Engineered Media for Removal of Fission Products from Aqueous Streams – 14580

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ABSTRACT

Nuclear fission products from fuel have the potential to be released into aqueous streams either from fuel processing operations or emergencies that cause the breakdown of nuclear fuel. Once fission products are entrained into aqueous streams, they present a threat of contaminating the surrounding environment. Therefore, methods of removing these contaminants from aqueous streams are desirable. Performance data associated with engineered media designed for removing the fission products cesium (Cs) and strontium (Sr) from aqueous streams has shown that such media is capable of achieving decontamination factors on the order of magnitude of 10^6 while reducing final waste forms by more than seven times compared to waste volumes generated by other technologies capable of removing Cs and Sr.

INTRODUCTION

Natural zeolites are known to be effective in removing Cs and Sr from aqueous streams. However, their performance can be limited by background water quality characteristics, such as highly acidic or basic conditions, or high concentrations of competing ions. Naturally occurring zeolites also have limited capacities leading to large amounts of associated waste. An engineered form of crystalline silico-titanate was developed to address performance constraints typically associated with natural zeolites.

UOP IONSIV™ R9120-B Selective Media, formed crystalline silico-titanate, was jointly developed by Sandia National Laboratories, Texas A&M University and UOP. Along with IONSIV R9150 and R9160, these are microporous, inorganic, crystalline adsorbents exhibiting high selectivity and capacity for fission products in the presence of high concentrations of competing cations. These adsorbents retain their physical integrity and selectivity over a broad pH range in the presence of high levels of ionizing radiation and exhibit a high resistance to attrition.

Description of Performance Evaluations

Performance evaluations of IONSIV selective media have been performed in numerous laboratory and pilot scale environments. Previous generations of these products have been used commercially for more than 30 years to treat radioactive waste streams in commercial nuclear power plants, alkaline tank waste and spent fuel storage pool water. The first commercial scale application of these adsorbents was implemented at the Fukushima Daiichi nuclear power plant in Japan for water decontamination purposes

following the March 2011 earthquake. Results from a range of evaluations and this commercial implementation are summarized in case studies discussed in this paper.

Discussion of Performance Data

Fukushima Daiichi

The Fukushima Daiichi nuclear power plant is located in Fukushima Prefecture in Japan. In March 2011, a 9.0 magnitude earthquake caused a tsunami to flood the plant and seawater was retained within the sub-basement on the plant site. Failure of the cooling systems increased temperatures in the fuel rods, which resulted in the release of fission products into cooling water that subsequently flowed to the sub-basement. Accumulation of this water caused the water level in the basement to rise and threatened to overflow the site and discharge radioactive water into the Pacific Ocean. The water level in the sub-basement needed to be lowered to prevent ocean discharge and achieve hydraulic equilibrium between the water in the sub-basement and the external groundwater to prevent groundwater contamination. The water from the sub-basement could then subsequently be used in the recirculation loop for cooling the reactor core. Water treatment was needed for removal of Cs and to facilitate storage and beneficial use of water contained in the sub-basement.

A water treatment system consisting of the following processes was originally installed:

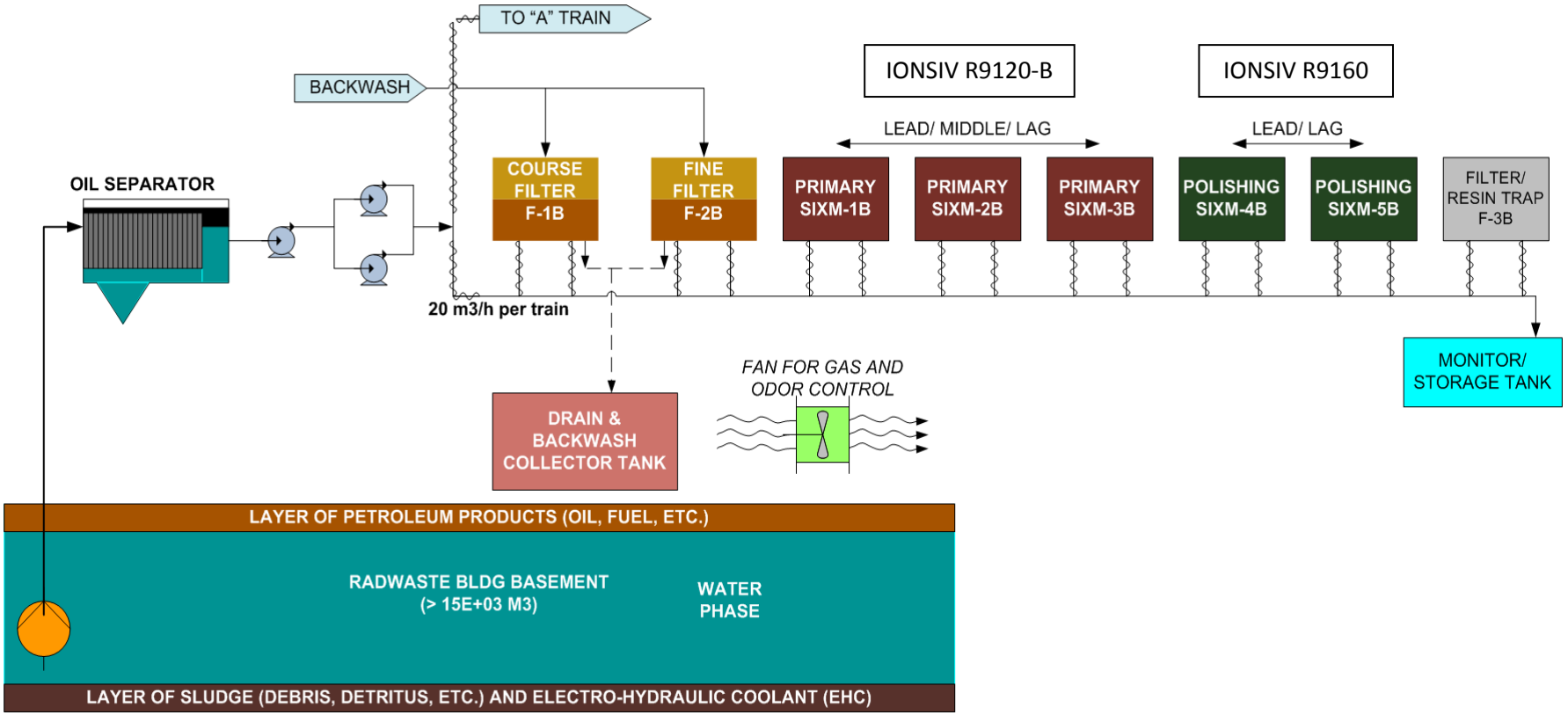
- Oil/water separation
- Cs removal adsorption columns
- Media filter
- Dissolved air flotation
- Coagulation/flocculation/sedimentation
- Disk filtration/reverse osmosis (RO)

This treatment process did not achieve the desired level of Cs removal and resulted in carryover of chemical precipitates that fouled the RO pre-filters and membranes. Consequently, the RO system could not operate at full capacity and resulted in higher levels of radioactivity in the RO membranes that are undesirable for worker exposure. This treatment process also generated large waste volumes that were undesirable.

A separate treatment process for Cs removal was subsequently installed to meet performance goals. IONSIV R9120-B and R9160-G selective media were utilized in conjunction with the Simplified Active Water Retrieve and Recovery System (SARRY^{TM}) system, which was developed by Toshiba Corporation, Shaw Global Services, LLC, and

AVANTech, Inc. and is depicted in Figure 1. As of April 2013, the SARRY system has treated over 500,000 m^3 of water since its installation.

Figure 1: SARRY System



Upon initial start up of the facility, decontamination factors for Cs were on the order of 100,000 due to the high initial concentrations. As Cs has been removed in the treatment process, concentrations in the influent have slowly been decreasing and the associated decontamination factors are lower compared to initial start up. Table 1 summarizes the system performance data as of April 30, 2013 based on publicly available data from TEPCO's reports on the situation at the Fukushima Daiichi facility.

