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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.

1.0 INTRODUCTION

The operation of CANDU power reactors produces a number of spent resin waste streams which 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 within 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) system resins,
- Moderator system resins,
- Heavy water upgrader resins, and
- CAN-DECON[1] decontamination resins.

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

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.

Physical, chemical, radiochemical and microbiological characteristics of the spent resins are required to develop options for their long-term management. As part of a program, initiated in 2000, to develop characterisation data, 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]. In addition, headspace gases and free water present at the bottom of the resin liners were also sampled. At the time of sampling, the resins had been in storage for periods ranging between 6.5 and 18 years. In 2003, samples were also collected from in-station, spent moderator resin storage tanks at Darlington Units 1 and 3. The tanks had accumulated resins since Units 1 and 3 started operating in December ‘90 and December ‘92, respectively.

Detailed findings from the characterisation of the resin samples are presented in this paper.

2.0 RESIN SAMPLING TECHNIQUE

Commercially available grain samplers were adapted for resin sampling. The sampler (see Figure 1) consists of two concentric tubes with 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 Figure 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.

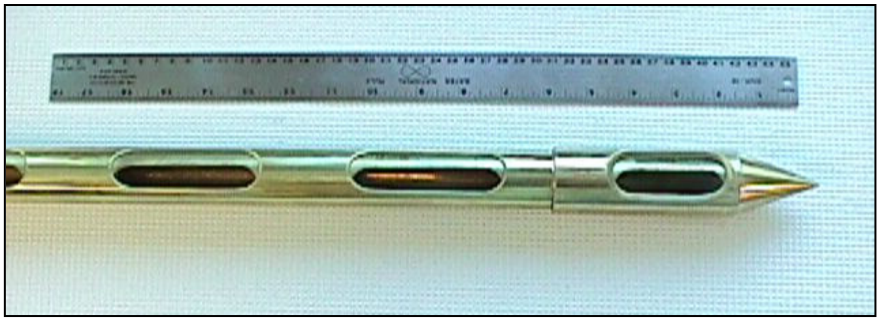

Figure 1. View of Resin Sampler with Partly Open Compartments

Lead blankets were used to minimise dose uptake during sampling. The highest dose rate (unshielded) recorded on top of a resin liner was about 1,200 mRem/h. The maximum dose rate in contact with the resin sampler was about 120 mRem/h.

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. When 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 Figure 3). This pipe normally houses an ultrasonic level transmitter probe, which was 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.

Figure 2. Resin Sampling from a Liner Stored Within an In-Ground Container

During sampling, the tritium level in the room was only about 0.02 MPCA[2]. The maximum field in contact with the sampler was about 100 mR/h.

3.0 CHARACTERISTICS OF SPENT RESINS SAMPLED AT THE WWMF

3.1 Resin Liners Investigated and Their Contents

Table 1 presents a list of the resin liners, which were sampled during the 2001/2. Note the following:

- The top liner within an IC is exposed to significant extremes in ambient temperature. The severity of freeze-thaw cycling in the top liner is, however, likely to be much less than for

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[2] MPCA denotes Maximum Permissible Concentration in Air

liners stored within the aboveground QCs. The lower resin liners within each IC experience stable above-zero temperatures year round.

- The storage duration of the sampled liners varied between 6.5 and 18 years. This represents the duration between the station shipment and the sampling dates and does not include the in-station storage period. The latter may exceed 5 years except in the case of CAN-DECON resins, which are shipped soon after generation.

- All liners, except IC-1207, contain mixed bed resins. The IC-1207 liner contains CAN-DECON cation exchange decontamination resins. The dose rates on top of the liners varied from 30 mR/h for the mixed bed CAN-DECON resin to 1,200 mR/h for the cation bed CAN-DECON resin.

- The system origin (last column of Table 1) for each sampled resin was deduced from a detailed assessment of its characteristics. Based on existing records, origin of the spent resins was not known with certainty prior to sampling.

