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Assessment of Alternate Ion Exchange Resins for Improved Antimony Removal from the Primary Heat Transport System

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ABSTRACT

Radiation fields around the CANDU heat transport system are a major contributor to worker dose during inspection, maintenance and refurbishment activities. While Co-60 is typically the dominant contributor to radiation fields in CANDU reactors, Sb-124, an activation product of antimony, is also a significant contributor, accounting for 5-20% of the radiation fields. The goal of this research project was to investigate resins for improved removal of antimony under both oxidizing and reducing conditions.Several candidate resins were tested and shortlisted through a sequence of iterative testing. The results of the laboratory testing have identified potential candidates for improved antimony removal. Further testing is required to ensure compatibility with existing station resin specifications.

1. INTRODUCTION

Radiation fields around the CANDU heat transport system (HTS) are a major contributor to worker dose during inspection, maintenance and refurbishment activities. While Co-60 is typically the dominant contributor to radiation fields in CANDU reactors, Sb-124, an activation product of antimony, is also a significant contributor, accounting for 5-20% of the radiation field [1].

The HTS is maintained at an alkaline pH using lithium hydroxide. Chemistry control of the HTS and limiting the growth of radionuclide concentrations in the coolant is achieved through a side stream purification system; the latter includes particulate removal using filtration and cleanup and pH control using ion exchange media. Lithium concentration in the HTS is maintained using lithiated mixed bed IX resin and supplemented as required by addition of lithium hydroxide. Some CANDU plants enrich the anion portion of mixed bed resins with a layer ofNRW 600LC anion resin (the specific configuration varies from station to station).

During the mid to late 1990s, in response to the significant issues with antimony transport during outages experienced at Gentilly-2 [2],a significant effort was expended to understand the behaviour of antimony under CANDU HTS conditions and to develop a method for its removal. During this work it was found that antimony was not effectively removed on HTS ion exchange resins because under normal reducing operating conditions, the major species in solution is uncharged and thus not strongly bound to either cation or anion resins. It was also found that under oxidizing conditionsantimony was very mobile and could be removed with high efficiency on anion resin; a high purification flow rate was important but not crucial as the first few applications were performed with purification half-lives of about four hours and there was little re-deposition as long as the coolant remained oxidizing.

During the previous studies, effort was also expended to identify alternate antimony-specific resins that might be used in CANDU HTS purification systems. Several chelating resins seemed promising, but were never evaluated for use. These types of resins need to be re-examined. In the decade since, new technologies have been developed for PWR/BWR applications which may also be suitable for CANDU applications; these should also be evaluated.

The goal of this research project was to investigate alternate resins for improved removal of antimony from HTS coolant both during normal operation (reducing conditions) and during outages (oxidizing conditions). Ultimately this will lead to reduction in dose to workers.

2. APPROACH

Potential candidate resins,as alternativesto the currently used standard anion resin (NRW 600LC), were selected based on discussions with major manufacturers, end-users, published information on resin characteristics and performance, as well as,their known chemistry properties. The shortlisted resinsare shown in Table 1according to their typesbased on vendor information; namely:chelating resins, inorganic media, conventional polymeric gel type resins, macroporous resins and hybrid resins (polymeric+inorganic).

Table 1: Table of resins considered for test program

Resin type	Resin ID	Description
Gel type resins	**PuroliteNRW-37LiLC**	Nuclear grade gel type mixed bed resin, composed of NRW600 LC and NRW100Li
	PuroliteNRW-600LC	Nuclear grade gel type strong base anion exchange resin.
Macroporous resins	A	Macroporous PS nuclear grade anioncrosslinked with DVB.
	B	Macroporous polystyrene chelating resincrosslinked with divinylbenzene with isothiouronium functional groups.
	C	Macroporous PS chelating resincrosslinked with DVB with N-methylglucamine functional groups.
	D	Macroporous PS chelating resincrosslinked with DVB with both phosphonic and sulphonic acid functional groups.
	E	Styrene-DVB based macroporous polymeric adsorbent.
	F	Mixed bed with macroporouscation and gel anion.
Inorganic media	G	Specially processed granular Titanium dioxide inorganic material.
	H	Inorganic oxide resin
	I	Inorganic hydrous zirconium oxide