August 2011	
Radioactivity density, initial (Bq/cm^3)	1.8 * 10^6
Radioactivity density ex Cs removal process (Bq/cm^3)	2.3
Decontamination Factor (Cs-137)	7.8 * 10^5
October 2013	
Volume of water treated (m3)	>500,000
Radioactivity density, initial (Bq/cm3)	3.7 * 10^4
Radioactivity density ex Cs removal process (Bq/cm3)	0.61
Decontamination Factor (Cs-137)	6.1 * 10^4

Table 1: Fukushima Performance Data

Application of IONSIV for cesium removal has resulted in essentially complete removal of Cs from seawater and achieved the following:

- Reduced Cs to non-detectable levels
- Allowed the RO system to operate at full design flows due to the fast kinetics of IONSIV and overall SARRY system design
- Minimized media replacement requirements due to the high capacity of IONSIV for Cs
- Reduced waste volumes by over 90% compared to those produced by the Cs removal process in the original treatment system

Simulated Wastes

Many Department of Energy (DOE) facilities have either operational or legacy needs for removing Cs and Sr from process or stored wastewater. IONSIV adsorbents have been evaluated in comparison to alternative treatment methods from various DOE facilities and results are summarized below.

Oak Ridge National Laboratories

Column testing of natural chabazite and IONSIV selective media were performed on a simulated waste as described in "A Comparative Evaluation of IONSIV IE-911 and Chabazite Zeolite for the Removal of Radiostrontium and Cesium from Wastewater[1]." The simulated and actual waste characteristics are shown in Table 2.

	Concentration (mg/L)	
Component	Simulant	Actual
Ca^{2+}	35-40	45
Cs^{+}	9.4×10^{-8} (3.0×10^{-2} Bq/L)	3.4×10^{-4} (1.12×10^{6} Bq/L)
K^{+}	1-3	1.2
Mg^{2+}	7-8	8.8
Na^{+}	14-30	18.3
Sr^{2+}	0.1	0.1
Sr^{2+}	5.3×10^{-8} as ^{90}Sr (2.70×10^{2} Bq/L)	1.14×10^{-6} as ^{85}Sr (1.0×10^{6} Bq/L)
pH	6.7-9	7-8

Table 2: Oak Ridge National Laboratories Water Quality Data

[1] A Comparative Evaluation of IONSIV IE-911 and Chabazite Zeolite for the Removal of Radiostrontium and Cesium from Wastewater; D.T. Bostick, S.M. DePaoli, and B. Guo; Oak Ridge National Laboratory. August 1998.

Test results demonstrate that IONSIV media showed substantially improved performance over natural chabazite, as shown in Table 3. This is due to the overall capacity of the media and its selectivity for Cs and Sr, which allows for greater media loading compared to chabazite.

	Cesium			**Strontium**		
	Natural Chabazite	IONSIV R9120B	**Performance Improvement**	Natural Chabazite	IONSIV R9120B	**Performance Improvement**
Sorption Ratio (L/Kg)	17,000	95,000	**5 x**	80,000	1,300,000	**16 x**
Max. Loading (meq/Kg)	0.17	5	**29 x**	24	200	**8 x**
Maximum DF	170	17,000	**100 x**	80	1,200	**15 x**
Relative Loading	1.0	29.4	**29 x**	1.0	8.3	**8 x**

Table 3: Media Performance Comparison on Oak Ridge National Laboratories Waste

The table below demonstrates the uptake performance for each media; the engineered form (IONSIV) has a much greater uptake rate, indicating volume of water treated per mass of media is substantially greater for the IONSIV selective media.

Savannah River Site

IONSIV selective media were evaluated for waste treatment from the Savannah River Site to remove Cs (137) from low-curie salt waste[2]. Results demonstrated the long term operational benefits of using IONSIV for treating tank waste at the Savannah River Site.

The "Early," "Middle," and "Late" waste designations are variations designed to reflect the expected composition trends during salt dissolution in a single saltcake tank. Table 4 shows the waste characteristics that require treatment.

