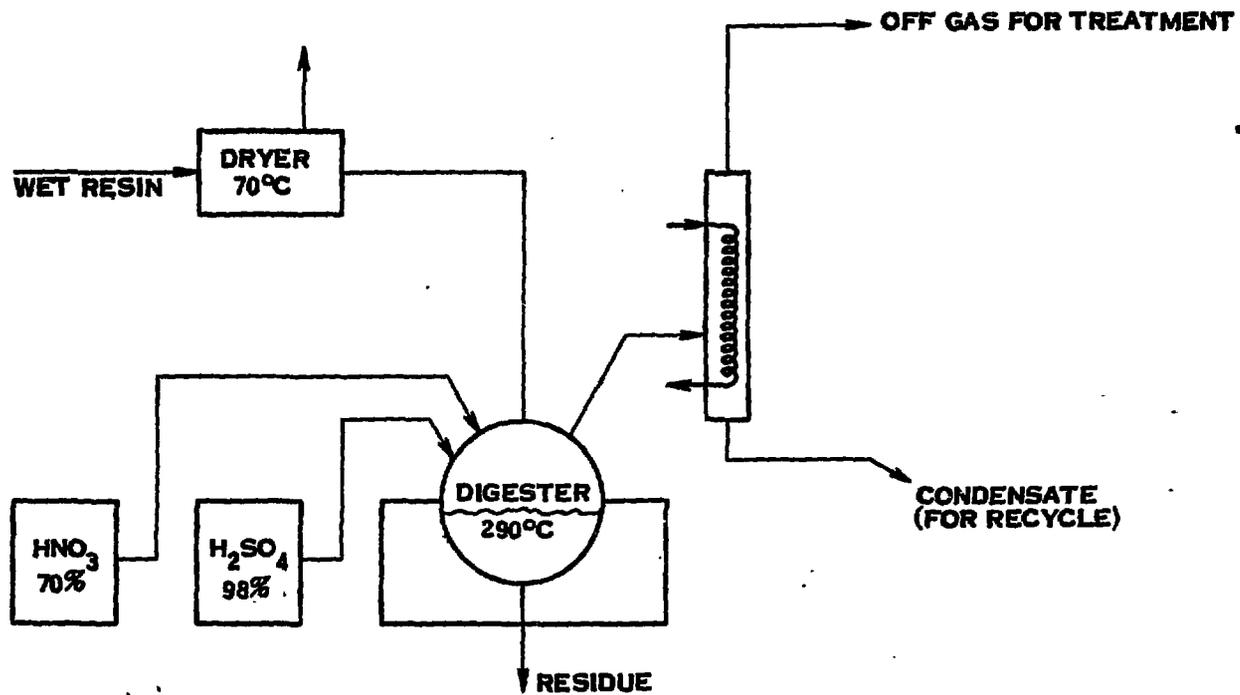


FIGURE 2
FLOW SHEET OF ACID DIGESTION SYSTEM

The off-gases contain N_2 , CO, CO_2 , SO_x , NO_x , as well as $^{14}CO_2$ removed from the resin and hence will require treatment for C-14 removal. The expected overall volume reduction factor is about 8. The process involves large capital and operating costs.

6. SPENT RESIN REGENERATION

In this scheme, the spent resins are regenerated with appropriate solutions, generally at ambient temperatures, and atmospheric pressures. The regenerated resins are reused in subsequent service cycles. The regenerant solutions containing radioactivity removed from the spent resins are evaporated and the small volume of radioactive residue will have to be incorporated in a suitable solid matrix for long-term storage. The unspent portions of regenerant effluents can be reused.

In conventional regeneration of mixed bed columns, the cation and anion resins are separated, usually by backwashing. The cation resin is regenerated with acid and the anion resin is regenerated with alkali. The regenerated resins are then mixed and the mixed bed returned to service. However, incomplete separation of the cation and anion resins, prior to regeneration invariably results in contamination of some cation resin with alkali and some anion resin with acid. The resulting ionic leakage during a service run of the mixed bed resin column is not acceptable in nuclear purification systems, particularly if the regenerants are NaOH and HCl.

6.1 Separation of Mixed Bed Resins

To eliminate the ionic leakage (described above) attempts were made to achieve a complete separation of the cation and anion components of a mixed bed resin column. A fluidization and entrainment technique was evaluated in the laboratory (7) for separating the mixed bed resins. The entrainment velocity ranges of the anion and cation resins were found to overlap due to the distribution of particle sizes of the resins. Consequently, poor separations were achieved, by entrainment, of mixed bed resins. The production of "fines" and the occasional tendency of the resin beads to stick together was considered to preclude reliable, complete separation of the mixed bed resins.

