Relative Determination of ^{14}C on Spent Ion-exchange Resins by Resin Regeneration and Sample Combustion

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Two techniques were tested for the recovery and analysis of carbon-14 in ion-exchange resins from nuclear power plants. Such determinations are necessary to classify spent resins before they are shipped and disposed of as low-level radioactive waste. Combustion/oxidation was used in the first method; the second used resin regeneration to evolve $^{14}CO_2$ for selective absorption in a scintillation cocktail. The resin regeneration procedure proved to be simple and somewhat more reproducible than the combustion/oxidation procedure for measuring ^{14}C on resin wastes from nuclear power plants. The resin regeneration procedure provided a recovery of $85 \pm 7\%$ as compared to $63 \pm 9\%$ for the combustion procedure.

Introduction

Generators of low-level radioactive waste (LLRW) are required (U.S. Nuclear Regulatory Commission, 1983) to report the quantities of carbon-14 and other radionuclides in such wastes destined for disposal. These quantities are important for classifying the waste for packaging prior to disposal and for establishing an inventory at the disposal site for performance assessment determinations. Ion exchange resins are an important waste form because they constitute >50% of the volume and 75% of the radioactivity in LLW shipped for disposal from nuclear power plants.

Analysis of ^{14}C content in spent ion-exchange resins can be accomplished using a method reported by Martin (1986), which uses an electric tube furnace to combust and oxidize the carbon in the sample. This procedure produces an off-gas which is quantitatively recovered in a liquid scintillation cocktail specific for trapping CO_2 and counted by liquid scintillation analysis (LSA).

Unlike other LLRW media, ion-exchange resins have the unique ability to be regenerated, releasing material ironically bound to them by stripping with acids or bases. Since most of the ^{14}C on the resin is believed to be a carbonate (Kunz, 1985), acidification will evolve it as $^{14}CO_2$, which can be selectively absorbed in trapping solutions for subsequent analysis by LSA techniques.

Chang *et al.* (1989) have developed a method based on acid regeneration to remove ^{14}C from spent resins

at Canadian reactors to reduce the overall volume of such wastes destined for disposal. They demonstrated this technique for the Ontario Hydro reactors using 2 M NaOH as a waste processing technique rather than an analytical method for LLRW resins. Snellman and Salonen (1982) have also reported use of an acid regeneration procedure for studies of ^{14}C in resins at Finnish reactors.

The purpose of this study was to compare the relative merit of determining ^{14}C content in LLRW resins by regeneration of the resin vs the more common technique of combustion/oxidation.

Experimental

Liquid scintillation analysis

A liquid scintillation analyzer (Packard Instrument Co.—Model 2000CA) was used with a preset region for counting the full spectrum of ^{14}C so that a strict energy calibration was not necessary. Sample quench was determined as a tSIE factor by ratioing the counts in this region to those observed from an external standard. Calibrations and a quench curve (Fig. 1) were obtained with a standard traceable to the National Institute of Standards and Technology and by quenching the solution with carbon tetrachloride. The CO_2-specific trapping solution was freshly prepared by mixing 410 mL of toluene, 270 mL methanol, 270 mL phenethylamine and 50 mL Liquifluor.*

Resin loading

The resin obtained for this project was a mixed anion/cation type, configured as small plastic beads

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*Liquifluor and the recommended mixture obtained from New England Nuclear Company, 549 Albany Street, Boston, MA 02118.
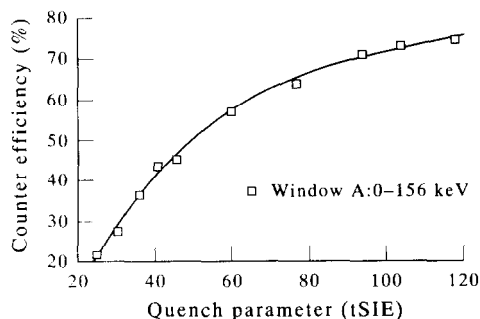
Fig. 1. ^{14}C counting efficiency vs quench for $^{14}CO_2$ LSA cocktail.

(Epicor EP-II, Dow Chemical Co.). A solution containing 1.35 μCi of ^{14}C in carbonate form was prepared and added to a 50 g sample of resin for a period of 4 h, accompanied by periodic agitation. This technique simulated the batch mode of operation commonly used for coolant cleanup systems in nuclear power plants. The sample was then vacuum filtered* to remove the spent solution. This vacuum filtration is similar to the dewatering step at a power plant. An aliquot of the solution was counted before and after resin treatment to determine the amount of activity deposited on the resin; 99.8% of the ^{14}C was transferred to the resin beads. There was no gaseous release of $^{14}CO_2$. Careful attention was made to maintain the pH above 7 to preclude any loss of gaseous CO_2. Weighed aliquots of the treated resin were processed to compare the off-gas and combustion/oxidation techniques.

