

## PROCESSING NUCLEAR WASTE FOR ISOTOPE PRODUCTION

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### ABSTRACT

A process developed by Ontario Hydro for recovering carbon-14 (C-14) contaminant from spent ion exchange resin waste and enriching it for isotope production is described. The process consists of three main steps: recovery of C-14 from spent resins, enrichment of the recovered C-14, and preparation of the final chemical product. A pilot scale plant capable of processing 4 m<sup>3</sup> of spent resins annually is being planned for demonstrating the technology.

### INTRODUCTION

Carbon-14 is produced in nuclear reactors by neutron activation of oxygen-17, nitrogen-14, and to a lesser extent carbon-13. It is a contaminant with an extremely long (5730 years) half-life. It can cause dosage to inhabitants by contact, inhalation or through the food cycle via photosynthesis. Release of carbon-14 to the environment must be minimized. According to U.S. Nuclear Regulatory Commission's classification given in the Code of Federal Regulations (10 CFR 61.55), wastes containing more than 8 Ci/m<sup>3</sup> are greater than class C (GTCC) and must be disposed of by stringent methods in geologic repositories.

In CANDU (CANada Deuterium Uranium) nuclear reactors, C-14 is produced mainly in the Moderator and Primary Heat Transport (PHT) systems. Control of C-14 emission from CANDU reactors is very effective. Over 90-95% of the C-14 produced is removed by the ion exchangers in the respective purification systems (1). The periodic release with purge gas from the moderator cover gas and the annulus gas systems is minimized by gas scrubbers and absorbers (2,3). The actual C-14 emissions from the generating stations are minimal. For example, the annual total C-14 production of a CANDU 600 MW reactor is estimated at 447 Ci/year for an 80% capacity factor, and the expected total C-14 emission is 10-20 Ci/year. This could be further reduced to about 1 Ci/year by adding control measures to the cover gas and annulus gas systems (4,5).

The ion exchange resins remove and contain the C-14 contaminant, but produce large volumes of spent resin wastes, which create a waste disposal problem. The measured C-14 activity levels on the spent resins ranged from 0.2-6.4 Ci/m<sup>3</sup> for PHT spent resins and 47-213 Ci/m<sup>3</sup> for Moderator resins (1,4). At Ontario Hydro, the annual resin usage is around 125 m<sup>3</sup> and is projected to reach 200 m<sup>3</sup> when Darlington Nuclear Generating Station comes into full service. Currently, the spent resin waste is stored in suitably engineered concrete structures. Because of the large volumes of spent resin waste generated each year this method of disposal by long term storage tends to be uneconomical; and may also be unsatisfactory considering the long half-life of the C-14.

However, C-14 can be a valuable commercial product for medical, pharmaceutical, agricultural, and organic chemistry research. At present, commercial C-14 is made artificially in research reactors by irradiating aluminum nitride targets for 4.5 years. If the C-14 containing resin wastes can be processed to reduce this artificial production of C-14, the total global build-up of this isotope can be reduced. There is, therefore, an incentive to remove C-14 from the spent resin for the waste volume reduction, and also to purify the recovered C-14 for the commercial market.

A process has been developed at Ontario Hydro to achieve both these objectives (6). The classification of the treated spent resin can be reduced from GTCC to Class A (ie, less than 0.1 times the 8 Ci/m<sup>3</sup> limit stipulated by U.S. Nuclear Regulatory Commission), which would qualify it for near-surface disposal.

### PROCESS DESCRIPTION

The process developed by Ontario Hydro consists of three main steps: C-14 recovery from spent resins, enrichment of the recovered C-14, and preparation of the final product.

Several alternative routes have been considered for this process which include thermal stripping vs. acid stripping for recovering C-14 from the spent resins, laser enrichment vs. cryogenic distillation for the enrichment of the gaseous intermediate product, and direct gas phase reaction vs. liquid phase ionic precipitation for preparing the final product. Analysis of the experimental results obtained at Ontario Hydro Research Division and also those reported in the literature has led to the selection of the following process (see Fig. 1) (6): The C-14 is first removed by acid stripping the resins to form carbon dioxide, which is converted to carbon monoxide by reaction with zinc. The carbon monoxide is then cryogenically distilled. Essentially pure C-14 monoxide (<sup>14</sup>CO) is obtained and oxidized to produce C-14 dioxide (<sup>14</sup>CO<sub>2</sub>). The gas is then converted to barium carbonate, which is the desired commercial product.