Therefore, it was concluded that regeneration (and reuse) of spent mixed bed ion exchange resins was not feasible and that separate cation and anion resin beds will have to be used at our nuclear stations, if spent resin regeneration is to be implemented for waste volume reduction.

6.2 Regeneration of Separate Beds

Attention was then directed to regeneration of separate cation and anion resin beds in future stations of Ontario Hydro. It was realized that, to achieve a high volume reduction factor economically, one has to:

1. minimize regenerant consumption,
2. use a volatile regenerant, where possible.

Laboratory experiments on inactive resins were carried out (8) employing very slow regenerant velocities (about 0.1 bed volume per hour) to minimize regenerant volume requirements. The results were not very encouraging.

Volatile acids such as hydrochloric acid and nitric acid were found to be quite effective for regeneration of simulated spent cation exchange resins and volume reduction factors approaching the theoretical (stoichiometric) limits of about 30 (before encapsulation of the evaporated residue in a solid matrix) were estimated.

Laboratory tests confirmed that strong base anion resins could not be effectively regenerated using a volatile base such as ammonium hydroxide.

Sodium hydroxide was determined to be an effective regenerant for spent anion resins - especially from the moderator system where non-radioactive boron is the major species. Because sodium hydroxide is non-volatile, any excess (unspent) sodium hydroxide in the regenerant effluent will have to be solidified along with the radioactive species eluted from the resins, resulting in low volume reduction factors. Two recycle schemes were examined (9), in which the unspent portion(s) of sodium hydroxide in the regenerant effluent from one cycle would be recycled and reused in subsequent regeneration cycles. The objective was to minimize the net regenerant consumption and thereby increase the volume reduction factor. The volume reduction factors obtainable with the recycle schemes are shown in Table 3. In the two stage recycle scheme, the unspent caustic in the regenerant effluent will be reused in two portions, the second containing a greater concentration of caustic and a lower concentration of boron than the first.

7. USE OF SEPARATE RESIN BEDS

The spent resin regeneration schemes described in the previous section are based on the use of separate cation and anion resin beds in the moderator and PHT purification systems. It is important to note that the use of separate beds, besides making spent resin regeneration feasible, might also result in substantial reduction in the amount of resin usage (due to more efficient use of the cation and anion components) and consequently in reduction in the volume of waste radioactive ion exchange resin. To evaluate the performance of separate beds in the purification systems, a

TABLE 3

**VOLUME REDUCTION FACTORS AND REGENERANT REQUIREMENT IN
CAUSTIC REGENERATION OF ANION RESIN
PARTIALLY LOADED WITH BORON**

Regeneration Scheme	Volume Reduction Factor*	Make-up Caustic Requirement (Bed Vols 2.8 N NaOH per Bed Vol of Resin)
Once-Through Regeneration	9.1	1.6
Single Stage Recycle	14.8	0.9
Two Stage Recycle	23.5	0.5

* Values were estimated based on crystal densities of NaBO_2 and NaOH . These are volume reduction factors prior to encapsulation of the regenerant waste

test loop consisting of a 200 mL cation resin (Amberlite, IRN-77) column in series with a 200 mL anion resin (Amberlite IRN-78, L/C) column, was installed on Unit 2 moderator purification system at Pickering generation station, in parallel with the existing mixed bed resin column. During the 8 week service period, the separate bed columns appeared to perform satisfactorily and their performance compared very favourably with that of the mixed bed column. The columns were valved out of the system when boron started breaking through the anion column. The gamma radiation field on the cation column was about 6 R/h on contact and the field on the anion column was about 100 mR/h. The anion resin column was shipped to the Radioactive Materials Laboratory of the Research Division. A complete chemical and radiochemical analysis of the resin was performed (10). This adds to our bank of knowledge on spent resin completion. The anion resin column was then regenerated with sodium hydroxide (for confirmation of the earlier regeneration studies), which removed practically all the boron from the resin. The regenerated anion column was shipped back to Pickering station. The cation and anion columns will be put back into service to commence the next service cycle. It is planned to study the performance of the separate bed columns over several service/regeneration cycles to examine their long-term behaviour.

