

**New Innovations in Highly Ion Specific Media for Recalcitrant Wastestream Radioisotopes**

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**ABSTRACT**

Specialty ion specific media were examined and developed for, not only pre- and post-outage wastestreams, but also for very difficult outage wastestreams. This work was carried out on first surrogate wastestreams, then laboratory samples of actual wastestreams, and, finally, actual on-site wastestreams. This study was particularly focused on PWR wastewaters such as Floor Drain Tank (FDT), Boron Waste Storage Tank (BWST), and Waste Treatment Tank (WTT, or discharge tank).

Over the last half decade, or so, treatment technologies have so greatly improved and discharge levels have become so low, that certain particularly problematic isotopes, recalcitrant to current treatment skids, are all that remain prior to discharge. In reality, they have always been present, but overshadowed by the more prevalent and higher activity isotopes. Such recalcitrants include cobalt, especially Co 58 [both ionic/soluble (total dissolved solids, TDS) and colloidal (total suspended solids, TSS)] and antimony (Sb). The former is present in most FDT and BWST wastewaters, while the Sb is primarily present in BWST wastestreams.

The reasons Co 58 can be elusive to granulated activated carbon (GAC), ultrafiltration (UF) and ion exchange (IX) demineralizers is that it forms submicron colloids as well as has a tendency to form metal complexes with chelating agents (e.g., ethylene diamine tetraacetic acid, or EDTA). Such colloids and non-charged complexes will pass through the entire treatment skid. Antimony (Sb) on the other hand, has little or no ionic charge, and will, likewise, pass through both the filtration and demin skids into the discharge tanks. While the latter will sometimes (the anionic vs. the cationic or neutral species) be removed on the anion bed(s), it will slough off (snow-plow effect) when a higher affinity anion (iodine slugs, etc.) comes along; thus causing effluents not meeting discharge criteria.

The answer to these problems found in this study, during an actual Nuclear Power Plant (NPP) outage cycle and recovery (four months), was the downselect and development of a number of highly ion specific media for the specific removal of such elusive isotopes. Over three dozen media including

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standard cation and anion ion exchangers, specialty IX, standard carbons, and, finally, chemically doped media (e.g., carbon and alumina substrates). The latter involved doping with iron, manganese, and even metals.

The media downselect was carried out on actual plant wastestreams so that all possible outage affects were accounted for, and distribution coefficients ( $K_d$ 's) were determined (vs. decontamination factors, DF's, or percent removals). Such  $K_d$ 's, in milliliters of solution per gram of media (ml/g), produce data indicative of the longevity of the media in that particular wastestream. Herein, the downselect is reported in pareto (decreasing order) tables. Further affects such as the presence of high cobalt concentrations, high boron concentrations, the presence of hydrazine and chelating agents, and extreme pH conditions.

Of particular importance here is to avoid the affinity of competing ions (e.g., a Sb specific media having more than a slight affinity for Co). The latter results in the snow-plow effect of sloughing off 3 to 4 times the cobalt into the effluent as was in the feed upon picking up the Sb.

The study was quite successful and resulted in the development of and selection of a resin-type and two granular media for antimony removal, and two resin-types and a granular media for cobalt removal. The decontamination factors for both media were hundreds to thousands of times that of the full filtration and demin.

## **EXECUTIVE SUMMARY**

Due to upset conditions not uncommon during outages, a selection of media capable of handling the removal of isotopes present in both normal and outage conditions was undertaken. Such a methodical approach to such packing materials is referred to as a media downselect. Especially in the case of the outage wastewaters in a typical PWR, the isotopes of interest include Mn 54, Co 57, Co 58, Co 60 and Sb 125, to mention a few.

Upset conditions during an outage (although also possible during normal operations) can include higher than normal levels of contaminants (e.g. Co 58), high concentrations of boron, the presence of hydrazine (normally only a problem for polymer systems), and chelating agents (e.g., ethylene diamine tetraacetic acid, or EDTA from common floor and respirator cleaners) that complex isotopes such as Co and carry it through membrane and media systems.

The object of this study was to downselect a media, or medias, capable of removing, particularly, soluble cobalt (Co) and antimony (Sb) from actual wastewater samples. This must be accomplished both during normal and upset conditions (such as addition of EDTA and high boron concentrations). Several such media have been selected from over thirty (30) standard and specialty medias that will accomplish this goal. Further, long-term testing at selected sites, in actual plant effluent conditions, and implementation on a full-scale is the final objective.

## INTRODUCTION

This summary report describes the testing performed by RWE Nukem Corp. (RNC) at its laboratories at Materials and Chemistry Laboratories, Inc. ( MCLinc) in Oak Ridge in support of field operations by RWE staff during a recent outage (April 1-28, 2005) at a Pressurized Water Reactor (PWR) facility. Results reported previously are compiled into a single narrative, with updated results obtained in subsequent testing. Test findings and results are organized in sections as different feed waters, interferences and complications arose during the outage and post-outage runs. Overall recommendations of the study are presented in the final Summary section.

As actual samples (FDT, BWST, WTT, and the treatment skid effluent) were taken and shipped by site personnel, some initial media scoping tests were performed with use of surrogate media (e.g., Co-60 traced water, or natural cobalt in non-radiological solution). These provided some insight (e.g., into the effects of added borate, and the relative poor performance by standard, commercial resins such as Purolite S-108, Dowex M4195 etc.), and select results are briefly discussed herein. However, results performed with use of actual Site wastewater samples are, of course, more relevant to future operations and are emphasized in this report. It is noted that authentic, site water compositions changed frequently (often by the hour), depending upon cleanup and treatment activities at the site, and thus the individual solutions received for testing represent “snapshots in time.”