These steps are discussed in more detail below.

### Recovery of C-14 from Spent Resins

A simplified process flow diagram of the recovery step is presented in Fig. 2.

The C-14 is first removed from the resin particles. Two alternative removal methods have been considered: thermal stripping and acid stripping. In a patented thermal stripping process (7), heated air (298-343 K) enriched with 10-50% of C-12 carbon dioxide ( $^{12}\text{CO}_2$ ) is used to displace the C-14 species on the spent resins. This method is not suitable for the current application because the removal efficiency (20-60% of the C-14 on the resin) is relatively low, and the large amount of  $^{12}\text{CO}_2$  added tends to make the subsequent steps of separating C-14 from the gas mixture more difficult.

The acid stripping technique developed at Ontario Hydro (8) has been selected for this process. This technique employs an inert carrier gas and can yield high removal efficiencies. A typical set of experimental results is shown in Table I. Similar efficiencies were obtained in experiments of different batch sizes ranging from 10 ml to 10 litres of resin (9,10,11). The high removal efficiency (98.5-100%) of this technique makes it attractive for this process. Although the spent acid will also remove other gamma emitting radionuclides from the resins and become an additional stream of radioactive waste, none of those species have very long half-lives. The disposal is relatively easy and the disposal cost is estimated to be about 5 K\$/m<sup>3</sup>.

As shown in Fig. 2, the spent resin is agitated with hydrochloric acid in an aerated reactor. Helium is used as a carrier purge gas. Both the radioactive and non-radioactive carbonates on the spent resins will react with the acid to generate carbon dioxide to be purged by the carrier gas. Should a significant amount of C-14 be present in organic forms, suitable oxidizing agents may be used instead of the acid. The off-gas is passed through a moisture trap, where any acid or water vapour carry-over is condensed by suitable cooling, and then delivered to a cryofreezer. Maintained at 77 K by liquid nitrogen, the cryofreezer separates the carbon dioxide from the carrier gas by forming solid carbon dioxide on the cooling surface. The helium is recovered in gaseous form and recycled. The solid carbon dioxide contains a mixture of  $^{12}\text{CO}_2$  and  $^{14}\text{CO}_2$  and will easily vaporize upon warm-up. The gaseous mixture is then reduced to a mixture of carbon monoxides by reaction with zinc powder supported on an inert material in a tubular reactor maintained at 673 K. Experimental measurements indicate that the conversion efficiency is greater than 99.98% (12). The zinc powder is replaced periodically because ZnO cannot be reduced to elemental zinc in the apparatus. The resulting mixture of  $^{14}\text{CO}$  and  $^{12}\text{CO}$  is stored as the feedstock to the subsequent stage of C-14 enrichment.

### Enrichment of Carbon-14

The carbon-14 found on the moderator ion exchange spent resins is equivalent to about 0.5 to 2% carbon-14 in the recovered carbon monoxide, with about 1%  $^{13}\text{CO}$  and the remainder  $^{12}\text{CO}$ . For the recovered carbon-14 to be a commercial product, it must be enriched to at least 95%. We have considered two different enrichment technologies, a laser method and cryogenic distillation.

The laser method is based on isotopically selective dissociation of a process molecule. The most suitable molecule in this case is formaldehyde, which is produced from the reaction between carbon monoxide and hydrogen in the presence of electronically excited mercury atoms. Experiments in this laboratory have shown large, single step enrichment factors for carbon-14 of around 1200, by using an ultraviolet laser (353.2 nm) to dissociate formaldehyde (13). Even with this high enrichment factor, at least two laser stages are required to reach 95% enrichment. However, recovering H<sub>2</sub> and  $^{14}\text{CO}$  dissociation products from the process stream to resynthesize formaldehyde for a second laser stage is too complicated for this application.

A simpler enrichment process is cryogenic distillation of carbon monoxide (14,15,16), which has the advantage of using CO from the previous recovery step directly. Also, it is a well tested technology, and almost all the world's carbon-13 is made by this method.