Resin type	Resin ID	Description
Chelating resins	**J**	Chelating resin of macroporous structure, with a PS crosslinked with DVB and substituted with weakly acidic aminophosphonic active groups.
	K	Polyacrylicchelating resincrosslinked with divinylbenzene with amidoxime.
	L	Weakly acidic macroporouschelating cation exchange resin with chelating iminodiacetate groups.
	M	Chelating resin with iminodiacetic functional group.
Hybrid resins	**N**	Strongly basic hybrid anion exchange resin (i.e., Iron oxide Styrene-DVB based and boron form polymeric resin) specially formulated to selectively remove antimony.

The iterative testing approach used to screen these resins,from an initially large number of resins down to the most promising candidate resins, is shown in the schematic below.

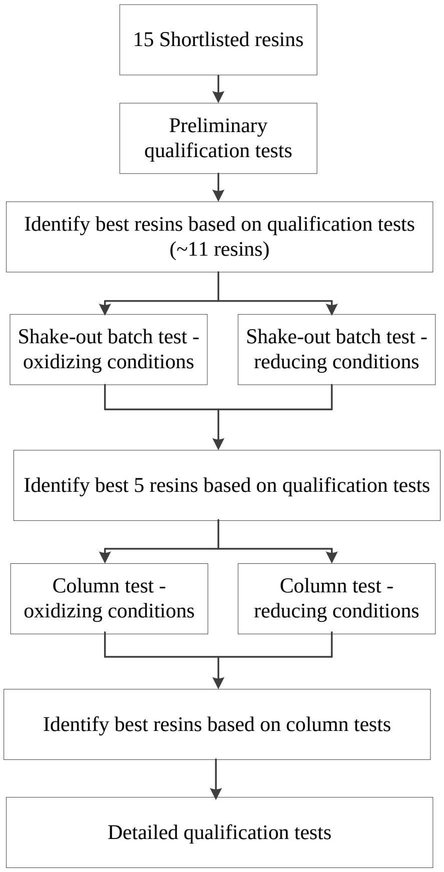

Figure 1: Schematic of iterative testing process

Thus, the evaluation of various shortlisted resins was done in a systematic manner as follows:

- Preliminary resin qualification tests
- Antimony removal tests under oxidizing as well as reducing conditions
    - Batch testing (‘shakeout’) tests
    - Column tests
- Detailed resin qualification tests

The resin bed in CANDU plants generally operates between 40-60 ºC. Testing in this program was generally performed at 60 ±5ºC.

3. PREPARATION OF SOLUTIONS

Two types of solutions were prepared for evaluating resin performance:

- an oxidizing solution, representative of shutdown conditions, where antimony is in the Sb(V) form, and

- a reducing solution, representative of normal operating conditions, where antimony is in the Sb(III) formas $Sb(OH)_3$.

Concentrations of antimony used were about 1ppm in order to facilitate detection of changes in antimony concentration during the tests. This is about three orders of magnitude higher than in the field.

Oxidizing solutions were prepared by sparging with air. H_2O_2 was not suitable as an oxidant since it could cause degradation of the ion exchange resins. Note that sparging is expected to yield dissolved O_2 concentrations higher than the 8-350 ppb levels required to convert Sb(III) to Sb(V) under HTS conditions [3].

Because of the difficulty in achieving antimony in a reduced state, hydrazine, typically a reducing agent and a good candidate for removal of oxygen, was employed: a limited number of tests involving a catalyst were carried out to determine an adequate hydrazine concentration.It was recognized that the solution conditions employed were not representative of those at the station. However, the aim was to employ a test solution with reduced antimony and these conditions are not readily achievable otherwise.

A neutral antimony species would not be removed by a strong base gel type anion exchange resin. The effectiveness of the respective oxidant/reductant was,therefore, assessed by measuring retention of antimony on the anion exchange resinprior to conducting shakeout or column testusing the prepared solutions and the test resins. Similar tests were reported in COG-93-336 for Sb speciation [4].

