CHARACTERISATION OF
ONTARIO POWER GENERATION'S SPENT RESINS

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ABSTRACT

This paper describes the results from a program undertaken to characterise spent resins produced from the nuclear operations of Ontario Power Generation. The resins were sampled from steel containers or liners located within storage structures at the Western Waste Management Facility (WWMF) in Tiverton, Ontario. At the time of sampling, the resins had been stored in these structures for durations ranging between 6.5 and 18 years. In addition, samples were also collected from in-station tanks at Darlington where resins have been stored for periods of up to 12 years. The sampled resins were physically, chemically and radiochemically characterised. For two of the resins sampled at the WWMF, results were correlated with characterisation data for both the liner headspace gases and the free water sampled from the bottom of the liners.

INTRODUCTION

There are twenty CANDU commercial power reactors in Ontario, Canada. These are located at Pickering, Bruce and Darlington. While the reactors are all owned by Ontario Power Generation (OPG), those at the Bruce site are operated by Bruce Power.

The operation of the power reactors produces a number of spent resin waste streams. These originate from clean-up systems in both light and heavy water circuits. In general, the spent resins are slurried out of the service columns, de-deuterated if they originate from heavy water service and then stored in in-station bulk resin storage tanks. Periodically, the spent resins are slurried out from the tanks into 3 m^3 steel shipping/storage containers or liners. These liners are shipped to OPG's Western Waste Management Facility (WWMF) in Tiverton, Ontario where they are stored within engineered 18 m^3 in-ground containers (designated IC-18s). Older resin liners are stored within 12 m^3 in-ground containers (designated IC-12s) and in above-ground structures called Quadricells (designated QCs). Resin liners are stacked four, six and two high within IC-12s, IC-18s and QCs, respectively.

The principal types of resin waste in storage are:

- Primary heat transport (PHT)[i] system resins,
- Moderator[ii] system resins,
- Heavy water upgrader[iii] resins, and
- CAN-DECON[iv] decontamination resins.

The spent resins generated from the moderator and PHT purification systems comprise the largest fraction of the radioactive resin waste. They are classified as intermediate level waste,

largely because of their C-14 content; the moderator resins, in particular, contain elevated levels of C-14.

Physical, chemical, radiochemical and microbiological characteristics of the spent resins are required to develop options for their long-term management. Physical characteristics are required to ascertain that the resins remain free flowing in order to facilitate their future retrieval. Chemical and radiochemical characteristics are required to classify the waste, assess gas generation potential during storage and disposal, and to perform safety assessments and design of the future repository. Microbiological characteristics are important for assessing corrosion and gas generation potential.

A program to sample resins was initiated in 2000 in order to develop characterisation data. As part of this program, spent resins were sampled from the topmost liners stored within seven ICs (three IC-18s in 2001 and four IC-12s in 2002) and one QC located at the WWMF [1]. At the time of sampling, the resins had been in storage at the WWMF for periods ranging between 6.5 and 18 years. In addition to sampling resins, gases present in the headspace and free water present at the bottom of the resin liners were also sampled.

In 2003, resin samples were also collected from in-station tanks at Darlington Nuclear Generating Station Units 1 and 3. The tanks contain spent moderator resin, which have accumulated since Units 1 and 3 started operating in December '90 and December '92, respectively.

Detailed findings from the physical, chemical and radiochemical characterisation of the resin samples collected are presented in this paper. The sampling methodology employed is also briefly discussed.

RESIN SAMPLING TECHNIQUE

Commercially available grain samplers were adapted for resin sampling. The sampler (see Fig. 1) consists of two polished concentric brass tubes; the tubes have registering slots, which are opened or closed by rotation of the inner tube. The outer tube has a conical tip to facilitate penetration. The sampler is approximately1.5 m long.

Sampling of resin from a liner contained within an IC is shown in Fig. 2. A concrete cap and a concrete shield were first removed from the storage structure to access the liner. This exposed the upper surface of the topmost liner with its various plugged openings. By unplugging the available openings as required, the headspace gases in each liner were monitored using a combustible gas meter, sampled and either purged with nitrogen or allowed to dissipate. The resin sampler was then inserted into the resin bed and a sample obtained.

Fig. 1   View of resin sampler with partly open compartments

Lead blankets were used to minimise dose uptake during sampling. The highest dose rate (unshielded) recorded on top of a resin liner was about 1200 mrem/h. The maximum dose rate, in contact with the resin sampler, was about 120 mrem/h.

Fig. 2   Resin sampling from a liner stored within an in-ground container

For sampling resin from the in-station storage tanks at Darlington, an overall probe length of approximately 4.5 m was required.   The 1.5 m sampler was, therefore, equipped with two extensions each approximately 1.5 m long.   For sampling, the probe was assembled piecewise with first, the sampler, and then, the extension pieces being lowered through a floor access into the 4 inch Schedule 40 pipe (this narrows down to 3 inch) located above the tank (see Fig. 3). This pipe normally houses an ultrasonic level transmitter probe, which can be removed along with the innermost 3 inch Schedule 40 pipe by unbolting the top flange plate. A funnel (for contamination control), equipped with an integral flange plate and a ring header for spraying water, was then bolted in place and the sampler introduced into the tank through the funnel opening.