The size of a distillation plant depends on the efficiency of separation per theoretical stage, which is defined as the length of column required for complete equilibrium between the liquid and vapour. The fundamental property describing this equilibrium is the separation factor, which is defined as the isotope mole fraction in the vapour divided by the mole fraction in the liquid. For a two component system, the separation factor,  $\alpha$ , is given by

$$\alpha = \frac{(N/N)_v}{(N/N)_l} \quad (\text{Eq. 1})$$

where N is a mole fraction, v refers to the vapour phase, l the liquid phase, and the prime (') refers to the light isotope. For ideal gases,  $\alpha$  is just the ratio of the vapour pressures of the isotopes ( $P'/P$ ).

A theoretical model has been developed to relate the separation factor to molecular constants obtained from spectroscopic data (17). In practice, however, it is sometimes more convenient to measure the vapour pressure for a given isotopic molecule (e.g.  $^{12}\text{C}^{16}\text{O}$ ), fit the vapour pressure-temperature data to the model, and use this result to calculate the vapour pressures of the other isotopic combinations. Based on measured vapour pressure data of  $^{13}\text{CO}/^{12}\text{CO}$  and  $\text{C}^{18}\text{O}/\text{C}^{16}\text{O}$  (18), vapour pressures, and thus the separation factors, for other isotopic combinations of carbon monoxide can be calculated (19) and the results

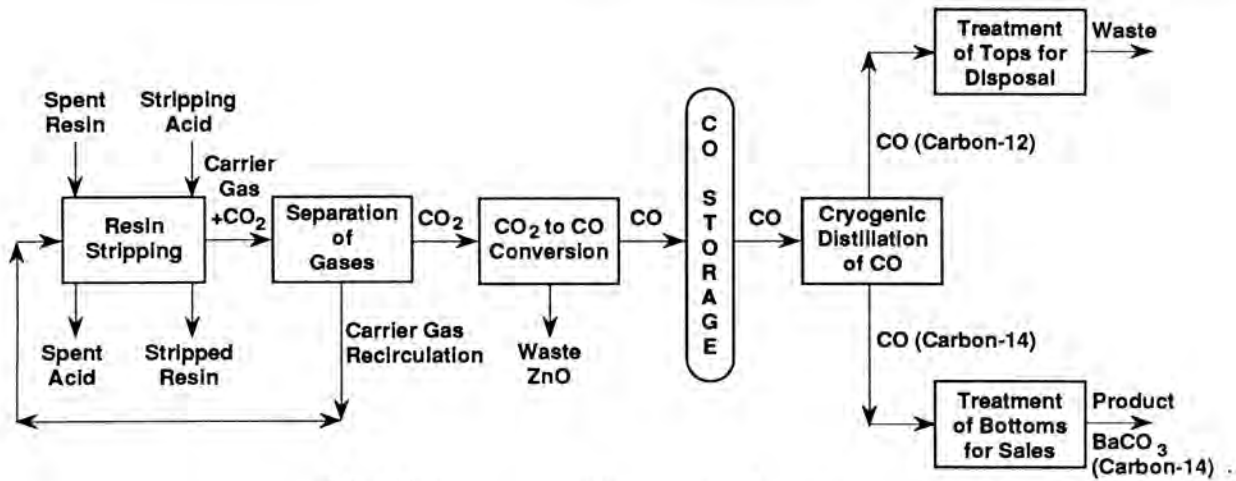


Fig. 1. Isotope recovery from spent resin waste.