Combustion procedure

An analytical procedure using combustion/oxidation in a tube furnace was used as a point of reference. The resin sample (0.5 g) was placed in a nickel boat, which in turn was placed inside the electric tube furnace for 30 min of combustion at 740 ± 6°C. A specially constructed 25 mm fused quartz tube was packed at one end with two catalysts: platinum on alumina beads and copper oxide wire. During combustion, the off-gases were drawn through the system using a flowrate of air at 200 mL/min through an ice bath and a system of dryers (see Fig 2) to remove water, followed by bubblers to trap the oxidized carbon (radioactive and not). The bubblers were filled with the LSA cocktail specific for CO_2. After the combustion was completed, the solutions were placed in vials and counted in a liquid scintillation analyzer. Backgrounds were determined prior to and following each sample by running blanks through the procedure. Six aliquots of the resin were analyzed to produce the data reported

*Apparatus: Porcelain Buchner funnel with 4.5 cm Whatman No. 1 paper, 125 mL filter flask and stopper.

here; however, numerous other samples have been processed with similar results.

Regeneration by acid stripping

Small samples (approx. 0.5 g) of the resin were regenerated by placing them in a 30 mL reaction vessel (midget bubbler) with impinger tip for adding reagents. The off-gas from the reaction vessel was drawn by vacuum through two bubblers (one for a backup) fitted with fritted glass tips (see Fig. 3). Each bubbler contained 15 mL of trapping solution to collect the evolved $^{14}CO_2$ in the off-gas. Air was pulled through the system at a flowrate of 200 mL/min; 10 mL of 6 M HCl were pipeted into the reaction vessel and swirled occasionally while the flowrate was continuously applied for 30 min to capture the off-gases in the trapping solution. The two 15 mL aliquots of trapping solution were then removed and counted in the LSA.

Dual regeneration by acid/base stripping

The resin regeneration procedure was also tested to determine whether the addition of KOH prior to the addition of HCl would improve recovery rates for ^{14}C on the resin since most reactors use mixed anion/cation resin beds, which may also capture organic forms of ^{14}C. Kunz (1985) has shown that some of the ^{14}C released from pressurized water reactors is in organic form, whereas the off-gases from boiling water reactors contain little organic carbon. A small aliquot (3 mL) of 6 M KOH was added to the reaction vessel. This amount was sufficient to cover the resin beads and still allow agitation by bubbling. The reaction vessel was swirled occasionally for 15 min, and the cocktail was collected from the bubblers and replaced with fresh cocktail. A 10 mL sample of 6 M HCl was then added to the reaction vessel containing the basic solution and resin to determine if additional $^{14}CO_2$ could be evolved. Flushing of the system continued for an additional 30 min.

Flushing time for resin regeneration

A determination was made of the effect of flushing time on recovery of $^{14}CO_2$ evolved from resin regeneration. Several identical aliquots of resin were regenerated for flushing times ranging from 5–45 min.