It should be noted that the use of separate cation and anion resin beds in Ontario Hydro's nuclear generating stations to facilitate spent resin regeneration for radioactive waste volume reduction, is still several years away. Mixed bed ion exchange resins have been in use thus far. Consequently, a large quantity of spent mixed resins have accumulated over the years. Attention was therefore directed to the treatment of the spent mixed resins employing non-reuse (non-regenerative) type processing schemes where the treated resin is not suitable for reuse. These considerations led to the development of the acid stripping process (11).

8. ACID STRIPPING PROCESS

A conceptual flow sheet of the acid stripping or activity stripping process for decontamination of spent radioactive ion-exchange resins is shown in Figure 3. The acid stripping process can be used for removing ionic, particulate and some carbon-14 activity from spent moderator and PHT resins. In the process, hydrochloric acid is passed through a column containing the spent resin, in the presence of an applied ultrasonic field. The ultrasonic energy is for removing particulate activity from the spent resins. The acid can be evaporated, the vapors condensed and reused. The concentrated acidic residue containing most of the radioactivity would be neutralized and bituminized for storage. The inorganic carbon-14 in the spent resins is liberated as $^{14}\text{C}\text{O}_2$ gas by the acid and the $^{14}\text{C}\text{O}_2$ gas is absorbed by an alkaline solid such as $\text{Ba}(\text{OH})_2$, for containment of the carbon-14. The acid-treated resin containing very low residual activity should be suitable for storage in the lower cost trench storage.

