Development and Testing of Two Novel and Vitrification Compatible Classes of Ion Specific Media for Application on the Hanford Waste Treatment Plant Supplemental Pretreatment and Secondary Waste Streams - 11001

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ABSTRACT

Having developed a two phase technology platform consisting of Ion Specific Media (ISM), and an Advanced Stabilization Technology (AST) featuring the Modular Vitrification System (MVS$^{®}$) to enhance and promote safe, clean and secure nuclear power, the ISMs have been further tested for the primary isotopes at Hanford that require Supplemental Treatment prior to vitrification. It is further planned that, in addition to surrogate testing and spiked surrogate testing, that actual waste testing will be carried out in hot-cells (e.g., at the 222S Labs at Hanford). While the primary focus of this paper is on the development of two novel classes of Ion Specific Media, it is important to note that these exclusively inorganic media were selectively designed to be compatible with advanced stabilization technologies (e.g., solidification and vitrification) and act as the final, stabilized waste forms required for storage or disposal on site. The purpose of developing such a class of high capacity and high specificity ISMs is to remove the recalcitrant isotopes (e.g., Cs-137, Sr-90,Tc-99 and I-129) during supplemental treatment (including Pretreatment, Off-Spec Tanks and Secondary Waste Treatment) and place them into very small packages for on-site storage or HLW vitrification. These ISMs must also be a very stable form themselves for such potentially long-term, in-tank or dry storage (i.e., inorganic in nature, leach resistant, non-hydrogen generating, sluiceable and amenable to future stabilization by thermal, or other, means). This driving to higher waste classification and smaller waste volumes allows the Waste Treatment Plant (WTP) the flexibility to minimize the in-tank HLW (for subsequent HLW vitrification) and maximize the lower level supernatant feed to further supplemental treatment and vitrification of the Low Active Waste, LAW.

Having done a full spectrum of ISMs with these qualifications and ones that will selectively handle the prominent class drivers and recalcitrant isotopes in Commercial Nuclear Power Plants (NPPs), a down select was done at our licensed facility, Materials and Chemistry Laboratories (MCL), in Oak Ridge, Tennessee for DOE specific isotope removal. This down select has been carried out on batch reactors and columns at an analytical- and bench-scale on **1)** near neutral pH surrogates and actual feeds, **2)** WTP secondary waste stream surrogates, pH ~8-9, **3)** strontium (Sr 90) removal from chelated tanks (e.g., AN 102 and AN 107), pH 12-13, and **4)** high alkali WTP Cs pretreatment, pH ~14. To further the efficacy testing here, prior to on-site hot-cell studies, testing was also successfully carried out on actual Commercial Nuclear Power Plant, NPP, waste streams, in both our Oak Ridge Lab as well as independently on site at the Seabrook Nuclear Power Station by the Electric Power Research Institute, EPRI, (including fuel pool and Boron Waste Storage Tank, BWST) waste waters.

INTRODUCTION

While one class of these inorganic Ion Specific Media is based on a proprietary, highly porous and stable glass microsphere (GMS) substrate, a highly specific engineered and/or modified mineral substrate has been included in the down select (specifically for cesium, cobalt, nickel, technetium, and iodine specificity). The glass microspheres can be produced in a fines (25-100 μ), or seeding agent form, or in a bead, or frit, version (20-50 mesh) for sluiceable column applications. These glass microspheres have huge surface areas, both external and internal, ~ 195 m^2 per gram, with crystalline structures of approximately 10 to 50 nm in diameter and a total porosity of about 35 to 40%. This extremely high internal surface area and nano-porosity allow for the internal placement of reactive moieties by chemical reactions and the subsequent entrapment of radio-isotopes within the matrix. Subsequent stabilization processes, such as microwave or glass former vitrification readily traps the isotopes in a leach-resistant and high quality waste form for long-term, safe storage. Similarly, the engineered mineral, fine or granular substrate, is a leafy structure with huge surface areas (500 m^2 per gram), as seen by electron microscopy, which, likewise, collapses around the captured isotopes during thermal processing. As mentioned, both media were designed to be vitrification and long-term storage friendly for application at the Hanford WTP or Commercial NPPs.

This novel class of Ion Specific Media has been developed with primary isotope areas of focus in mind for Hanford waste streams. Previously reported for Commercial NPPs, these ISMs are applied herein to many high level wastes, HLW, and low active wastes, LAW, applications at the Department of Energy (DOE) sites as well. The primary areas of interest for waste classification drivers and recalcitrant isotopes at DOE sites, include the following: Cesium (Cs-137), Strontium (Sr-90, (which also includes the Actinides for DOE waste streams, such as Am- 241 and Pu-239), Nickel (Ni-63), Cobalt (Co-58/60) and Iron (Fe-55), (while these three isotopes are more of an issue with NPPs), Technetium (Tc-99), Iodine (I-129) and Selenium (Se-79). The latter three isotopes are semi-volatile, oxy-anions, as is Antimony (Sb-125) in commercial NPPs. These isotopes are above the Waste Acceptance Criteria, WAC, in the off-gas condensate feeding the Effluent Treatment Facility (ETF) at Hanford and are a significant issue in the WTP vitrification off-gas stream.

Testing was carried out on select ion specific media (ISMs) at **1)** Near-Neutral pH, PWR Surrogate, traced PWR surrogate, actual samples and on-site tanks (e.g., Cs, Co, Ni, and Sr), **2)** WTP Secondary, or Recycle (vitrification off-gas volatiles, e.g., Tc, I, Se and Hg), surrogate (pH 8-9), **3)** Envelope C (e.g., chelated Sr-90) surrogates for Tanks AN 102 and AN 107 (pH 12-13), and **4)** traced species (primarily Cs) from Hanford WTP LAW simulant (50% AN 104, pH 14). The following represents the nomenclature of the media tested:

- Engineered Herschelite = H
- KCCF Herschelite = KH
- CTMA Herschelite = CH
- Iron Impregnated EH = IH
- HydroxyApatite Microspheres = HAM
- KCCF HydroxyApatite Microspheres = KHAM

- Strontium Apatite Microspheres = SAM
- Glass Microspheres = GMS
- CTMA HydroxyApatite Microspheres = CHAM
- Silver Impregnated Zeolite = AGZ
- Silver Impregnated Herschelite = AGH

Table I. Represents the cross-walk between DOE and Commercial NPP isotopes of concern, as well as the media applied therein.