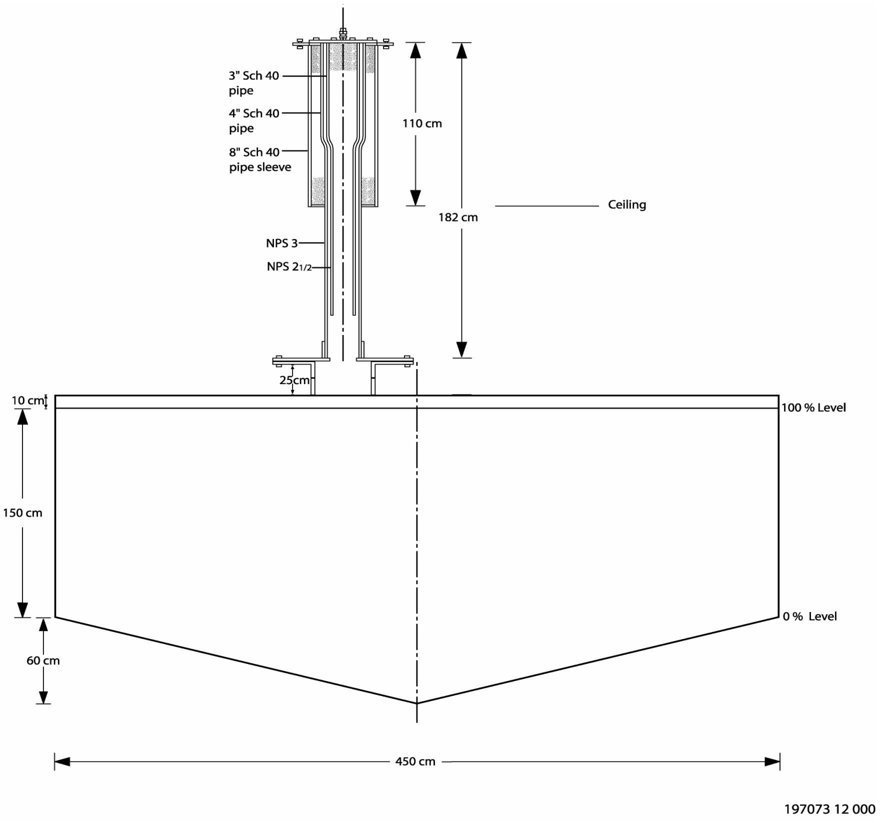

Figure 3. Schematic of Darlington Moderator Resin Storage Tank

Table 1 Resin Liners Investigated and Their Contents

Location of Liner	Station of Origin of Liner	Storage Duration (years)*	Type of Resin	Dose Rate (mR/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 when resin was sampled.

3.2 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 findings at Brookhaven [2] where IRN-77 cation resins, irradiated in a sealed environment to a dose of 1.2×10^9 rad, experienced no 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 Figure 4. The presence of both the cation and anion components is evident. The component resins typically differ in colour[3] and size[4]. The photomicrographs of the IC-1207 sample showed only one type of resin bead, consistent with the resin being a cation exchange resin.

All samples, except the two CAN-DECON resins, also showed evidence of small amounts of granular activated carbon (GAC). This 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

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[3] 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.

[4] 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.

in storage for shorter periods, suggests other factors besides the severity of freeze-thaw conditions may influence cracking. These include:

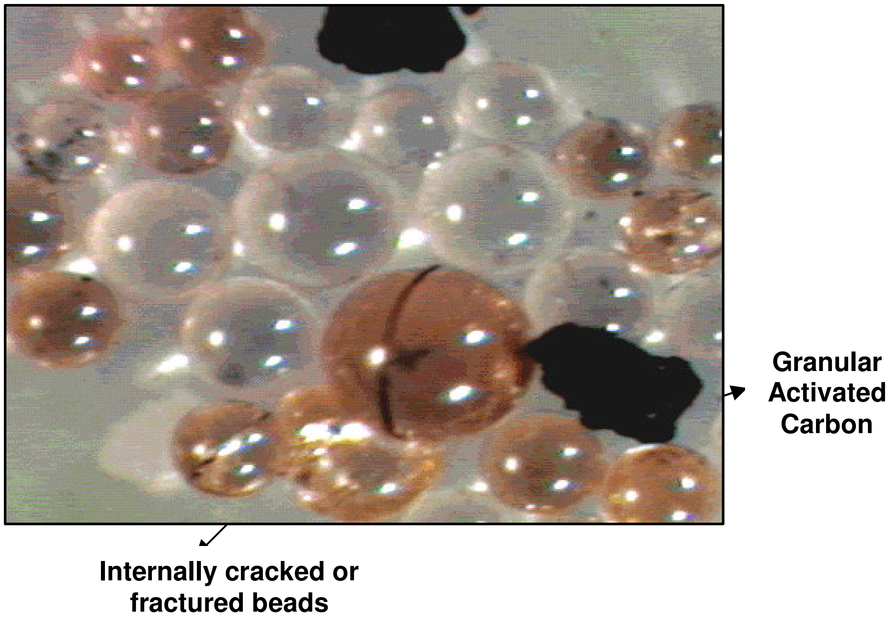

Figure 4. A Typical Photomicrograph of Resin Sampled from the Liner at WWMF

- 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.

3.3 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. Sulfur levels for the IC-18 samples were determined after stripping with tri-sodium phosphate (TSP). The overall results are summarised in Table 2.

The total elemental loadings for the various sampled resins varied between approximately 1 and 4 %. 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 - gadolinium is typically added to moderator water for reactivity control, while LiOH is used for pH control in PHT systems.

Table 2 Chemical Characteristics of Sampled Resins – A Summary

Liner	Storage Period* (years)	Dose Rate (mR/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	1,200	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	1,100	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 when sampled.

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 found in the IC-12 and QC resins by acid stripping. 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[5] 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 sampled resins (excluding the IC-18 resins) varied approximately between 10 and 40 % of their original sulfur content. Some of the strippable sulphur on the IC-1207 resin may, however, be attributed to the possible use of Rodine 31 sulfur-bearing inhibitor during the decontamination. Similarly, some of the strippable sulphur on the IC-1208 and IC-1220 resins may in fact arise from the possible use of service water for slurrying spent resins into storage tanks (the presence of Na, Ca and K suggests that service had been used; service water is also expected to contain sulphate anions). These

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

factors must be considered in order to derive a correlation between the level of strippable sulfur and self-irradiation dose. Unfortunately, such a correlation was not developed. The data in Table II does, however, suggest the existence of such a correlation considering that the high activity QC-21 resin, which had been in storage the longest, also had the highest level of strippable sulphur loading.

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) in spent mixed bed resins and potentially lead to C-14 releases.

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.

3.4 Radiochemical Characteristics

Radiochemical constituents of the resin samples were determined using gamma spectrometry and liquid scintillation counting. 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-carbonate (NC) form of C-14 and the non-HTO form of H-3.

Radiochemical results are shown in Table 3. The H-3 results for IC-18 samples do not include the non-HTO contribution. The measured radiochemical activities of the various resins are consistent with expectations based on their service conditions and their previous, albeit, limited characterisation data. 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 solvent regeneration during the decontamination. The relatively low value for C-14 activity of the IC-1207 resin is also consistent with the acidic process conditions during a CAN-DECON; under such conditions, the C-14 is likely released as $^{14}CO_2$.

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 4:

- Over the storage period, a significant proportion of H-3 (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 H-3 in non-HTO form is greater than the proportion of C-14 in NC form. This may be attributed to the greater mobility of H-3 in the resin matrix.

- The non-HTO levels of H-3 were also measured in the headspace gas present within the liners. This H-3 would be associated with both hydrogen and methane present in the headspace gas. Possibly because of uncertainty in the data, there appeared to be no correlation between the level of non-HTO H-3 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 NC form of C-14 in the resin and that present in the headspace gases.