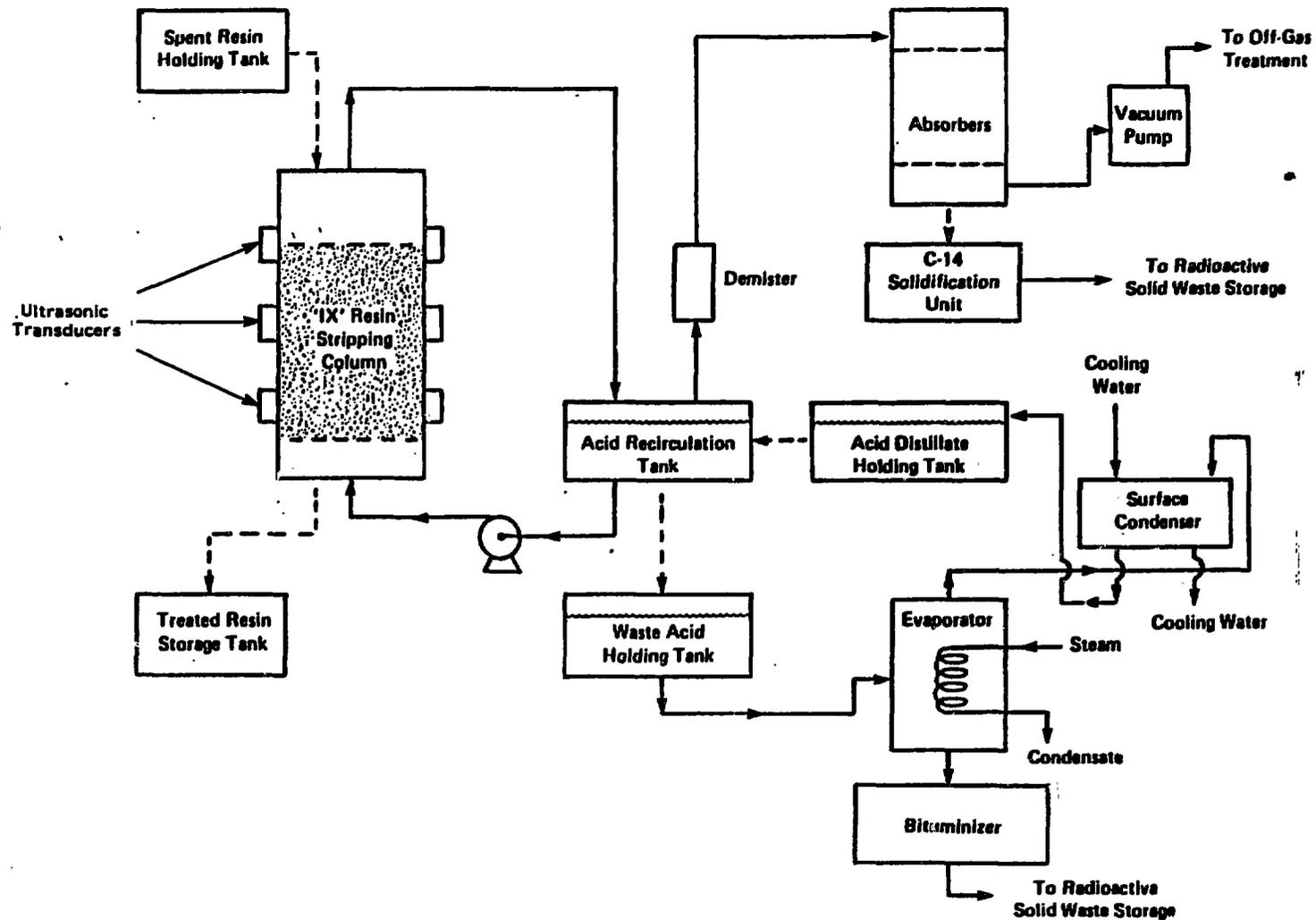


FIGURE 3
ACID STRIPPING OF SPENT ION EXCHANGE RESINS

8.1 Carbon-14 on Spent Ion-Exchange Resins

Carbon-14 on spent ion-exchange resins was recognized as a serious problem in the context of processing of the spent resins for long term storage. Carbon-14 is produced, primarily by the (n, α) reaction of oxygen-17 in the moderator and PHT circuits of CANDU reactors. It was believed that the carbon-14 on the spent resins was primarily inorganic ($^{14}\text{Co}_3/\text{H}^{14}\text{Co}_3$) in nature. Attention was therefore focussed on carbon-14 in spent resins - its concentration in the resins and the effectiveness of its removal by acid stripping.

Carefully controlled laboratory tests were performed (12) in which fresh resin samples loaded with known amounts of C-14 labelled $\text{NaH}^{14}\text{Co}_3$ were stripped with acid, the $^{14}\text{Co}_2$ liberated was absorbed in NaOH and estimated by liquid scintillation counting. The objective was to estimate the carbon-14 recovery and establish a mass balance for carbon-14. A schematic of the experimental apparatus is shown in Figure 4. During operation, the apparatus was kept under a slight vacuum to prevent escape of $^{14}\text{Co}_2$ gas from the system. The function of the ultrasonic probe was to aid in removing the fine carbon dioxide gas bubbles from the resin beads. Problems arising due to the dependence of carbon-14 counting efficiency on sodium hydroxide concentration, were overcome by adjusting the sodium hydroxide concentrations of all the counting samples to the same value. From the experimental results, it was established that practically all the bicarbonate (H^{14}Co_3) carbon-14 was removed from the resins by acid stripping. The mean carbon-14 recovery was about 97 per cent.

It should be noted that the acid stripping technique will not be effective in removing organic carbon-14 from spent resins. Work is currently in progress at Ontario Hydro's Research Division to determine the concentrations of organic and inorganic carbon-14 on spent ion exchange resins. If significant concentrations of organic carbon-14 are found on the spent resins, then modifications to the activity stripping process, such as the use of oxidizing agents for oxidizing the organic carbon-14 into $^{14}\text{Co}_2$, will have to be adopted.

The concentrations of (inorganic) carbon-14 on two samples of spent moderator resin obtained from Ontario Hydro's Pickering Nuclear Generation Station was determined (13) by the acid stripping technique to be about 177 $\mu\text{Ci}/\text{mL}$ resin and 213 $\mu\text{Ci}/\text{mL}$ resin, respectively. It is interesting to note that these values are considerably greater than those previously reported (see Table 1). Also of interest is the fact that 94% of Co-60, the principal radionuclide on the spent resin, was removed during the acid stripping experiment.

Further developmental work on the activity stripping process is planned to optimize the process for removal of ionic, particulate and carbon-14 activities from spent resins including the evaporation and immobilization aspects.