During sampling, the tritium level in the room was about 0.02 MPCA[v]. The maximum field in contact with the sampler was about 100 mrem/h; the contact field decreased to 55 mrem/h after the sampler was placed inside an aluminum transportation sleeve. The fields at 0.3 m from the sleeve were about 10 mrem/h.
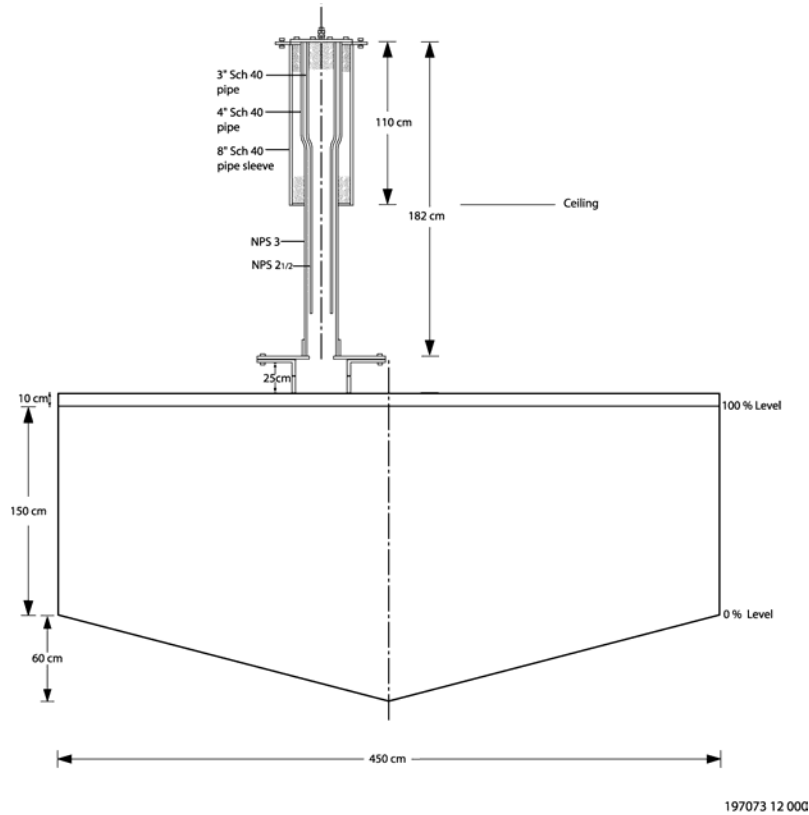
Fig. 3   Schematic of Darlington moderator resin storage tank

CHARACTERISTICS OF SPENT RESINS SAMPLED AT THE WESTERN WASTE MANAGEMENT FACILITY

Resin Liners Investigated and Their Contents

Table I presents a list of the resin liners, which were sampled during the 2001/2. Note the Following:

- The top liner within an IC is possibly exposed to significant fluctuations in ambient temperature. The severity of freeze-thaw cycling in the top liner is, however, likely to be much less than in the case of liners stored within the aboveground QCs. Other resin liners, stored lower within the ICs, probably experience stable above-zero temperatures year round.

- The storage duration of the sampled liners varied between 6.5 and 18 years. This period represents the duration between the shipment and the sampling dates. It does not, however, include the in-station storage period. Excluding decontamination resins, which are shipped soon after generation, the in-station storage period may extend beyond 5 years.

- All liners, except IC-1207, contain mixed bed resins. The IC-1207 liner contains CAN-DECON cation exchange decontamination resins.

- The dose rates recorded on top of the liners varied from 30 mrem/h for the mixed bed decontamination resin to 1200 mrem/h for the cation bed decontamination resin.

- The system origin, i.e., the plant system which generated the resin, shown in the last column of Table I, were surmised from the detailed assessment of the physical, chemical and radiochemical characteristics of the sampled resins. Based on existing records, these conditions were not known with certainty prior to sampling.

Table I   Resin Liners Investigated and Their Contents

Location of Liner	Station of Origin of Liner	Storage Duration (years)*	Type of Resin	Dose Rate (mrem/h)	System Origin
IC-1809	Pickering	9	Mixed Bed	50	Heavy water upgrader
IC-1834	Bruce A	7	Mixed Bed	150	Heavy water upgrader
IC-1208	Pickering	13	Mixed Bed	200	Heavy water upgrader
IC-1220	Pickering	10	Mixed Bed	1100	Heavy water upgrader
IC-1826	Pickering	6.5	Mixed Bed	450	Mixture of resins from PHT and moderator systems
QC-21	Bruce A	18	Mixed Bed	700	Mixture of resins from PHT and moderator systems
IC-1209	Pickering	12	Mixed Bed	30	CAN-DECON decontamination
IC-1207	Pickering	13	Cation Resin	1200	CAN-DECON decontamination

*storage period at WWMF, at the time of sampling.

Physical Characteristics

All sampled resins were free-flowing and showed no signs of agglomeration despite being in storage for up to 18 years. This observation is consistent with results from Brookhaven [2] where IRN-77 cation resins, irradiated in a sealed environment to a dose of 1.2×10^9 rad, did not experience any adverse effects (they congealed partially when irradiated under vented conditions). Note that the cumulative dose for spent OPG resins is not expected to exceed 10^8 rad.

