

**Fukushima Nuclear Crisis Recovery: A Modular Water Treatment System
Deployed in Seven Weeks - 12489**

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ABSTRACT

On March 11, 2011, the magnitude 9.0 Great East Japan earthquake, Tohoku, hit off the Fukushima coast of Japan. This was one of the most powerful earthquakes in recorded history and the most powerful one known to have hit Japan. The ensuing tsunami devastated a huge area resulting in some 25,000 persons confirmed dead or missing. The perfect storm was complete when the tsunami then found the four reactor, Fukushima-Daiichi Nuclear Station directly in its destructive path. While recovery systems admirably survived the powerful earthquake, the seawater from the tsunami knocked the emergency cooling systems out and did extensive damage to the plant and site. Subsequent hydrogen generation caused explosions which extended this damage to a new level and further flooded the buildings with highly contaminated water. Some 2 million people were evacuated from a fifty mile radius of the area and evaluation and cleanup began.

Teams were assembled in Tokyo the first week of April to lay out potential plans for the immediate treatment of some 63 million gallons (a number which later exceeded 110 million gallons) of highly contaminated water to avoid overflow from the buildings as well as supply the desperately needed clean cooling water for the reactors. A system had to be deployed with a very brief cold shake down and hot startup before the rainy season started in early June. Joined by team members Toshiba (oil removal system), AREVA (chemical precipitation system) and Hitachi-GE (RO system), Kurion (cesium removal system following the oil separator) proposed, designed, fabricated, delivered and started up a one of a kind treatment skid and over 100 metric tons of specially engineered and modified Ion Specific Media (ISM) customized for this very challenging seawater/oil application, all in seven weeks. After a very short cold shake down, the system went into operation on June 17, 2011 on actual waste waters far exceeding 1 million Bq/mL in cesium and many other isotopes. One must remember that, in addition to attempting to do isotope removal in the competition of seawater (as high as 18,000

ppm sodium due to concentration), some 350,000 gallons of turbine oil was dispersed into the flooded buildings as well.

The proposed system consisted of a 4 guard vessel skid for the oil and debris, 4 skids containing 16 cesium towers in a lead-lag layout with removable vessels (sent to an interim storage facility), and a 4 polishing vessel skid for iodine removal and trace cesium levels. At a flow rate of at least 220 gallons per minute, the system has routinely removed over 99% of the cesium, the main component of the activity, since going on line. To date, some 50% of the original activity has been removed and stabilized and cold shutdown of the plant was announced on December 10, 2011.

In March and April alone, 10 cubic feet of Engineered Herschelite was shipped to Seabrook Nuclear Power Plant, NPP, to support the April 1, 2011 outage cleanup; 400 cubic feet was shipped to Oak Ridge National Laboratory (ORNL) for strontium (Sr-90) ground water remediation; and 6000 cubic feet (100 metric tons, MT, or 220,400 pounds) was readied for the Fukushima Nuclear Power Station with an additional 100 MT on standby for replacement vessels. This experience and accelerated media production in the U.S. bore direct application to what was to soon be used in Fukushima.

How such a sophisticated and totally unique system and huge amount of media could be deployable in such a challenging and changing matrix, and in only seven weeks, is outlined in this paper as well as the system and operation itself.

INTRODUCTION

There were ten major prior experience steps leading up to the readiness and acceptance by Tokyo Electric Power Company, TEPCO, of a modular emergency technology recovery system: 1) successful EPRI U.S. testing and introduction to EPRI Japan, with subsequent introduction to TEPCO, 2) Three Mile Island (TMI) media and vitrification, 3) commercial NPP media, 4) DOE low and high level waste media and vitrification in high salt and pH, 5) national laboratory ground water media, 6) Gulf oil spill media in seawater, 7) all media demonstrated at high rad. levels in seawater, 8) final waste form and disposal, 9) immediate availability of 100 metric tons of media, and 10) remote operation, modular water treatment equipment design and fabrication in both commercial and DOE canyon operations.