The feed compositions employed were as follows:

- pH of DI wateradjusted to ~9.5-9.9[1] with lithium hydroxide
- 1.1-1.3 ppm Sb concentration using antimony oxide (Sb_2O_3)
- 0.05 ppm[2]sulphate, 0.05 ppm chloride, 5 ppb nitrate, 5 ppb nitrite and 50 ppb ammonia
- Redox conditions: oxidizing conditions by spargingwith air for 25-30 minutes; reducing conditionsby using 1000 ppm hydrazine (catalyzed with 20% Cu/HNO_3).

While not measured, naturally occurring carbonate species may also be present, especially in the oxidized solution whereno effort was made to exclude oxygen.

The solutions were analysed for Total Organic Carbon (TOC) andfor elemental composition using Inductively Coupled Plasma Mass Spectrometry (ICP-MS); these analyses were conducted under Kinectrics' Standard Council of Canada ISO 17025 Accreditation program. Resin testing and Neutron Activation Analysis (NAA) were performed in accordance with ISO 9001 procedures. The instrument precision for TOC was ± 5% and ±2 %for Sb via ICP-MS.

4. SCREENING OF CANDIDATE RESINS

This section presents the results of screening tests which led to the identification of the best resin options as per Figure 1; the latter were then subjected to the detailed qualification testing which is described in Section 5.

Fourteen resins were initially identified for screening (plus two standard Purolite resins). These were subjected to 2 physical tests/measurements to assess their minimum qualifications for service, namely, friability crush strength and Perfect Whole Bead (PWB). Both tests are based on ASTM D2187. For friability testing, at least 25 beads retained on a US#30 mesh screen are crushed one at a time with a force rate of 1.961 N/second. A pass is received if the crush strength is greater than 3N/bead. For the PWB count, at least 80 beads are assessed under a microscope; a resin receives a pass if the average number of PWBs is greater than 90%. Based on the results of the physical assessments, 11 resins, shown in bold in Table 1, were selected for antimony removal tests as described next.

4.1 Resin Shakeout Batch Uptake Tests

In order to further shortlist the resins, batch antimony uptake tests were conducted. These were performed by equilibrating 0.2g of resin with 100mL of both oxidizing and reducing solutions prepared as previously described; the equilibration period was 2 hours at 60ºC with the solution agitated at approximately 300 rpm.The initial antimony concentration in the oxidizing and reducing solutions was 1.16 ppm and 1.02 ppm, respectively.

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[1] pH is related to the apparent pH (pH_a) in heavy water by the relationship pH_a=pH+0.47. This was used to convert pH_a range of 10.0-10.4 to pH in light water of 9.53-9.93.

[2] A suitable iron, lithium or sodium salt was used since these elements have been reported in previous analysis of HTS coolant.

Test results are presented in Table 2. The 5 resins (IDs B, C, H, K and N) which showed significant promise for Sb capture are highlighted in bold; these 5 resins were selected for column performance testing along with NRW-600LC as the benchmark.

Table 2: Results of batch uptake testing

Resinsample ID	Sb removalunder oxidizing conditions (%)	Sb removalunder reducing conditions (%)
NRW-600LC	0±0	0-0±0
NRW-37LiLC	0±0	0-0±0
B	96±2	4±1
C	92±0	74±3
E	0±0	0±0
H	83±2	81±1
K	57±6	67±1
J	30±2	12±1
L	0±0	0±0
M	0±0	0±0
N	86±1	85±1

Surprisingly, the NRW resins displayed negligible Sb uptake under both the oxidizing and reducing test conditions employed even though they are known to manifest some degree of effectiveness in the field, particularly under oxidizing conditions. To understand this result, supplementary batch tests with an increased amount (doubled resin quantity for the same volume of test solution) of NRW-600LC were performed under oxidizing conditions. These resulted in approximately 5±3% removal of antimony (an increase from 0%). This indicated that NRW-600 is required in greater quantity than the better performing resins, in order to achieve antimony removal. Thus the batch test was considered to be a valid screening tool for identifying resins with more effective performance.