A typical photomicrograph of the sampled mixed bed resin is shown in Fig. 4. The presence of both the cation and anion components is evident. The component resins typically differ in colour[vi] and size[vii]. The photomicrographs of the IC-1207 sample showed only one type of resin bead, consistent with the resin being a cation exchange resin.
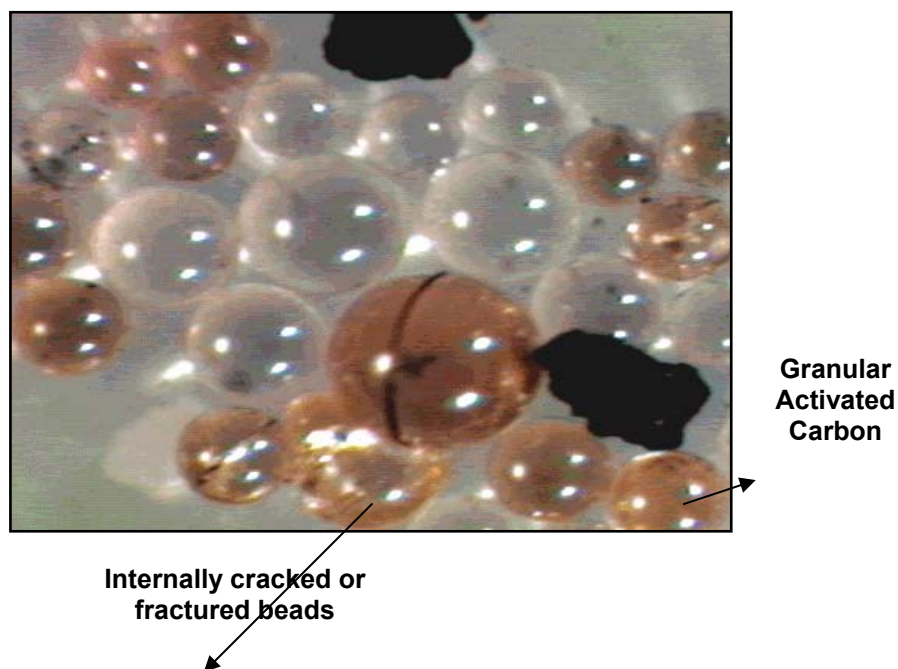
Fig. 4   A typical photomicrograph of resin sampled from the liner at WWMF

All samples, except the two decontamination resins, showed evidence of small amounts of granular activated carbon (GAC), in addition to the resin. The presence of GAC mixed with resin is of concern with respect to the potential for biogenic gas formation [3]. However, the fraction of GAC in these particular samples was relatively small. GAC is used for organics removal in the heavy water clean-up process. Historically, used GAC has not been rigorously segregated from the spent resins, with some GAC having been transferred to the in-station bulk spent resin storage tanks.

All sampled resins indicated signs of cracking (incidence of cracking in new resin beads is ≤ 5%); the severity of the cracking was, however, not quantified. Amongst the sampled liners, the resin in QC-21 has probably experienced the harshest freeze-thaw conditions. The presence of cracking in the other resins, which have likely experienced less harsh conditions and have been in storage for shorter periods, suggests other factors besides the severity of freeze-thaw conditions may influence cracking. These include·

- Cracking may occur from exposure to high temperatures, high radiation doses or to oxidising environments; in the case of moderator resins, cracking may arise from exposure to radiolytically produced deuterium peroxide, D_2O_2 [4].

- Anion resins, upon irradiation, release substantial amounts of free liquid [2].   The accompanying bead shrinkage may lead to cracking.

Chemical Characteristics

The chemical constituents of the resins were analysed to determine the loadings of the major cationic and anionic species. For this purpose, the IC-18 resins were microwave digested while the remaining samples were acid stripped. Although, the resin matrix is destroyed during

digestion, more representative results are obtained by acid stripping because of the larger sample size used. Induction Coupled Plasma-Mass Spectrometry (ICP-MS) was employed to analyse for the concentrations of over 20 elements. Halogen and nitrogen contents were determined using the neutron activation technique and the Kjeldahl method, respectively. The strippable levels of sulfur for the IC-18 samples were determined after stripping with tri-sodium phosphate (TSP). The overall results are summarised in Table II.

Table II Chemical Characteristics of Sampled Resins – A Summary

| Liner | Storage Period* (years) | Dose Rate (mrem /h) | Total Elemental Loading Mass % | Principal Contributors to Elemental Loading | Strippable Sulfur Loading | | Extent of Resin Capacity Utilised |
					Mass %	% of Original Sulfur Present	
IC-1809	9	50	4.2	Ca, Na, Mg, Fe	-	-	Likely exhausted
IC-1826	6.5	450	2.9	Ca, Na, K, Li	-	-	Likely exhausted
IC-1834	7	150	3.7	Fe, Ca, Ni, Na	-	-	Significant unused capacity
IC-1207	13	1200	3.5	Fe, S, Ni	0.91	10	Some unused capacity
IC-1208	13	200	2.1	S, Na, Ca, K	0.94	<32	Exhausted
IC-1209	12	30	1.0	S, Ni, Mn, Fe, K	0.53	19	Significant unused capacity
IC-1220	10	1100	2.1	S, Na, Ca, K	0.86	<32	Exhausted
QC-21	18	700	2.0	S, Gd, Li	1.1	39	Exhausted

* storage period at WWMF, at the time of sampling.

The total elemental loadings for the various sampled resins varied between approximately 1 and 4 %. As stated earlier, the elemental and radiochemical loading data for each sampled resin were used to identify the system origin for that resin, i.e., the plant system, which generated it. Thus, the dominant presence of iron on the IC-1207 resin is consistent with the resin having been used to regenerate iron-loaded solvents during the decontamination. Similarly, the dominant presence of gadolinium and lithium on the QC-21 resin suggests that it is a mixture of moderator and PHT resins because gadolinium is typically added to the moderator water for reactivity control, while LiOH is used in PHT systems for pH control.

The levels of strippable sulfur associated with IC-18 resins, as determined by stripping with TSP, were not reproducible and were substantially lower (generally << 1%) than the levels associated with the IC-12 and QC resins. This observation suggests that the strippable sulfur associated with the IC-18 resins may be dominantly in a non-sulfate form, because sulfate ions are known to be readily displaced from resins using TSP. This is consistent with the known fact, that radiolytic scission of sulfonic acid groups[viii] leads to the formation of soluble organic acids, (e.g., benzenesulfonic acids) which are subsequently oxidised radiolytically to sulfates [2]. It is conceivable that significant formation of sulfates may not have occurred yet in the IC-18 resins because of their younger age.