The primary deciding factor for Fukushima NPP involvement was likely based on previous Three Mile Island (TMI) experience in the most similar nuclear experience available to date. The Ion Specific Media used at TMI in 1979 was the base substrate based on what has now become the highly engineered and developed KurionHerschelite media. Further, this inorganic precursor material was immobilized and stabilized into glass utilizing a modular vitrification system by Pacific Northwest National Laboratory (PNNL). Over the last three decades, this technology has been developed into the Kurion Modular Vitrification System (MVS®). A secondary factor was

the very unusual previous experience with using this same media in an oil laden seawater matrix (i.e., the Gulf oil spill). Combining the high competition of seawater, with its associated pH, with the presence of oil fouling made this a particularly unique and challenging remediation situation. This required a highly specialized and robust media, likely one never seen before in the history of nuclear power. Also of utmost importance was the ironically fortunate timing of completing testing at the Seabrook Nuclear Power Station for the Electric Power Research Institute (EPRI). This long range testing for cesium and other isotope removal was carried out using the same media as was ultimately utilized at the Fukushima Dai-ichi Plant. It was also EPRI U.S. that was asked by their member company TEPCO to offer technical assistance during the nuclear crisis.

Having already developed a two phase technology platform consisting of an Isotope Separation System (ISS), utilizing 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 had been further tested for the primary isotopes at Hanford that required Supplemental Treatment, as well as at Commercial Nuclear Power Plants (NPPs) that require removal prior to vitrification. In addition to surrogate testing and spiked surrogate testing, actual waste testing (e.g., Seabrook and Diablo Canyon Power Stations) was carried out at our licensed laboratories in Oak Ridge, Tennessee. At the heart of the ISS is the development of two novel classes of Ion Specific Media (ISM). The AST features an Advanced Microwave Evaporator System (AMES) and Modular Vitrification System (MVS[®]). While the primary focus of this paper is on the development and successful full-scale deployment of Ion Specific Media in very challenging conditions, it is important to note that these exclusively inorganic media were selectively designed to be compatible with the 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 a class of high capacity and high specificity Ion Specific Media is to surgically remove the recalcitrant isotopes (e.g., Cs-137, Sr-90, I-131 and Tc-99) during remediation and/or decontamination and decommissioning 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-vessel or in-tank storage (i.e., inorganic in nature, leach resistant, non-hydrogen generating and amenable to future stabilization by thermal, or other, means). Driving to higher waste classification and smaller waste volumes allows the plant the flexibility to minimize the higher level waste streams and maximize the clean supernate product water for use as recycle cooling water to the reactors and fuel pools.

Subsequent stabilization processes, such as microwave or vitrified glass products readily traps the isotopes in a leach-resistant and high quality waste form for long-term, safe storage. The modified mineral, fine or granular substrate, is a leafy structure with huge surface areas (500 m² per gram), as seen by electron microscopy, which collapses around the captured isotopes and dissolves into the glass during thermal processing. As mentioned, all media applied were designed to be both vitrification and long-term storage friendly.

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 Materials and Chemistry Laboratories (MCL) facility, in Oak Ridge, Tennessee for DOE and NPP specific isotope removal. This down select was carried out in batch reactors as well as columns at an analytical- and bench-scale, on near neutral pH feeds and surrogates, but also included very high alkali WTP pretreatment, pH ~14, and WTP secondary waste stream, pH ~8-9, surrogates (very similar to pH 8.3 seawater).

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 as well as seawater samples.

The figures of merit for performance were the distribution coefficient, K_d , and the decontamination factor, DF (equivalent to C_0/C) [1 and 2]. The value of the distribution coefficient is computed using the formalism:

$$K_d \text{ (mL/g)} = (V/M) \cdot (C_0 - C) / C \quad (1)$$

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 and FINDINGS

Three Mile Island Experience

As mentioned, of critical importance during the Fukushima crisis was the base line experience of the Three Mile Island (TMI) nuclear incident of 1979[3,4,5 and 6]. While TMI was a level 5 event, Fukushima was quickly reassessed as a level 7 event putting it in the same category as the Chernobyl incident of 1986. The latter did not have the complications of huge amounts of contaminated water and especially not oil laden seawater. There were three current Kurion staff members involved in the TMI clean up that proceeded from 1979 to 1982. *Dr. Mark Denton, who began his career at Oak Ridge National Laboratory in 1977, was involved in various media development and applications as he is today.* The ion specific media (ISM), based on what is now a highly engineered and developed Kurion Herschelite, was used as the base substrate at

TMI in 1979. *Jack Sprucinski, who acted as Kurion's Fukushima radiation protection officer, was the radiation safety officer (RSO) for the TMI cleanup effort. Jack McElroy, a Kurion scientific advisor, was involved in the vitrification of the TMI high level waste (HLW) utilizing a Pacific Northwest National Laboratories (PNNL) modular vitrification unit.* This inorganic precursor material was immobilized and stabilized into glass utilizing this modular vitrification system at PNNL. Over three decades, this has been developed into the Kurion Modular Vitrification System (MVS[®]). TMI studies ironically involved wastewater feed onto substrate media at a range of temperatures (e.g., experienced during the emergency cooling of exposed fuel at Fukushima).