DOE Sites	Commercial Sites
[In order of loading]	[In order of loading]
Supplemental Treatment Drivers	**Waste Class Drivers**
• Cs 137 [KH, H & KHAM]	• Cs 137 [KH, H & KHAM]
• Sr 90 [HAM, KHAM, SAM & H]	• Ni 63 [H & HAM]
	• Sr 90 [HAM, SAM & H]
Effluent Release Drivers	
• Am 241 (Actinide) [HAM & IH]	**Effluent Release Drivers**
• Pu 239 (Actinide) [HAM & IH]	• Co 58, Co 60 [H, HAM & KHAM]
• Tc 99 [CHAM, CH & IH]	• Fe 55 [H & HAM]
• I 129 [AGH, AGZ & IH]	• I 129 [AGH, AGZ & IH]
• Se 79 (Sb, As, Bi) [AGH, AGZ & IH]	• Sb 125 (Se, As, Bi) [AGH, AGZ & IH]
• Hg [EH & HAM]	
• Pb [EH]	

This report summarizes additional performance evaluations for some of the more promising treatment media, as identified from previous screening tests, as well as for some recently prepared novel modified phases. The emphasis is upon identifying inorganic media that are compatible with subsequent vitrification of the spent media. Table II provides a description of the test media actual characteristics.

A silver-modified zeolite product (hereafter noted as AGZ) and silver impregnated Engineered Herschelite (AGH) were notably effective for many priority cationic and anionic priority radionuclides in near-neutral oxic surrogate and actual waste water systems. After repeating the original AGZ testing with the inorganic AGH (engineered, granular media with no binder) with very similar results, the AGZ (zeolite with binder) was replaced with the AGH in the final downselect. Granular (14 x 50 mesh), Engineered Herschelite mineral (09-1772-SW), modified Herschelite and Hydroxy Apatite Microspheres (HAM, 10-0577) are all notably effective for cationic contaminants of interest.

From previous discussions, priorities remain for identifying effective media for select radionuclides. In oxic, near-neutral pH waste waters, priority cationic species are represented by Cs-137, Sr-90, Ni-63, Fe-55 and Co-58 & 60. Under these same aqueous conditions, priority (oxy) anionic species are represented by pertechnetate, TcO_4^-, (Tc-99), I^- (I-129), $Sb(OH)_6^-$ (Sb-125) and $HSeO_3^-$ (Se-79) [1,2 and 3].

Two near-neutral surrogate aqueous systems have been formulated for use in testing. For commercial nuclear power plant (NPP) surrogate, we have used a formulation of de-ionized water supplemented with ~ 1 g/L boron (added as B_2O_3), simulating waste water from pressurized water reactors (PWRs). When this water is spiked with metal cations prepared in dilute nitric acid solution, the pH value was subsequently re-adjusted to ~ 5.6 by addition of a small amount of sodium carbonate solution. Solution aliquots, before and after media contact, are filtered to remove any metal ions that may have been precipitated by the pH adjustment.

The Hanford Waste Treatment Plant, WTP, condensate surrogate (off-gas from melters) was prepared to mimic the average composition described by Rutland and Thompson [4] (see Tables IIIa and IIIb). The solution, before spiking with select priority metal cations prepared in dilute nitric acid solution, is pH ~ 8.6.

Table II. Test Media Description (Final Down select media in bold)

Laboratory Preparation *or* MCLinc Sample ID	Vendor ID	Comments
09-1772-SW **H**	Engineered Herschelite ZS500RW	Engineered Herschelite (washed with NaCl before use), 14x50 mesh
AGH	Ag Impregnated Herschelite	Silver impregnated Engineered Herschelite, 14x50 mesh
AGZ		A wide-pore synthetic aluminosilicate zeolite, modified by the exchange of cations (silver) in the crystal lattice, 10x20 mesh. *(Baseline).*
ASM	RTP-10357	Iron-doped anion exchange resin. *(Baseline).*
IH	Iron Impregnated Herschelite	Iron-doped Engineered Herschelite, 14x50 mesh
KUR-31-3 MDPA + H	MCLinc	Herschelite contacted with MPDA solution. 14x50 mesh
KUR-31-4 CTMA + H, **CH**	MCLinc	Herschelite contacted with CTMA solution. 14x50 mesh
KCCF + H, **KH**	MCLinc	KCCF modified Herschelite, 14x50 mesh
KUR-31-6 CTMA+HAM **CHAM**	MCLinc	HAM GMS contacted with CTMA (mixture in solution)
LOCKIT-1 (10-0629)	JV Mfg., Green Bay WI 54304	Organophilic clay. *(Baseline).*
KCCF + HAM, **KHAM**	MCLinc	KCCF modified Hydroxy Apatite Microspheres
HAM (10-0577)	MO-SCI Rolla, MO	Synthetic Hydoxy Apatite Microspheres (HAM), prepared from Glass Microspheres

Table IIIa. Hanford Effluent Treatment Facility (ETF) WAC Compared with Average WTP Recycle: Major Radionuclides *

Inorganic Species	WTP (ppm)	ETF Limit (ppm)	Multiples over
Cl^-	810	59	13.7
F^-	1240	4	310
K^+	28	6.5	4.3
Na^+	596	59	10.1
NH_4^+	1133	737	1.5
NO_2^-	328	39	8.4
PO_4^{3-}	22.5	1.3	17.3
SO_4^{2-}	349	84	4.2

Table IIIb. Hanford Effluent Treatment Facility (ETF) WAC Compared with Average WTP Recycle: Major Inorganic Species *

Radionulclide	WTP (Ci/L)	ETF Limit (Ci/L)	Multiples over
Am-241	7.69E-08	1.40E-09	55**
Cs-137	1.66E-04	9.90E-06	17
Se-79	3.36E-07	1.50E-07	2.2
Sr-90	1.11E- 05	4.20E-05	0.3
Tc-99	***	***	10

*Adapted from Rutland-Thompson Presentation [4]
** Over the WAC, but currently being reevaluated
*** Tc-99 is also reported to partition significantly to this WTP waste stream, but reported units are suspect.