The levels of strippable sulfur associated with the various resins (excluding the IC-18 resins) varied approximately between 10 and 40 % of their original sulfur content. Thus, aging appears

to result in a significant loss of cation exchange capacity. The resulting sulfate ions would possibly displace other anions (such as carbonates) and potentially lead to C-14 releases.

The strippable sulfur level for IC-1207 was the lowest. This can be rationalised based on the fact that the resin is exclusively of the cation type while the remaining resins are of the mixed bed type and are constituted only of about one-third cation resin. For a given amount of self-irradiation dose, the percentage of sulfonic acid sites cleaved would be lower for a resin constituted only of the cation type. Although, estimates for the self-irradiation dose were not developed; a correlation may exist between the level of strippable sulfur and self-irradiation dose.

Given that the IC-1207 resin is constituted exclusively of cation resin, it follows that the strippable sulfur associated with this resin must be in a complexed cationic form. This is plausible because the resin is likely to contain residual levels of organic chelating agents (EDTA, oxalic and citric acids) used during the decontamination.

It was instructive to also examine the elemental loadings after converting the data into the equivalent anionic and cationic loadings. Charges for the various species were assigned to make the conversion. The anionic and cationic loadings were then compared with the typical values for cation and mixed bed capacities. On this basis, it was concluded that IC-1834, IC-1207 and IC-1209 had residual unused capacities while the remaining resins were essentially exhausted. The exhausted resins would be most susceptible to C-14 releases as a result of carbonate ion displacement by sulfate ions.

Radiochemical Characteristics

Radiochemical constituents of the resin samples were determined using gamma spectrometry and liquid scintillation counting. C-14 was measured in both its carbonate and non-carbonate (NC) forms. H-3 was measured in both its tritiated water (HTO) and non-tritiated water (non-HTO) forms. The carbonate form of C-14 and the HTO form of H-3 were obtained by acid stripping; combustion of the stripped resin provided values for the non-HTO form of H-3 and the NC form of C-14.

Radiochemical results are shown in Table III.   The H-3 results for IC-18 samples do not include the non-HTO contribution. The measured radiochemical activities are consistent with expectations based on the system or systems of origin for these resins and also with the previous, albeit, limited characterisation data for these resins. For example, Co-60 was observed to be the dominant gamma emitter on the IC-1207 resin; this along with the dominant presence of iron on this resin (noted earlier) is consistent with the IC-1207 resin having been used for chelant regeneration during the CAN-DECON PHT system decontamination. The relatively low value for C-14 activity of the IC-1207 resin is also consistent with the acidic process conditions during the decontamination: C-14 levels in the PHT system are significantly lower than in the moderator water and under the acidic conditions prevailing during a decontamination, the C-14 is likely released as $^{14}CO_2$.

Table III Radiochemical Characteristics of Sampled Resins

Nuclide	Activity at Measurement Time (Bq/m^3)							
	IC-1809	IC-1826	IC-1834	IC-1207	IC-1208	IC-1209	IC-1220	QC-21
Mn-54				<2.5E+07	<1.7E+06	<8.9E+04	2.2E+07	2.3E+07
Co-60	8.8E+07	9.5E+09	2.3E+09	3.9E+10	2.6E+09	6.9E+08	1.4E+10	1.9E+10
Zr-95						8.9E+06		
Nb-94				<1.8E+07	2.3E+06	3.3E+06	<2.1E+07	<2.4E+07
Sb-125	7.8E+06	2.7E+07	2.7E+07	6.1E+07	<5.0E+06	3.7E+07	<1.1E+08	<1.0E+08
Cs-134	1.3E+07	8.0E+04	8.5E+06	<1.2E+07	1.9E+07		1.6E+09	1.8E+08
Cs-137	1.7E+09	2.2E+10	5.1E+08	2.8E+08	4.6E+09	1.2E+08	2.0E+11	1.5E+11
Eu-154				<3.2E+07	<2.7E+06	1.5E+07	<4.2E+07	3.4E+08
Eu-152				9.1E+07	3.6E+06	2.3E+07	<4.7E+07	2.9E+09
Eu-155				2.1E+08	9.4E+06	7.0E+06	8.6E+08	7.9E+08
Gd-153				<2.3E+07	<2.8E+06	1.4E+06	<6.7E+07	<6.8E+07
Am-241	1.3E+06	5.4E+07	3.8E+07	1.3E+08	2.0E+06	6.3E+07	1.2E+08	1.2E+08
C-14	4.4E+09	1.3E+12	4.2E+09	7.2E+06	2.0E+11	3.0E+08	9.7E+10	5.2E+11
H-3[a]	2.7E+11	2.3E+09	1.4E+11	2.7E+10	1.8E+11	2.9E+10	2.8E+10	1.3E+11

a   The non-HTO form of H-3 was not measured for IC-18 samples.

The percent of H-3 in the non-HTO form and the percent of C-14 in the NC form for both resins are shown in Table IV:

Over the storage period, a significant proportion of tritium (as observed, particularly in the cases of IC-1220 and QC-21) appears to have become incorporated within the resin matrix and hence is not released by acid stripping. However, C-14 does not appear to be significantly bound within the resin matrix except in two cases, namely, the IC-1209 and QC-21 resins. Overall, the proportion of tritium in non-HTO form is much greater than the proportion of C-14 in NC form. This may arise from the greater mobility of H-3 in the resin matrix.