EPRI Commercial Nuclear Power Plant Experience

Several Kurion Ion Specific Media (ISM) were selected for EPRI testing on actual NPP waste waters for later use in outage conditions. Testing was carried out at the Seabrook Nuclear Power Station in New Hampshire from August through September, 2010 utilizing the EPRI Multiple Bed Test Unit (MBTU) (see Figure 1). As can be seen in the figure, less Kurion media was required than any other due to the high specificity and capacity of the media (far left column). This was also an essential requirement at the Fukushima site to minimize the final waste product.



Figure 1. Multiple Bed Test Unit. and KHAM lower.

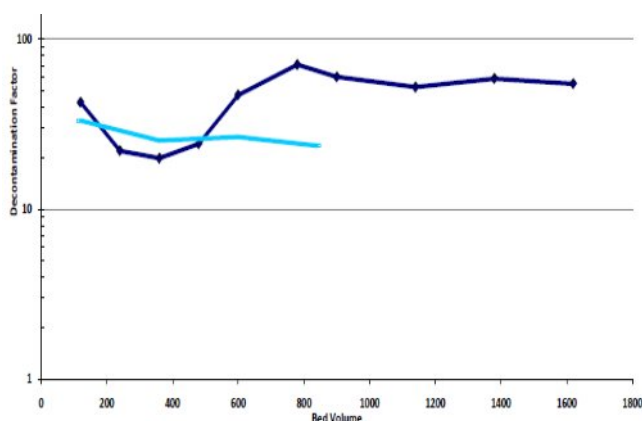


Figure 2. Herschelite (KUR-EH) upper

Both ISMs were tested specifically for cesium (Cs) and cobalt (Co) removal, among other common isotopes. Both media achieved below Minimum Detectable Activity (<MDA) throughout the testing. The plant actually ran out of tank feed waste water before breakthrough of the media occurred. See Figure 2 for the spent fuel pool curves for Cs removal, as an example. All effluent Cs-137 was less than Minimal Detectable Activity (< MDA) and Decontamination Factors (DF) were calculated from MDA values.. A high number of Bed volumes (BVs) were achieved in all cases. While Figure 2 illustrates results out to approximately 1800 BVs, the test was carried out ultimately to 3500 BVs without Cs breakthrough. Again, this was essential during the Fukushima cleanup to minimize the change out of loaded vessels and minimize the number of vessels going to the interim storage facility. Importantly, the media was tested for both

Fuel Pool and Boron Waste Storage Tanks (BWST). It was later proposed to utilize boron as a neutron moderator in the Fukushima project and it was important to prove that the boron had no deleterious effect on the media. It was further essential that the media was stable under flow requirements and did not degrade or produce fines. As anticipated, the media showed no plugging of the filters during the prolonged testing as did some of the other media that was tested. The ISM demonstrated at the Seabrook NPP for cesium removal was subsequently chosen for full-scale outage operation beginning April 1, 2011 and continues to perform to date without Cs breakthrough.

Further Essential Commercial NPP Simulant and Actual Wastewater Testing

Even more ironic, the final results of media development and down select, testing protocols and results for both Commercial NPPs and DOE waste streams was reported at the 2011 Waste Management Conference in Phoenix, Arizona seven days before the Great East Japan earthquake was to occur, allowing an unprecedented insight into the selection of critical media (7).

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 Na₂CO₃ solution, and then filtered at 0.40- μ m 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 I summarizes the computed values for cobalt ion. Hydroxy Apatite Microspheres (HAM) and Engineered Herschelite (EH) (as-received or after contact with MDPA or CTMA solutions) removed soluble Co to non-detect levels. Silver (Ag) impregnated Herschelite, AGH, used as a *baseline*, was also very effective ($K_d \sim 2.5 \times 10^3$ mL/g). Herschelite that had been contacted with cetyltrimethyl ammonia, CTMA, was transformed into an anion exchange medium (for I 129, Sb 125 and Se 179) and has little affinity for cations (e.g., Co²⁺).

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

Table I further 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 K_d are likely more valid [8].