* Adapted from Rutland-Thompson Presentation [4]
EXPERIMENTAL

Media performance has been assessed by batch "equilibrium" testing (typically, 3 to 16-h phase contact) with the use of either single isotopic tracers (with subsequent liquid scintillation counting, LSC), or with natural (non-radioactive) elements in mixture (with subsequent analysis by inductively-coupled plasma-mass spectroscopy, ICP-MS). Earlier tests with single isotopic tracer testing in WTP condensate surrogate or de-ionized water utilized Tc-99, Cs-137 and Sr-90. This investigation also presents data for I-129 in WTP condensate surrogate.

The figures of merit for performance were the distribution coefficient, Kd, and the decontamination factor, DF (equivalent to C_0/C). [5 and 6]

The value of the distribution coefficient is computed using the formalism:

$$K_d \ (mL/g) \ = \ (V/M)*(C_0-C)/C \qquad (1)$$

Where

V = volume (mL) of aqueous phase taken

M = mass (g) of solid phase taken

C_0 = original concentration of analyte in filtered test solution (i.e., with no solid medium added)

C = final ("equilibrium") concentration of analyte in filtered solution after phase contact with test sorbent

RESULTS

1. a. Simultaneous Batch Testing for Cations in PWR Simulants and Actuals (Test Series KUR-32)
Cobalt (Co), nickel (Ni), strontium (Sr) and iron (Fe) were spiked into de-ionized water with boron added (~ 1 g-B/L). After spiking with dilute nitric acid solutions, the solution pH was adjusted to ~ 5.6 with dilute Na_2CO_3 solution, and then filtered at 0.40-μm for use in phase contact studies.

ICP-MS results (cation series) for the gravity-sedimented supernatant solution phase after overnight phase contact with select media was carried out for Co, Sr, Ni and Fe. Table IVa summarizes the computed values for cobalt ion. Hydroxy Apatite Microspheres (HAM) and Engineered Herschelite (as-received or after contact with MDPA or CTMA solutions) removed soluble Co to non-detect levels. Silver (Ag) impregnated zeolite, AGZ, used as a *baseline*, was also very effective (Kd ~ 2.5 E 3 mL/g) as was silver impregnated Herschelite (AGH). Herschelite that had been contacted with CTMA (exclusively, or in a mixture with MPDA) is transformed into an anion exchange medium (for I 129, Sb 125 and Se 179) and has little affinity for cations (e.g., Co^{2+}).

Table IVb summarizes the computed values for nickel (Ni) ion. Results are very analogous to those described for cobalt (Co) ion.

Table IVc summarizes the computed values for strontium (Sr) ion. Again, results are similar to testing with the other cations of interest. Since media may also contain traces of leachable natural strontium, results from previous testing with use of Sr-90 are included for comparison. Selective measurement of Sr-90 shows the same trend as natural Sr, but estimates for Kd are likely more valid [7].

Data for iron suggests that iron was not appreciably soluble in the test solution, except in the presence of media previously contacted with MDPA.

Results for surrogate testing vs 09-1772-SW Herschelite (H) at near-neutral pH value are very similar to those previously seen, with target metal distribution coefficients (K_d) on the order of ~ 10^4 mL/g ($\log_{10}(K_d)$ ~ 4) for most cationic analytes.

Table IVa. Cobalt Series (C_0 = 0.69 mg/L)

Test Series	Medium	C/C_0	V/M	Kd (mL/g)	DF = C_0/C
32-1	10-0577 (**HAM**)	≤ 0.01	199.47	**$\geq$ 1.36E+04**	≥ 69
32-2	09-1772-SW (**H**)	≤ 0.01	194.65	**$\geq$ 1.32E+04**	≥ 69
32-3	MPDA + H	≤ 0.01	197.51	$\geq$ 1.34E+04	≥ 69
32-4	CTMA + H (CH)	0.49	197.54	2.03E+02	2.03
32-5	MPDA + CTMA + H	0.77	298.32	9.01E+01	1.30
32-6	AGZ *(baseline)*	0.07	192.90	2.47E+03	13.8

Table IVb. Nickel Series (C_0 = 0.69 mg/L)

Test Series	Medium	C/C_0	V/M	Kd (mL/g)	DF = C_0/C
32-1	10-0577 (**HAM**)	≤ 0.01	199.47	**$\geq$ 1.36E+04**	≥ 69
32-2	09-1772-SW (**H**)	≤ 0.01	194.65	**$\geq$ 1.32E+04**	≥ 69
32-3	MDPA + H	≤ 0.01	197.51	$\geq$ 1.34E+04	≥ 69
32-4	CTMA + H (CH)	0.80	197.54	5.03E+01	1.25
32-5	MDPA + CTMA + H	0.86	298.32	5.06E+01	1.17
32-6	AGZ *(baseline)*	0.06	192.90	3.13E+03	17.2

Table IVc. Strontium Series (C_0 = 0.79 mg/L)

