

**Isotope Specific Remediation Media and Systems- 13614**

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**ABSTRACT**

On March 11, 2011, now two years ago, the magnitude 9.0 Great East Japan earthquake, Tohoku, hit off the Fukushima coast of Japan. While, of course, most of the outcome of this unprecedented natural and manmade disaster was a negative, both in Japan and worldwide, there have been some extremely invaluable lessons learned and new emergency recovery technologies and systems developed. As always, the mother of invention is necessity.

Among these developments has been the development and full-scale implementation of proven isotope specific media (ISMs) with the intent of surgically removing specific hazardous isotopes for the purpose of minimizing dose to workers and the environment. The first such ISMs to be deployed at the Fukushima site were those removing cesium (Cs-137) and iodine (I-129). Since deployment on June 17, 2011, along with treated cooling water recycle, some 70% of the curies in the building liquid wastes have been removed by the Kurion system alone. The current levels of cesium are now only 2% of the original levels. Such an unprecedented, "external cooling system" not only allowed the eventual cold shut down of the reactors in mid-December, 2011, but has allowed workers to concentrate on the cleanup of other areas of the site. Water treatment will continue for quite some time due to continued leakage into the buildings and the eventual goal of cleaning up the reactors and fuel pools themselves.

With the cesium removal now in routine operation, other isotopes of concern are likely to become priorities. One such isotope is that of strontium, and yttrium (Sr-90 and Y-90), which is still at original levels causing further dose issues as well as impediments to discharge of the treated waste waters. For over a year now, a new synthetic strontium specific media has been under development and testing both in our licensed facility in Oak Ridge, Tennessee, but also in confirmatory tests by the Japan Atomic Energy Agency (JAEA) in Japan for Tokyo Electric Power Company (TEPCO). The tests have proven quite successful, even in high salt conditions, and, with loading and dose calculations being completed, will be proposed to add to the existing cesium system. There is no doubt, as high gamma isotopes are removed, other recalcitrant isotopes such as this will require innovative removal media, systems and techniques.

Also coming out of this international effort are other ISM media and systems that can be applied more broadly to both Commercial Nuclear Power Plants (NPPs) as well as in Department of Energy (DOE) applications. This cesium and strontium specific media has further been successfully tested in 2012 at a Magnox station in the UK. The resulting proposed mitigation systems for pond and vault cleanup look quite promising. An extremely unusual ISM for carbon 14 (C-14), nickel (Ni-63) and cesium (Cs-137)

has been developed for Diablo Canyon NPP for dose reduction testing in their fuel pool. These media will be deployed in Submersible Media Filter (SMF) and Submersible Columns (SC) systems adapted to standard Tri-Nuclear<sup>®</sup> housings common in the U.S. and UK. External Vessel Systems (mini-Fukushima) have also been developed as a second mitigation system for D&D and outages. Finally, technetium (Tc-99) specific media developed for the Waste Treatment Plant (WTP) recycle or condensate (secondary) waste streams (WM 2011) are being further perfected and tested for At-Tank Tc-99 removal, as well as At Tank Cs media.

In addition to the on-going media development, systems for deploying such media have developed over the last year and are in laboratory- and full-scale testing. These systems include the fore mentioned Submersible Media Filters (SMF), Submersible Columns (SC) and external pilot- and full-scale, lead-lag, canister systems. This paper will include the media development and testing, as well as that of the deployment systems themselves.

## INTRODUCTION

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. A tremendous effort has been made, by many nationalities, since this time to restore this damaged plant and surrounding area and to return a great deal of the residents to their homes and farm lands.

A little more than a month after the March 11, 2011 Great East Japanese Earthquake and Tsunami damaged the Fukushima Daiichi Nuclear Plant, TEPCO announced the selection of Toshiba (oil/grease separation), Kurion (cesium removal), AREVA (cesium downstream removal) and Hitachi (desalination) to provide an external reactor water cooling system rated at 1200 MT/day (317,000 gallons/day). The mission was to reduce the dose to workers, allow access to the turbine and reactor buildings and protect the environment by the removal of a very large volume of highly radioactive, oily and saline water. As mentioned, the system went on line June 17, 2011, less than 100 days after the tsunami, compared to approximately 18 months for startup of the cesium removal at Three Mile Island, TMI (1979 U.S. incident). That system was used to process 2990 MT (790,000 gallons) of high activity water, or 2.5 days of processing for the TEPCO system.

An extremely important milestone was met by the TEPCO team on December 16, 2011 when the plant officially reached cold shutdown status. As of the Waste Management conference in March 2012, the Kurion system alone had processed more than 137,340 MT (36 million gallons) of waste water and was responsible for the removal of approximately  $3.1 \times 10^{17}$  Becquerel, Bq (8.4 million curies) of cesium (see Figure 1). By this anniversary date, Kurion had removed > 70% (75% by TEPCO estimate) of the total activity and 53% of the total volume, while the SARRY system had removed ~ 30% (25% by TEPCO estimate) and AREVA 0.1%. By this date, the combined water cooling system had processed more than 258,780 MT (68 million gallons), reduced salinity by almost 90% and estimated to have removed  $4.4 \times 10^{17}$  Bq (12 million curies) of the estimated original  $5 \times 10^{17}$  (13.6 million curies) cesium inventory. To put this into perspective, the initial inventory represented nearly 27 times the annual disposal of all curies of activity for the U.S. fleet of 104 reactors, some  $1.9 \times 10^{16}$  Bq (507,000 curies) (Figure 1).

