DEVELOPMENT AND IMPLEMENTATION OF METHODOLOGIES FOR REMOVAL OF PROBLEMATIC RADIONUCLES AT COMMERCIAL U.S. PRESSURIZED WATER REACTOR FACILITIES

A. Tavares,
Graver Technologies, Inc.

G. Austin
Duratek, Inc.

HISTORY

Commercial nuclear facilities in the U.S. and elsewhere have struggled for years to implement cost effective technologies for the removal of problematic isotopes from radioactive liquid waste streams. During the fledgling years of the U.S. nuclear power industry, evaporation was the preferred and relatively efficient method for the treatment of radioactive liquid waste. However, as plant systems aged and solid waste disposal costs increased, evaporation became much less cost effective, spawning the search for alternate technologies.

In the early to mid 1980's, a number of nuclear facilities began utilizing demineralization systems, typically supplied by vendors, to process liquid waste. These demineralization systems initially utilized large volume atmospheric vessels that provided for marginally efficient ion exchange kinetics. The atmospheric vessel systems then evolved into pressure vessel systems that were inherently safer and more efficient. As the use of pressure vessel systems became more predominant in the industry, more emphasis was placed on the removal of specific radioisotopes such as Cobalt and Cesium, and less emphasis on total deionization of the waste streams. This increased emphasis led to the development of ion specific media that had a higher affinity for the removal of these targeted radioisotopes.

There were several variations of ion specific media, and most proved very efficient for the removal of Cesium, even in hard to treat waste streams. This success effectively eliminated Cesium as a problematic isotope at most nuclear stations, except in cases where efficient polishing of trace amounts of Cesium is required to meet specific plant discharge goals. The ion specific media that were developed for the removal of Cobalt isotopes were not as effective in every application, and this challenge led to the research and development of other treatment methods such as chemical pretreatment and membrane filtration. Although some Cobalt specific media are still in limited use today, chemical pretreatment and/or membrane filtration have become the technologies of choice for Cobalt removal, and in the vast majority of applications have proven very effective. As with Cesium, Cobalt has been effectively eliminated as a problematic isotope except where polishing of trace amounts is required to meet specific plant discharge goals.

Presently, because of the aforementioned successful treatment methodologies, efficient removal of Antimony, along with trace amounts of Cobalt and Cesium have become the primary areas of radwaste treatment concern.

Duratek, Inc. and Graver Technologies have recognized this concern and have developed two alternate treatment methodologies to address the Antimony and trace Cesium/Cobalt issue.

Antimony Removal Process

Historically, removal of Antimony in a Pressurized Water Reactor (PWR) waste stream has been accomplished by utilizing standard strong base anion resins. The primary problem with this treatment method is that, due to contaminant concentrations, anion resin is much more selective for various other constituents in a PWR waste stream than it is for Antimony. The result is that Antimony is retained on the anion column but typically "sloughed" after a minimal period of retention. In early 2004, Duratek, Inc. teamed with developmental scientists from the Vitreous State Laboratory (VSL) of Catholic University in Washington, D.C. to research various alternative Antimony treatment methods that would eliminate or significantly reduce this sloughing phenomenon. This research was conducted in two phases.

In Phase one, wastewater from a commercial U.S. PWR was shipped to the VSL and testing was conducted using various commercially available resins along with VSL generated ion exchange media. The results from this VSL testing led into Phase two, which was actual onsite slipstream testing at the same commercial U.S. PWR.

Testing Chronology

In the spring of 2004, tests were conducted at the VSL in two stages using a total of ten (10) various ion exchange media and two waste water sources. One source was actual waste from a commercial PWR and the other was a surrogate prepared by the VSL to match the average conditions at the commercial PWR.

Stage 1

In stage 1, ten different ion exchange media were tested using a bulk capacity test method to determine the optimum performer. Six of these were commercially available products and four were prepared at the VSL. The bulk capacity testing consisted of adding a specific amount of each of the ion exchange media to equal volumes of the wastewater. The bottles were sealed and rolled in a tumbler for several hours (all equal time periods). The samples were then filtered and the filtrate analyzed for all detectable isotopes. Since the primary focus of the study was the evaluation of Sb125 removal efficiency, the selection of optimum performers was made on the basis of Sb125 decontamination factors (DF's). The results revealed a few ion exchange media that performed better than the rest.