Test Series	Medium	C/C_0	V/M	Kd (mL/g)	DF = C_0/C
32-1	10-0577 (**HAM**)	0.04	199.47	**5.05E+03**	26.3
32-2	09-1772-SW (**H**)	0.04	194.65	**4.93E+03**	26.3
32-3	MDPA + H	0.03	197.51	7.60E+03	39.5
32-4	CTMA + H (CH)	0.32	197.54	4.27E+02	3.16
32-5	MDPA + CTMA + H	0.81	298.32	6.99E+01	1.23
32-6	AGZ *(baseline)*	0.06	192.90	2.85E+03	15.8

Table IVd. Gamma Activity in Treated Waste Water Aliquots

	Medium	NA	Engineered Herschelite (**H**)	BC-WL (Bone Char) *(Baseline)*
	Sample ID	1073-73-0	1073-73-1	1073-73-2
Nuclide	Unit	Result ± 2σ	Result ± 2σ	Result ± 2σ
Co-57	pCi/g	< 1.08	< 0.61	< 1.07
Cs-137	pCi/g	134 ± 8.01	< 1.81	112 ± 7
Am-241	pCi/g	29.9 ± 7.78	< 5.78	< 9.27

Tables IVd and IVe suggests that Engineered Herschelite (H) is very effective for both Cs-137 (Kd $\geq$ 7.68E+03 mL/g) and for Am-241 (Kd $\geq$ 440 mL/g), whereas BC-WL (Bone Char) shows minimal removal of Cs-137 (Kd ~ 20 mL/g). [8] The high over-all removal of gross nonvolatile activity by Herschelite reflects the fact that this medium is highly effective for both Cs-127 and Sr-90. See Tables IV c and IV d.

Table IVe. Removal of Gross Total Nonvolatile Activity from actual fuel pool waste water (As Estimated by LSC)

Solid	L/S (g/g)	Kd (mL/g)	DF (A_0/A)
Herschelite (**H**)	105.15	**2.23E+03**	22.19
BC-WL	102.67	9.15E+01	1.89

1. b. Simultaneous Batch Testing for (Oxy)Anions in PWR Simulant (Test Series KUR-33)
Iodine ion (from KI), and dilute nitric acid solutions of selenium (Se) and antimony (Sb) were added into de-ionized water with boron added (~ 1 g-B/L). After spiking with dilute nitric acid solutions, the solution pH was adjusted to ~ 5.6 with dilute Na_2CO_3 solution, and then filtered at 0.40-μm for use in phase contact studies. Under the final solution conditions, the predominant chemical species in the prepared solution are expected to be I^-, $HSeO_3^-$, and $Sb(OH)_3^-$ [2,3, 9 and 10].

ICP-MS was again carried out for the gravity-sedimented supernatant solution phase (anion series) after overnight phase contact with select media for Se, Sb and I. Tables Va-Vc outline the media results.

Table Va. Selenium Series (C_0 = 0.70 mg/L)

Test Series	Medium	C/C_0	V/M	Kd (mL/g)	DF = C_0/C
33-1	Fe(OH)$_3$ on Porous Glass Beads	0.61	191.82	1.20E+02	1.63
33-2	ASM (Anion IX) *baseline*	≤ 0.01	199.49	≥ 1.38E+04	≥ 70.0
33-3	LOCKIT (modified clay)	0.74	196.75	6.81E+01	1.35
33-4	CTMA + H (**CH**)	0.13	199.93	**1.36E+03**	7.78
33-5	MDPA + CTMA + H	0.11	191.82	1.49E+03	8.75
33-6	AGZ *(baseline)* & **AGH**	≤ 0.01	199.65	**1.38E+04**	≥ 70.0
33-7	MDPA + CTMA + HAM	0.77	202.53	6.00E+01	1.30

Table Vb. Antimony Series (C_0 = 0.96 mg/L)

Test Series	Medium	C/C_0	V/M	Kd (mL/g)	DF = C_0/C
33-1	Fe(OH)$_3$ on Porous Glass Beads	0.44	191.82	2.47E+02	2.29
33-2	ASM (Anion IX) *baseline*	≤ 0.01	199.49	≥ 1.90E+04	≥ 96.0
33-3	LOCKIT (modified clay)	0.76	196.75	6.20E+01	1.32
33-4	CTMA + H (**CH**)	0.14	199.93	**1.28E+03**	7.38
33-5	MDPA + CTMA + H	0.10	191.82	1.65E+03	9.60
33-6	AGZ *(baseline)* & AGH	0.36	199.65	3.48E+02	2.74
33-7	MDPA + CTMA + HAM	0.09	202.53	1.96E+03	10.67

Table Vc. Iodine Series (C_0 = 0.36 mg/L)

Test Series	Medium	C/C_0	V/M	Kd (mL/g)	DF = C_0/C
33-1	Fe(OH)$_3$ on Porous Glass Beads	1.28	191.82	~ 0	~ 1
33-2	ASM (Anion IX) *baseline*	≤ 0.03	199.49	≥ 6.98E+03	≥ 36.00
33-3	LOCKIT (modified clay)	0.06	196.75	3.34E+03	18.00
33-4	CTMA + H (CH)	1.22	199.93	~ 0	~ 1
33-5	MDPA + CTMA + H	1.47	191.82	~ 0	~ 1
33-6	AGZ *(baseline)* & **AGH**	≤ 0.03	199.65	**≥ 6.99E+03**	≥ 36.00
33-7	MDPA + CTMA + HAM	5.56	202.53	~ 0	~ 1

2. Hanford WTP Secondary/Recycle Stream surrogates.

2. a. Sorption Batch-Test Using I-129 Tracer in WTP Secondary/Recycle Condensate Simulant
Dilute stock I-129 was prepared using Eckert & Zeigler Analytics standard PN 82387. The test solution was WTP Condensate Simulant with ~ 5E-03 M Na_2SO_3 added (to keep iodine in the form of I^-), pH ~8.6, and total iodine ("cold carrier") ~ 3.2 mg/L. A number of commercial and laboratory-prepared media were contacted with the test solution, but only two of them were notably effective (Table VI). One was an organic anion exchange resin and the other a modified engineered inorganic media.