## BACKGROUND

According to companion data received from the site, the Floor Drain Tank (FDT) composition of 4/18/2005 had the highest total gamma activity ( $\sim 5.2\text{E-}03 \mu\text{Ci/mL}$ , almost exclusively ( $\sim 97\%$ ) due to Co-58 (a beta and gamma emitter)). Initial testing with this sample at MCLinc using beta counting was confounded by the presence of tritium (H-3), a low-energy beta emitter with no gamma radiation “signature.” Tritium represented  $> 98\%$  of the total activity present, but because H-3 readily exchanges with ordinary hydrogen in water, it was effectively removed by drying the sample at  $\sim 110$  deg. C. Without the H-3 interference, the fate of Co-58 could be monitored by liquid scintillation counting (LSC). The activity in this sample predominantly behaved as a cation (presumably due to  $\text{Co}^{2+}$  and/or  $\text{Co}(\text{OH})^{+}$ ); the cobalt activity was effectively removed by conventional (sulfonated) cation exchange resins (Dowex 50-X8 and specialty resin, GX), a specialty thiol-based cation exchange resin (GT), and bone char (BC), all of which have a strong preference for cations. However, several other media, including Ebony T (100%) (super pure  $\text{MnO}_2$ ), a silver-impregnated carbon (AGC 5860), activated alumina (AA) and even some forms of activated carbon were also judged very effective.<sup>1</sup>

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<sup>1</sup> In order to compare the relative effectiveness of solid media for the removal of soluble contaminants, or the removal of a given contaminant under variable test conditions, we compute a conditional distribution (or partition) coefficient,  $K_d$ , using the relationship:

$$K_d = S/C \quad \text{mass ratio/concentration} \quad \text{mg/g / mg/ml} = \text{ml/g} \quad (\text{Eq. 1})$$

Where S = mass (or activity) of contaminant “sorbed” at equilibrium per mass of sorbent, and C = equilibrium concentration (or activity) of soluble contaminant in the aqueous phase.

The value of  $K_d$  obtained from equilibrium batch testing can be used to roughly estimate the packed bed capacity or retardation factor,  $R_f$  (i.e., reactor breakthrough, in cumulative bed pore volumes passed), with the caveat that solute mass transport and reaction kinetics significantly affect the performance of actual dynamic flow reactors.; see, e.g., Relyea, J.F. (1982), “Theoretical and Experimental Considerations for the Use of the Column Method for Determining Retardation Factors,” *Radioactive Waste Management and the Nuclear Fuel Cycle*, 3, 151-166.

Another water composition received from the site originated from the boron waste storage tank (BWST) on 4/18/2005. According to site data, this sample had a total gamma activity  $\sim 1.1\text{E-}05$   $\mu\text{Ci/mL}$ , comprised of  $\sim 60\%$  Co-58 and  $\sim 40\%$  Sb-125 activities. Again, the preponderance of total activity was due to tritium (a pure beta emitter). In contrast to the FDT composition, the beta activity (with H-3 removed) in this sample of BWST waste had considerable anionic character. The contaminant anion behavior may be due to the Sb-125 component (Sb(V) forms an anionic complex,  $\text{Sb(OH)}_6^-$ ; see Krupka and Serne, 2002), and/or complexation of Co-58 by EDTA to form an anion (vide infra). Removal of activity by all media was less than that observed for the FDT composition, with activated alumina (AA) and bone char (BC) being more effective than conventional (sulfonated) cation exchange resin or thiol-based cation exchange resin (GT).

Additional testing was performed on mixtures of FDT and BWST water, both with and without added EDTA. Without added EDTA, radioactive contaminants in the mixture behaved predominantly as cations (as was the case for the higher-activity FDT component alone). When  $< 2$  ppm of the potent chelant, disodium ethylenediamine tetraacetate ( $\text{Na}_2\text{EDTA}$ ) was added to a mixture of FDT and BWST water, the responsiveness to treatment was significantly altered. EDTA has a strong affinity for cobalt, forming an anionic complex ( $\text{Co(EDTA)}_2^-$ ); see Szecsody et al., 1994; Krupka and Serne, 2002. For the mixture without added EDTA, the most effective media tested were the same as those that were effective for FDT alone, i.e., cation exchange resin, Ebony T (100%), and bone char (BC). With added EDTA, all media affinities were notably lower, with the most effective media now being thiol resin (GT), silver-impregnated carbon (AGC 5860), and Dowex 2-X8 (Type II strongly basic anion exchange resin).

A third Site wastewater, originating from the Waste Treatment Tank (WTT) on 4/29/05 was also run. This waste represents pre-treated wastewater (Total gamma activity  $\sim 1.9\text{E-}5$   $\mu\text{Ci/mL}$ , essentially all as Co-58). This wastewater needed slight additional “polishing” to meet a target treatment goal of  $< 1\text{E-}5$   $\mu\text{Ci/mL}$ . For this composition, treatment with either silver-impregnated carbon (AGC 5860) or bone char (BC) was most effective (both media yielding  $K_d > 1,000$  mL/g). Thus, specialty carbon media was shown to be useful for final “polishing” of wastewater. As noted in an attachment, bone char does release phosphate ion (and increase water conductivity), and thus should not be used prior to anion exchange medium (as most anion exchange resins have a high affinity for phosphate ion).