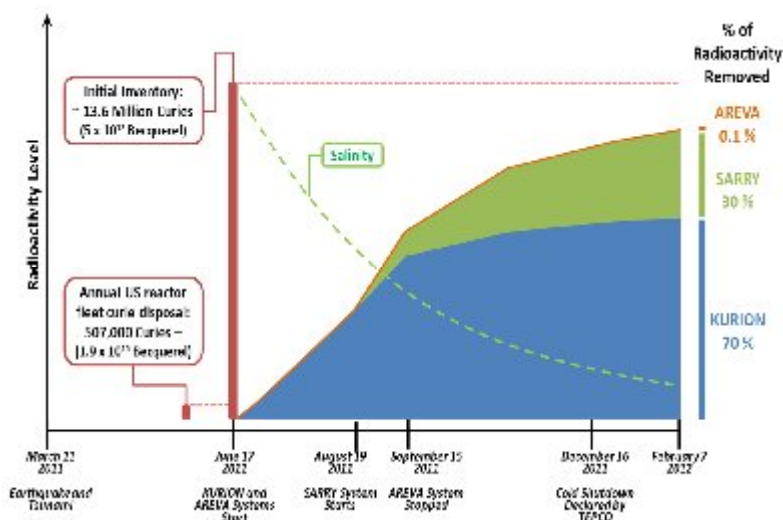


Figure 1. Reduction of initial radioactivity inventory by cesium absorption systems.

- 1) Estimated initial inventory of radioactive based on TEPCO data showing 118,390 m<sup>3</sup> of water at 4.2 million Becquerel/cc of total cesium. Historic salinity data from TEPCO for 2011 and March 6, 2012 (3).
- 2) Estimated activity of radioactive cesium removed following start of treatment based on conservative assumptions derived from data made available publicly by TEPCO via handouts and press releases.
- 3) Curie disposal for the US fleet of 104 reactors for all sources (e.g. cesium, nickel, cobalt) averaged over 1997 through 2006 per the DOE Manifest Information Management System (MIMS). Approximately 10 percent was added to this figure to arrive at the total annual US curie disposal for all sources and generators.

Of the cesium removal systems, the Kurion system is the only system to see the high-activity, high-salinity (100% seawater) water present during the initial system startup. This was due to the fact that the AREVA system operated downstream and was designed to remove the last tenths of a percent of the activity. Further, by starting up more than two months later and initially located behind the Kurion system, the SARRY system never saw more than 60% of the initial cesium level or 50% of the salinity present in June.

After one year of actual operation (June 15, 2012), Kurion had achieved ~ 71% and SARRY 29% activity removal (TEPCO press releases). Estimates from the latest public data available showed that the TEPCO full system had processed, by 2012 year end, a total of 540,000 MT (>140 million gallons). In doing so, the Kurion system had removed 17 x 10<sup>16</sup> Bq (4.6 million curies) and the SARRY system 8 x 10<sup>16</sup> Bq (2.16 million curies), an impressive total of 25 x 10<sup>16</sup> Bq (6.75 million curies) to bring the total activity down to ~2% of the original value.

## 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 spectrometry, 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<sub>d</sub>, and the decontamination factor, DF (equivalent to C<sub>0</sub>/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 contacted

M = mass (g) of solid phase contacted

C<sub>0</sub> = 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

### Evaluation of Media for Strontium Removal

While cesium levels have been reduced to some 2% of original concentrations at Fukushima Daiichi Station due to extensive treatment and recycle, strontium levels have remained at initial levels of  $1 \times 10^5$  Bq/mL. While the dose contribution is approximately 3% of the cesium (gamma) equivalent, to further reduce dose to workers and the environment, development and testing of ion specific media (ISM) for strontium (Sr-89 & 90/Y-90) began in June of 2011. Since this time, verification testing of the work done in Oak Ridge, TN was carried out at the Japan Atomic Energy Agency (JAEA).

Five media were studied as batch reactions for uptake of the strontium (Sr<sup>2+</sup>) cation in five percent seawater with no additional Cs. The media studied were: KUR-TS-G, KUR-EH, KUR-SSM and KUR-HAM. The media were studied at two volume to mass ratios (V:m) for comparison to confirmatory data: 100 mL/g (JAEA batch reaction reports) and 1000 mL/g (Previous Kurion studies simulating column operations). At a V:m of 100, the best media to excel in batch reactions was KUR-TS-G (granular titanasilicate) with a K<sub>d</sub><sup>Sr</sup> of  $5.4 \times 10^4$  mL/g, while KUR-HAM (hydroxyapatite microspheres, 740 mL/g), KUR-SSM, (strontium specific media, 490 mL/g) and KUR-EH, (Engineered Herschelite 41 mL/g) followed. While it has been reported that other media appear to be excellent Sr<sup>2+</sup> removal candidates, these products are often found to lose physical stability in dilute seawater, and would not be a practical media for Sr<sup>2+</sup> removal in column applications. KUR-TS-G, is a very stable granular, titanasilicate synthetic product with a high K<sub>d</sub><sup>Sr</sup>, even in high competition (e.g., seawater, Ca and Mg) making it an excellent choice for removal of Sr in column/vessel applications. The media even proved stable in DOE high molarity, extreme pH conditions.

Strontium-89 and 90 are both products of the fission process and the continued dissolution of spent nuclear fuel. The data from TEPCO has suggested that there is a high level of <sup>89/90</sup>Sr<sup>2+</sup> in the cooling water. What is known, is that there is approximately 400 ppb of natural Sr<sup>2+</sup> in 5% seawater (8 ppm in 100% SW). The amount of radioactive Sr, is of course a small fraction of this. Unfortunately it is necessary to remove all of the Sr<sup>2+</sup> (and yttrium, Y) as the isotopes cannot be separated.

Two scenarios were tested for this report: Sr removal in the treatment skid (ie, in the presence of Cs), and Sr removal after the treatment skid (Polisher position without Cs). Two volume to mass ratios were explored. The physical stability of the media tested were also explored to observe whether they would hold up in the extreme conditions of high throughput vessel processing.

The media tested is listed in Table 1. A solution of 5% seawater was made up from 100% InstantOcean<sup>®</sup> and deionized water. The final concentration of Sr<sup>2+</sup> was ~ 900 ppb, as measured by ICP-MS. The media were dried by air, and weighed out to either 10 mg or 100 mg. To each of these media was added 10 mL of 5% seawater, resulting in a final V:m of 100 and 1000 mL/g. The phases were contacted overnight on a TCLP rotator and were filtered with a 0.2 μm syringe filter. The experiment was run in triplicate and analyzed by ICP-MS.