Table VI. Iodine Series (I-129, A_0 ~ 201.55 DPM/g) (Minimum Detectable Activity, MDA)

Test Series	Medium	A/A_0	V/M	Kd (mL/g)	DF (A_0/A)
34-6	AGZ & **AGH**	0	94.98	**<MDA**	**<MDA**
34-10	ASM (Anion IX)	0.08 (< MDA)	96.18	≥ 1.15E+03	≥ 13

As for the testing using natural iodine (Table VI), AGH (Ag impregnated Herschelite) and ASM (iron doped organic anionic resin base) were very effective. LOCKIT (organophilic clay), the other reagent that was shown to be effective in Table Vc, was not included in the screening vs I-129 due to the substrates inability to be used in the column mode and tendency for plugging. It was concluded that the silver doped inorganic media had the highest removal and capacity for total iodine, as well as being the best candidate for thermal treatment (e.g., vitrification). [11]

2. b. Sorption Batch-Test Using Sr-90 Tracer in WTP Secondary/Recycle Condensate Simulant

Table VII. Media Testing with use of **Sr-90** in Hanford WTP Condensate Simulant
(Contact time ~ 3.5-h)

Test Series	Medium	A/A_0	V/M	Kd (mL/g)	DF (A_0/A)
10-1	10-0581 **HAM**	0.00	110.72	**≥ 5E+04**	**<MDA***
10-2	10-0577 **HAM**	0.00	101.61	**≥ 5E+04**	**<MDA***
10-6	09-1772- SW (H) Herschelite	0.44	89.14	1.14E+02	2.28

* Final activity less than minimum detectable activity (< MDA) or DF > 300.

2.c. Removal of Technetium (Tc-99) from WTP Secondary Waste Waters

The aqueous phase used was Tc-99 (from NH_4TcO_4 stock solution) diluted in de-ionized water. Forty (40) milliliters of solution was contacted with 99.8-mg as-received medium for ~ 4-h by tumbling the phases (at 30 RPM) in a sealed centrifuge tube with use of a TCLP extraction apparatus. Note that bentonite is a swelling clay, and the fine powder initially formed gummy particles upon surface hydration (in this instance, aqueous phase was added to the dry solids). Initial vigorous shaking of the phases failed to completely disperse the solids, but did produce some light foaming (suggesting that the organic modifier could be a cationic surfactant). The suspension formed after tumbling the phases clarified fairly rapidly, but hydrated bentonite tended to adhere to the container walls. Phases were separated by centrifugation (1000 RPM for 5-min), and then small aliquots of the supernatant solution were taken for subsequent counting.

Technetium activity in the solution phase was estimated by liquid scintillation counting (LCS), with alpha and beta discrimination (MCL-7759), using aliquots of the original and treated solution. Under the count conditions used, the estimated minimum detectable activity (MDA) was 6.65 dpm, and results for all QA specimens were acceptable.

Attempts were made to impregnate a more suitable matrix (ie, less hydrophobic, swelling and plugging material), with the same or equivalent surfactant. As can be seen in Table VIII, modification of HAM provided such a robust media with excellent affinity and capacity.

Table VIII. Technetium removal media tests
Tc-99 Series   Ao = 1.17E+04 DPM/mL (311 µg/L)

Solid	L/S (g/g)	A (DPM/g)	Kd (mL/g)	DF (A$_o$/A)
Lockit (clay) *Baseline*	100.49	19.42	6.07E+04	605
Modified Lockit	105.93	19.49	6.37E+04	603
CTMA+HAM,**CHAM**	106.81	82.16	**1.52E+04**	143
CTMA + H, **CH**	92.22	498.7	**2.17E+03**	24.2

Comments:

L/S = mass ratio of liquid phase to solid phase, as-tested
Ao = Initial activity of traced solution
A = Final activity of equilibrated solution (filtered at 0.45-µm)
MDA = Estimated Minimum Detectable Activity
Kd = Computed conditional distribution coefficient, mL/g
DF = Decontamination Factor, under specific test conditions (i.e., at indicated L/S)
"Modified" = medium pre-contacted with CTMA solution, then rinsed and dried before use.
Tc-99 Series were tested as NH_4TcO_4 prepared in DI-water (phase contact overnight).
Pre-treatment of HAM (substrate = 10-0577) with CTMA solution did not appreciably affect its ability to remove Sr-90 from WTP surrogate, but gave it good Tc-99 removal efficiency.

2.d. Removal of Mercury (Hg) from Hanford WTP Secondary Waste Surrogate
Mercury (Hg) as Hg (II) was added to the Hanford WTP Secondary waste surrogate (off-gas condensate) at a pH of ~8.0. The contact time was ~ 3 hours and the Hg was analyzed in the treated supernatant by cold vapor AAS. Four newly developed media were run in this test series as well as the *baseline* Nucon Mersorb-3. This is a 14x50 sulfur-impregnated carbon normally used in gaseous streams rather than waste water streams.

The four ISM media with likely the best affinities and capacities [Kd (mg/L) and DF (Ao/A)] for Hg compared to the *baseline* were:

- AGH (Ag doped inorganic)   Kd = 1.41 E +03   DF = 14.71
- Herschelite (H)   Kd = 2.96 E +03   DF = 31.25
- HAM (HA Microspheres)   Kd = 1.20 E +03   DF = 13.33
- Herschelite + MDPA (KUR-31-3)   Kd = 2.77 E +03   DF = 29.41
- Mersorb-3 *(baseline)*   Kd = 3.08 E +02   DF = 4.17