Results for surrogate testing vs Engineered Herschelite (EH) at near-neutral pH value are very similar to those previously seen, with target metal distribution coefficients (K_d) on the order of ~ 10⁴ mL/g ($\log_{10}(K_d) \sim 4$) for most cationic analytes.

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

Test Series	Medium	C/C ₀	V/M	Kd (mL/g)	DF = C ₀ /C
32-2	09-1772-SW (EH)	≤ 0.01	194.65	≥ 1.32E+04	≥ 69
32-6	AGH(baseline)	0.07	192.90	2.47E+03	13.8

Table Ib. Nickel Series (C₀ = 0.69 mg/L)

32-2	09-1772-SW (EH)	≤ 0.01	194.65	≥ 1.32E+04	≥ 69
32-6	AGH(baseline)	0.06	192.90	3.13E+03	17.2

Table Ic. Strontium Series (C₀ = 0.79 mg/L)

32-2	09-1772-SW (EH)	0.04	194.65	4.93E+03	26.3
32-6	AGH(baseline)	0.06	192.90	2.85E+03	15.8

These results suggest that Engineered Herschelite (EH) is very effective for both Cs-137 (Kd ≥ 7.68E+03 mL/g) as well as for Am-241 (Kd ≥ 440 mL/g), not shown. The high over-all removal of gross nonvolatile activity by Herschelite reflects the fact that this medium is highly effective for both Cs-137 and Sr-90.

Table Id. Removal of Gross Total Nonvolatile Activity from actual fuel pool waste water (As Estimated by liquid scintillation counting, LSC)

Solid	L/S (g/g)	Kd (mL/g)	DF (A ₀ /A)
Herschelite (EH)	105.15	2.23E+03	22.19
BC-WL	102.67	9.15E+01	1.89

Simultaneous Batch Testing for (Oxy)Anions in Commercial NPP Simulant

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 Na₂CO₃ 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⁻, HSeO₃⁻, and Sb(OH)₃⁻ [9,10, 11 and 12].

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 IIa-IIc outline the media results.

Table IIa. Selenium Series (C₀ = 0.70 mg/L)

Test Series	Medium	C/C ₀	V/M	Kd (mL/g)	DF = C ₀ /C
33-4	CTMA + EH (CH)	0.13	199.93	1.36E+03	7.78
33-6	AGH	≤ 0.01	199.65	1.38E+04	≥ 70.0

Table IIb. Antimony Series (C₀ = 0.96 mg/L)

33-4	CTMA + EH (CH)	0.14	199.93	1.28E+03	7.38
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Table IIc. Iodine Series (C₀ = 0.36 mg/L)

33-6	AGZ (baseline)&AGH	≤ 0.03	199.65	≥	≥ 36.00
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				6.99E+03	
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Hanford Waste Treatment Plant, WTP, Secondary/Recycle Stream surrogates.
(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 $\sim 5\text{E-}03$ 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 III). One was an organic anion exchange resin and the other a modified engineered inorganic media.

Table III. Iodine Series (I-129, $A_0 \sim 201.55$ DPM/g) (Minimum Detectable Activity, MDA)

Test Series	Medium	A/A_0	V/M	Kd (mL/g)	DF (A_0/A)
34-6	AGH	0	94.98	<MDA	<MDA

As for the testing using natural iodine (Table III), AGH (Ag impregnated Herschelite) was very effective. 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). [13]

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

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

10-2	10-0577 HAM	0.00	101.61	$\geq 5\text{E}+04$	<MDA*
10-6	09-1772- SW (EH) Herschelite	0.44	89.14	$1.14\text{E}+02$	2.28

* Final activity less than minimum detectable activity ($< \text{MDA}$) or $\text{DF} > 300$.

Removal of Technetium (Tc-99) from Waste Treatment Plant (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. 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. 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 successfully made to impregnate a more suitable matrix (ie, less hydrophobic, swelling and plugging material), with the same or equivalent surfactant.

Table V. Technetium removal media tests

Tc-99 Series $A_o = 1.17E+04$ DPM/mL (311 $\mu\text{g/L}$)

Solid	L/S (g/g)	A (DPM/g)	Kd (mL/g)	DF (A_o/A)
CTMA+HAM, CHAM	106.81	82.16	1.52E+04	143
CTMA + EH, CH	92.22	498.7	2.17E+03	24.2

Removal of Traced Cesium (Cs 137) from Hanford WTP Secondary Waste Surrogate

The Hanford WTP condensate surrogate (Secondary/Recycle Waste) was prepared to mimic the average composition. The surrogate, as originally prepared, 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.