Dual regeneration of cobalt contaminated reactor resins

An aliquot of the resin containing ^{14}C was dual-loaded with ^{60}Co solution (1.75 nCi/g). Counts of the ^{60}Co solution before and after resin treatment indicated that 98% of the ^{60}Co was ionically bound to the resin beads. The sample was regenerated using 6 M HCl to determine whether a significant amount of the ^{60}Co contaminant would be evolved and trapped in the liquid scintillation cocktail to introduce interfering counts.
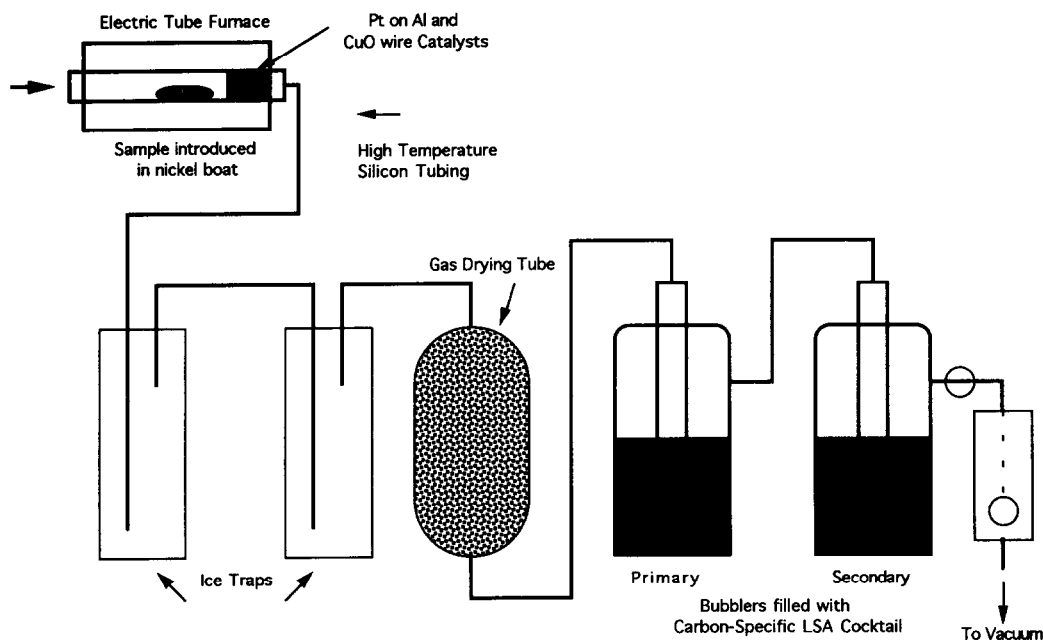
Fig. 2. Apparatus for combustion/oxidation of resin to recover $^{14}CO_2$.
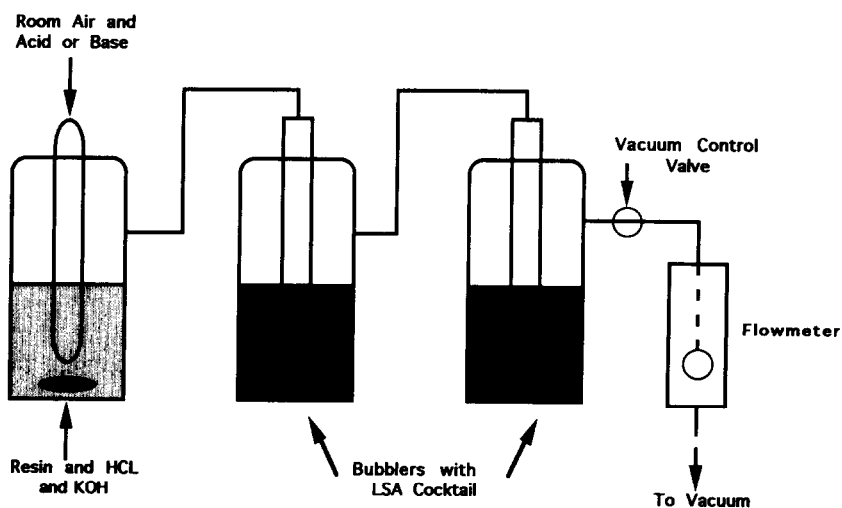

Fig. 3. Apparatus for regeneration of resin to recover $^{14}CO_2$.

Results and Discussion

The recovery results of the combustion/oxidation procedure are summarized in Table 1. The mean percent recovery for this procedure was $63 \pm 9\%$, with a combustion time of 30 min at $740 \pm 6°C$. The resin regeneration procedure with a bubbling time of 30 min yielded a mean recovery of $85 \pm 7\%$ (Table 2). The recoveries for the regeneration technique using HCl were highly efficient with less variation than the combustion procedure.

Table 1. Measured recovery of ^{14}C from reactor resins by the combustion/oxidation technique

Trial	Recovery (%)
1	58.3
2	62.6
3	69.6
4	66.3
5	65.3
6	57.7
	Average $= 63.3 \pm 9.2\%$

Table 2. Measured recovery of ^{14}C from reactor resins by regeneration with HCl

Trial	Recovery (%)
1	91.7
2	86.7
3	81.3
4	86.6
5	84.0
6	82.5
	Average $= 85.4 \pm 7.4\%$

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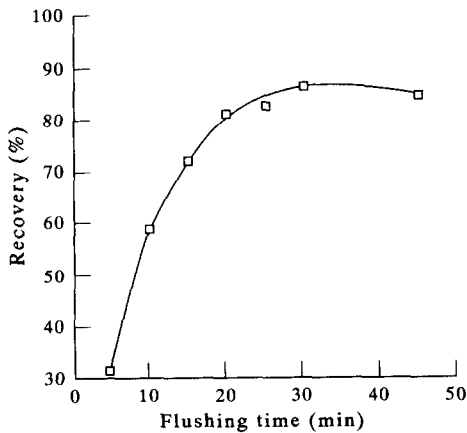

Fig. 4. Percent recovery of $^{14}CO_2$ vs flushing time for the resin regeneration technique.