An important attribute of the “outage” waste waters is the presence of boron (a neutron poison) at elevated concentrations (Table I). The boron is added as boric acid, a very weak acid; Pourbaix (1974) gives the dissociation of boric acid as a function of pH value:

$$\text{Log}_{10} ([\text{H}_2\text{BO}_3^-]/[\text{H}_3\text{BO}_3]) = - 9.21 + \text{pH} \quad (\text{Eq. 3})$$

As shown in Table I, at near-neutral pH values (e.g., as for the raw FDT waste), appreciable  $\text{H}_2\text{BO}_3^-$  anion will be formed, which may compete for binding sites on anion exchange resin. It would be preferable to place

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$$R_f = [1 + K_d(\rho_b/\theta)] \quad (\text{Eq. 2})$$

where

- $R_f$  = Maximum number of bed pore volumes that can be treated before breakthrough,
- $K_d$  = Conditional contaminant distribution coefficient (mL/g), determined from the sorption isotherm,
- $\rho_b$  = Packed bed density (g/mL),
- $\theta$  = Total void fraction of the packed bed.

A relatively large value for  $R_f$  indicates that the contaminant has been immobilized to a great extent.

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the cation exchange resin (with effluent pH ~ 3.5) before the anion exchange resin (thus lowering the pH of the anion exchange resin influent solution), to minimize loading of the anion resin with borate. (At pH 3.5, H<sub>2</sub>BO<sub>3</sub><sup>-</sup> anion is only 2E-06 of the total B, and thus subsequent loading of the anion resin would be minimal).

Table I. Effect of Water Composition on the Formation of H<sub>2</sub>BO<sub>3</sub><sup>-</sup> Anion

Water Composition	FDT	BWST	WTT
B (total), ppm	1330	1200	700
pH	6.8	5.2	4.7
[H <sub>2</sub> BO <sub>3</sub> <sup>-</sup> ]/[H <sub>3</sub> BO <sub>3</sub> ]	3.89E-03	9.77E-05	3.09E-05
H <sub>2</sub> BO <sub>3</sub> <sup>-</sup> , ppm	29.1	0.66	0.065

Data was summarized and media performance ranked in pareto tables.

## APPROACH AND RESULTS

### Testing with FDT Waste Sample, Pre-Treated with Purolite

The sample (INF FDT “A”) proved to be problematic and refractory to bench-scale treatment. The boron level was estimated at 1330 ppm as B, due to cross contamination. The total activity is estimated by liquid scintillation counting as ~ 1.08E5 CPM/g.

The liquid sample used for this series of tests was contacted for ~ 5.4-h with Purolite (a Boron specific resin) as the solid phase, at a mass ratio, L/S ~ 41. Phases were separated by filtration at 0.45- $\mu$ m, and the liquid phase was used for further testing. The total activity of the filtered liquid was ~ 1.03E5 CPM/g (little or no activity removal by the Purolite). The initial pH of the filtered Purolite-equilibrated sample was ~ 6.6; it was adjusted to a value ~ 3.2 with a single drop of HCl.

The solution was contacted with the media used for the surrogate testing (Part 1), at a nominal mass ratio, L/S, ~ 40. The phases were sampled after two contact intervals (~ 0.5-h and again after an additional ~ 3.2-h, for a total ~ 3.7-h), and phases were separated at two effective pore sizes (0.2- $\mu$ m with use of a syringe filter, and ~ 0.03- $\mu$ m with use of a 50,000 Dalton cut-off hollow fiber UF system).

As noted in Table II below, none of the media tested removed appreciable activity, and there was negligible effect of longer phase contact or filtration medium.

Table II. Removal of Gross Activity from FDT at Initial pH ~ 3.2

Solid Phase (L/S ~ 40)	Filter at 0.2- $\mu$ m		UF Membrane
	Contact ~ 0.5-h	Contact ~ 3.7-h	Contact ~ 3.7-h
Dowex M4195	Removed ~ 7.1 %	Removed ~ 8.2 %	Removed ~ 6.4 %
Dowex M4195 (saturated with natural cobalt)	Removed ~ 3.4 %	Not tested	Not tested
Dowex 50WX8, sodium form	Removed ~ 7.2 %	Removed ~ 4.9 %	Removed ~ 5.0 %

NOTE: did not remove H-3 before counting, so results are not specific to Co-58

### Revised Testing with FDT Water Composition

The site samples contained high levels of tritium (H-3), which had previously confounded total activity measurements at by Liquid Scintillation Counting (LSC).

In both water compositions, the volatile component (assumed to be tritium) is predominant (> 97 % of total activity for sample 05-0186, and > 99 % of total activity for sample 05-0207).

Table III ranks initial media tested by the magnitude of the measured distribution coefficient,  $K_d$  (mL/g), where a large value of  $K_d$  represents strong partitioning to the solid phase (and a longer time to breakthrough, if exchange kinetics are favorable). Table III data are based on activities measured after evaporation of the H-3 component from FDT composition; the liquid to solid mass ratios (L/S) used in testing varied from ~ 10 to ~100, and contact times varied from ~ 0.7 to > 5-h.

From Table III, the highest ranked medium for removal of nonvolatile activity (Co-58) from the FDT water sample was the experimental resin, GX ; at an L/S ~ 88 and a contact time of ~ 1.6-h (on a wrist-action shaker), this medium removed > 98% of the non-tritium activity. A mercury-selective (thiol) resin GT removed a comparable amount of Co-58 under the same contact conditions, but at L/S ~ 55.