The Herschelite and modified Herschelite were the top performers with the Hydroxy Apatite Microspheres (HAM) also performing quite well. Figure 1 illustrates the removal of Hg, utilizing distribution coefficients (Kd's), for each of the media.
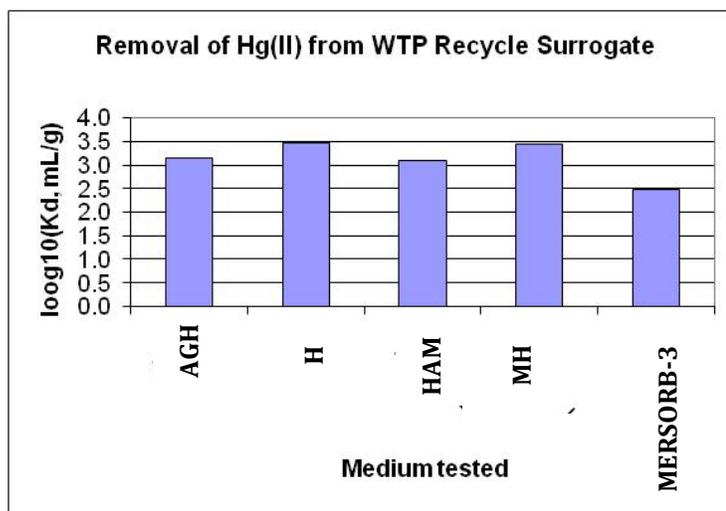
Figure 1. Removal of Mercury from Hanford WTP Condensate Surrogate
These inorganic media should also be applicable to the mercury contamination at the Savannah River Site (SRNL).

2.e. Removal of Traced Cesium (Cs 137) from Hanford WTP Secondary Waste Surrogate
Preparation of Traced WTP Secondary Surrogate Solution

The Hanford WTP condensate surrogate (Secondary/Recycle Waste) was prepared to mimic the average composition described by Rutland and Thompson [4] (Tables IIIa and IIIb). The surrogate, as originally prepared (See Tables IX and X), had pH value ~ 8.7. Select metals of interest, including natural Cs, Sr, and Ce (surrogate for Am-241) were subsequently added as standards in dilute nitric acid, yielding a solution with pH ~ 8.6.

The relatively volatile components, such as ammonium ion, are concentrated into the actual WTP waste stream by volatilization and subsequent condensation. Some less volatile components (e.g., Am-241 and Tc-99) also partition to the WTP by entrainment in the evaporator off-gas.

Table IX. Hanford WTP Surrogate Formulation

Compound	FW	Compound (mol/L)	Compound (g/L)
NaF	41.99	6.53E-02	2.74
KCl	74.55	7.16E-04	0.05
NH$_4$Cl	53.49	2.28E-02	1.22
NaNO$_2$	69.00	7.13E-03	0.49
(NH$_4$)$_2$SO$_4$	132.13	3.63E-03	0.48
NH$_4$H$_2$PO$_4$	115.03	2.37E-04	0.03
(NH4)$_2$CO$_3$	96.09	1.62E-02	1.56

Table X. Hanford WTP Surrogate (Compared to Target Values from Table IX)

Inorganic ion	Formulated (mol/L)	Target (mol/L)
Cl$^-$	2.28E-02	2.28E-02
F$^-$	6.53E-02	6.53E-02
K$^+$	7.16E-04	7.16E-04
Na$^+$	7.24E-02	2.59E-02
NH$_4^+$	6.28E-02	6.28E-02
NO$_2^-$	7.13E-03	7.13E-03
PO$_4^{3-}$	2.37E-04	2.37E-04
SO$_4^{2-}$	3.63E-03	3.63E-03

In order to more quickly screen for uptake of cesium ion (priority radionuclide, see Table IIIb) by select media, a portion of the WTP secondary surrogate, with added natural Cs, was mixed with 10% (v/v) of a radiological standard of low-level Cs-137 in 0.1 M HCl. This traced mixture contained a total Cs concentration ~ 10 mg/L (ppm), but a low Cs-137 activity (~ 4,200 pCi/L), and had a pH value ~ 7.4. This total cesium concentration more nearly mimics that of typical caustic tank waste than the more dilute WTP waste. The general assumption for Cs in Hanford waste streams is that Cs-137 represents approximately 1/3 of the total Cs present (radiological and natural). From this assumption, the total Cs in the traced WTP surrogate (~ 10 mg/L) would represent the activity equivalent of approximately 0.3 Ci/L in actual Hanford waste, whereas the value reported in Table IIIb for the WTP is ~ 0.2 mCi/L (or estimated total Cs ~ 6 μg/L).

Media Preparation: Media tested are briefly described in Table XI. Some media were prepared by addition of potassium hexacyanoferrate (KCCF). The method of preparation was simplistic, and not optimized. Briefly, the medium was saturated with a solution of concentrated cobalt nitrate (~ 0.4 M), and then oven-dried (~ 120 C). Next, a solution of concentrated (~ 0.4 M) potassium ferrocyanide ($K_4Fe(CN)_6$) was added to the substrate. The intent was to precipitate KCCF within the media pores or surface. Treated media were rinsed with DI-water, to remove excess reagent and/or KCCF product that was not bound to the medium), and again dried before use as a sorbent.

Phase Contact: Aliquots of traced liquid and media in sealed centrifuge tubes were contacted by tumbling the phases overnight on a TCLP extraction apparatus.

Analytical: Aliquots of the traced WTP surrogate, with elevated level of natural Cs and low-level Cs-137 tracer, were counted by liquid scintillation counting (LCS).

For traced solution aliquots that were contacted with media, phases were separated by low-speed centrifugation, and aliquots of the supernatant phase were counted (without filtration). This analytical preparation penalizes media preparations that yield substantial colloids.

Table XI. Preliminary estimates of Kd for Cs on select media. Initial Cs (total) ~ 9 mg/L in synthetic Hanford WTP medium. Media tested at L/S ~ 100 (mL/g), after overnight phase contact. The activity of "soluble" Cs-137 tracer in the supernate phase was counted by liquid scintillation. Porous soda lime glass spheres (GL0191B4, -200+270 mesh) and porous glass frit were provided by MO-SCI Corp., Rolla, MO.