The non-HTO levels of tritium were also measured in the headspace gas present within the liners. This tritium would be associated with both the hydrogen gas and methane present in the headspace gas. There appeared, however, to be no correlation between the level of non-HTO tritium in the resin and that in the headspace gases.

The NC form of C-14 was also measured in the headspace gas present within the liners. This C-14 would be associated principally with carbon dioxide, methane and carbon monoxide; these gases were detected to varying extents in the headspace gas. In general, as with tritium, there appeared to be no correlation between the concentration of the non-carbonate C-14 in the resin and that present in the headspace gases.

Table IV Non-HTO Form of Tritium and Non-Carbonate Form of
Carbon-14 in Sampled Resin

Liner	Percent of Tritium in Non-HTO Form	Percent of C-14 in Organic Form
IC-1809	-	2.5
IC-1826	-	0.1
IC-1834	-	2.5
IC-1207	3	-
IC-1208	24	0.3
IC-1209	25	13
IC-1220	72	0.1
QC-21	53	26

Relationship between Resin Characteristics and Characteristics of Free Water

It is interesting to compare the characteristics of resins with those of the associated free waters[ix]. The characteristics of free water sampled from the bottom of the IC-1207 and QC-21 resin liners are summarised in Table V.

Sulfur was present at comparable levels in both the IC-1207 and QC-21 water samples. The presence of sulfur in the water is consistent with the significant levels of strippable sulfur associated with both these resins. Sulfur in the QC-21 water can arise only from the radiolytic scission of sulfonic acid groups. In the case of the IC-1207 free water, it may also arise from the residual sulfur-bearing inhibitor (Rodine 31A) used during the CAN-DECON decontamination.

The presence of sulfur as sulfate ions may be partly responsible for the low pH observed in both water samples. For instance, the sulfur level of 140 μg/g in the IC-1207 water would correspond to a sulfuric acid concentration of 4.4 x 10^{-3} moles/L. If this acid is fully dissociated, a pH of 2.06 would result rather than the observed value of 3.0.

Iron and Co-60 were, respectively, the dominant element and radionuclide present in the IC-1207 water. This and the negligible C-14 activity in the water are consistent with the IC-1207 resin being a used CAN-DECON cation exchange resin. The presence of iron and Co-60 in solution, rather than being exchanged on the resin, is surprising considering that the resin is not fully spent. Based on the Co-60 specific activity (Co-60 activity per mass of iron) values, it can, however, be reasoned[x] that the iron in the free water originates, not from the resin degradation products, but from corrosion of the liner steel material.

The presence of significant levels of total organic carbon (TOC) in the water is consistent with the generation of resin degradation products during storage. The lower TOC level in the QC-21 water compared to that in the IC-1207 water (a factor of 3-4) may be explained by the lower cation content of the QC-21 resin (this resin contains only about one third of the cation content of the IC-1207 resin).   Residual CAN-DECON reagents (organic chelating acids EDTA, citric acid and oxalic acids) present in the resin bed may also be a contributor to the TOC in the case of the IC-1207 water.

The conductivity of the QC-21 water was a factor of ~9 lower than that of the IC-1207 water. This observation is consistent with the significantly lower elemental loading of the QC-21 water (220 ppm versus 1100 ppm for the IC-1207 water).

Table V Characteristics of Free Water Sampled from the Bottom of Resin Liners

Parameter	IC-1207	QC-21
Total Chemical Loading (µg/g)	1100	220
Principal Elements	Fe, S, Si	S, B, Li
Iron Loading (µg/g)	870	1.2
Sulfur Loading (µg/g)	140	110
Co-60 (nCi/kg)	1.9E+05	1.0E+02
Cs-137 (nCi/kg)	2.7E+03	5.7E+03
C-14 (nCi/kg)	-	9.3E+02 (all in NC form)
H-3 (nCi/kg)	5.7E+05	3.8E+06
pH (measured)	3.0	3.15
pH (calculated)	2.06	2.17
Conductivity (mS/m)	850	90
Total Organic Carbon (µg/g)	1850	455

CHARACTERISTICS OF SPENT RESINS SAMPLED FROM IN-STATION STORAGE TANKS AT DARLINGTON NUCLEAR GENERATING STATION

Samples were collected in 2003 from storage tanks at DNGS Units 1 and 3 containing spent moderator resin. The extended sampling probe was utilised. The Unit 1 tank contained about 11 m^3 of resin on December 2002 (the contents in the tank were at the 33 % level; see Fig. 3), of which 9.7 m^3 consisted of moderator resins, the balance being end shield and liquid zone control system purification resins. No resin shipments have taken place from this tank since the Unit 1 start-up in December 1990. The Unit 3 tank had accumulated approximately 17 m^3 resin since its start-up date in December 1992 (the tank contents in February 2003 were at the 62% level). The tank contained approximately 15.7 m^3 of moderator resins, the balance consisting of end shield and liquid zone control system resins. Approximately 4.2 m^3 of resin was transferred out of this tank and shipped in 1998. Because the resin outlet nozzle is located at the bottom of the tank, the oldest resin would have been discharged.

The samples drawn from the Units 1 and 3 tanks filled six and nine compartments of the sampler, respectively. Resin from each compartment was segregated and analysed separately to determine the variation in resin characteristics with depth in the tanks. Table VI summarises the mass and dose rate data for these sub-samples.   Note the significant variation in radiation field or activity with depth in the tanks.

