Removing Antimony from PWR Waste Streams

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Abstract

Light water, pressurized nuclear reactors (PWRs) with borated primary systems are often plagued with Sb^{125} (antimony). This isotope is problematic in that it is not readily removed from liquid radwaste (LRW) by conventional ion exchange processing.

While hydroxide-form anion resin is initially effective at removing Sb^{125}, when fully borated, this media tends to slough the accumulated Sb^{125}. This necessitates frequent changes of the anion resin, a process that is both costly and operationally burdensome.

Based on testing at Arkansas Nuclear One, Vogtle, Fort Calhoun, Turkey Point and other sites, a new media has been developed that selectively removes Sb^{125} from a borated stream while remaining unaffected by the boric acid concentration. In most cases, 10 to 20 cubic feet (0.28 to 0.56 m^3) of Sb^{125}-selective DT-47 media is sufficient to treat a plant's LRW for a year.

This paper reports on the in-plant antimony removal performance of the DT-47 Sb-selective media, as well as on follow-up testing conducted to date.

Background

Before the mid-1990's, the primary focus of PWR LRW processing was waste minimization. With waste treatment and disposal such substantial contributors to operating costs, reduced volumes could help make nuclear power economically competitive.

This push for volume reduction was remarkably successful. Disposal volumes dropped sharply with LRW volumes often reduced by a factor of 5 -- and in extreme cases a factor of 20 -- over prior operating periods.

Reducing activity releases to the environment was a secondary goal, and discharges decreased somewhat with waste volumes. But after the mid-1990's, industry insurance ratings and peer audit groups placed steadily increasing emphasis on this performance criterion. Plant performance was now being evaluated in terms of millicuries of activity released, instead of cubic feet of waste generated, though, for cost reasons, volume reduction targets were never eliminated.

Ion-selective processing media, refined primary chemistry management, improved fuel integrity, reductions in volume of water generated, implementation of chemical control programs, and training of plant personnel about the impact of introductions to the LRW system have all contributed to the steady downward trend in activity releases. In the 1980's, activity releases of 1,000 mCi/yr (3.7E+10 Bq) were common. By the 1990's, plants were routinely targeting releases of 400 mCi/yr (1.48E+10 Bq). Today, releases of 20 to 30 mCi/yr (7.4E+8 to 1.11E+9 Bq) are the norm.

New Challenges

Despite a high biological uptake for cesium, source reduction and the introduction of new cesium-selective media have reduced concern for this isotope, except as a waste classification issue. Likewise, improved primary chemistry, chemical cleaning campaigns, and chemical control programs have reduced the impact of cobalt on LRW processing and activity releases.

Coincident with the reduction of these two primary contributors, secondary isotopes such as antimony started claiming a higher percentage of released activity at many plants. In effect, as the more abundant isotopes of cesium and cobalt were reduced, the remaining isotopes became more apparent. As a result, effective treatment methods were needed to mitigate the impact of the now-noticeable Sb concentrations.

Many Approaches, Few Results

In the 1980s, the Vitreous State Laboratory (VSL) at the Catholic University of America engaged in a several years of on/off efforts to identify or develop an Sb-specific media. These efforts were generally unproductive. The only material identified, powdered activated alumina, showed the required affinity for antimony. Unfortunately, it was difficult to apply, and was quickly overwhelmed in borate solutions -- a serious shortcoming when processing PWR waste streams.

In the mid 1990's, EPRI supported a number of investigative efforts that yielded "interesting" results, but did not identify a material viable for use in power plants. For instance, stannis chloride was found to show efficacy, but its highly corrosive nature made introduction to plant systems impossible.

Several plants and vendors saw measurable reductions in antimony when using coagulants and precipitants to remove cobalt and other particulate material, but the decontamination factors (DFs) were insufficient to effect the desired improvements in effluent quality. The gains were small in light of the shortcomings of pretreatment: additional equipment, chemical handling, inconsistent results, increased filter usage, and potential media fouling.

Slow Progress

In the late 1990's Diversified Technologies deployed three different, but related, media for column testing at plant sites. While the three showed varying degrees of affinity for antimony, all exhibited the tendency for borates to overwhelm this selectivity.

Through literature search and testing, it was determined that a pH reduction resolved the competition problem, as boric acid does not compete in the same way as borates. When a range of pH levels were tested, a pH of 4.5 seemed to provide the maximum benefit, with minimal adjustment. The small incremental gains that came from lowering the pH further were offset by the additional chemical treatment required, and the prospect of having to re-adjust the pH higher to meet the discharge limits at some plants.

When the DT-47 was used on various process streams, the DFs varied from 5 to 50, with most results in the 10 to 20 range, at the adjusted pH of 4.5. Though these DFs were no better than anion resin (OH^- form), DT-47 has three notable advantages: longer life, transparency to boric acid and resistance to elution. When fully borated, anion resin loses virtually all affinity for antimony; if not removed from service, it may elute a significant portion of the antimony already collected.