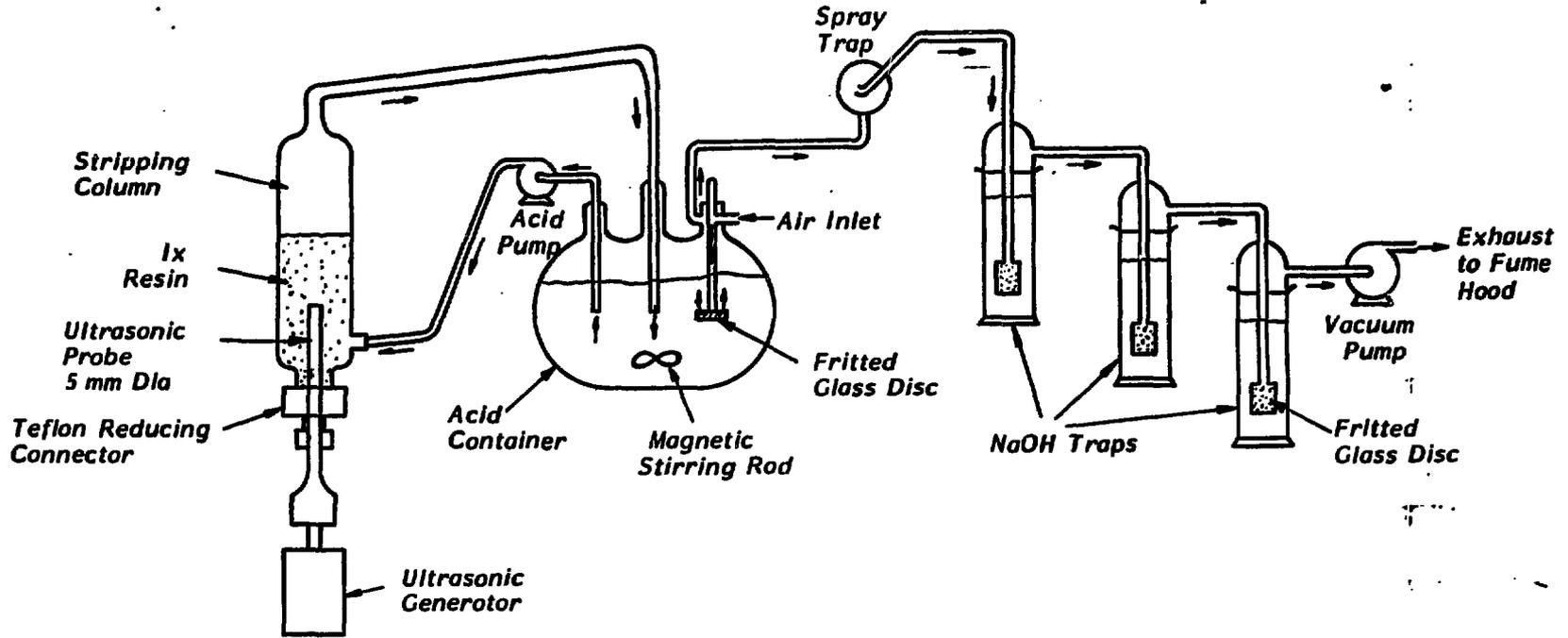


FIGURE 4
ACID STRIPPING APPARATUS FOR CARBON-14 DETERMINATION

9. ION-EXCHANGE RESIN SLURRY SAMPLER

More samples of spent ion-exchange resins from our nuclear generating stations are needed to allow us to better characterize the spent resins chemically, and to facilitate development of processes for the treatment of the spent resins. With these in mind, development of a resin slurry sampler, has recently been undertaken by Ontario Hydro's Research Division. The sampler is being designed to enable collection of representative samples of spent resins directly from spent resin slurring lines at the stations, without adversely affecting the slurry operations. The resin slurry sampler is being fabricated at the present time and will be tested in the Ion-Exchange Pilot Plant facility of Ontario Hydro's Research Division.

10. CONCLUSIONS

The opportunities for reducing the volume of waste radioactive ion-exchange resins produced in nuclear station purification circuits are many and varied. Ontario Hydro Research Division's efforts have been directed towards: (1) developing technology that could be used to reduce the volume of waste resin that has been and is generated at existing stations and, (2) developing purification processes that will be more efficient in terms of impurity removal and the volume and form of active waste generated. This paper has reviewed the evolution of studies under the first objective. The acid stripping process will be further developed, since it has potential as a final treatment step for high level active waste resins yielding low level waste resin and a high level low volume waste, the economic advantage arising from the differential in costs of high and low level waste storage. However, as far as the resin is concerned, acid stripping is a non-conservative process - the resin must be replaced by new resin. The use of separate ion-exchange beds and regeneration of the resins would save on both waste storage costs and resin replacement costs; in addition, separate beds may facilitate more effective use of the resin capacity. This regeneration process is being studied as and when resins in the in-station separate bed test loop become exhausted. The development of a spent resin sampling method is an important part of the overall resin treatment study since real samples are needed for verification of the acid stripping process and generally to provide information about the degree of exhaustion of the spent resins and the type and level of activity on the resins.

Implementation of any of the newly developed processes will necessarily be based on economic evaluations of all the process options. While the Chemical Research Department has frequently done preliminary cost studies of various processes, detailed estimates and economic comparisons are generally the purview of the Design and Development Division, hence cost data for the resin regeneration and acid stripping processes will be discussed in the following papers.

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