In order to more quickly screen for uptake of cesium ion 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 ($\sim 4,200$ 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 for the WTP is ~ 0.2 mCi/L (or estimated total Cs ~ 6 $\mu\text{g/L}$).

Media Preparation: 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 ($\text{K}_4\text{Fe}(\text{CN})_6$) 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 VI. 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.

Code ID	Substrate ID		KCCF Added	Kd (mL/g)
KUR-7-1	09-1771	Herschelite (EH)(~ 15- μ m)	No	1500
KUR-7-2	09-1773	Clinoptilolite(16x20 mesh)	No	570
KUR-7-3	09-1771	Herschelite (EH) + KCCF = KH	Yes	12,600

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

(Engineered Herschelilite Removal of At-Tank Cesium)

Engineered Herschelilite was tested at several mesh sizes (Zeofume is 15 micron while column media is a granular 14x50 mesh) Our high grade clinoptilolite zeolite was also tested at the various pH values. Surface area definitely effects the capacities and kinetics of the media. 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). At the extreme pH of 14 and at this high salt molarity, only the EngineeredHerschelite (EH) continued to remove the Cs (also Co and Ni) with respectable Kd's, while the standard zeolite lost all affinity.

ALL MEDIA HAD TO BE FULLY DEMONSTRATED AT HIGH RAD LEVELS AND IN SEAWATER BEFORE APPLICATION AT FUKUSHIMA

All media proposed for use at Fukushima were tested in advance of initial presentations to TEPCO in synthetic seawater known as “Instant Ocean,” Marineland Labs. This was prepared with a specific gravity (SG) of 1.033 by hydrometer at a pH of 8.3. Ironically, this high salt content waste was very similar to the Hanford WTP Recycle/Secondary wastes outlined herein. 4 mL of seawater (4.0711 g) at a SG of 1.020 by gravimetry was mixed with 4 mL deionized water (3.9901 g) at 22 °C. The two most important isotopes of concern were cesium and iodine.

Table VII Cs-137 traced synthetic seawater

<u>Sample</u>	<u>Medium</u>	<u>Kd (mL/g)</u>
11-2070	H	533
10-7595	EH	626
09-1773	Clino	123

I-129 traced seawater

<u>Sample</u>	<u>Medium</u>	<u>Kd (mL/g)</u>
10-7109	AGH	>3.25E+03

Note that >Kd for I-129 means below Minimum Detectable Activity (MDA), which limits the Kd calculation

While iodine removal was not affected by seawater, its removal efficiency was affected by excess turbine oil. It was proven that, with proper oil removal by the prefilter vessel media (SMZ), iodine removal remained optimum. On the other hand, while cesium removal by the Herschelites or zeolites was not affected by the oil, it was notably affected by the percent seawater (% SW) as can be seen in Figure 3 below. The media's performance greatly increased with diminishing seawater as dilution continued. Kurion laboratory results were in very good agreement with those of TEPCO and CRIEPI (Central Research Institute for Electrical Power Industry) as can be seen in Figure 4 (14, 15, 16, 17 and 18).

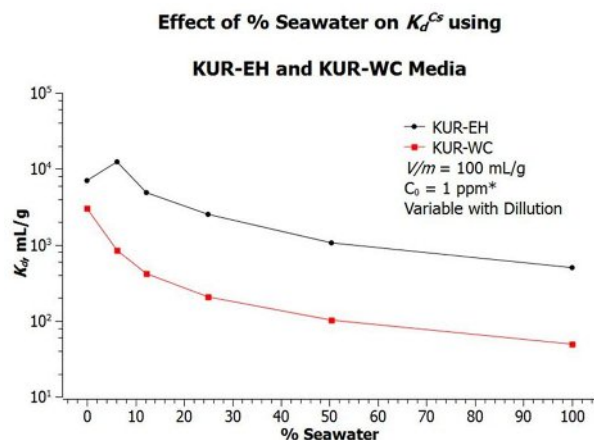


Figure 3. Effects of seawater dilution: The two media compare almost linearly. The distribution coefficients for this are much more parabolic, likely due to the decrease of the initial C_s concentration before contact with the media.