Table 3. Measured recovery of $^{14}CO_2$ from reactor resin by dual regeneration with KOH and HCl

Trial	Recovery (%)
1	93.4
2	78.8
3	87.2
4	79.1
5	91.7
6	81.5
	Average $= 85.3 \pm 12.5\%$

Figure 4 demonstrates that $^{14}CO_2$ recovery is a function of sample flushing, and as the data indicate, the resin does not release all of the $^{14}CO_2$ immediately, but with agitation, releases ^{14}C from the resin as $^{14}CO_2$ at various rates over a period of 5–45 min. Based on the data, a 30 min flushing time was selected; longer flushing times (up to 45 min) provided no significant recovery advantages for $^{14}CO_2$.

Dual regeneration recoveries using both KOH and HCl are shown in Table 3. These data indicate that the combination of KOH–HCl yields essentially the same recovery rate for $^{14}CO_2$ as regeneration with just HCl; however, the resin tested contained only the carbonate.

The resin regeneration procedure was found to be selective for carbon. Regeneration of a resin containing both ^{14}C (β_{max}—156 keV) and ^{60}Co (β_{max}—318 keV) yielded a LSA spectrum containing only ^{14}C (Fig. 5). Although the ^{60}C bound to the resin could be stripped (regenerated) from the resin by acidification, it was retained in solution rather than evolved for capture in the cocktail specific for $^{14}CO_2$. The amount of ^{60}C stripped from the resin was determined by vacuum filtering the resin and counting the liquid regenerant and the filtered resin sample separately in a NaI(Tl) well-counter. Eighty-two percent of the ^{60}C remained ironically bound to the resin. Beta spectra are routinely run for LLRW resin samples from reactors, and these too show no contamination by ^{60}C or other radionuclides that may be cross contaminants.

Both techniques of ^{14}C analysis continue to have one primary drawback in that each depends on use of a LSA cocktail that contains toluene, methanol and phenethylamine, which require that the cocktail be managed as a hazardous waste. It is also important to carefully manage the sample concentrations to avoid having a concentration of ^{14}C in the LSA cocktail that would classify it as a mixed waste.

Conclusion

The resin regeneration procedure proved to be simpler and somewhat more reproducible than the combustion/oxidation procedure for measuring ^{14}C in resin wastes from nuclear power plants. The resin regeneration procedure yielded a recovery of $85 \pm 7\%$ as compared to $63 \pm 9\%$ for the combustion procedure. The gain in system recovery is not a sufficient basis for using the regeneration technique for measuring ^{14}C in LLRW resins; however, the procedure offers advantages due to simplicity and reduction of contamination of equipment by other radionuclides.

The off-gas technique using only HCl is comparable to the KOH–HCl recoveries; thus, no particular
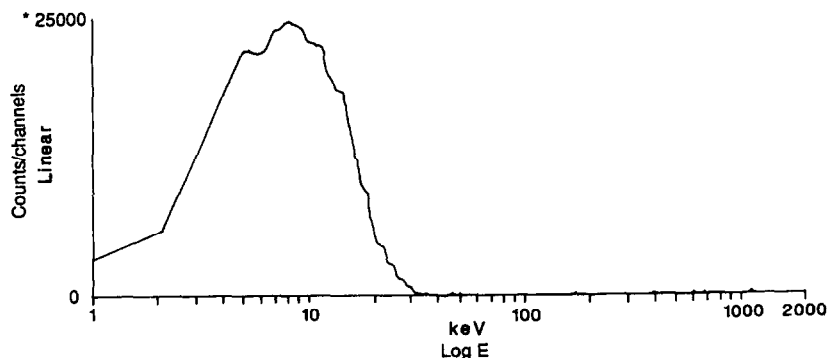

Fig. 5. Beta spectrum of the recovered off-gas from acid regeneration of a resin sample containing 13.5 nCi of ^{14}C and 3.5 nCi of ^{60}Co. *CPM value displayed is the maximum full scale count of the Y-axis.

advantage was obtained for LLW forms by dual regeneration. The procedure is also relatively free of entrained contaminants such as ^{60}Co, which is essential for analyzing reactor waste resins which contain copious quantities of this and other radionuclides which have the potential to interfere with the analysis of ^{14}C in LLRW.

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