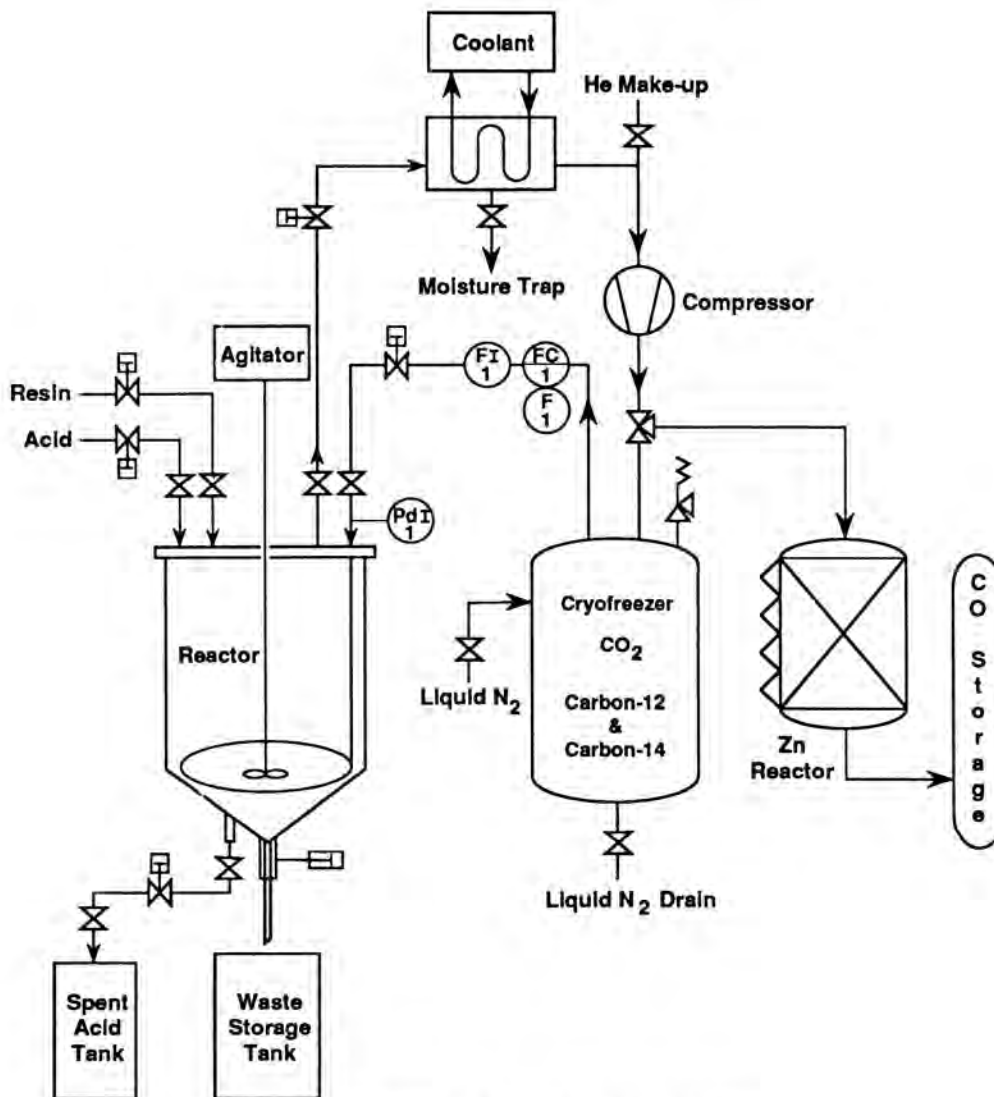


Fig. 2. Recovery of C-14 from spent resins.

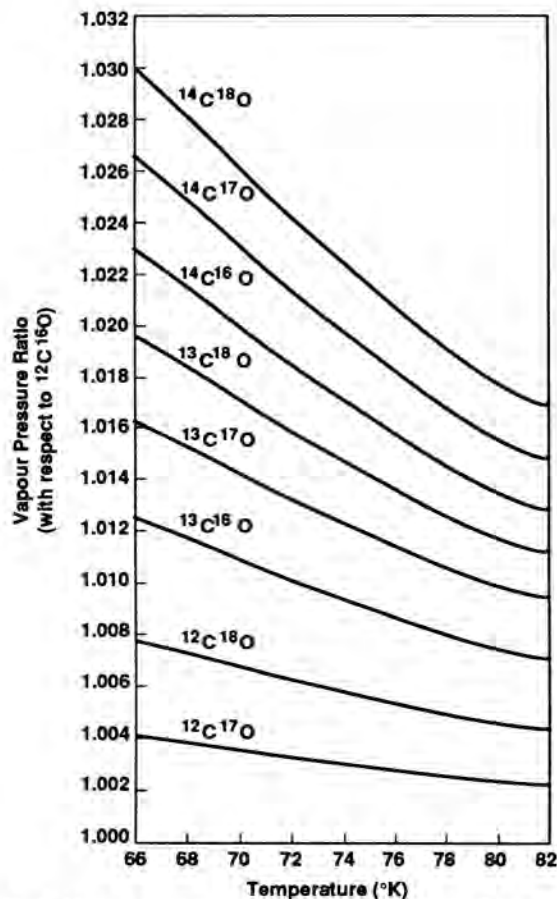


Fig. 3. Vapor pressure ratios for isotopic carbon monoxide.