Though DT-47 demonstrated marked performance improvements over anion resin, it was not problem-free. Besides requiring pH adjustment for optimum performance, it had an irregular grain size, and exhibited a friability that caused an abundance of fines. These fines often resulted in elevated pressure drops and restricted flow early in bed life. Backflushing or sparging was rarely effective in reestablishing good flow, as the sparging simply carried the fines to the top of the bed, further aggravating the problem. As a result, some beds were removed from service because of pressure drop before they were completely exhausted.

Media Improvements

In order for DT-47 to become commercially viable, three improvements were needed: better DFs, longer bed life, and reduced pressure drops. All three of these were addressed by changes in formulation and manufacturing. Subsequent field testing was used to determine which changes were actually improvements.

Based on processing results from 2005, the fruit of this development effort was an improvement of DFs to the point that MDA was more consistently reached, and for longer periods. This improvement was "perceived" as much as proven. A direct comparison between media tested at different times is always problematic, due to the variability of the streams used for testing.

There was a quantifiable improvement in larger grain size, fewer fines and reduced friability. Previously, fresh DT-47 beds would experience progressive flow restrictions within a few months; the new formulation showed little change in pressure drop after a year of operation.

A newer formulation being deployed in 2006 has larger grain size without an apparent loss of decontamination efficacy (that might be expected due to the smaller surface area of these larger grains). This formulation has a stronger media-antimony bond that may prove beneficial for decontamination, as well as a long-lived process bed that is evidenced by greater throughput. Interestingly, the stronger media-antimony bond seems to reduce the dependency on pH adjustment. Preliminary application shows consistent antimony removal to MDA, even in the mid-6 pH range. To date, there has not been enough time to determine whether this holds true over the life of the bed, or whether is it just the transient behavior of new media. Clearly, elimination of the pH adjustment for optimum performance would be favorable.

Turkey Point

In the past, antimony has accounted for as much as 65% of the gamma activity releases at Turkey Point. Introduction of the DTS Waste Processing System (WPS™) and DT-47 antimony-selective media has resulted in a sharp improvement in antimony removal.

The following table shows the weighted average antimony processed during the first quarter at Turkey Point.

Table 1

Turkey Point Antimony Removal (451,000 gallons, 1,707 m^3)

Isotope	Weighted Average Influent (μCi/ml)	Weighted Average Effluent	DF	% Removed
Sb-124	3.42E-6 (127 mBq/ml)	MDA	∞	100.0
Sb-125	4.27E-5 (1580 mBq/ml)	3.01E-7 (11.1 mBq/ml)	141.7	99.29
Total	4.61E-5 (1706 mBq/ml)	3.01E-7 (11.1 mBq/ml)	153.1	99.35

Arkansas Nuclear One

ANO was an early-adopter of Sb-selective media, and has used it continually since 2001. Antimony was a particularly chronic problem in Unit 2, and Unit 1 saw intermittent concentrations of concern. DT-47 has mitigated, if not eliminated, the antimony problem at ANO by routinely delivering DFs of >10.

New Media, Plant Testing and Performance

To obtain results rapidly, plant column testing was conducted at a 10X flux, for an equivalent total throughput of >40,000 gallons per cubic foot (5.4 m^3 per liter). Most of the testing was conducted at an average pH of 3.5, though a short test run was conducted at pH 4.5 to compare the influence of pH on media performance. A slight increase in conductivity was observed, with no discernable pH shift across the columns.

In the 3.5 pH range, there was no measurable boron uptake. This was expected, since virtually all of the boron would be present as boric acid. At a pH of 4.5, boron removal, as borate, was in the single digit to 10% range. The column was not run to borate saturation. If it had been, as in full-scale applications, it is not expected that the collected antimony would be eluted.

During initial column testing, an affinity for Co-58 was observed, though it was not analyzed for during later testing. During full-scale application, the same affinity (likely the result of association with organics and formation of a weakly anionic state) was seen for Co-58, but the Co-58 later eluted. Sample results below were typical.

Table 2

Typical Column Test Results for DT-47

Isotope	Influent (pH 6.2)	DT-47C Effluent (20 Bed Volumes)	DF
Mn-54	2.05E-06 (75.8 mBq/ml)	1.11E-06 (41.1 mBq/ml)	2
Co-58	4.71E-05 (40.7 mBq/ml)	1.54E-05 (570 mBq/ml)	3
Co-60	5.92E-06 (219 mBq/ml)	1.81E-06 (67.0 mBq/ml)	3
Sb-125	8.99E-06 (332 mBq/ml)	MDA	Infinity

The rest of the column test results for antimony were MDA. Influent antimony concentrations ranged from low E-5 uCi/ml (370 mBq/ml) to high E-7 uCi/ml (3.7 mBq/ml) throughout. No affinity for cobalt, cesium or other isotopes was observed during the test runs.