Table VI Mass and Dose Rate Data for Sampled Resins

Sub-sample #	Unit 1 Tank		Unit 3 Tank	
	Mass of Sub-sample (g)	Contact Dose Rate* (mrem/h)	Mass of Sub-sample (g)	Contact Dose Rate* (mrem/h)
1 (bottom compartment)	45.6	4	41.5	38
2	55.0	29	53.8	1
3	58.6	75	45.1	6
4	60.2	170	48.3	25
5	60.5	280	52.3	17
6	55.7	140	45.2	18
7	-	-	50.1	106
8	-	-	42.6	46
9	-	-	42.9	97

*   Dose rates were recorded in contact with sample bottle.

Distribution in Age of Resin within the Tanks

It was desirable to estimate the age distribution of resin in the tank in order to suitably decay correct the measured radioactivity data. Estimated age distributions of the sampled resins are shown in Table VII.

The volume of resin above the centre of each sampler compartment was estimated considering the resin levels in the Units 1 and 3 tanks to be at the 32 % and 61% levels, respectively (i.e. water above the resin bed was assumed to represent 1% of the level in the tanks). These resin levels were consistent with the number of sampler compartments filled in each case. This assessment was based on the physical dimensions and location of the sampler within the tank during sampling (as shown in Fig. 3, the axis of the inserted sampler would be laterally displaced from the vertical axis of the tank), and the dimensions and shape of the tank.

Table VII Estimated Age Distribution of Resin Sampled from Storage Tanks

Compartment Number	Unit 1 Tank		Unit 3 Tank	
	Volume of Resin Above Centre of Compartment (m³)	Storage Duration of Resin at Centre of Compartment (years)	Volume of Resin Above Centre of Compartment (m³)	Storage Duration of Resin at Centre of Compartment (years)
1 (Bottom)	10.6	11.9	17.4	10.2
2	10.0	11.1	16.8	9.9
3	8.9	10.0	15.8	9.3
4	6.7	7.5	13.6	7.9
5	4.5	5.0	11.3	6.6
6	2.2	2.5	9.1	5.3
7			6.9	4.0
8			4.6	2.7
9			2.4	1.4

The resin volumes in the tanks, corresponding to 32 % and 61% levels, were estimated to be 10.7 and 17.6 m³, respectively. Based on the overall resin storage duration of 12 years for the Unit 1 tank and 10.2 years for the Unit 3 tank, and taking into account the volume of discharged resins, the average resin accumulation rates in these tanks were estimated to be 0.9 and 1.7 m³/y, respectively. These rates were then applied, respectively, to the volumes shown in Table VII (Columns 2 and 4) to estimate the corresponding age of resin sub-samples (see Columns 3 and 5 in Table VII).

Chemical Characteristics

The elemental compositions of resin sampled from DNGS Units 1 and 3 tanks are shown in Tables VIII and IX, respectively. As before, these compositions were obtained by acid stripping. For each sub-sample, the copper/zinc ratio, the major elements in decreasing order of importance and the total elemental loading are also shown.

The copper/zinc ratios, with two exceptions (sub-samples 1 and 2 from Unit 1 tank), were generally consistent with the corrosion of the brass material of construction of the sampler[xi]. Evidently, the corrosion occurred despite the sampler surfaces having been nickel coated. The corrosion led to significant levels of nickel being also present in the sub-samples. Considering copper, zinc and nickel to be extraneous to the sample, the elemental loadings for both resins were dominated by lithium, boron, gadolinium, sulfur and iron and ranged between 0.4 to1.7 wt % (4.3E+03 to 1.7E+04 ppm).

Gadolinium and Gd-153 (see next section) were present in all sub-samples; the correlation between the gadolinium concentration and the Gd-153 activity was not as strong as one might expect.

Table VIII Elemental Composition of Spent Resin Sampled from
Darlington NGS Unit 1 Moderator Tank

Element/ Sub-sample	Elemental Composition (µg/g of 'as is' resin)					
	1	2	3	4	5	6
Boron	2.0E+03	1.5E+03	1.8E+02	1.0E+02	1.0E+02	2.4E+02
Copper	4.1E+00	7.1E+00	1.0E+03	5.6E+02	1.5E+03	1.9E+01
Gadolinium	1.9E+03	9.5E+03	1.3E+04	1.2E+04	8.0E+03	2.3E+03
Iron	6.9E+01	7.3E+01	5.1E+02	7.5E+02	3.7E+03	3.0E+02
Lithium	4.2E+03	6.5E+02	1.0E+03	5.7E+02	4.6E+02	2.1E+02
Nickel	1.7E+03	1.4E+03	1.0E+04	6.5E+03	1.0E+04	1.7E+03
Sulfur	7.9E+02	4.5E+02	6.9E+02	5.2E+02	8.2E+02	8.5E+02
Copper/Zinc	0.4	0.2	2.0	2.0	2.0	1.4
Major elements	Li, B, Gd, Ni, S	Gd, B, Ni, Li, S	Gd, Ni, Li, Cu, S	Gd, Ni, Fe, Li, Cu, S	Ni, Gd, Fe, Cu, S	Gd, Ni, S, Fe, B
Total loading	1.2E+04	1.4E+04	2.8E+04	2.1E+04	2.6E+04	6.0E+03
Total loading (excl Ni, Cu, Zn)	1.0E+04	1.3E+04	1.6E+04	1.4E+04	1.4E+04	4.3E+03

Table IX Elemental Composition of Spent Resin Sampled from Darlington NGS Unit 3
Moderator Tank