Table 1. Media Tested, Size and Provider

Media	Grain Size	Provider
KUR-TS-G	14 x 50 Mesh	Kurion, Inc.
KUR-EH	14 x 50 Mesh	Kurion, Inc.
KUR-SSM	14 x 50 Mesh	Kurion, Inc.
KUR-HAM	14 x 50 Mesh	Kurion, Inc.

### Strontium Removal in 5% Seawater

To emulate the polishing skid (post Cs treatment), the media were tested in 5% seawater without the addition of Cs. The results are summarized in Table 2 and are shown graphically in Figure 2 and Figure 3.

Table 2. Distribution coefficients of media tested in 5% seawater (900 ppb Sr<sup>2+</sup>, 0 ppb Cs<sup>+</sup>) at V:m ratios of 100 (batch reactions) and 1000 mL/g (column flow).

Media	K <sub>d</sub> <sup>Sr</sup> V:m 100 (mL/g)	K <sub>d</sub> <sup>Sr</sup> V:m 1000 (mL/g)
KUR-TS-G	5.4 x 10 <sup>4</sup>	2.9 x 10 <sup>3</sup>
KUR-EH	41	1.7 x 10 <sup>2</sup>
KUR-SSM	4.9 x 10 <sup>2</sup>	2.3 x 10 <sup>2</sup>
KUR-HAM	7.4 x 10 <sup>2</sup>	Not Measured

All of the tested media appeared to remove some amount of the strontium ion, but one media stood out in the experiment, KUR-TS-G. Typically media with a K<sub>d</sub><sup>Sr</sup> of the 10<sup>3</sup> magnitude are reliable and are considered good. Media with a K<sub>d</sub><sup>Sr</sup> of 10<sup>4</sup> or higher are considered very good or excellent. KUR-TS-G demonstrated a distribution coefficient in the very good to excellent range (10<sup>4</sup> mL/g). Both of these media are titanosilicate or silicotitanate based, and perform relatively closely to one another. However, their physical (granular) properties do differ, and will be discussed in the stability section.

EH media was used as a baseline because it is currently being used in the cesium treatment train at Fukushima. However the large error bars shown in both Figure 2 and Figure 3 show that the EH, designed for Cs removal, is not best suited for removing Sr<sup>2+</sup> in seawater conditions.

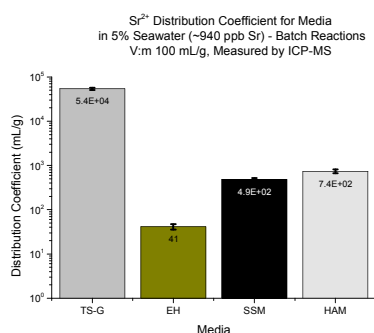


Figure 2. Strontium distribution coefficient of several media using 5% seawater (940 ppb Sr<sup>2+</sup>, no Cs) and a V:m of 100 mL/g. The numbers presented are averaged between three trials.

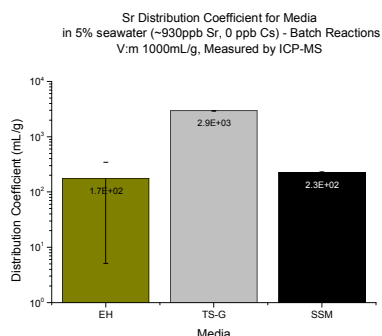


Figure 3. Strontium distribution coefficient of several media using 5% seawater (940 ppb Sr<sup>2+</sup>) (no added Cs<sup>+</sup>) and a V:m of 1000 mL/g. The numbers here are averaged between three trials.

### Strontium Removal in 5% Seawater and 60 ppb Cs<sup>+</sup>

To emulate the lead skid, the media were tested in 5% seawater with the addition of 60 ppb Cs<sup>+</sup>. The results are summarized in Table 3 and are shown graphically in Figure 4 and Figure 5.

Table 3. Sr<sup>2+</sup> and Cs<sup>+</sup> distribution coefficients of media tested in 5% seawater (900 ppb Sr<sup>2+</sup>, 60 ppb Cs<sup>+</sup>) at a V:m ratio of 1000 mL/g.

Media	K <sub>d</sub> <sup>Sr</sup> V:m 1000 (mL/g)	K <sub>d</sub> <sup>Cs</sup> V:m 1000 (mL/g)
KUR-TS-G	2.32 x 10 <sup>3</sup>	2.9 x 10 <sup>3</sup>
KUR-EH	2.41 x 10 <sup>2</sup>	7.5 x 10 <sup>3</sup>
KUR-KH	Not Measured	>1.3 x 10 <sup>5</sup>

The best Cs media for the lead position in the treatment train continues to be KH with a K<sub>d</sub><sup>Cs</sup> of 1.3 x 10<sup>5</sup> mL/g. However, the focus in these experiments is on the Sr<sup>2+</sup> removal. While the data shows that this Sr media does remove Cs in these conditions, it can be considered an added benefit as it may help remove Cs in the polishing position. When the Cs<sup>+</sup> distribution coefficients are compared, it is clear that KUR-TS-G has a much higher affinity for Cs<sup>+</sup> and is likely to help remove any additional Cs<sup>+</sup> that gets through the treatment train. If used as a polisher, it appears that TS-G would still be able to remove small amounts of Cs<sup>+</sup> while still maintaining a competitive Sr uptake.

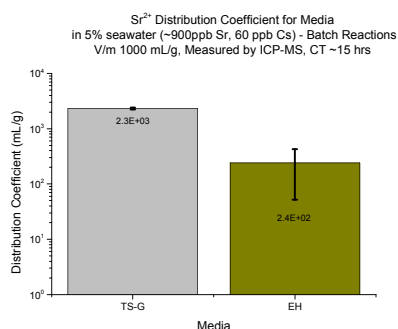


Figure 4. Strontium distribution coefficient of several media using 5% seawater (900 ppb Sr<sup>2+</sup>), added Cs (60 ppb) to simulate the front of the treatment train, and a V:m of 1000 mL/g. The numbers here are averaged between three trials.