Code ID		Substrate ID	KCCF Added	Kd (mL/g)
KUR-7-1	09-1771	Herschelite (**H**)(~ 15-μm)	No	1500
KUR-7-2	09-1773	Clinoptilolite(16x20 mesh)	No	570
KUR-7-3	09-1771	Herschelite (**H**)	Yes	12,600
KUR-7-4	09-1773	Clinoptilolite	Yes	9,400
KUR-7-5	10-0886	porous glass frit	Yes	45
KUR-7-6	10-0578	porous glass bead	Yes	160
KUR-7-7	10-0579	Barium titanate	No	0

3. Envelope C (e.g., chelated Sr-90 removal) Surrogates for Tanks AN 102 and AN 107 (pH 12-13)
Hydroxy Apatite Microspheres (HAM) not only survived the extremes of chelants (Nearly every imaginable chelant, see Table XII), and the two pH extremes tested (12.4 and 13), but did so with a fairly good Distribution Coefficient (Kd). In the most extreme case of pH 13, the **Kd was ~360 (3.6 E +2)**, while at pH 12, the **Kd was 215 (2.15 E +2)**. Of course, the pH range on AN 102 and 107 might not be this severe (some samples are reported at pH 10.8, etc.), so this might be a worst case scenario.

Table XII. Chelated **Sr-90** surrogate.

Constituent	unit	Simulent (As-Tested) 68-1F	Simulent (As-Tested) 68-2F
		68-1F	**68-2F**
pH	N/A	**13**	**12.4**
Sodium	Mol/L	4.9	4.7
HEDTA	Mol/L	4.82E-03	4.59E-03
EDTA	Mol/L	7.11E-03	6.78E-03
NTA	Mol/L	4.67E-03	4.44E-03
IDA	Mol/L	6.77E-03	6.44E-03
Gylcolate	Mol/L	3.71E-02	3.53E-02
Citrate	Mol/L	2.11E-02	2.01E-02

In most cases, there are very limited data for chelants. The as-tested caustic waste stimulant (Series 68) was prepared from AN-104 Simulant by addition of chelate solution, pH adjustment (HNO3), and filtration.

Chelants added	pH 13	pH 12.4
	mol/L	mol/L
HEDTA	4.82E-03	4.59E-03
Na2EDTA*2H2O	7.11E-03	6.78E-03
NTA	4.67E-03	4.44E-03
IDA	6.77E-03	6.44E-03
Glycolic acid (70%)	3.71E-02	3.53E-02
Citric acid	2.11E-02	2.01E-02

4. At-Tank Pretreatment (primarily Cs) Removal from Hanford WTP LAW Simulant (50% AN 104, pH 14)

4.a. Engineered Herschelite Removal of At-Tank Cesium

Figure 2 depicts the removal capability of Engineered Herschelite at several mesh sizes (09-1771 is 15 micron while 09-1772 is a granular 14x50 mesh and 09-1774 is standard clinoptilolite zeolite) and pH values. Surface area definitely effects the capacities and kinetics of the media as can be seen in this figure. The isotopes of concern in this test were Cs, Sr, Ni and Co and the surrogate was a Hanford high salt content surrogate which was adjusted to three pH values (6.2, 11.7 and 14). At the near neutral pH, all three media performed well for all four isotopes. At pH 11.7, distribution coefficients (Kd's) decrease by an order of magnitude and some isotopes (e.g. Sr) begin to lose their affinity (with the exception of Cs and Co and Ni). Cerium (Ce) was added here as a surrogate for uranium, but had little or no solubility at this pH. At the extreme pH of 14 and at this high salt molarity, only the Herschelite (H) continued to remove the Cs (also Co and Ni) with respectable Kd's, while the standard zeolite lost all affinity.
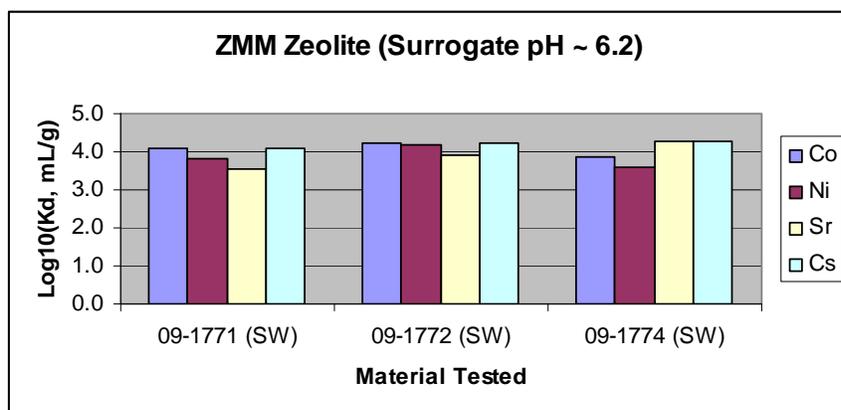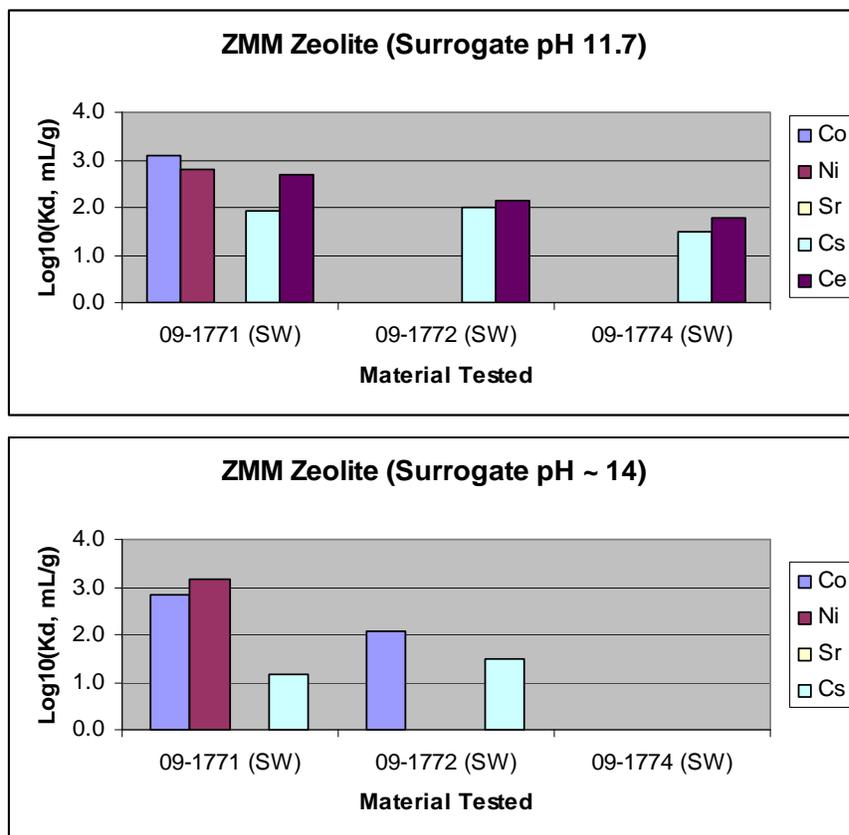
Figure 2. Engineered Herschelite Series (Filtered at ~ 20-µm after overnight contact)
4.b. Crystalline Silicotitanate (CST) *Baseline* Comparison