Table 3 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.

Table 4 Non-HTO Form of H-3 and NC 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

3.5 Relationship between Resin Characteristics and Characteristics of Free Water

The characteristics of free water[6] sampled from the bottom of the IC-1207 and QC-21 resin liners are summarised in Table 5.

Table 5 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

- 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. 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 4.4×10^{-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 was the dominant element and Co-60 the dominant radionuclide present in the IC-1207 water. This is consistent with the IC-1207 resin being a spent 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 (activity per mass of iron) values for the water and the resin, it was reasoned[7] that the free water iron originated from corrosion of the liner steel and not from the resin degradation.

- 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 higher TOC level in

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

[7] 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.

the case of the IC-1207 resin (a factor of ~4 compared to the QC-21 resin) can be attributed partly to the presence of residual CAN-DECON reagents (organic chelating acids EDTA, citric acid and oxalic acids) in the resin bed and partly because the IC-1207 resin is 100% cationic whereas the mixed bed QC-21 resin contains only about one third cationic resin.

- 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).

4.0 CHARACTERISTICS OF SPENT RESINS SAMPLED AT DARLINGTON

Spent moderator resin samples were collected in 2003 from storage tanks at DNGS Units 1 and 3 using an extended sampling probe.

- The Unit 1 tank contained about 11 m^3 of resin (the tank contents were at the 33 % level; see Figure 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 contained about 17 m^3 resin since its start-up date in December 1992 (the tank contents 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 shipped from this tank in 1998. Because the resin outlet is located at the bottom of the tank, the oldest resin would have been discharged first.

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 6 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 6 Mass and Dose Rate Data for Sampled Resins

Sub-Sample #	Unit 1 Tank		Unit 3 Tank	
	Mass of Sub-Sample (g)	Contact Dose Rate* (mR/h)	Mass of Sub-Sample (g)	Contact Dose Rate*(mR/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.

4.1 Age Distribution of Resin within Tanks

Age distributions of the sampled resins were estimated (see Table 7) in order to suitably decay correct the measured radioactivity data.

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 Figure 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 7 Estimated Age Distribution of Resin Sampled from Storage Tanks

Compartment Number	Unit 1 Tank		Unit 3 Tank	
	Volume of Resin Above Centre of Compartment (m^3)	Storage Duration of Resin at Centre of Compartment (years)	Volume of Resin Above Centre of Compartment (m^3)	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 volumes of resin in the Units 1 and 3 tanks were estimated to be 10.7 and 17.6 m^3, respectively. Based on the overall storage duration of 12 years in the Unit 1 tank and 10.2 years in the Unit 3 tank, and taking into account the volume of discharged resins, the average resin accumulation rates were estimated to be 0.9 and 1.7 m^3/y, respectively. Based on these rates and the volumes shown in Table 7, the corresponding ages of resin sub-samples were estimated as shown.

4.2 Chemical Characteristics

The elemental compositions of resin sampled from DNGS Units 1 and 3 tanks are shown in Tables 8 and 9, 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[8]. 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; there did not appear to be a strong correlation between the gadolinium concentration and the Gd-153 activity.

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.

4.3 Radio-chemical Characteristics

The radiochemical activities of the sampled resins, after decay correction (according to the storage durations in Table 7), are shown in Table 10. Because the radioactivity data varied randomly with depth in the tank, they are presented in the form of Log Mean[9] (LM) and Log Dispersion[10] (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

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

[9] LM is equivalent to the geometric mean.

[10] 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.

slurry transfer the spent resins into storage tanks. The activation product radionuclides of most interest are Co-60, Gd-153 and C-14.

Table 8 Elemental Composition of Spent Resins from Darlington Unit 1 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 9 Elemental Composition of Spent Resins from Darlington Unit 3 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

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[11] 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 10 Radiochemical Characteristics of Resins 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

5.0 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 up to approximately 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

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

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.

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