Stage 2

The ion exchange media that provided the optimum results in the bulk capacity tests were then subjected to column testing. The column tests were performed using equal volumes of the chosen ion exchange media using 80 mesh discs at the bottom of the columns to simulate full scale vessel retention elements. The columns were initially back flushed with deionized water to

remove air bubbles, and then wastewater was introduced using piston driven pumps. The flow rate was adjusted to simulate full-scale vessel flow conditions. The column test effluents were analyzed and two important findings were realized.

Finding #1

All but one of the tested ion exchange media exhausted at around 300 column volumes. The one ion exchange media that proved most efficient exhibited much longer run times while maintaining effective Sb125 removal capacity.

Finding #2

During the column testing stage a phenomenon was observed that required a specific operational technique to resolve. Due to pending patents and the proprietary nature of this discovery, the specifics of this operational technique cannot be divulged. However, when employed during the stage 2 testing, this technique resulted in Sb125 removal capacity remaining effective for over 5000 column volumes. At this capacity, a typical ion exchange vessel with a volume of 30 ft3 could process in excess of 1 million gallons and remain efficient for Sb125 removal.

Plant Specific Testing/Full Scale Operation

The Sb125 process developed during the VSL column testing was then reproduced on a laboratory scale at the commercial PWR that provided the initial waste sample. The results were similar to those achieved at the VSL. After successful completion of the plant laboratory scale testing, the Sb125 removal process was installed in the full-scale Duratek, Inc. liquid waste processing system in October 2004. Data has been collected for each processing event since full-scale operations commenced on 10/12/04, and the results are summarized in the Table I below.

Table I. Sb125 Process Data

Date	Influent Activity uCi/ml	Effluent Activity uCi/ml	Decontamination Factor
11/29/04	3.57E-05	MDA	446
11/30/04	3.57E-05	MDA	446
12/01/04	3.57E-05	MDA	446
12/13/04	1.24E-05	MDA	155
12/14/04	4.04E-06	MDA	50
12/21/04	3.88E-05	MDA	485
01/11/05	1.32E-04	MDA	1650
01/17/05	6.50E-06	MDA	81
01/18/05	6.50E-06	MDA	81

NOTE: For purposes of calculating decontamination factors, an MDA value of 8.0E-08 uCi/ml was utilized. Actual MDA at this commercial PWR is ZERO counts during the live time period.

A total of 283,651 gallons was processed during this data collection period with MDA activity reported for each processing event. The media throughput since the Sb125 process was initiated is 9,455 gallons/ft3, or 1,266 column volumes.

Ion Selective Filters

The predominant method for polishing trace amounts of Cobalt isotopes in the effluent of granular media based radioactive liquid waste processing systems has been to utilize mechanical filters – typically 0.1 micron absolute cartridges. While this is normally an effective removal mechanism for trace amounts of Cobalt isotopes, it is not effective for removing trace Cesium isotopes. A substantial percentage of the Cobalt is likely to be present as a colloid, a small particle or group of particles that can be mechanically filtered with fine filtration. Conversely and with rare exception, Cesium exists as a soluble ionic species, and requires ion exchange media for removal. Additionally, the 0.1 micron filter cartridges are very easily fouled by any suspended solids that remain in the waste stream. This results in low volume throughputs, high solid waste generation, and premature replacement due to high differential pressure and reduced flow concerns.

Graver Technologies, Inc. has developed a new and unique functional filter methodology. The Functionalized Liquid Polishing (FLiP^{TM}) Filter combines the mechanical filtration capability of a cartridge with the ion exchange capability of ion selective granular media. This new technology operates best as the final polisher on a comprehensive liquid waste processing system. The functional ion selective media provides the removal mechanism for soluble isotopes. This media is uniquely manufactured to provide enhanced hydraulic properties that allow the FLiP filter system to run for long periods and to filter insoluble particles without being susceptible to premature fouling.

These filters have been utilized in several Duratek supplied liquid waste processing systems since early 2004, and exceptional results have been documented. In one U.S. PWR application, a throughput in excess of 200,000 gallons per filter change-out has been achieved while producing less than Minimum Detectable Activity (<MDA) Antimony effluent for nearly every batch of radioactive liquid waste processed. Overall system and filter performance also achieved impressive decontamination factors for Cesium and Cobalt.