are given in Fig. 3. These separation factors were used to estimate the length of packed column required to enrich carbon isotopes. A demonstration unit (Fig. 4) was built in 1984 to study temperature and flow control systems, and to test various column packings for a CO distillation column. The packed length in the test column was 147 cm with a column diameter of 17.3 mm. Figure 5 shows the performance of two column packings, Heli-Pak 3012 (type A) (Podbielniak, Inc., Bensenville, Illinois) and Heli-Pak 3013 (type B); both are made of rectangular, coiled stainless steel wire, and type B packing is slightly larger than type A packing. Measurements of the number of theoretical plates in the column showed that column performance was independent of reboiler power from 20 W to 60 W. For type B packing, the H.E.T.P. (height equivalent to a theoretical plate) was 2.4 cm; for type A packing, the H.E.T.P. increased to 3.8 cm.

Figure 5 also shows that changing the condenser temperature from 77 K (liquid nitrogen at atmospheric pressure) to 68.4 K (liquid nitrogen at reduced pressure) does not change the number of theoretical plates. However, because the vapour pressure ratios (Fig. 3) between  $^{14}\text{CO}$  and  $^{12}\text{CO}$  are quite different at these two temperatures, the

separation per unit column length is greater at the lower temperature. The advantage of greater separation at the lower temperature is partially offset by reduced column throughput because the CO density is lower at this temperature.

The distillation column, liquid nitrogen reservoirs, and outer vacuum jacket were built from 304 stainless steel. The condenser and reboiler were constructed of oxygen-free electrolytic copper and brazed to the column. A vacuum ( $< 10^{-3}$  Pa) surrounds the column to insulate it from room temperature. In addition, 60 layers of aluminized mylar film surround the column as a radiation shield. Radiation leakage to the column is less than 0.25 W.

The distillation column is cooled by liquid nitrogen in the condenser. The coolant temperature is adjusted by reducing the pressure over the liquid nitrogen; a typical operating range is 101 to 31 kPa, which changes the temperature from 77 K to 68 K. A pressure controller between the reservoir and the vacuum pumps maintains the pressure over the liquid nitrogen at a preset level. The same controller can also keep the reservoir at pressures above atmospheric without a vacuum pump by venting the boiloff. The liquid nitrogen control system has operated for 48 months under a variety of column conditions and a further six months unattended, with the distillation column at 15 W. During this time, the supply pressure of liquid nitrogen was changed from 275 kPa to 620 kPa. The control system drops these pressures to the current operational pressure of the liquid nitrogen reservoir, without disturbing the temperature or pressure within the column.

A production distillation unit should operate continuously. In our design, gas enters the middle of the column (feed) while portions of gas from the condenser (waste) and reboiler (product) are simultaneously removed (Fig. 6). During operation, the size of the feed stream must be balanced by the product and waste streams to keep a constant quantity in the column. Because the product flow rate in the proposed pilot plant is so low ( $\sim 80$  g per year) continuous flow control at this rate is impossible. An alternative procedure is to add or remove fixed volumes of gas at regular time intervals. Varying the time controls the flow rate.

A logic circuit operates the feed and withdraw system. This circuit sets the time that each valve is open or closed, prepares the system for sampling by an operator, and counts the total number of pulses of gas that have entered or left the column. To correct for small variations in the material flows, the control circuit also monitors the amount of carbon monoxide in the reboiler by measuring the differential pressure across the reboiler. This pressure difference is due to the weight of liquid CO and is thus proportional to the number of moles of CO. If the liquid level is outside preset limits, the circuit automatically corrects the level by sus-