Table XIII represents a direct comparison of cesium removal at various pH values utilizing the same Hanford WTP surrogates used for Engineered Herschelite in Figure 2 above, showing similar pH trends.

Table XIII. CST Cs-137 Removal as a function of pH.

pH	DF (A_o/A)	Kd (mg/L)
10.7	1.80	600
11.0	1.43	414
11.37	1.47	433
11.74	1.57	466
12.3	1.27	151
>13.8	1.21	208

CONCLUSIONS

The primary objectives of this ion specific media (ISM) development and down select study were to provide high selectivity and high capacity media to remove the isotopes of concern for secondary/recycle waste (off-gas condensates), off-spec tanks (e.g., chelated Sr) and pretreatment (In-Tank columns) at DOE's Hanford Site, as well as the class driving isotopes (e.g., Cs, Ni and Sr) and recalcitrant isotopes

(e.g., Cs, Ni, Sr, Sb, I, Co, and Fe) for commercial nuclear plants [12 and 13]. Additionally, an attempt was made to offer two separate and distinct types of media. One with an engineered, mineral substrate and the other with a Glass MicroSphere base. While the dose levels and history of the two sources varies widely, there is considerable overlap between the two challenges which provides the advantage of synergistic development. A further objective was to carry out test runs on a wide variety of conditions, ranging from near neutral solutions, to condensate waste streams, and, finally, to extremely high salt molarity and pH waste streams. Lastly, and of significant importance, is the development of media with end processing and disposal in mind (e.g., thermal processing). In summary, eight media have been produced and tested with extremely high selectivity and capacity (H, HAM, KH, KHAM, AGH, CH, CHAM and IH) for the isotopes of concern . See Table XIV below (Kd values are maximums).

Table XIV. Summary of Media Down Select

Isotope	Affinity Series	DF (A_o/A)	Kd (mg/L)
Cs	KH > H > KHAM	H	1.5 E +3
		KH	1.26 E +4
Sr	HAM > H	HAM >300 (<MDA)	>5 E +4
Am	HAM	>30 (<MDA)	> 2000 (< MDA)
Pu	HAM		
Hg	H > AGH ~ HAM >> MERSORB-3	H 31.25	3 E +3
I	AGH ~ IH	AGH < MDA	<MDA
As	IH > CH ~ SMZ > AGH		
Se	CHAM >> IH > CH ~ AGH ~ SMZ	AGH >70 (pH ~ 7)	1.38 E +4
Sb	CHAM > IH > AGH > CH ~ SMZ	CHAM 10.67	1.96 E +3
Tc	CH > CHAM ~ SMZ	CH 200	2.55 E +4
		CHAM 150	1.52 E +4
Ni	H > HAM	H >69	1.32 E +4
		HAM >69	1.36 E +4
Co	H > HAM > KHAM	H >69	1.32 E +4
		HAM >69	1.36 E +4
Pb	H or CH		

The inorganic media criteria, to be successful for DOE waste streams, must also include the following physical parameters:
- **Sluicability**- Into and out of the in-riser columns (both of the media bases are sluiceable/pumpable).
- **Mixability/Pumpability**- After settling. (All of down selected inorganic media are low density- 0.7 and ~ 1.3 g/cc) vs higher density media (e.g., CST at 2.5 g/cc).
- **Density**- To allow for optimal settling rates, our media at lower effective bulk densities, should have advantages here over media more dense than the existing sludge.
- **Abrasivity-** Besides the mixing/pumping issue, this is a primary concern. CST is abrasive by nature in the piping, etc. Engineered Herschelite (and the Glass Microspheres) are not. Engineered Herschelite can be further "hardened," but remains non-abrasive.

- **pH –** CST is acidic by nature (and contains Niobium, another problem) and causes 3 species to precipitate out when contacted with caustic solutions. Thus, the partial rocking up at West Valley and the column plugging at SRNL. Engineered Herschelite is pH 8-9, thus eliminating this concern. It also has no niobium or titanates (which makes the CST work) causing other (glass solubility) issues.
- **Capacity/Affinity-** Kurion Engineered Herschelite and GMS media, Kds/DF's (from surrogate and actual nuclear plant test runs), could be the first real alternative to sRF, CST and the old Super-Ligs. Ideally, these media will go into testing at 222S Labs soon due to the need to make decisions by FY end to allow proceeding on one design or the other. We feel that the timing is good.

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