Table III. Batch test results using FDT

<b>Efficacy Ranked by <math>K_d</math> (excludes H-3 activity)*</b>		
<b>Medium</b>	<b><math>K_d</math> (mL/g)</b>	<b>Comments</b>
GX	<b>4510</b>	(Experimental cation resin)
GT	<b>2815</b>	Hg selective Cation
Bone char (BC EM)	<b>1721</b>	Fine powder
NUCON NUSORB KINA-3	<b>1569</b>	Crushed pellets (KI on coal)
Dowex 50W-X8 (pH 5.1)	<b>1429</b>	Strongly-acidic CIX, Na form
Ebony T (100%)	<b>1326</b>	RNC high purity $MnO_2$
Alumina Grade A-1	<b>1298</b>	Kaiser (Tested as crushed fine powder)
Bone Char (BC W)	<b>1170</b>	Bone char pellets
AGC 5860 (pH 6.7)	<b>1040</b>	Silver-impregnated carbon
AWC	<b>752</b>	Cameron CG6/AW12X40 (acid-washed coal)
Bayoxide E33	<b>716</b>	Bayer AG pelletized iron oxides (equiv. SP-60)
Durasil 70	<b>332</b>	MCL sample 05-0211
Ebony T (80%)	<b>151</b>	RNC Crude $MnO_2$
AGC 5860 (pH 5.1)	<b>99</b>	After reduction by hydroxylamine
M4195 + Co (pH 3.2)	<b>79</b>	Dowex Cu-selective CIX; Co-saturated
M4195 (pH 3.2)	<b>73</b>	Dowex Cu-selective CIX
Mn(OH)O (hydrous)	<b>25</b>	Sigma-Aldrich 243442 (60-230 mesh)
Dowex 21K XLT	<b>16</b>	Anion exchange resin
Purolite ( at pH 6.7)	<b>5</b>	Boron-selective resin
Calgon HGR	<b>4</b>	Sulfonated carbon
Mersorb-3	<b>0</b>	Sulfur-impregnated carbon

\* Activity measured on dried residue, referenced to original liquid sample volume.

#### **Testing of BWST and FDT/BWST Mix with and without EDTA Interferant**

Table IV summarizes select properties of the blended waste water composition. The two water samples that were blended had comparable boron levels (~ 1,330 ppm-B in FDT and ~ 1,200 ppm-B in BWST), for an average ~ 1,265 ppm B.

As illustrated in Table V, addition of < 2 ppm  $Na_2EDTA$  had a profound effect on the removal of Co-58 by select media. EDTA converts cationic cobalt (as  $Co^{2+}$  and/or  $Co(OH)^+$ ) to the anion complex,  $Co(EDTA)^-$ . EDTA had a more adverse effect on the GX (sulfonated) cation exchange resin than on the GT (thiol) specialty resin. Bone char (BC) is a medium that is most effective for sorption of cations. EDTA had an adverse effect

on the uptake of Co-58 on bone char, but uptake was enhanced for the silver-impregnated carbon (AGC 5860). As expected, addition of EDTA causes more Co-58 to be captured on anion exchange media (Dowex 2-X8). EDTA significantly affects the uptake by Ebony T (and EDTA is likely to strip Co-58 that had been previously loaded on cation-selective media, such as Ebony T and cation exchange resin). In the absence of EDTA, the mixture of BC and AGC 5860 gives a Kd for Co-58 that is equivalent to the weighted-average value for the individual components; with EDTA, the Kd for sorption to the mixture is greater than the weighted-average value expected, and may reflect the pH-buffering by the bone char.

Table IV. Select Properties of a 50:50 Mixture of FDT and BWST

Property	Unit	Value	Comment
Co-58	μCi/mL	2.53E-03 (~ 97% of Total Gamma)	Estimated from Site gamma data
Sb-125	μCi/mL	2.12E-06 (~ 0.1% of Total Gamma)	Estimated from Site gamma data
H-3	μCi/mL	5.54E-02 (~ 98% of Total Beta)	Estimated from MCL data
pH	Standard	6.75	Measured at MCL

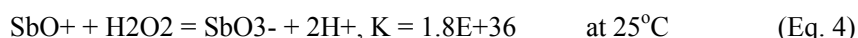
Table V. Effect of Added Na2EDTA on Uptake of Radioactivity (~ 97% as Co-58) by Select Solid Media, as Reflected in the Partition Coefficient (Kd, mL/g).

Solution:	FDT + BWST (~ 50:50)		FDT + BWST (~ 50:50)
Na2EDTA Added	None		~ <b>1.9 mg/L</b>
Solid Phase	pH after Phase Contact	Kd (mL/g)	Kd (mL/g)
GX	3.62	2349	450
GT	2.52	<b>2037</b>	1161
BC- W	7.43	1585	51
AGC 5860	7.08	<b>609</b>	<b>1066</b>
Ebony T (100%)	6.77	1818	2
AA (Al2O3)	7.20	619	20
Dowex 2-X8, Cl form	5.47	19	941
BC + AGC 5860 (~ 50:50)	7.30	1146	926

Note: Beta activity is estimated after drying the sample aliquots to evaporate the H-3 component.

### Uptake of Sb-125 by Select Media

Stock Sb-125 certified standard, tracer, (70275-728) was obtained from Analytics (Atlanta, GA 30318), in the form of Sb(III) in 6 M HCl, with 30 μg/g natural Sb carrier. The sample was transferred quantitatively from the sealed ampoule, and was converted to the anionic Sb(V) form by the addition of excess hydrogen peroxide (Eq. 4). The excess H2O2 was subsequently destroyed by heating the sample to 40-50°C.



Thermodynamic values used to estimate the equilibrium constant, K, are taken from Pourbaix (1974), Atlas of Electrochemical Equilibria in Aqueous Solutions. The large value for K computed in Eq. 1 indicates that the oxidation of Sb(III) by peroxide is highly favored (thermodynamically) under the reaction conditions used. An aliquot of the Sb-125 standard was added to the BWST water composition, and the pH and redox potential

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values were adjusted to give values comparable to the original BWST water (pH = 5.2, Eh = 0.514 V). Pourbaix gives the limit of the domain of relative predominance of the dissolved species ( $[Sb(III)]/[Sb(V)]$ ) as illustrated in Figure 1. The adjusted solution (sample 1057-71-2) gave pH = 5.2 and Eh = 0.56 V, which is in the thermodynamic stability domain of anionic Sb(V) (Figure 1). (Note from Fig. 1: under mildly reductive conditions – e.g., upon addition of hydrazine – and over a wide range of pH values - the uncharged Sb(III) species,  $HSbO_2$  (or  $Sb(OH)_3$ ), can predominate; this uncharged species will not sorb well to solid surfaces; see Report PNNL-14126).