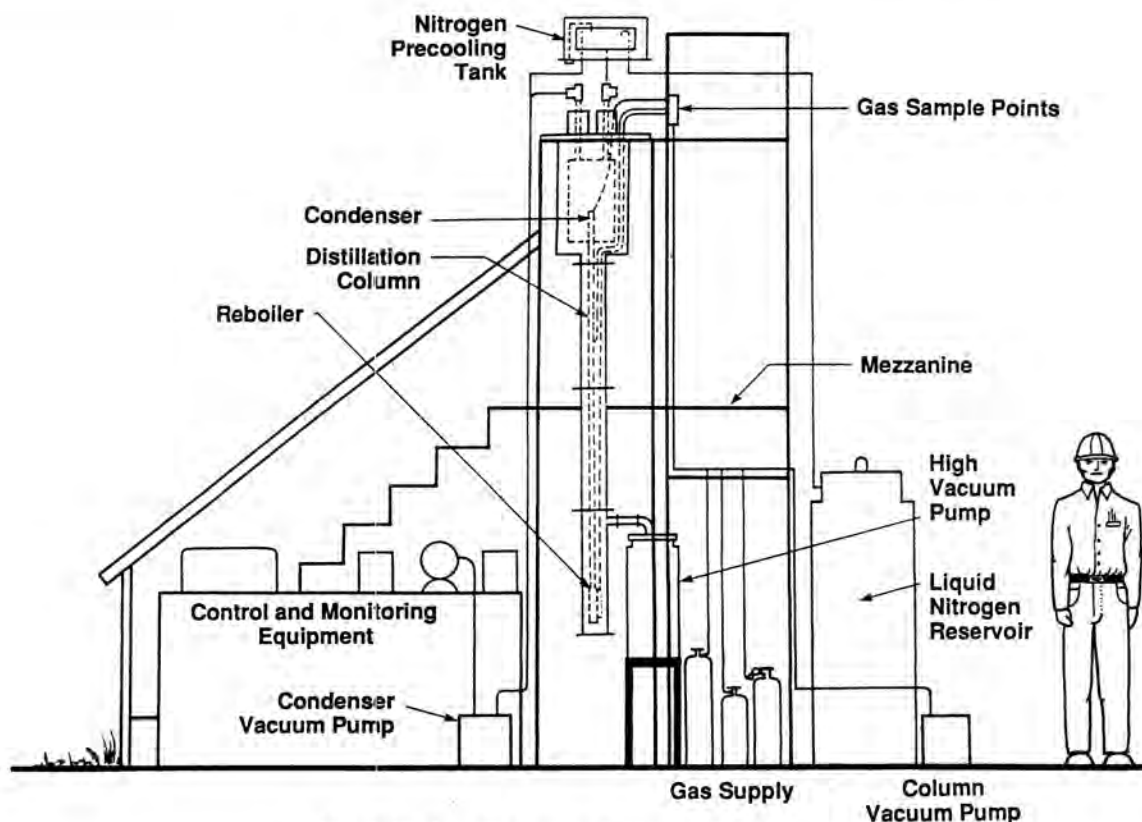


Fig. 4. Carbon-14 cryogenic demonstration unit.

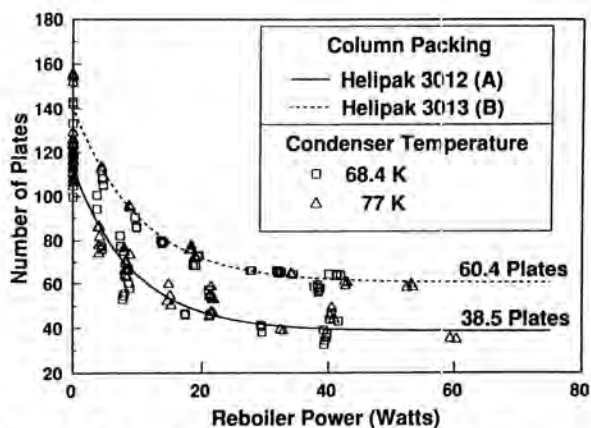


Fig. 5. CO distillation performance curves. Two types of packing tested in 147 cm long, 17.3 mm diameter test columns.

pending either a feed or a withdraw cycle. Lamps on the front of the control box show the operator the status of each solenoid valve.