Element/ Sub-sample	Elemental Composition (µg/g of 'as is' resin)								
	1	2	3	4	5	6	7	8	9
Boron	8.2E+02	1.5E+03	2.9E+03	1.3E+03	1.5E+03	2.6E+02	1.2E+02	1.4E+02	6.1E+01
Copper	5.8E+03	9.4E+01	8.3E+03	9.6E+03	1.9E+02	2.6E+03	5.7E+03	6.6E+03	3.2E+03
Gadolinium	9.7E+03	6.0E+03	3.8E+03	3.5E+03	2.1E+03	2.5E+03	6.2E+03	8.2E+03	6.4E+03
Iron	2.2E+03	9.0E+02	5.1E+02	2.0E+03	1.3E+03	2.4E+03	8.4E+02	2.8E+03	2.1E+03
Lead	1.8E+02	3.0E+01	8.7E+01	1.2E+02	8.2E+02	2.9E+02	2.0E+02	1.3E+02	5.0E+01
Lithium	4.3E+02	1.7E+02	2.8E+02	1.2E+02	8.7E+01	8.3E+01	2.2E+02	1.0E+02	1.3E+01
Nickel	1.1E+04	9.0E+03	8.6E+03	1.3E+04	5.9E+03	8.8E+03	1.0E+04	9.7E+03	9.1E+03
Phosphorus	3.3E+02	3.6E+02	3.2E+02	2.6E+02	1.5E+02	2.4E+02	2.9E+02	2.1E+02	2.5E+02
Sulfur	2.2E+03	1.0E+03	1.7E+03	1.8E+03	1.5E+03	1.6E+03	2.3E+03	2.3E+03	2.5E+03
Zinc	3.3E+03	7.1E+01	4.2E+03	5.2E+03	1.1E+02	1.5E+03	3.3E+03	3.9E+03	2.1E+03
Copper/ Zinc	1.8E+00	1.3E+00	2.0E+00	1.8E+00	1.6E+00	1.7E+00	1.7E+00	1.7E+00	1.6E+00
Major elements	Ni, Gd, Cu, Zn, Fe, S	Ni, Gd, B, S, Fe, P	Ni, Cu, Zn, Gd, B, S	Ni, Cu, Zn, Gd, Fe, S, B	Ni, Gd, S, B, Fe, Pb	Ni, Cu, Gd, Fe, S, Zn	Ni, Gd, Cu, Zn, S, Fe	Ni, Gd, Cu, Zn, Fe, S	Ni, Gd, Cu, S, Fe, Zn
Total	3.7E+04	2.0E+04	3.1E+04	3.7E+04	1.4E+04	2.0E+04	3.0E+04	3.4E+04	2.6E+04
Total (excl Ni, Cu, Zn)	1.7E+04	1.0E+04	9.8E+03	9.2E+03	7.6E+03	7.5E+03	1.0E+04	1.4E+04	1.2E+04

Observed lithium levels are attributable to the presence of small quantities of end shield resins (lithium and lithiated resins are used in the end shield purification system) in the tanks. The distribution of lithium with depth in the tanks depend on when these resins were introduced into the tanks and, in the case of the Unit 3 tank, also on the disturbance associated with the discharge of resin from the tank in March 1998.

Boron is generally present at a higher level at the bottom (older resin) of both tanks. This is consistent with the use of boron in the moderator system during plant commissioning to control excess core reactivity. The observed trend in boron levels with depth suggests that mixing may not occur to a significant extent in the tank.

It is surprising that the observed levels of strippable sulfur in both tanks are generally constant with depth or alternately with the age of the resin. The levels of strippable sulfur in the Units 1 and 3 tanks were 690±167 ppm and 1900±470 ppm, respectively; it is not clear why the levels of strippable sulfur in the Unit 3 tank are about 3 fold higher. The levels in both tanks, however, are lower than those measured in older (13-18 years not including in-station storage duration) resins sampled from IC-12 and QC liners (5,300 to 11,000 ppm).

The presence of iron is expected based on the large surface area of carbon steel shielding used in the end shield system. It is likely that most of the observed iron is associated with the end shield cooling system purification resins that are also stored in these tanks. The contribution of iron from moderator resins is expected to be small, since that system is largely comprised of stainless steels and zirconium alloys. The levels in both tanks vary widely.

Radio-chemical Characteristics

The radiochemical activities of the sampled resins, after decay correction (according to the storage durations in Table VII), are shown in Table X. Because the radioactivity data varied

randomly with depth in the tank, they are presented in the form of Log Mean[xii] (LM) and Log Dispersion[xiii] (LD) values.

Radiochemically, moderator resins are expected to contain only activation product radionuclides. Typically, however, fission products such as Cs-137, Cs-134, Eu-152 and Eu-154 are also observed as a result of the fission of trace levels of uranium contained in the Zircalloy calandria tubes and possibly also from cross-contamination from equipment used to slurry transfer the spent resins into storage tanks. The activation product radionuclides of most interest are Co-60, Gd-153 and C-14.

In general, the radiochemical characteristics of the resin in both tanks are very similar. The Co-60, Cs-137, C-14 and H-3 activity concentrations are generally consistent with their historic values. Most of the C-14 activity is present in acid strippable form; the C-14 present in NC form is significantly lower than the values for the resins sampled at the WWMF. Despite the similar LM activity values for resins in both tanks, the LM value for the C-14/Co-60 scaling factor[xiv] differed significantly between resins in the two tanks.

LD values were the highest for Gd-153 amongst the various radionuclides detected. The large dispersion can be attributed to resins arising from both normal operation as well as from gadolinium pull operations being stored in the tanks. Following gadolinium pull, low levels of gadolinium (~1 ppm) may persist in the moderator water after the reactor becomes critical. Activation of Gd-152 results in the formation of Gd-153.