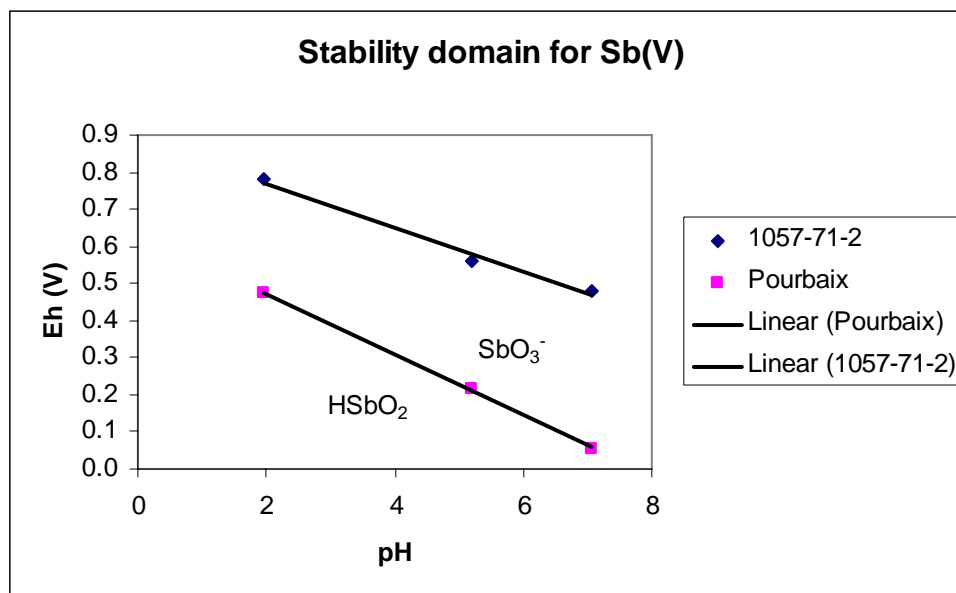
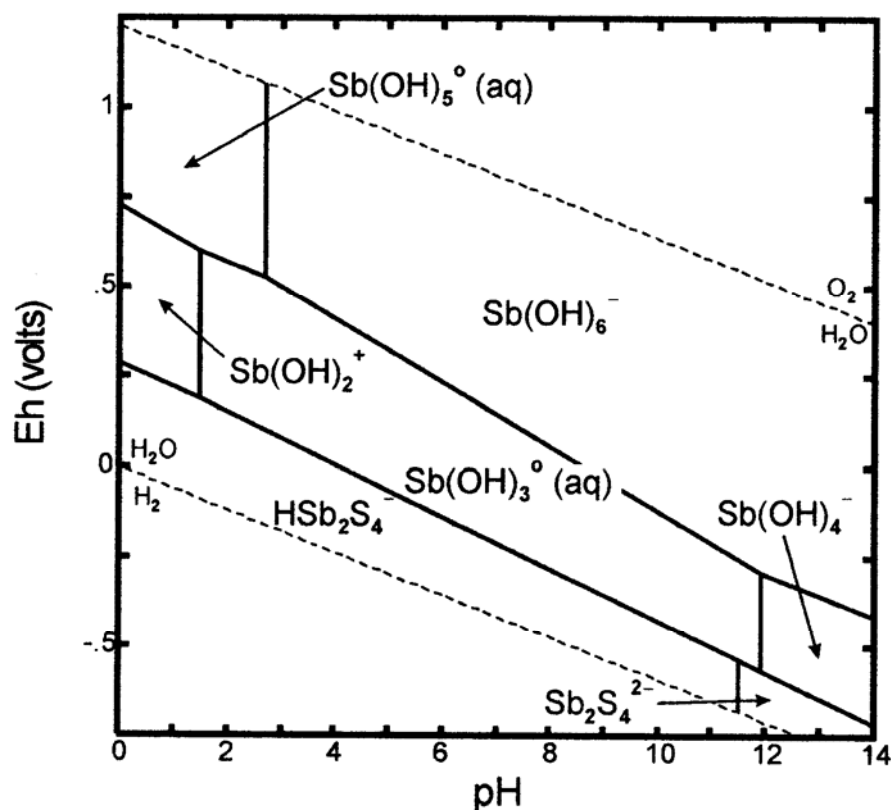


Fig. 1. Solution 1057-71-2 (BWST plus added Sb-125 tracer) is in the thermodynamic equilibrium stability domain of anionic Sb(V) (as  $SbO_3^-$  or  $Sb(OH)_6^-$ ).

Similar thermodynamic prediction is depicted in Figure 2 (from Report PNNL-1426).





**Figure 2.1.** Eh-pH Diagram Showing Dominant Aqueous Species of Antimony [Diagram was calculated at 25 °C and a concentration of  $2.90 \times 10^{-10}$  mg/L ( $10^{-14.6}$  mol/L) total dissolved antimony.]

Fig. 2. Eh-pH Domain for Antimony Species (from Krupa and Serne (2002), Report PNNL-1426).

The added Sb-125 spike is estimated at 4.41E+03 DPM/g-solution for sample 1057-71-2. The measured non-volatile beta activity for the sample (i.e., after evaporating the H-3 component) is estimated at 4.31E+03 CPM/g-solution. Other select properties are given in Table VI.