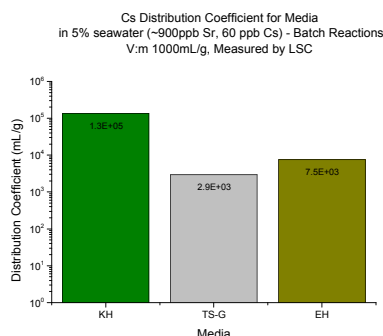


Figure 5. **Cesium** distribution coefficient of several media using 5% seawater (900 ppb Sr<sup>2+</sup>), added Cs (60 ppb) to simulate the front of the treatment train, and a V:m of 1000 mL/g. KH was the best media with a K<sub>d</sub><sup>Sr</sup> of >1.3 x 10<sup>5</sup> mL/g, followed by EH (7.5 x 10<sup>3</sup> mL/g), and TS-G (2.9 x 10<sup>3</sup> mL/g). The numbers here are averaged between three trials.

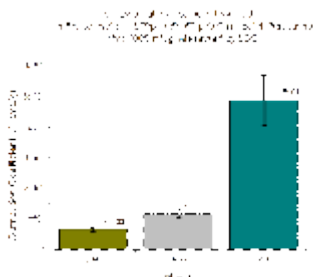


Figure 6. Further shows the superiority of the KH media for Cs removal at current conditions.  
**Physical and Chemical Stability of Media**

The physical and chemical stability of the media is of the utmost importance when selecting a suitable product for a treatment train. As these media are being used in a high flow column system, the ability for the media to maintain their granular form without fines or gels creation is essential. There are several titano-silicate [Na<sub>2</sub>(TiO<sub>2</sub>)<sub>x</sub>(SiO<sub>4</sub>)<sub>y</sub>] based materials. Despite their similar compositional formulation, the physical stability of these materials is quite different and KUR-TS-G clearly excels under these conditions.

The instructions for the use of some media warn of several precautions that can influence the media: contact with deionized water, long contact in tap water, and formation of colloids and powders when shaking the media. These notes were taken into account in the preparation of the experiments. However, even when gentle rotating was used for less than 10 minutes, some granular products seem to degrade and create fines/gel. KUR-TS-G exhibits good stability in DI water and in seawater for extended periods of time.

These experiments tested the ability of several media to remove Sr<sup>2+</sup> from different conditions. Figure 7 represents a long-term column on KUR-TS-G to make sure that the media can perform in the at least 80 GPM flow rates (145% of design specification) currently being used at the Kurion treatment system. Competing media was not applied to column tests due to instability.

As Kurion's treatment train runs two systems into one polisher at an increased rate (80 GPM), the column was tested at an equivalent laboratory rate of 0.15 mL/min (Fukushima Equivalent, FEQ, of 94 GPM). One bed volume of media was equivalent to approximately 0.527 mL of solution. The column was hand packed and the 5% seawater solution (~900 ppb Sr<sup>2+</sup>) was run countercurrent to gravity to reduce

channeling. An autocollector was used to collect a fraction of samples. The resulting effluents were measured by ICP-MS for Sr<sup>2+</sup> concentration.

The results of the experiment are visually represented in Figure 7. The K<sub>d</sub><sup>Sr</sup> is traditionally measured at a C/C<sub>0</sub> of 50%. Since the density of KUR-TS-G is approximately 1 g/mL, the K<sub>d</sub><sup>Sr</sup> is equivalent to the number of Bed Volumes treated: 2.24 x 10<sup>3</sup> BV: 2.24 x 10<sup>3</sup> mL/g.

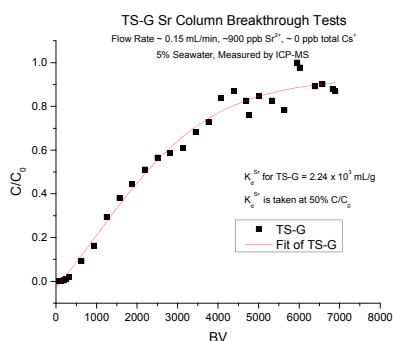


Figure 7. Column Test Results of TS-G as a Polisher. 5% seawater, 900 ppb of total Sr<sup>2+</sup>, 0 ppb of Cs<sup>+</sup> 0.15 mL/min (94 GPM FEQ).

An additional concern has arisen during operations due to the increased competition from calcium (Ca) and magnesium (Mg), likely being leached from the concrete in the containment and basement areas of the plant. In order to insure that this increasing competition did not adversely affect the media's removal of Sr, tests were also run comparing K<sub>d</sub>'s for Sr against those of Ca and Mg for a variety of media. The key here is to compare the Separation Factors (SF) of Sr/Ca and Sr/Mg. The two most important current waste water conditions are the system influent 5% seawater and the reverse osmosis (RO) 10% seawater reject shown in Figure 8 and Figure 9, respectively.

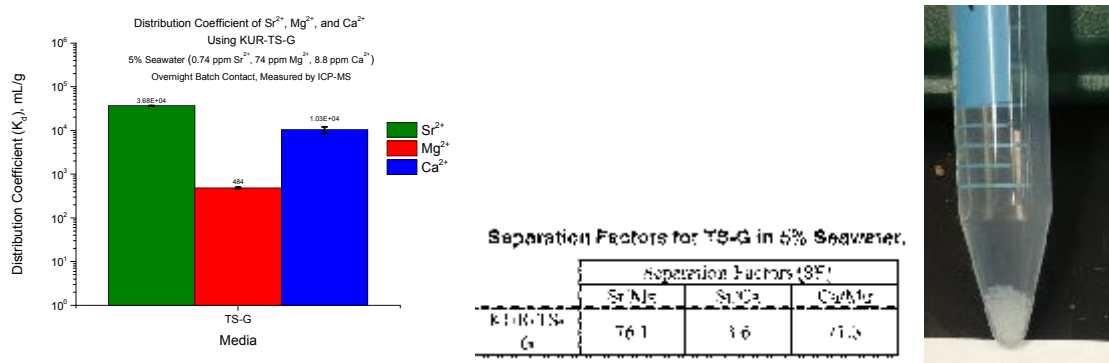


Figure 8. Comparison at current 5% Seawater conditions (Left) and TS-G in 5% Seawater over 24 hours (Right).