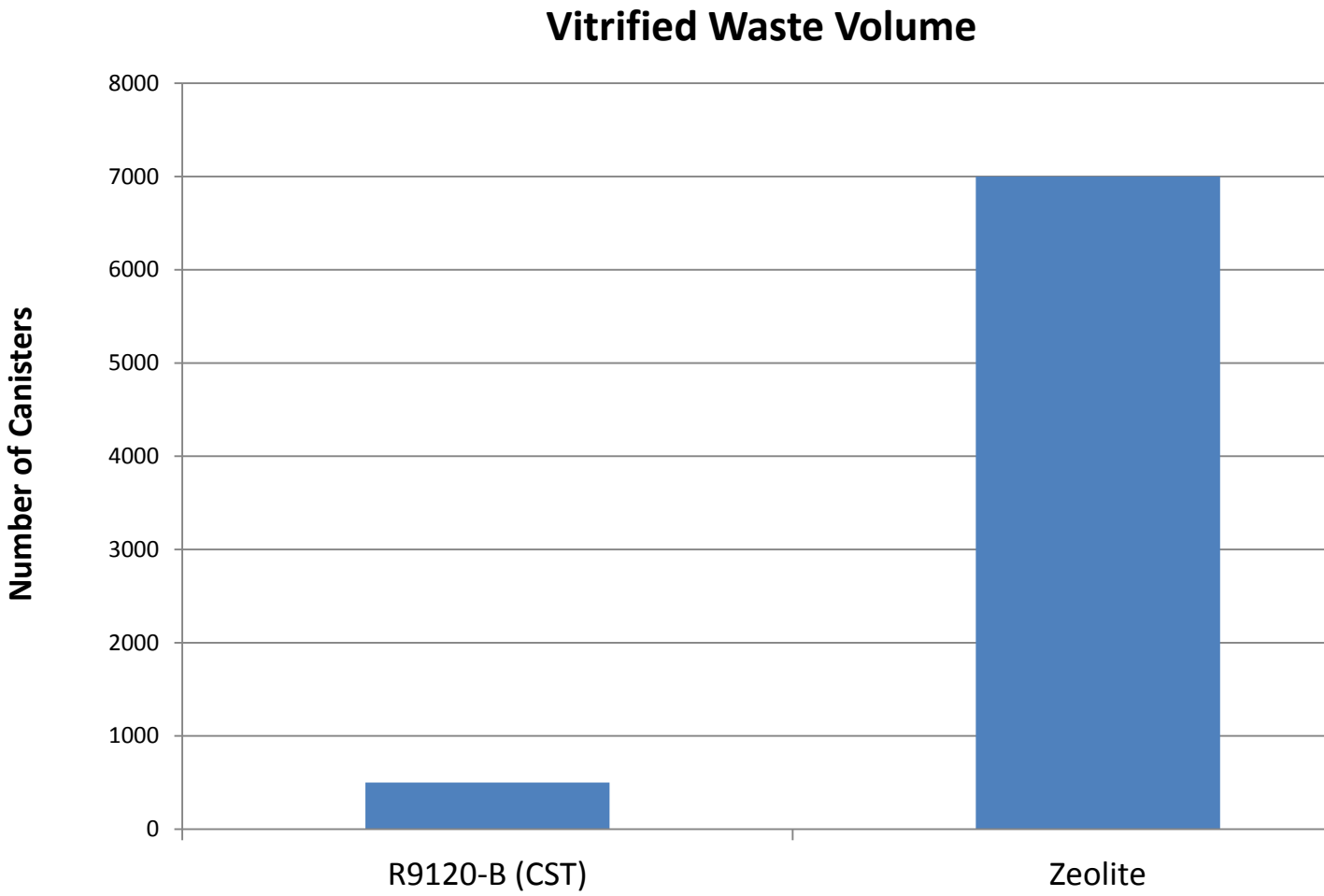
Concentration (Molar)					
Component	Early	Middle	Late	Average	Tank 41H
Na^+	7.0	7.0	4.2	6.0	7.9
K^+	0.0070	0.0070	0.0042	0.006	0.0079
Cs^+	0.00020	0.00020	0.00020	0.000040	0.00038
OH^-	1.90	1.00	0.30	1.60	0.85
NO_3^-	2.60	4.00	0.50	2.30	4.9
NO_2^-	0.90	0.10	0.020	0.71	0.24
ALO_2^-	1.20	0.40	0.010	0.35	0.45
CO_3^{-2}	0.13	0.45	1.08	0.12	0.45
SO_4^{-2}	0.050	0.30	0.55	0.16	0.23
PO_4^{-3}	0.0070	0.0020	0.010	0.13	0.035
Cl-	0.035	0.035	0.035	0.033	0.001
F-	0.033	0.033	0.033	0.031	0.001

Table 4: Savannah River Waste Composition

[2] Small-Column Ion-Exchange Alternative to Remove ^{137}Cs From Low-Curie Salt Waste: Summary of Phase 1; J.F. Walker, Jr. et al; May 2004.