4.2 Column Tests

The effectiveness of the 5 resins short-listed in Table 2 was next assessed under flow conditions in column tests. For this purpose, the IX column contained a layer of the test resin on top of thelithiated mixed bed resin NRW-37LiLC, in a 1:3 volume ratio at 60 ºC (± 5 ºC). The test column had a 1 cm ID anda 25 cm length. The test flow rate was1.2 BV/min. The initial antimony concentration in the oxidizing and reducing solutions was 1.2 ppm.

The results of column testing under both oxidizing and reducing conditions are shown in Table 3.

Table 3: Results of column testing for Sb removal

Resinsample ID	**Sb removalunder oxidizing conditions (%)**	**Sb removalunder reducing conditions (%)**
NRW-600LC	0.0	0.0
B	-	74
C	36	80
H	70	73
K	36	73
N	69	72
J	12	-

Resins B, C, H, K, and N removed antimony well under reducing conditions. Resins H and N additionally also removed antimony well under oxidizing conditions. The top four resins (shown in bold), specifically resinsC, H, K and N were carried forward for further characterization. Consistent with its behavior under batch testing, the NRW 600LC was ineffective at removing antimony from the solution.

5. DETAILED QUALIFICATION OF SHORTLISTED RESINS

5.1 Leachable residue and species

In order to assess the suitability of the resins for use in nuclear stations, the resins were further assessed for water leachables[3]. The testing was based on ASTM D5627-94. A known quantity of resin was contacted with water (50 g in 200 mL) for 18 hours in a stoppered flask at 60 ºC ± 5 ºC. After the exposure, a portion of the test solution was evaporated and weighed to determine leachables (residues). Another portion was submitted for Total Organic Carbon (TOC) analysis and Induction Coupled Plasma Mass Spectrometry (ICP-MS) analysis.The results of these analyses are shown in Table 4 along with the resin specification for mixed bed resinleachables. It is clear from the elevated level of leachables that the resins in their current formulationdo not meet the Mixed Bed Resin Leachate specification(e.g., especially resins K and N). Only two of the resins were tested in duplicate because of limited sample availability.

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[3] Assessment of leachables is part of the IX resin specification. It is also defined in the referenced ASTM test. The test method covers the measurement of water soluble extractable residue from ion-exchange resins based on elevated temperature extraction and gravimetric determination of residue.

Table 4: Measured leachablesincluding TOC from the resin

Resin sample ID	% leachates	mg leachables/L resin	Leached TOC (ppm)
C	0.058 ± 0.001	339 ± 4	60.4
H	0.037 ± 0.000	296 ± 0	3.80
K	0.27	1718	35.2
N	0.88	6287	2.87
NRW600LC	0.005	33.5	8.58
Mixed Bed Resin Specification	NA	200	NA

The ICP analysis of the resinleachatesindicated that the leachable Cl in resinsC and H were7.5 ppm and 58.8 ppm, respectively with instrument precision being ± 2%.The leachate of ResinN showed elevated levels of B (640 ppm). Sodium levels in leachates from all resins were also elevated as compared to the NRW-600LC standard. Because no station specifications exist for the leachable concentration for these elements, values were benchmarked against thosefor NRW-600LC; levels of Cl, B and Na in the leachates for NRW-600LC were <1, 0.04, and 0.193 ppm, respectively.

Due to the higher concentration of leachables in K and N, only resins C and Hwere progressed to the long term stability challenge test.

5.2 Challenge Test

In order to test the integrity of the resins under a chemically challenging environment, a known amount of resin was exposed to an aqueous solution of peroxide and iron (as ferric chloride) in a flask at 80 ºC (± 5 ºC) for 7 days. Shown below are photographs of the reaction flasks after testing was completed. Resin Cappeared similar toNRW-600LC, with the supernatant being essentially clear. The red residue within the flask was likely iron-based. In contrast, the ResinH supernatant was uniformly red-coloured.

A portion of the cooled supernatant was then filtered through a 0.45 µm filter and submitted for TOC and ICP analysis. Additionally, the physical characteristics (PWB, friability, and fines) of the resin were re-assessed.