Table X   Radiochemical Characteristics of Resins Sampled from DNGS Spent
Moderator Resin Storage Tanks

Nuclide	Resin From Unit 1 Tank		Resin From Unit 3 Tank	
	Log Mean (Bq/kg)	Log Dispersion	Log Mean (Bq/kg)	Log Dispersion
Mn-54	6.1E+08	5.4E+00	4.6E+07	5.7E+00
Co-60	5.2E+07	4.3E+00	5.0E+07	2.9E+00
Sb-125	2.5E+06	-	1.6E+06	2.2E+00
Cs-134			2.9E+05	2.5E+00
Cs-137			3.8E+04	2.7E+00
Eu-152	5.4E+05	5.6E+00	2.4E+06	7.1E+00
Eu-154			9.2E+05	3.2E+00
Gd-153	2.1E+11	1.4E+01	5.0E+10	1.1E+01
C-14	2.7E+09	3.7E+00	4.4E+09	3.6E+00
H-3	1.0E+08	4.7E+00	3.6E+08	1.1E+00
% C-14 (NC)	1.2E-01	1.9E+00	8.6E-02	3.2E+00
C-14/Co-60	5.2E+01	3.2E+00	8.8E+01	2.3E+00

CONCLUSIONS

Resins sampled from dewatered shipping liners were free-flowing and indicated no signs of agglomeration despite being in storage for up to 18 years. However, signs of bead cracking were evident in all samples. Because of incomplete information, the station systems from which the resins originated were not known with certainty, prior to sampling. Their origin was, however, identified based on the measured chemical and radiochemical characteristics. The total elemental loadings for the various sampled resins varied between approximately 1 and 4 % on a mass basis. In addition to the signature elements for each type of resin, significant levels of strippable sulfur were also observed in all sampled resins. These represented between 10 and 40 % of the original sulfur present as sulfonic acid groups on the cation resin component.

The presence of strippable sulfur is attributed to the radiolytic degradation of the cation resins, which ultimately leads to the formation of sulfate ions and other resin degradation products. These may possibly displace other anions such as carbonate from the resins leading to potential C-14 releases. The formation of sulfate ions leads to low pH (a pH of approximately 3 was observed in two cases) in the free water associated with the resins further mitigating against the retention of C-14 carbonate. The radiochemical characteristics indicated that, in some cases, significant levels of tritium and C-14 had become incorporated within the resin matrix as non-HTO tritium and non-carbonate C-14, respectively. The percent levels of non-HTO tritium and non-carbonate C-14 did not correlate with the corresponding levels in the headspace gases.

Compared to the mostly dewatered resin samples collected from the shipping liners, the samples collected from the in-station tanks represent resins which have been stored, immersed in water, for durations of up to 12 years. These resins originated mostly from the moderator system and were generated during both normal and gadolinium pull operations. The elemental loadings ranged between 0.4 and 1.7 % on a mass basis, which is significantly lower than the resins sampled from IC-12 and QC liners. In addition to being loaded with the characteristic signature elements, namely, boron, gadolinium and iron (lithium was also present as a result of lithiated end-shield resins having been introduced into the tanks), the resins also contained up to 2500 ppm of strippable sulfur. In both tanks, the levels of strippable sulfur did not vary significantly with depth or the age of the stored resin. The levels are, however, significantly lower than those measured in older (13-18 years not including in-station storage duration) resins sampled from IC-12 and QC liners (5,300 to 11,000 ppm). It is conceivable that cation resins stored under water experience less radiolytic degradation because the shielding effect of water would result in less deposited dose. As expected, C-14 was present at an elevated level in the sampled resins. In contrast to the non-carbonate levels of C-14 in resins sampled from the IC and QC liners, the non-carbonate C-14 levels in the moderator resins were essentially negligible.

ACKNOWLEDGEMENTS

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FOOTNOTES

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[i] The PHT system in a CANDU plant refers to the heavy water coolant circuit that includes the fuel channels i.e., the pressure tubes with fuel bundles located inside them.

[ii] `The heavy water moderator is contained within the calandria vessel. This vessel is a cylindrical horizontal shell enclosed at each end with integral endshields and spanned axially by several hundred (380 and 480 depending on the unit) calandria tubes. The fuel channels are located within the calandria tubes, separated by a carbon dioxide filled, recirculated gas annulus.

[iii] The heavy water upgrader system is used to process downgraded heavy water originating from the PHT and moderator systems.

[iv] CAN-DECON refers to a regenerative process for decontaminating the PHT system using organic chelating acids.

[v] MPCA denotes Maximum Permissible Concentration in Air

[vi] Cation resins are usually darker in colour than anion resins because of the sulfonation process used to functionalize them; in some mixed beds, the colour difference may be nearly indiscernible, while in others, the colour differences are obvious. Cation resin can range from pale amber to black, while anion can range from colourless to dark amber.

[vii] The mean effective size of resin beads is 0.3 to 0.7 mm; on average, cation beads are slightly larger than anion beads, although their size ranges overlap greatly.

[viii] The sulfonic acid group is attached directly to the phenyl group (phenyl-SO_3H).

[ix] Because of the design limitations, about 2 inch of water remains at the bottom of the liner after the resin is dewatered.

[x] If the iron in the free water arises from resin degradation products, then one would expect the Co-60 specific activity in the water to be comparable to that in the resin. If the iron in the free water originates from liner corrosion, then the specific activity of Co-60 in the water should be significantly lower than the value for the resin.

[xi] The composition of yellow brass is typically 62-68 % copper and 38-32 % zinc.

[xii] LM is equivalent to the geometric mean.

[xiii] LD is calculated by estimating the standard deviation of log of the data and then taking its antilog. For a lognormal distribution, the 68.3 % confidence limits are defined by LM/LD and LM*LD.

[xiv] A scaling factor refers to the ratio between a Difficult-to-Measure radionuclide and an Easy-to-Measure radionuclide.