Table VI. Select Properties of BWST with Added Sb-125 (Sample ID 1057-71-2)

Property	Unit	Value	Comment
Co-58	μCi/mL	6.39E-06	Estimated from Site gamma data
Sb-125	μCi/mL	1.99E-03	Estimated from Sb-125 Spike
H-3	μCi/mL	6.61E-02 (~ 98% of Total Beta)	Estimated from MCL data
Sb (total)	mg/L	1.63	Contributed by tracer
pH	Standard	5.19	Measured at MCL
Eh	V (vs. SHE)	0.489	Measured at MCL
Solids	Wt%	0.49	Measured at MCL

The relatively large amount of total Sb (1.6 ppm) and the distinct possibility that oxidation of Sb(III), although thermodynamically favorable, may not have been kinetically favorable, resulted in low values estimated for the computed Kd (Table VII). (Again, if oxidation is not kinetically favorable, uncharged Sb(III) may predominate).<sup>2</sup> The observation that minimal Sb-125 was removed by either strong acid cation exchange resin (GX) or by Type II strong basic anion exchange resin (Dowex 2-X8) suggests that under the conditions of testing, neutral species or low charge density complexes may predominate. Of the media tested under these conditions (liquid to solid mass ratio ~ 70:1), only Ebony T and AA (alumina) had favorable removal.

Table VII. Removal of Sb-125 traced BWST (Trial #1)

Solid Phase	pH after Phase Contact	Kd (mL/g)
GX	1.94	17
GT	1.95	18
BC-W	7.57	17
AGC 5860	7.31	0
Ebony T (100%)	5.80	<b>87</b>
AA (Al <sub>2</sub> O <sub>3</sub> )	7.16	<b>74</b>
Dowex 2-X8, Cl form	3.34	26
BC + AGC 5860 (~ 50:50)	7.42	0

Note: Beta activity is estimated after drying the sample aliquots to evaporate the H-3 component.

Table VIII. Removal of Sb-125 traced BWST by Anion-Exchange Media and by Ebony T (MnO<sub>2</sub>)

Solid Phase	pH after Phase Contact	Kd (mL/g)
DOWEX® 2X8 (Anion IX)	3.4	30
DOWEX® 21K XLT (AIX)	5.9	13
Ebony T (100%)	5.8	<b>212</b>

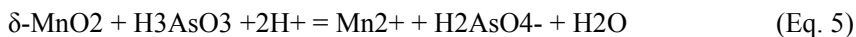
These data suggest that oxidized Sb-125 is very difficult to remove from solution by sorption. This may be a consequence of a relatively large complex (Sb(OH)<sub>6</sub><sup>-</sup>) having low charge density. In Table VIII, 100% Ebony was the most effective solid medium tested. The 100% Ebony medium was evaluated against the persulfate-oxidized solution (Table VII; at a liquid:solid mass ratio ~ 40 (or liquid:solid volume ratio ~ 90); Ebony T removed ~ 84% of the Sb-125 activity, for Kd ~ 212 mL/g (cf. Table VII: Kd ~ 87 mL/g for peroxide-oxidized Sb-125).

### **BWST Wastewater Testing with and without Added Antimony Tracer**

High levels of Sb-125 (as represented in this series of tests with use of Sb-125 spiked borated waste storage tank (BWST) water composition) have proved to be relatively difficult to treat. In results reported previously, organic ion exchange media were shown to be relatively ineffective for this purpose, with the exception of a specialized iron-doped resin (experimental FDR and subsequent commercial ASM 125). Inorganic media judged to be relatively effective for removal of Sb(OH)<sub>6</sub><sup>-</sup> anion from a borated waste stream included AA (activated alumina), Ebony T (100%) (MnO<sub>2</sub>), and GFH (granulated ferric hydroxide) (tested as Bayoxide-33, an equivalent to Apyron SP-60).

<sup>2</sup> See p. 2.1 of Report PNNL-14126: "However, contrary to thermodynamic predictions, Sb(V) and Sb(III) have been found coexisting in natural aqueous systems." A slow rate of Sb(III) oxidation is thus inferred.

Alumina is relatively inexpensive, with good mechanical stability (e.g., it is crush-resistant), and it removes a variety of anionic contaminants from mildly acidic to near-neutral pH value (see “Discussion” section). Manganese dioxide may function as a sorbent, co-precipitant and as an oxidant. Power et al. (2005) have demonstrated that MnO<sub>2</sub> can oxidize arsenite (As(III)), forming arsenate (As(V)), the latter of which is much more amenable to sorption:



Manganese dioxide, as demonstrated with Ebony T, similarly, is able to oxidize Sb(III), which forms an uncharged hydrolysis product at near-neutral pH values (pH ~ 5-8), to yield anionic Sb(V) complex, for enhanced sorption (See U.S. Patents, M.S. Denton, et al). Granulated ferric hydroxide (GFH) is generally effective for sorption of oxyanions (such as arsenate) over a range of pH values, but it has very poor mechanical properties (e.g., poor mechanical strength), making it difficult to use in packed bed reactor configurations. Also, operational experience at various sites using GFH has not always been successful, especially under “outage” situations, when borate is elevated and EDTA may be present.

The actual mechanism for the sloughing of Co 58 by the SP-60 column during outage conditions has not been positively identified at this time. Joint EPRI tests on antimony removal focused on antimony without extreme cobalt levels. It is thought, at this time, that the hydroxide portion of the ferric oxy-hydroxide is simply slowly dissolving at this low pH. It is further thought that the Co on the media is exchanged onto the EDTA in the solution allowing Sb uptake and Co “snow plowing”.