(a) Resin H (b) Resin C

Figure 2: Photographs of two flasks after the performance challenge test

The results of the chemical analysis of the initial and final supernatant solutions are presented in Table 5. Comparison between the compositions of the supernatant and the initial solutions indicated that TOCs and Na were leached from each type of resin; on the other hand, uptake of Cl from the solution occurred on each type of resin. Both Resin H and Resin C supernatants had lower Na levels than the reference NRW-600LC supernatant; however, only the Resin H supernatant had lower TOC than the reference NRW-600LC supernatant. Thus, ResinHwas judged to have superior chemical stabilityunder the test conditions employed. Note that the values of chloride and TOC in the supernatant solutions cannot be compared withprevious data because of the specific solution formulationemployed in the challenge tests.

Table 5: Chemical analysis following challenge testing

	Initial solution	**NRW-600LC supernatant**	**Resin H supernatant**	**Resin C supernatant**
TOC (ppm)	1.03	460	29.4	713
Cl (ppm)	198	1.88	91.2	26.6
Na (ppm)	0.45	50.6	44.1	1.37

Results of the physical characterizationof the exposed resins are shown in Table 6.While exposure to the challenge solution did not alter the fines content (fraction of resin held up on No. 50 mesh) of Resin C, a slight increase was experienced in the case of Resin H.While Resin C met the fines requirements;it failed the crush tests early in the loading algorithm.No significant change in the bead strength was observed following exposure to the challenge solution.

Table 6: Results of the physical characterization of exposed resins

	NRW-600LC	Resin C	Resin H
Average force to fracture (N)	6.25 +/- 2.49	too soft to crush	4.98 +/- 1.90
% of beads with >3N strength	96	cannot determine	88
Fines content (%)	<0.01	0.06 (0.06)	0.27 (0.20)
Perfect whole beads (%)	98.1 +/- 0.1	98.3 +/- 1.0	99.3 +/- 0.7

Values in brackets for fines indicate valuesbefore exposure.

6. TESTING OF ALTERNATE RESINS

While the qualification testing focused on Resins C and H, neither resin met all the requirements. This included their chloride and sodium contents which hitherto had not been determined. Belatedly, neutron activation analysis (NAA) indicated the chlorine content of as-received Resin C and Resin H to be 4345 ± 7 ppm and 56,250 ± 636 ppm, respectively; the corresponding sodium levels were < 2 ± 0 ppm and 335 ± 7 ppm, respectively[4]. For reference, the QA specification for both elements in strong base anion resins is ≤ 100 ppm. Clearly, the high chlorine content, in particular, of both resins was unacceptable.

Given this, a discussion with resin vendors led to a new formulation,Resin N,being made available in OH-form (initially Kinectrics was made aware of the resinonlyin boron-form) and also Resin H in OH-form (the previous form provided was in Cl-form). Both resins were, however, available only in non- nuclear grade. Analysis of these resins by NAA yielded data for chlorineand sodium as shown in Table 7.

Table 7: Total chlorineand sodium measured by neutron activation analysis (NAA)

Resin sample ID	Total chlorine (ppm)	Total Sodium (ppm)
H-OH form	156 ±5	611±1
N-OH form	144±1	585±1
SBA Specification	≤ 100	≤ 100

Reported error is approximately ± 10 ppm for both elements and both resins.

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[4] Reported error in NAA results is ±45ppm for Chlorine in Resin C, ±13ppm for Sodium in Resin H and ±280 ppm for Chlorine in Resin H.

Although the chlorine and sodium contents of both resins still exceeded specifications, it was felt that with appropriate changes to the manufacturing technique, the resins could be brought into specification. Accordingly, small scale column tests were performed with the new resins to quantify their antimony removal. The results of this work are tabulated below.

Table 8: Results of column testing under oxidizing and reducing conditions

Resinsample ID	Sb removal oxidizing conditions (%)	Sb removal reducing conditions (%)
H (OH form)	74	78
N (OH form)	69	62

Both resins adequately removed oxidized as well as reduced antimony. It was subsequently discovered that resins H and Nwere in-fact the same resin, with one vendor rebranding another's resin material as their own. This narrowed the selectiondown to one final resin. This resin appears to be a promising candidatebut requires more detailed testing.