One of the key study results showed that the high capacity of IONSIV selective media capacity reduces final waste forms. Figure 2 demonstrates the substantial reduction in projected final waste volumes when using IONSIV selective media compared to natural chabazite.

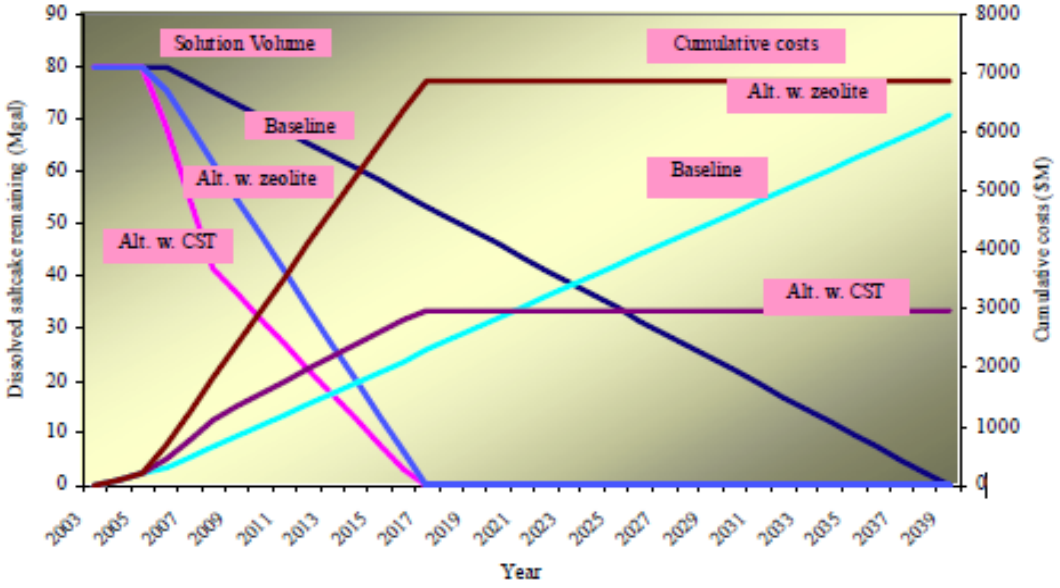
Figure 2: Comparison of Final Waste Form Volumes



The overall project timeline and economic impacts of using media with a greater capacity that results in lower final waste volumes are demonstrated in Figure 3. The 'Baseline' approach assumes the use of monosodium titanate sorption and cross-flow filtration for removal of strontium and actinides followed by caustic-side solvent extraction for removal of the cesium. The option designated as 'Alt w. CST' incorporates the IONSIV selective media. Earlier projections indicate that using IONSIV for waste treatment has the potential to reduce overall treatment costs by up to $3B and decrease

the treatment timeframe by approximately 20 years (Figure 4 reflects these projections). As canister costs have increased, projected savings have also increased to around $5.5B.

Figure 3: Operational Comparison of Savannah River Waste Treatment Options



CONCLUSION

Results from full scale operations, laboratory and pilot scale evaluations demonstrate that IONSIV selective media is highly effective in removing the fission products Cs and Sr from aqueous streams. The capacity and selectivity of this media result in the following benefits for wastewater treatment where Cs and Sr removal are required:

- Minimal volumes of loaded media are generated for subsequent storage/disposal
- Removal of Cs and Sr from streams containing high levels of competing ions over the full pH range is achievable, facilitating improved downstream process performance and reducing liquid waste and sludge volumes from downstream processes
- Increased treatment rate resulting in faster project completion timelines and overall decrease in treatment costs

REFERENCES

1. A Comparative Evaluation of IONSIV IE-911 and Chabazite Zeolite for the Removal of Radiostrontium and Cesium from Wastewater; D.T. Bostick, S.M. DePaoli, and B. Guo; Oak Ridge National Laboratory. August 1998.
2. Small-Column Ion-Exchange Alternative to Remove ^{137}Cs From Low-Curie Salt Waste: Summary of Phase 1; J.F. Walker, Jr. et al; May 2004.