The pilot plant will have 4 columns of progressively smaller diameter. Each column will be 15 m in length with the diameters ranging from about 25 mm at the waste end of the plant to 8 mm at the product end. The columns will

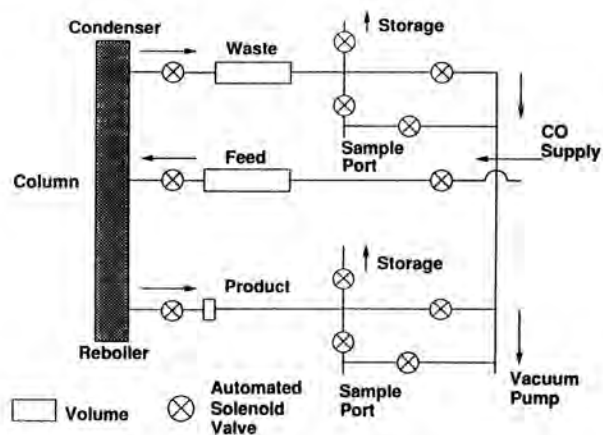


Fig. 6. Schematic of pulse flow system in the demonstration column.

be packed with Heli-Pak B packing. This design will produce 99%  $^{14}\text{CO}$ .

**Product Packaging**

Enriched  $^{14}\text{CO}$  is then oxidized over a platinum catalyst (not shown) at about 673 K in oxygen to generate  $^{14}\text{CO}_2$  for packaging into a suitable form for marketing. One such stable form for the wholesale commercial market is C-14

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**TABLE I**  
**TYPICAL RESULTS OF REMOVING C-14 BY ACID STRIPPING (8,9)**

Experimental Conditions

Resin Volume	= 10 ml of Amberlite IRN 150
Acid Concentration	= 6 N HCl
Acid Volume	= 120 ml
Reaction Time	= 45 minutes
Agitation Speed	= 60 rpm
Aeration Rate	= 135 ml/min

Results

Percent recovery of C-14 from simulated moderator spent resin  
 (50 Ci/m<sup>3</sup> loading of NaH<sup>14</sup>CO<sub>3</sub> on IRN 150 resin) in 10 Trials:

(1)	99.90%	(2)	100.02%	(3)	102.20%	(4)	98.56%	(5)	101.46%
(6)	99.36%	(7)	100.31%	(8)	102.65%	(9)	99.34%	(10)	99.70%

Statistical Tests

Mean recovery efficiency:	$\bar{x} = 100.35\%$
Sample standard deviation:	$S = 1.3285$
Null Hypothesis	$H_0$ : Recovery efficiency, $U_0 = 100\%$
Alternative Hypothesis	$H_A$ : $U_0 \neq 100\%$
Student-t Statistic:	$T_9 = \frac{(\bar{x} - U_0)}{S/\sqrt{n}} = 0.833$

$$t_{9,0.005} = 3.25$$

Since  $T_9 < t_{9,0.005}$ , therefore do not reject  $H_0$ .

barium carbonate. Barium carbonate can be prepared by either direct reaction of CO<sub>2</sub> gas with barium hydroxide solution or by adding barium ions to a sodium carbonate solution (20). Preliminary experiments indicated that the former method of direct gas phase reaction would encounter technical problems from the clogging of the CO<sub>2</sub> gas aspirator. The experiments to precipitate barium carbonate from sodium carbonate solution with barium ions have indicated quantitative recovery and experienced no technical difficulties. Therefore, precipitation by barium ions is the preferred method.

### DISCUSSION AND CONCLUSIONS

In this paper we presented a process which has the potential of reducing the volume of carbon-14 waste and at the same time producing a marketable isotope. If Ontario Hydro's nuclear waste can replace the artificial production of this isotope, we will reduce the global build-up of C-14.

We have described the components of the process in detail and compared the alternative methods. The reasons for our selections were presented. Key components have been successfully tested at Ontario Hydro's Research Division, but the integration of the process is yet to be demonstrated. A pilot scale plant capable of processing 4 m<sup>3</sup> of spent resins annually is being planned for demonstrating the technology at Ontario Hydro. For an estimated average C-14 activity level of 100 Ci/m<sup>3</sup>, a total of 400 Ci of C-14 can be produced each year. Based on the current wholesale value of the C-14 isotope, the cost of the demonstration plant estimated at \$3 million can be recovered in less than two years. Parties that are interested in joint ventures with Ontario Hydro on this project are welcome to contact our New Business Ventures Division.

Upon successful demonstration, the process can be scaled up and the volume of resin wastes produced by the

stations can readily supply a full scale production of 2000 Ci or more per annum.

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