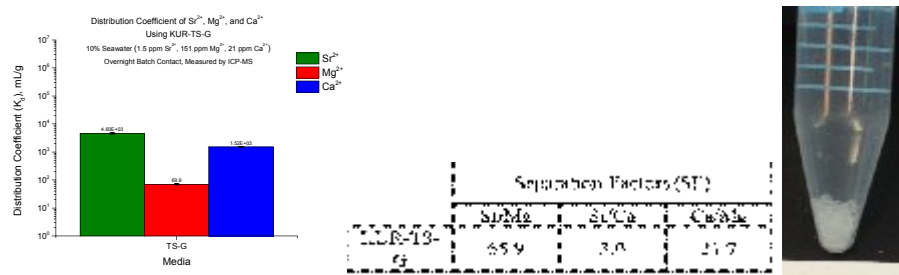


Figure 9. Comparison at current Reverse Osmosis (RO) Reject conditions and TS-G in 10% Seawater over 24 hours (Right).

For full validation of all test results, it has been the practice since the beginning of the crisis to do verification test in Japanese laboratories that can confirm results to TEPCO. This has normally been done by the Central Research Institute of Electric Power Industry (CRIEPI) or the Japan Atomic Energy Agency (JAEA). In the case of Sr studies, the collaboration was with JAEA (4).

**Materials:** Kurion Sr media: TS-G

MSDS: Chemical composition; Titanium silicate, H, Na, Ca mixed salt

Properties; White granular, bulk density 56kg/m<sup>3</sup>

TS-G received on 6th June 2012 was used without conditioning.

Seawater (SW) used for adsorption experiments:

Synthetic seawater of three salt concentrations was used (Table 4). The 100% SW was Aquamarine(TM) from Yashima Pure Chemicals Co.,Ltd. available for a corrosion test. Its ingredients are selected according to ASTM D1141 (Standard Practice for the Preparation of Substitute Ocean Water). The 200% SW was prepared by JAEA by using high purity reagents. The 5%SW was prepared by dilution of 200%SW with pure water.

Table 4 Composition of synthetic seawater(SW).

mg/L	100 %SW(CRC*)	100 %SW	5 %SW	200 %SW
Mg	1290	1334.4	66.72	2668.8
Ca	412	418.5	20.925	837
Sr	<b>7.9</b>	<b>14.0</b>	0.7	28
K	399	397.3	19.865	794.6
Na	10800	11033.4	551.67	22066.8
B	4.44	4.7	0.235	9.4
Cl	19400	19858.5	992.925	39717
F	1.3	1.4	0.07	2.8
SO <sub>4</sub>	2715	2768.8	138.44	5537.6
Br	67.3	67.5	3.375	135

\*CRC handbook of chemistry and physics, 92nd ed. (5). The Sr conc. in CRC book seems more appropriate for the performance experiment.

**Adsorption experiment and Analyses:** Aquamarine(TM) was used after filtration (0.45 micron)

- Solution / Media ratio : 100 ml/g in 9 or 20 ml glass bottle
- Mixing : Rotation of the glass bottle at 10 rpm for 20 hours, Temp. 23 – 24°C
- Analyses : Sr concentration by ICP-OES, initial and final pH (pHi and pHf)
- Calculation of parameters:

$$\text{Uptake (\%)} = (\text{Initial Sr conc.} - \text{Final Sr conc.}) / (\text{Initial Sr conc.}) \times 100$$

$$\text{Distribution coefficient of Sr, } K_d (\text{Sr}) (\text{ml/g})$$

$$= (\text{Initial Sr conc.} - \text{Final Sr conc.}) / (\text{Final Sr conc.}) \times \text{Seawater vol.} / \text{media weight}$$

**Results:** Uptake ratios, distribution coefficients and pH values are shown in Table 5. As a reference, values for Herschelite, AGH and SMZ obtained by the same procedure are also listed.

Table 5. Uptake ratios, distribution coefficients and pH values.

Sample	Seawater		Media mg	Initial Sr mg/L	Final Sr mg/L	Uptake %	K <sub>d</sub> (Sr) ml/g	Initial pH	Final pH
	%	ml							
TS-G	5	10	101.73	0.71	0.004	99.4	17350	7.1	8.1
TS-G	5	10	101.45	0.71	0.004	99.4	17398	7.1	8.1
TS-G	5	10	101.78	0.71	0.004	99.4	17341	7.1	7.9
TS-G(*)	100	4.5	45.32	15.3	7.81	48.9	95	7.7	7.3
TS-G	100	4.5	45.26	14.5	8.24	43.4	76	7.9	7.7
TS-G	100	10	100.61	14.7	8.56	41.8	71	7.8	7.7
TS-G	100	10	102.87		8.55	41.8	70	7.8	7.7
TS-G	200	10	99.11	29.7	23.1	22.2	29	7.8	7.5
TS-G	200	10	100.91	29.7	22.9	22.9	29	7.8	7.5
TS-G	200	10	100.90	29.7	22.3	24.9	33	7.8	7.5
Herschelite	5	10	101.01	0.71	0.61	14.1	16	7.1	7.9
Herschelite	100	10	101.90		15.3	-4.1	-4	7.8	7.9
Herschelite	200	10	103.44	29.7	29.5	0.7	1	7.8	7.7
AGH	100	10	101.27		14.8	-0.7	-1	7.8	7.7
SMZ	100	10	100.99		15.7	-6.8	-6	7.8	7.7

(\*)Reported as the JAEA TEST No.TS-G-1

**Evaluation**

**Reproducibility:**  $K_d^{Sr}$  value in 100% SW was 95 ml/g in the report on TEST No.TS-G-1. We conducted additional three measurements. The average  $K_d^{Sr}$  value was 78 (+ - 10) ml/g. Reproducibility of experiments using 5 - 200%SW was good.