Note that while the above assessment indicatedResin H and Resin N to be identical, Table 1 indicates these to be of different types based on the manufacturer's categorization information.

7. DISCUSSION

The mixed bed NRW37LiLC and anionic NRW600 resins were noteffective in removingSb(III) because the latter exists as an uncharged species. Their limited success with removal of anionic Sb(V) species could be attributed to the relatively intermediate base characteristics, as well as lower ionic potential[5], of Sb(V) compared to other competing anionspresent in solution (e.g., carbonate, chloride, nitrate).

Removal of both Sb(III) and Sb(V) species by Resins H or N can be explained by anion exchange and chelation mechanism respectively. Resins H andNarestrongly basic hybrid anion exchange resins. Hybrid ion exchangers have an absorbent inserted into the polymer structure, conferring unique properties to the media that are not present either in the ion exchanger or the absorbent alone. In this case the ion exchange material is a Type I strong base anion resin (quaternary amine) and the absorbent is hydrated iron oxide-hydroxide. The anion exchanger portion of the resin plays a role when Sb is in the oxidized form. The mechanism is shown pictorially below. The manufacturer has presented information which suggests that the antimony, once captured, is held very tightly and released only by contact with hot sulfuric acid or caustic solutions. In short, the antimony is tightly held onto the resin matrix. This explains the success observed in the testing program.

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[5] Ionic potential refers to the charge to radius ratio of the ionic species in solution and is a measure of the effective charge of the species. If the ionic potential of Sb(V) is lower than that of other competing anions, it would be less likely to be retained.

Resin N-OH form is not routinely produced and thus its shelf life has not been characterized yet. Strong base anion nuclear grade resins have a shelf life of about 2 years [5] but hydroxide form resins degrade slowly even at room temperature to produce some weak base functionality at the expense of the strong base groups with an accompanying small (almost insignificant) loss of total capacity. While chloride and sulfate forms are more stable, hydroxide resins are recommended for only limited storage before use. It would be useful to ascertain the shelf life and stability of the Resin N-OH-form for potential use in nuclear stations.

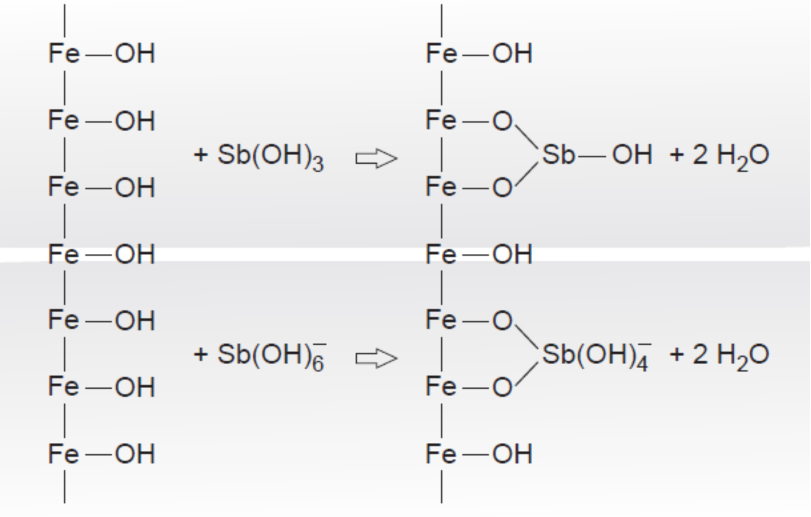

Figure 3: Schematic representation of the formation of bidentate inner-sphere complexes between $Sb(OH)_3$ and $Sb(OH)_6^-$ and iron hydroxide surface [6]

8. CONCLUSIONS

The goal of this research program was to investigate resins for improved removal of antimony under both oxidizing and reducing conditions. The results of the laboratory testing have identified a potential candidate for improved antimony removal. This resin has been used for antimony removal in various forms in US nuclear utilities, although mainly in waste water treatment. Initial testing using the identified resin has shown an order of magnitude improvement in antimony removal compared to the current benchmark resin. However, the resin needs to be further evaluated before a final decision regarding its station use can be made.

9. REFERENCES

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