In this series of tests, created surface deposits of hydrated metal oxide (either MnO<sub>2</sub> or ferrihydrate, “Fe(OH)<sub>3</sub>”) on select porous media [activated alumina (AA) and activated carbon (GAC)]; the resulting alumina-based products were tested. The objective was to form an effective composite phase that is less-dense than “Ebony” (hence easier to sluice the material into or out of packed bed reactor columns), and to discover whether there are possible synergistic effects between surface coating and substrate.

Manganese-doped alumina (MDA), or Ebony A is shown to sorb Sb-125 in a manner essentially equivalent to pure MnO<sub>2</sub>; additionally, the MDA has a packing density that is half that of Ebony T (100%). Iron-doped alumina (FDA) has an affinity for Sb-125 intermediate between that of the substrate (alumina) and MDA. One form of FDA is currently commercially available in adequate batches.

One can also achieve a granular activated carbon (GAC) based iron containing adsorbent that is highly effective for removal of soluble arsenic oxyanions. We show that the preferred substrate steam-activated lignite) is itself relatively effective for removal of Sb-125 (in contrast to other GAC products tested to-date). Iron-doped carbon (FDC) is shown below to be especially effective for removal of Sb-125. The FDC has a relatively low packing density, but the carbon substrate (Darco) has poor mechanical stability. There currently does not appear to be a commercially-available equivalent to the FDC product. An initial attempt to produce a stable (non-friable) manganese-doped carbon was not successful.

**Activated Alumina Substrate**

Table IX. Testing vs. Sb-125 Traced Wastewater (a) – Alumina Substrate

Property	Units	Solid Substrate			
		Al <sub>2</sub> O <sub>3</sub> (b) AA	MnO <sub>2</sub> -doped Al <sub>2</sub> O <sub>3</sub> (MDA)	“Fe(OH) <sub>3</sub> ”-doped Al <sub>2</sub> O <sub>3</sub> (FDA)	Ebony T (100%) (MnO <sub>2</sub> )
Solid tamp density	g/cc	0.91	1.0	0.83	1.98
As-tested: Liquid:solid	V(cc)/g	24.6	24.6	25.1	24.5
Activity Removed	%	86.5	<b>94.6</b>	90.8	<b>95.1</b>
Distribution coefficient (K <sub>d</sub> )	mL/g	158	<b>430</b>	232	<b>475</b>
Final pH	standard	7.4	6.5	7.2	6.2

Solution tested: initial nonvolatile activity = 1153 CPM/g (~ 2.56E-5  $\mu$ Ci/mL) Sb-125, initial solution pH ~ 4.6. Alumina substrate used is MCB AX0610-3, 8-14 mesh.

As noted in Table IX, the Mn-doped alumina (MDA) maintained the Sb-selectivity of pure MnO<sub>2</sub> [Ebony T (100%)], while having a bulk density comparable to the alumina substrate. The surface coating of MnO<sub>2</sub> enhanced performance relative to the alumina substrate alone. The surface coating appears to be very well adhered to the substrate. The iron-doped alumina (FDA) prepared for this study was not greatly superior to alumina alone. The alumina substrate has excellent crush-resistance (i.e., it is physically robust).

**Activated Carbon Substrate**

Some thirteen commercially available granular activated carbon (GAC) products have been examined for their ability for iron impregnation and for the utility of the iron-doped product to remove arsenic oxyanions. It was concluded that Norit Darco, steam-activated lignite, was superior for achieving these objectives. The grade of activated carbon used in this investigation (Norit Darco HD 3000, Batch 19.86) is apparently equivalent to Norit hydrodarco 3000. Test results are summarized in Table X.

Table X. Testing vs. Sb-125 Traced Wastewater (a) – GAC Substrate

Property	Units	Solid Substrate		
		Darco <b>GAC (b)</b>	MnO <sub>2</sub> -doped GAC ( <b>MDC</b> )	“Fe(OH) <sub>3</sub> ”-doped GAC ( <b>FDC</b> )
Solid tamp density	g/cc	0.39	0.37	0.38
As-tested: Liquid:solid	V(cc)/g	25.2	31.5	24.6
Activity Removed	%	84.4	78.2	<b>97.4</b>
Distribution coefficient	mL/g	136	113	921
Final pH	standard	5.6	5.3	5.2

Solution tested: initial nonvolatile activity = 1153 CPM/g (~ 2.56E-5  $\mu$ Ci/mL) Sb-125, initial solution pH ~ 4.6.

GAC substrate is DARCO activated carbon HD 3000 (American Norit Company, Jacksonville, FL)

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The GAC substrate is very friable (low crush-resistance); all of the GAC-based media fell apart upon tumbling liquid and solid phases overnight on a TCLP apparatus.

Surprisingly, the MDC [Mn(IV)-doped GAC] did not perform better than the GAC alone. [Unlike metal doping on alumina substrate, it is not possible to visually confirm reactive metal loading on the black carbon substrate.]

The Sb-removal performance of FDC [Fe(III)-doped GAC] was the most promising (Table X).

The inorganic solid substrates described above are best used as final “polish” media, after the effluent water has become slightly acidic from treatment by the cation exchange resin bed.

#### **Testing of FDT:BWST Mix with the Addition of EDTA**

Select media were evaluated against an approximately 50:50 mixture of archived site floor drain tank and archived borated waste storage tank waste compositions. Additionally, a total of ~ 2 ppm disodium ethylenediamine tetraacetate (Na<sub>2</sub>EDTA) was added to an aliquot of the blended wastes, to determine any adverse effect of this potent chelating agent on the uptake of radioactivity. (~ 97% of the nonvolatile activity is due to Co-58). As noted in our previously, EDTA has a strong affinity for cobalt, forming an anionic complex (Co(EDTA)<sup>2-</sup>).