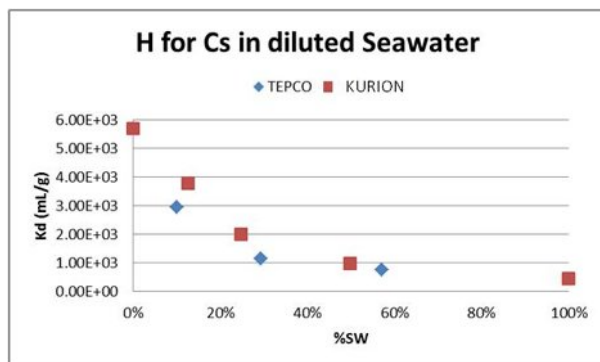


Figure 4. Sorption of Cs from diluted seawater by Herschelite, plotted as linear isotherm.

Once the initial cesium concentration diminished where initial dose build up on the media was not as significant of an issue (as well as a decrease in % SW), it was proposed to introduce an even more efficient media that had been developed and produced in mass quantities for the project. This media has extremely high K_d s and DF capabilities and was proposed as a polishing media to maintain the extremely aggressive decontamination factors required (e.g., $10^5 - 10^6$) of the system. These KH (or H) vessels have now replaced the AGH polishing vessels since iodine is no longer an issue.

Sorption of cesium on Herschelite modified by addition of potassium hexacyanoferrate (KCCF) is best represented by Freundlich isotherms (see KH curve and graph below). Sorption data in the form of isotherms allow estimates of the ultimate mass loading ($x/m = S = \text{g-Cs/g-solid}$) for a medium at full saturation (equilibrium concentration, C_e , equal to influent concentration C_o). Results for the mass concentration of natural cesium at equilibrium (from surrogate testing) can be converted

to an equivalent activity in contaminated water from Fukushima by assuming that all of the cesium is present as the isotope Cs-137 (specific activity $3.12\text{E}+12$ Bq/g).

The plot in Figure 5 is based upon an assumed equivalent activity $\sim 1\text{E}+03$ Bq/mL (total Cs $\sim 3.1\text{E}-10$ g/mL). At this low value of [Cs], the K_d (mL/g) on KH is relatively constant at $\sim 1\text{E}+05$ mL/g, with minimal effect of % SW (Figure 5). In contrast, “standard” Herschelite is affected by salinity (see Figures 3, 4 and 5).

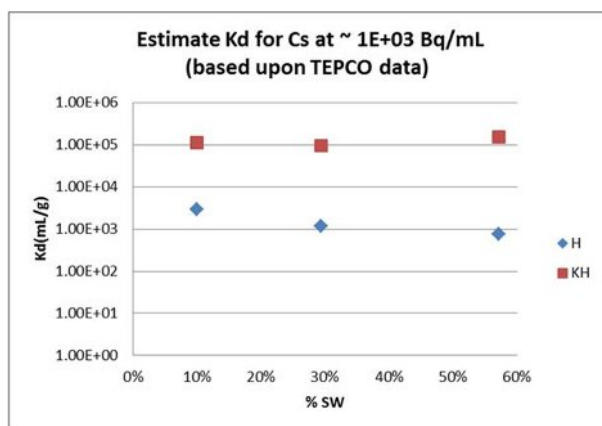


Figure 5. Estimated values of K_d (mL/g) for Cs-137 at $\sim 3.1\text{E}-10$ g/mL, as a function of seawater dilution.

While KH has exceptional Cs removal and capacity efficiencies, pure (100%) KH was only proposed when Cs levels were low enough to not cause rapid dose issues on the media, which would cause more rapid vessel change outs and dose to workers. As a polishing vessel, 100% KH is the ultimate application of this media. Until such Cs levels reach such safer levels however, mixtures of H and KH are being applied in the polisher vessels. This could also be done in the primary cesium tower skids in the center of the system. The effect of % KH in H on K_d and DF can be seen in Figure 6 below.

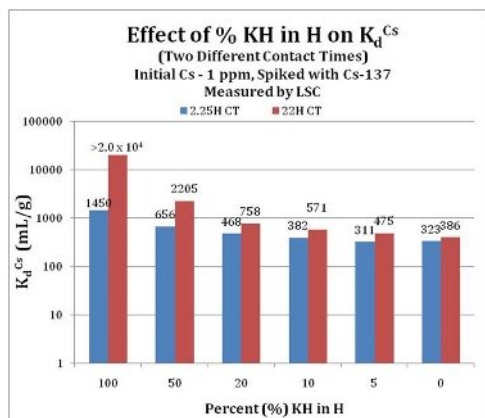


Figure 6. Effect of Super Media Mix or Polisher Vessel on K_d and DF

Oil and Filtration Media: Front Protection Vessels

Almost as importantly as the lack of effect (competition) of seawater components on the media was the proof that the media's performance was not appreciably effected by the presence of oils. Both turbine oils, as well as several other oil sources, had been found in the waste water present in the flooded building basements. As one could imagine, such a situation would be totally untenable for standard organic ion exchange resins. Fouling of such media would be extremely rapid. This is not to mention storage issues (e.g., hydrogen generation) and the lack of subsequent disposal/disposition pathways (i.e., not vitrifiable or readily solidified).