Functionalized Liquid Polishing (FLiP) Filter

The FLiP Filter is engineered to perform a final polishing function, removing **trace amounts** of radionuclide contaminants that remain in the liquid radioactive waste stream. The FLiP Filter will remove both suspended and dissolved contaminants.

Ion Selective Configurations:

- Cesium
- Cobalt
- Antimony – a secondary specificity for Antimony removal has been demonstrated
- Others to be determined

Design Features:

- Lightweight, and can be disposed of in a similar manner to other filter cartridges
- No additional chemical pretreatment or precoat required
- Polypropylene core and outer cage for strength and stability
- Inner and outer polypropylene filter wraps
- The annulus region (area lying between the inner and outer filter wraps) is packed with ion selective material
- Standard filter size of 30" length X 2.5" diameter – can be custom sized for any specific application

Performance:

The FLiP Filters were utilized at three separate commercial nuclear plants in conjunction with Duratek, Inc. supplied liquid waste processing systems in 2004. At two of those facilities, the FLiP Filters were used sporadically as part of the overall liquid waste processing system testing. Test data are still being collected and evaluated. At one commercial nuclear facility, the FLiP Filters were (and continue to be) utilized during full-scale liquid waste processing operations. Following is a summary of the operational data collected during the full-scale operational period from February 2004 through October 2004:

- Processing system consisted of four (4) deep bed filtration/ion exchange vessels preceded by Duratek, Inc.'s. AIM™ chemical pretreatment system and followed by one (1) cartridge filter housing
- One (1) process vessel contained activated carbon and was utilized as a deep bed filter
- Remaining process vessels were loaded with various types of ion exchange media
- Cartridge filter housing contained six (6) FLiP Filters

Table II. Performance Data

Process Events	Average Total Influent (uCi/ml)	Average Sb125 Influent (uCi/ml)	Average Filter Influent (uCi/ml)	Average Total Effluent (uCi/ml)	Average Sb125 Effluent (uCi/ml)	Average System DF	Average Sb125 DF	Average Filter DF
28 (1)	4.14E-04	1.024E-05	4.37E-05	4.27E-07	<MDA (6)	970	512	102
20 (2)	2.21E-03	1.52E-05	N/A (3)	4.22E-06 (4)	1.26E-06 (5)	524	12	N/A (3)
1	1.52E-03	1.35E-03	N/A (3)	1.71E-07	<MDA (6)	8888	67,500	N/A (3)

(1) 225,100 total gallons
2) 258,700 total gallons
(3) Insufficient data
(4) Data include one (1) processing event with 5.73E-05 uCi/ml effluent. Average effluent for remaining nineteen (19) processing events was 1.43E-06 uCi/ml.
(5) Data include one (1) processing event with 2.45E-05 uCi/ml effluent. Average effluent for remaining nineteen (19) processing events was 3.68E-08 uCi/ml.
(6) MDA value 2.0E-08 uCi/ml

Although the FLiP filter technology has proven effective for removal of trace amounts of problematic radioisotopes, it is imperative that a gross filtration/ion exchange system is operated upstream of the FLiP filter installation to ensure efficient overall radioisotopic removal.

SUMMARY

Duratek, Inc. and it's partners the Vitreous State Laboratory at Catholic University and Graver Technologies, Inc., have developed and implemented technologies that enhance the ability to remove problematic isotopes from liquid radioactive waste streams.

Regarding Sb125, a process that has the capability of achieving throughputs in excess of 5000 column volumes while maintaining satisfactory Sb125 removal efficiency has been implemented at a commercial U.S. PWR. The full-scale operational data collected to date supports the conclusions derived during the various developmental and testing phases. Throughputs significantly higher than those historically recorded have been achieved with MDA Antimony 125 activity being discharged. Duratek, Inc. plans to implement this process at other commercial utilities that utilize Duratek Inc.'s liquid waste processing services in 2005.

The FLiP Filter technology provides a proven method for the removal of trace amounts of problematic isotopes such as Cesium, Cobalt, and Antimony. A FLiP Filter array effectively processed in excess of 250,000 gallons of liquid radioactive waste at a commercial U.S. PWR. MDA of Sb125 was achieved for more than 225,000 of those gallons. The Flip Filters are commercially available to interested parties and may be configured and utilized for the final polishing reduction of one or more of the aforementioned isotopes.