Data has been previously reported for testing on these blended water compositions. Comparable data for the present developmental media are presented in Table XI below. Hydrous metal oxides sorbed onto either alumina (AA) or granular activated carbon (GAC) were not particularly effective for the near-neutral FDT-BWST blend; metal-doped alumina performed no better in this series of experiments than did the bare alumina substrate. Adding EDTA (metal chelant) to the blend resulted in even less sorption to the alumina-substrate solid media.

Reversing the trend for alumina substrate, the iron-doped GAC (FDC) had little tendency to sorb predominantly cationic Co-58 ( $K_d \sim 22$  mL/g), but performed very well for anionic (chelated) Co-58 ( $K_d \sim 1,254$  mL/g). This is consistent with its enhanced performance for anionic Sb-125, and is similar in this respect to the performance of silver-doped carbon (AGC 5860).

Since the net surface charge determines whether an inorganic medium is predominantly a cation- or anion-exchanger, it may be worthwhile investigating pH dependence over the range of expected values based upon historic data from the site, to determine whether the contaminant-laden medium will subsequently desorb contaminant when water condition changes (pH, redox condition, added EDTA, etc.).

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Table XI. Effect of Added Na<sub>2</sub>EDTA on Uptake of Nonvolatile Radioactivity (~ 97% as Co-58) by Select Solid Media, as Reflected in the Partition Coefficient (K<sub>d</sub>, mL/g). The blended waste has an initial pH value ~ 6.7 and contains ~ 1,265 ppm B. Phase contact time is ~ 3-h, and media are tested at average mass ratio (liquid/solid) ~ 69.

Solution:	FDT + BWST (~ 50:50)		FDT + BWST (~ 50:50)
Na <sub>2</sub> EDTA Added	None		~ <b>1.9 mg/L</b>
Solid Phase	pH after Phase Contact	K <sub>d</sub> (mL/g)	K <sub>d</sub> (mL/g)
GX	3.62	2349	450
GT	2.52	<b>2037</b>	<b>1161</b>
BC- W	7.43	1585	51
AGC 5860	7.08	<b>609</b>	<b>1066</b>
Ebony T (100%)	6.77	1818	2
AA (Al <sub>2</sub> O <sub>3</sub> )	7.20	619	20
Dowex 2-X8, Cl form	5.47	19	941
BC + AGC 5860 (~ 50:50)	7.30	1146	926

Note: Beta activity is estimated at MCLinc after drying the sample aliquots to evaporate the H-3 component. (H-3 is ~ 98% of total beta activity, before drying)

Table XII. Effect of Added Na<sub>2</sub>EDTA on Uptake of Nonvolatile Radioactivity (~ 97% as Co-58) by Select Solid Media, as Reflected in the Partition Coefficient (K<sub>d</sub>, mL/g). The blended waste has an initial pH value ~ 6.7 and contains ~ 1,265 ppm B. Phase contact time is ~ 16.5-h, and media are tested at average mass ratio (liquid/solid) ~ 61.

Solution:	FDT + BWST (~ 50:50)		FDT + BWST (~ 50:50)
Na <sub>2</sub> EDTA Added	None		~ <b>1.9 mg/L</b>
Solid Phase	pH after Phase Contact	K <sub>d</sub> (mL/g)	K <sub>d</sub> (mL/g)
MnO <sub>2</sub> -doped Al <sub>2</sub> O <sub>3</sub> ( <b>MDA</b> )	6.6	314	13
"Fe(OH) <sub>3</sub> "-doped GAC ( <b>FDC</b> )	7.0	537	17
MnO <sub>2</sub> -doped GAC ( <b>MDC</b> )	5.0	22	1254

Note: Beta activity is estimated after drying the sample aliquots to evaporate the H-3 component. (H-3 is ~ 98% of total beta activity, before drying)

From Tables XI and XII, the media that appear to be most effective in upset conditions (higher levels of Sb-125, EDTA and boron) appear to be granular AGC 5860, GT (resin), and (possibly) MnO<sub>2</sub>-doped alumina (MDA).

## SUMMARY & CONCLUSIONS

As witnessed in the pareto ranking tables (diminishing distribution coefficients, or K<sub>d</sub> values), some extremely high K<sub>d</sub> values were achieved in total activity removing of FDT and BWST wastewaters (primary activity from cobalt and antimony, respectively).

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While removal efficiencies, percentages or decontamination factors (DFs) are useful measurements in media selections, distribution coefficients (Kds) supply an additional benefit in giving a better idea how long such a media might last prior to breakthrough as opposed to a snapshot percent removal of a particular isotope. Thus the definition of Kd as the mg of the isotope of interest per g of media divided by the mg of isotope per ml of solution (in mL/g). This represents the number of mL of solution that can be processed per g of media. The next step, of course, was to run long-term breakthrough curves on actual on-going wastewaters. This is on-going and will be presented in a subsequent paper.

It was found, and quite dramatically, that such high Kd values could be reduced or completely eliminated with the introduction of some outage upset additives. A drastic reduction occurred (by a factor of 1000) in Kds with the addition of extremely small amounts of complexing agents such as EDTA. There were several exceptions to this case including GT resin and AGC 5860 5860 specialty media. Some media such as standard Dowex 2-X8 (anion IX) and AGC 5860 5860 actually improve with the addition of EDTA, but only AGC 5860 5860 performs during normal operations, as well, successfully.

Removal of antimony (Sb) has long been the most challenging undertaking at a PWR and remains so to this day. This is particularly the case during outages and/or high boron concentrations. Like the media downselect for cobalt removal, Sb required an even more specialized media, and one that could also operate under normal and upset conditions.

Fortunately, after extremely involved studies, several media were found successful. These included: MDA (a manganese doped alumina), FDC (an iron doped carbon), and the final downselect resin, ASM 125.