The final irony was that the ultimate final media selected for the Fukushima Project had, in fact, been applied to the Gulf oil spill in the U.S., thus some very rare experience with oily seawater conditions. To re-prove the ability to, not only filter out fines/crud, but to remove the oil, two techniques were applied. For a qualitative determination of oil uptake by the media, a fluorescence technique was developed. As can be seen in Figure 7a, surfactant modified clinoptilolite (SMZ, left), or modified Herschelite (CH), agglomerates the oil in the center of the vial while the untreated media (Clino, right) does not and the oil remains floating on the surface (as it does in the basements). Actual turbine oil was used in the tests (Chevron GST 3200 Turbine Oil Iso 32) compliments of the Diablo Canyon Nuclear Power Plant, U.S. It was further necessary to prove that the surfactant was not simply washed off during processing. Since the surfactant modified media (SMZ or SMD) has a very high affinity for technetium (Tc 99), it was found that one could follow the retention of surfactant as a parallel to the removal capability of Tc 99. Unlike the fluorescence technique, this is a quantitative analysis. With the previous determination of Tc 99 Kd values for the media, it was determined (see Figure 7b) that there was no erosion of removal efficiency over time; thus no loss of surfactant or oil removal capability.

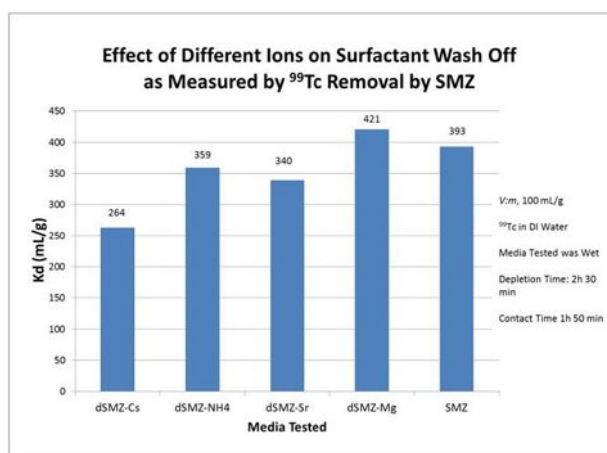


Figure 7.a) Qualitative determination of media oil uptake by fluorescence b) quantitative determination of surfactant retention of oil by the indirect removal of Tc 99.

KURION PROCESS AND SKID DESIGN

With all these process pieces put together and proof of concept proven both in U.S. laboratories and those of numerous Japanese labs (including TEPCO, CRIEPI and

JAEA), the following process flow diagram (Figure 8a) and processing skid design (Figure 8b) was finalized.

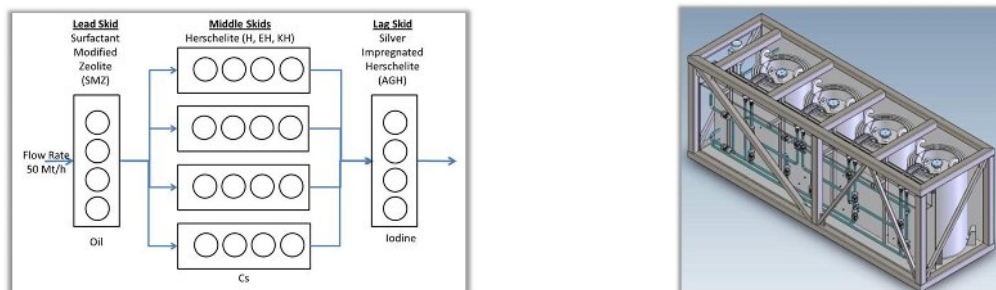


Figure 8. a) High level flow sheet b) Processing skid design (The four fully loaded Herschelita skids, Cesium Towers, weigh 90 MT each, while the lead and lag skids weigh 65 MT each).