Full-scale plant use confirmed column test results. The DT-47 was positioned in the process logic downstream of the cation resin, in order to take advantage of the low pH already present. Influent pH to the antimony-selective media bed ranged from 3.5 to 4. Boric acid concentrations were not tracked, but covered the usual range found in PWR LRW, and had no quantifiable effects. The influent antimony concentrations were routinely mid E-5 (370 mBq/ml), with effluents routinely MDA through the equivalent of 30,000 gallons per cubic foot (4.1 m^3 per liter) of DT-47. This throughput performance is consistent with the earlier DT-47 formulation, though with better DFs and reduced pressure drops.

Fort Calhoun
An early application of the new formulation was at Fort Calhoun nuclear plant. The results in the table below is indicative of the enhance antimony removal efficacy as well as broader spectrum removal of cobalt and manganese isotopes. The processing results also indicated the media is less dependent (or independent) of pH adjustment required with the older formulation.

Minimum detectable activity (MDA), used for calculation of the decontamination factor (DF) is 1.0E-7 uCi/ml (3.7 mBq/ml).

Isotope	Influent (pH 5.4)	DT-47 Effluent (1,100 Bed Volumes)	DF
Ag-110M	2.93E-06 (108.4 mBq/ml)	MDA	29
Co-58	5.07E-06 (187.6 mBq/ml)	MDA	51
Sb-125	2.06E-05 (762.2 mBq/ml)	MDA	206

Unique Use
PWR's with Bora-Flex spent fuel pool racks have chronic problems with silica elution. Since the mid-1990s, the Boric Acid Recovery System (BARS™) provided by Diversified Technologies has used reverse osmosis (RO) membrane technology to remove silica from borated spent fuel pool and reactor water storage tank systems.

The reject from this RO process, rich in silica, cobalt, cesium, and antimony (if present in SFP/RWST systems), is sent to LRW for processing. This high concentration of antimony was a removal challenge, even for plants using DT-47 media.

To capture the antimony at the source, the BARS™ reject outlet was fitted with a dolly-mounted, 1.5 cubic foot (43 liter) shielded antimony-capture vessel loaded with DT-47. This vessel proved highly effective, removing 100% of the antimony from the reject stream that had influent antimony concentrations as high as 1.0E-3 uCi/ml (37 Bq/ml), while allowing cobalt and cesium to pass. No affinity for cobalt has been observed in this application, likely because of absence of complexing organics and particulate form of cobalt. This selectivity for antimony prevents the mobile vessel from accumulating an unduly high dose rate from cobalt and cesium accumulation.

Because the antimony was intercepted before it could mix with organics and other chemicals in the sumps and waste tanks, antimony removal was significantly improved with minimal media consumption. The small vessel showed no breakthrough after several weeks of round-the-clock operation.

Current Users
A number of plants, including ANO Units 1 & 2, Fort Calhoun, Wolf Creek, Rancho Seco, Vogtle, Indian Point, Millstone, Seabrook and Turkey Point have applied DT-47. Users of the early formulation are easily upgraded to the new, improved material, as the transition requires no changes in MSDS, material handling or operating procedures.

The Cons
The efficacy of DT-47 compared to that of anion resin -- the traditional antimony removal media -- is obvious. Nonetheless, DT-47 has two shortcomings. The first is pH adjustment to the acid form for improved decontamination, and the second is that DT-47, a metal oxide, cannot be volume-reduced by thermal treatment.

The need for pH adjustment is easily accommodated. In most instances, the reduced pH from upstream cation beds is adequate to effect the pH shift in the already boric acid buffered stream. In those instances where the cation beds are run past chemical exhaustion (a good practice), an automated pH adjustment skid controls the pH of the process stream to the desired level without operator intervention. The day-tank of the pH skid must be refreshed every few weeks.

Longer-term use of the newest DT-47 formulation indicates little need for pH adjustment. In most instances, the natural bias of the LRW process stream toward acidity as well as the acid pH shift induced by upstream H+ form action resin results in satisfactory performance without pH adjustment.

The ineffectiveness of thermal treatment for volume reduction cannot be remedied, but is of little consequence. The 10 to 20 cubic feet (0.28 to 0.56 m^3) of DT-47 media used for antimony removal will be low dose, Class A waste that benefits little from volume reduction and is well suited for direct burial.

Summary

PWR plants have chronically had problems removing antimony from borated LRW process streams. Today, these problems are being addressed through application of a new media designed specifically for selectivity for antimony. This media has undergone several generations of development, and is currently being used successfully in eight plants. The latest formulation of the media has exhibited the ability to produce MDA antimony with little or no pressure drop for the duration of bed life. To date, full-scale application of the new formulation indicates little, or no, pH adjustment is required for optimum performance.

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