**Effect of salt concentration:** The TS-G exhibited high Sr removal performance in 5% SW. The  $K_d^{Sr}$  value, however, does decrease, as expected, with salinity. The relationship between  $K_d^{Sr}$  value for TS-G and the salinity of seawater is described by the line in Figure 10. The slope is -1.75. This suggests that the dominant reaction for Sr removal is ion-exchange between Sr(II) and large amount of Na(I) ion.

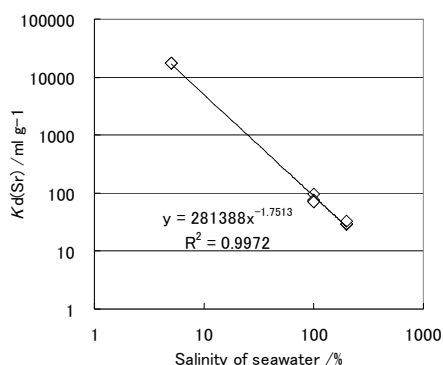


Figure 10. Relationship between  $K_d^{Sr}$  for TS-G and the salinity

Two additional studies were then carried out: 1) At lower Sr concentration to represent current conditions, and 2) Kinetics tests in 5% seawater, also current condition; both at the same conditions as the original studies, except all tests were run at 5% seawater. Table 6 illustrates the effect of Sr concentration on  $K_d$ 's.

Table 6. Effect of Sr concentration on  $K_d^{Sr}$  values

Sample	Sample (mg)	Initial Sr conc. (ppm)	Final Sr conc. (ppm)	Sr removal (%)	$K_d$ (ml/g)	Final pH	Adsorbed Sr (ppm)
KUR-TS-G	101.3	0.11	0.00033	99.7	31697	7	10.4
KUR-TS-G	102.9	0.18	0.00038	99.8	45997	7	17.5
KUR-TS-G	99.3	0.31	0.00077	99.8	40265	7	30.8
KUR-TS-G	101.8	0.42	0.00094	99.8	43674	7	41.2
KUR-TS-G	98.7	0.80	0.00191	99.8	42184	8	80.4
KUR-TS-G	105.5	1.00	0.00419	99.6	22497	8	94.2
KUR-TS-G	102.0	2.02	0.00842	99.6	23378	7	196.9
KUR-TS-G	103.6	2.24	0.00604	99.7	35761	8	215.9
KUR-TS-G	99.3	2.83	0.01163	99.6	24410	7	283.8
KUR-TS-G	101.2	9.85	0.04671	99.5	20742	7	968.8
KUR-TS-G	98.1	20.0	0.13224	99.3	15280	7	2020.6
KUR-TS-G	108.1	28.5	0.16517	99.4	15864	7	2620.2
KUR-TS-G	109.2	98.9	2.01860	98.0	4394	7	8869.1
KUR-TS-G	105.4	298	30.03487	89.9	847	7	25450.7
KUR-TS-G	108.0	1000	499.72601	50.0	93	7	46326.2

10ml of 5%SW, Shaking for 20h

Table 7 represents an attempt at establishing the true equilibrium of the TS-G media and the effect of shaking time on Sr removal. This appears to be ~ 240 hours under these conditions.

Table 7. Effect of shaking time on Sr removal.

Sample	Shaking time Hrs	Sample (mg)	Initial Sr conc. (ppm)	Final Sr conc. (ppm)	Sr removal (%)	$K_d^{Sr}$ (ml/g)	Final pH ( $\pm 0.1$ )
KUR-TS-G	0	-	10.09	10.09	-	-	-
KUR-TS-G	1	98.5	10.09	0.476	95.3	2051	7
KUR-TS-G	3	100.5	10.09	0.239	97.6	4101	7.1
KUR-TS-G	5	98.4	10.09	0.124	98.8	8185	6.9
KUR-TS-G	8	102.1	10.09	0.072	99.3	13621	7.4
KUR-TS-G	16	100.9	10.09	0.051	99.5	19382	7.5
KUR-TS-G	24	101.2	10.09	0.043	99.6	22935	7.1
KUR-TS-G	28	102.6	10.09	0.050	99.5	19660	7.6
KUR-TS-G	28	100.7	9.90	0.044	99.6	22939	7.1
KUR-TS-G	28	100.8	9.90	0.044	99.6	22515	7.1
KUR-TS-G	28	100.4	9.90	0.044	99.6	22558	7.1
KUR-TS-G	48	101.1	10.09	0.037	99.6	26785	7.3
KUR-TS-G	48	101.2	10.09	0.039	99.6	25548	7.5
KUR-TS-G	72	100.7	10.09	0.038	99.6	26572	7.3
KUR-TS-G	72	100.0	10.09	0.038	99.6	26703	7.3
KUR-TS-G	96	99.9	10.09	0.032	99.7	30981	7.3
KUR-TS-G	96	101.0	10.09	0.032	99.7	31619	7.3
KUR-TS-G	120	100.8	9.90	0.027	99.7	36793	7.5
KUR-TS-G	120	100.8	9.90	0.027	99.7	36450	7.5
KUR-TS-G	140	100.5	10.09	0.028	99.7	35848	7.3
KUR-TS-G	240	100.1	10.09	0.022	99.8	46345	7.5

## Media Systems and Decontamination Applications

In addition to the development of a number of unique ion specific media, Fukushima experience also led to the development of three new media delivery systems to be deployed in 2013 in Commercial NPP applications. These three media systems are:

1. **Submersible Media Filters (SMF):** These submersible units are designed for any type of fuel pool, pond or underwater isotope specific remediation. They fit into existing Tri-Nuc (Tri Nuclear Corp.) filter housings (single, dual or quad.) commonly used in the industry and use standard Tri-Nuc tools. They have an annulus (between two sheet filter) filled with an appropriate ion specific media (ISM) developed for each application (e.g., Cs, Sr, Ni, Co, C14, etc.) and are inside to out flow. Applications for these units would include the remediation of low activity levels such as for decontamination & decommissioning, D&D, or outages and operate in the recycle mode. See Figure 11.
2. **Submersible Columns (SC):** These are also submersible units for similar applications but are able to remediate higher levels of activity due to the fact that the entire unit is filled with ISM (vs annulus only) with top to bottom flow with discharge out the screened insert into the Tri-Nuc housing. Like the SMF, they too are designed to fit into a Tri-Nuc filter housing by utilizing this reusable screen insert (including lifting bales).
3. **External Modular, Skid-Mounted, Lead-Lag Vessel System:** These are basically mini-Fukushima ISM vessels capable of being used in a merry-go-round configuration and utilizing different media in each vessel. The vessels can be either sluicable or disposable as a whole. The vessels come with no, light or heavy shields depending on the application. As one would expect, these units are capable of much higher capacities and run times due to the amount of media present and added flexibility. Again, applications include fuel pool or pond applications allowing for remediation and dose reduction during outages, D&D or pool draining. See Figure 12.

The primary reasons these media systems were developed and to be deployed are to 1) Supply dose reduction/mitigation to workers and the environment during pool/pond outages, area D&D or even draining of the entire containments, 2) Offer a portable, skid-mounted mitigation system allowing the larger plant waste treatment system to be augmented, or by-passed (outages) or even shut down in the case of plant D&D, and 3) Offer a system that requires no plant modifications or license amendments.

In order to offer an end disposition path for the small amount of secondary waste produced and full life-cycle cost, all of the systems have been designed to be vitrified into glass utilizing the Kurion GeoMelt<sup>®</sup> System, to be covered in a separate document.

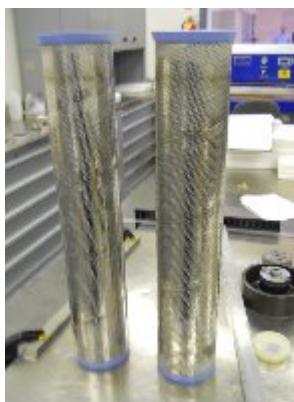


Figure 11. Submersible Media Filters (SMF) readied for inserting into Tri-Nuc housings.

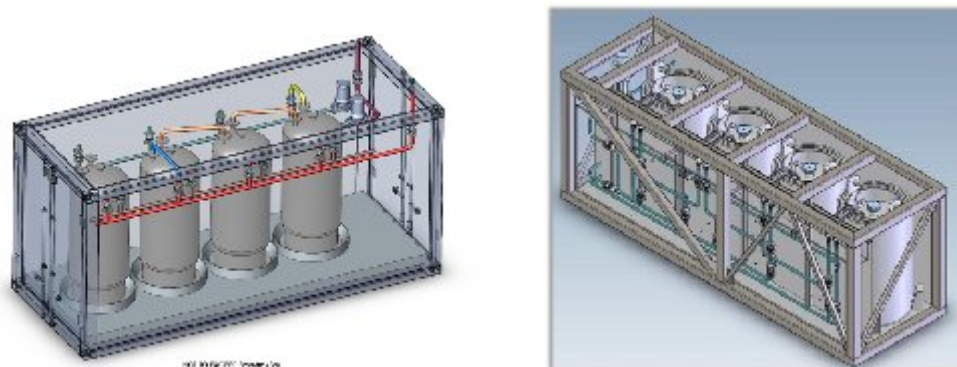


Figure 12. External, Skid-Mounted Lead-Lag Vessel System (Left). Fukushima 60 or 90 MT Skid (Right).

### Applications Utilizing ISM Mitigation Systems

**Fuel Pool Outage:** Kurion’s licensed facility in Oak Ridge received shipment of fuel pool water from Diablo Canyon Power Plant (DCPP) for the purpose of developing an ion specific media and system for the removal of C-14, Ni-63 and Cs-137. Several media were tested using this feed and a media down-select made which has been incorporated into SMF and SC units previously described. The surfactant-modified Herschelite (CH), developed for Fukushima was not especially effective for C-14 in this instance, suggesting that C-14 was not predominantly in the form of a hydrophilic species that would have affinity for the reagent. The iron impregnated Herschelite (IH) medium was effective for the elusive C-14 (

Table 8), and extremely effective (high  $K_d$ , value) for Ni-63 (Table 9) and Cs-137 (Table 10) in the as-received wastewater.

**Table 8. Fate of C-14 in DCPW wastewater**

Medium	Result (pCi/L)	A/A <sub>o</sub>	V/M (mL/g)	K <sub>d</sub> (mL/g)
NA	1.72 x 10 <sup>4</sup>	1.00		
CH-G	1.75 x 10 <sup>4</sup>	1.02	136.81	-2.23
CH-G	1.51 x 10 <sup>4</sup>	0.88	37.87	5.24
IH	1.09 x 10 <sup>4</sup>	0.63	93.47	<b>53.88</b>

**Table 9 Fate of Ni-63 in DCPW wastewater**

Medium	Result (pCi/L)	A/A <sub>o</sub>	V/M (mL/g)	K <sub>d</sub> (mL/g)
NA	8.50 x 10 <sup>5</sup>	1.00		
CH-G	2.32 X 10 <sup>5</sup>	0.27	136.81	364.77
CH-G	1.1717 x 10 <sup>5</sup>	0.14	37.87	237.71
IH	209x 10 <sup>4</sup>	0.02	93.47	<b>3716.40</b>