The features of the processing skids include:

- 3 vessels operating, 1 vessel for replacement for middle Cs skids
- 4 vessels operating in parallel for Lead (Pre-filter and Oil) and Lag Skids (Polishing Vessels)
- Each vessel has $\sim 42.4 \text{ ft}^3$ (1.2 m^3) of media
- Dedicated shields for each vessel to mitigate dose during operation, hoisting/change out, and storage (7" thick shields for vessels in center towers and 3" shields for Lead and Lag vessels, and 1" skid shields)
- Shield placement guides (trunnion guides for alignment of 33,000 lbs shield) for precise positioning
- Removable redundant feed pumps
- Manually operated valves for high reliability and merry-go-round positioning for middle skids
- Manual valves in fixed piping operated using reach rods through external shielding to minimize worker dose
- Dose monitored at shielding external surface

FINAL WASTE FORM AND DISPOSAL OPTION: MODULAR VITRIFICATION SYSTEM (MVS[®])

As mentioned previously, in time, it will become equally important to have a clear waste disposition path as well as a successful isotope removal system. The Kurion system and approach advocated a media that was readily stabilized/immobilized after its use. As with the TMI cleanup sequence, once the media in the submerged demineralization vessels was spent, it was further proven that this type of media could be melted into glass (vitrified) in a modular vitrification unit. This work was carried out by PNNL in support of the 1979 TMI recovery on portions of the waste stream and was summarized in the Reference [3]. Similarly, the Kurion system proposed utilizing a vitrification friendly media to be subsequently vitrified in a Modular Vitrification System. The recent, featured article in Radwaste Solutions "Two Novel Approaches"(19) discusses the

application of Kurion Ion Specific Media and Modular Vitrification System to achieve excellent isotope separation and glass making; resulting in a stabilized vitrified waste form.

All of the media utilized during the Fukushima Project have been melted in numerous glass formulations at our Vitrification Pilot Facility in Rolla, Missouri. As an example, excellent waste loadings of 70-75% (at 1100-1200 °C) have been achieved with spent Herschelite (see Figure 9 to show before and after). Of extreme importance, even at these elevated temperature melts, cesium retention was 100% based on XRF analysis.

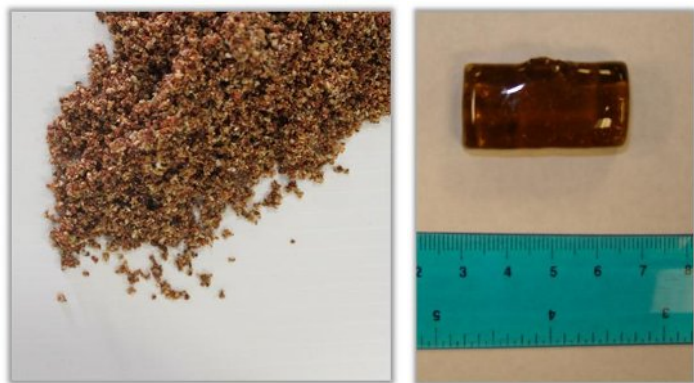


Figure 9. Spent Herschelite (left) and Vitrified Herschelite (right) at 1100 °C for 3-4 hours.

CONCLUSIONS

As demonstrated herein, all ten major steps leading up to the readiness and acceptance of a modular emergency technology recovery system were met and in a very short period of time, thus utilizing three decades of experience to produce and deliver such a system literally in seven weeks:

- EPRI - U.S. Testing and Experience Leading to Introduction to EPRI – Japan and Subsequently TEPCO Emergency Meetings
- Three Mile Island (TMI) Media & Vitrification Experience by PNNL
- Commercial Nuclear Power Plant Media Experience (including long term Cs removal)
- DOE Low Active Waste (LAW) and High Level Waste (HLW) in High Salt and pH Conditions Media and Vitrification Experience
- National Laboratory (e.g. Oak Ridge National Laboratory, ORNL) Ground Water Media Experience
- Gulf Oil Spill Media Experience in Seawater
- All Media Had to be Fully Tested at High Rad Levels in Seawater and Oil Before Arriving in Japan
- Final Waste Form and Disposal Experience (e.g., vitrification)
- 100 Metric Tons (6000 cubic feet or 220,400 pounds) of Media had to be Immediately Available with the same amount in production as replacement

media. [To date, for 2011, 400 MT of media have been prepared for Japan alone.]

- Remote Operation, Modular Water Treatment Equipment Design and Fabrication in both Commercial NPP and DOE Canyon Operations

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