**Table 10. Nuclides identified by gamma spectroscopy**

Nuclide	Activity (μCi/mL)	As-received	Cs-spike	CH treat	IH treat
Mn-54	Result	2.85 x 10 <sup>-6</sup>	ND	ND	ND
	2SD	3.53 x 10 <sup>-6</sup>			
	MDA	5.79 x 10 <sup>-6</sup>	1.14 x 10 <sup>-5</sup>	4.64 x 10 <sup>-6</sup>	3.91 x 10 <sup>-6</sup>
Co-57	Result	4.51 x 10 <sup>-6</sup>	5.95 x 10 <sup>-6</sup>	ND	ND
	2SD	2.69 x 10 <sup>-6</sup>	2.53 x 10 <sup>-6</sup>		
	MDA	4.29 x 10 <sup>-6</sup>	3.91 x 10 <sup>-6</sup>	2.33 x 10 <sup>-6</sup>	2.11 x 10 <sup>-6</sup>
Co-58	Result	4.97 x 10 <sup>-4</sup>	4.98 x 10 <sup>-4</sup>	2.87 x 10 <sup>-5</sup>	1.82 x 10 <sup>-5</sup>
	2SD	2.52 x 10 <sup>-5</sup>	2.53 x 10 <sup>-5</sup>	4.79 x 10 <sup>-6</sup>	4.07 x 10 <sup>-6</sup>
	MDA	1.04 x 10 <sup>-5</sup>	9.14 x 10 <sup>-6</sup>	5.23 x 10 <sup>-6</sup>	3.71 x 10 <sup>-6</sup>
Co-60	Result	1.96 x 10 <sup>-4</sup>	2.02 x 10 <sup>-4</sup>	1.23 x 10 <sup>-5</sup>	7.37 x 10 <sup>-6</sup>
	2SD	1.27 x 10 <sup>-5</sup>	1.27 x 10 <sup>-5</sup>	2.72 x 10 <sup>-6</sup>	2.33 x 10 <sup>-6</sup>
	MDA	8.02 x 10 <sup>-6</sup>	5.79 x 10 <sup>-6</sup>	2.26 x 10 <sup>-6</sup>	3.53 x 10 <sup>-6</sup>
Cs-137	<b>Result</b>	<b>ND</b>	<b>3.01 x 10<sup>-4</sup></b>	<b>4.14 x 10<sup>-6</sup></b>	<b>ND</b>
	2SD		2.27 x 10 <sup>-5</sup>	2.38 x 10 <sup>-6</sup>	
	MDA	1.35 x 10 <sup>-5</sup>	1.36 x 10 <sup>-5</sup>	3.27 x 10 <sup>-6</sup>	6.45 x 10 <sup>-6</sup>

Aliquots of the as-received wastewater, wastewater supplemented with Cs-137, and traced wastewater aliquots after contact with select media (at V/M ~ 100 mL/g) were counted with use of gamma spectroscopy. Counting results are summarized in Table 10.

**Pond Trial Mitigation Plan:** A second scheduled application of all three ISM media systems involves deployment at a Magnox Plant in the UK in order to reduce dose and provide redundant (submersible and external) mitigation systems during D&D. This again involves the application of very specific media systems to surgically remove recalcitrant isotopes. In this case, strontium (Sr) being the primary and cesium the secondary (the opposite of Fukushima). The trials included Kurion EH-G and EH-P (granular and powder) for and TS-G and TS-P for Sr<sup>2+</sup> and Cs<sup>+</sup>.

Several trials were run on-site and on actual wastewaters for Total “others” (beta including Sr/Y) and Cs-137 including:

- Vault water at pH 10.4 and conductivity 3.0 mS: Table 11 illustrates the success of these trials for Total “others” while Table 12 summarizes the Cs-137 trials.
- Pond water at pH 7 and conductivity 3.0 mS
- Pond Water + Powdered Pond Paint/Concrete, pH 11.4, Conductivity 3.66 mS: These trials, even at the higher competition and pH, showed removal efficiencies as high as 98.7% removal of beta and 98.3% for Cs-137.
- Pond Water + Pond Sludge, pH 11.09, Conductivity 6.4 mS: Again high removal efficiencies were reported as high as 99.6% removal of beta and 99.2% for Cs-137.

**Table 11. Packed Column Total ‘Others’ Tests : Magnox Vault Water**

<b>Packed Column Total 'Others' Test</b>		
<b>Test Liquid - R2 Magnox Vault Water, pH 10.4, Conductivity 3.0 mS</b>		
<b>Sample</b>	<b>Total 'Others'</b>	<b>Removal</b>
	<b>MBq/m<sup>3</sup></b>	<b>Efficiency %</b>
R2 Magnox Vault bulk	351.02	-
Kurion EH Short Column (~6cm)	72.68	79.3
Kurion EH Long Column (~12cm)	5.38	98.5

Kurion TS-G Short Column	11.88	96.6
Kurion TS-G Long Column	0.28	99.9

**Table 12. Packed Column Cs-137 Tests : Magnox Vault Water**

<b>Packed Column Cs-137 Test</b>			
<b>Test Liquid - R2 Magnox Vault Water, pH 10.4, Conductivity 3.0 mS</b>			
<b>Sample</b>	<b>Cs-137</b>	<b>Removal</b>	
	<b>MBq/m<sup>3</sup></b>	<b>Efficiency %</b>	
R2 Magnox Vault bulk	97.29	-	
Kurion EH Short Column	1.19	98.8	
Kurion EH Long Column	1.704	98.2	
Kurion TS-G Short Column	1.614	98.3	
Kurion TS-G Long Column	0.858	99.1	MDA result used

## CONCLUSIONS

While the Three Mile Island (TMI) in 1979 and Fukushima-Daiichi (2011) crises caused not only considerable local damage, but damage to the nuclear industry as a whole, they did provide extremely valuable lessons learned and were the birth place for technology developments which have widespread and long-term benefits for that same industry as they might be deployed for dose reduction to workers and the environment in both operating and decommissioned plants. Both the development and testing of highly specific ISMs for enhanced removal of Cs and Sr have been reported herein, but also several very unique deployment systems have been described. These media have been tested both in the laboratory and on-site (Oak Ridge and Magnox) and at full-scale (Fukushima) on actual waste waters. The deployment systems (e.g., Submersible Media Filters and Submersible Columns) have been tested at full-scale in fuel pool conditions (flow rate, pressure drop, etc.) and will be tested in actual pool and pond trials in the near future.

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