# Development of Ion Specific Media to Treat Sr-Contaminated Water at Fukushima Daiichi Nuclear Power Plant – 15486

Joshua Mertz, Brett Simpson, Carly Nelson, Wesley Bratton
Kurion, Inc.

## ABSTRACT

Since April of 2011, Kurion, Inc. contracted with the Tokyo Electric Power Company (TEPCO) to remediate cooling water using Ion Specific Media targeting cesium (Cs). The effluent of the Cs-sorption systems routed into a reverse osmosis (RO) system. While the RO permeate was recirculated into the cooling loop, the RO reject was captured in carbon-steel tanks.

However, the cesium-extracted tank water at Fukushima Daiichi also has a high strontium (Sr) activity (~4 x $10^5$ Bq/mL) and needs to be reduced to lower the onsite and boundary doses. To treat this highly contaminated water, Kurion developed the Kurion Mobile Processing System (KMPS). The KMPS uses a powder batch-contact addition step in concert with a series of ion exchange vessels to decontaminate the high Sr-activity water.

Kurion tested and developed several ion specific media to treat the water. Several inorganic media were evaluated in the down-select for the system. Equilibrium batch tests, shortened contact time batch tests and column tests were performed to assess the media depending on water conditions. Two media were selected for KMPS: FAS-P (a powdered zeolite) to reduce $Ca^{2+}$ and $Sr^{2+}$ concentrations and TS-G (a synthetic titanosilicate) to polish the $Sr^{2+}$ downstream. The results of these laboratory tests and their performance in the field will be discussed.

The operation of the system has led to the continued reduction of dose at the Fukushima Daiichi nuclear power plant. This system and these media can be applied to other difficult wastewater solutions involving high levels of contaminants and salinity.

## INTRODUCTION

On March 11, 2011, the magnitude 9.0 Great East Japan earthquake, Tohoku, hit off the Fukushima coast of Japan. The earthquake and subsequent tsunami knocked out station power, the backup generators, and pumps at the facility, shutting down reactor core cooling loops. A partial meltdown of the cores at Fukushima resulted. As an emergency response, seawater was temporarily used to cool the reactors. The resulting incident at the Fukushima Daiichi Nuclear Power Plant has created an international response to help contain and clean up the contaminated buildings and cooling water that was supplied to the cores after meltdown.

The Kurion Ion Specific Media System (ISMS) was an integral part of the initial cooling loop to cool the reactor cores [1]. This cooling loop uses the basements of various process buildings at Fukushima as staging tanks, before pumping water into the reactor buildings to cool the cores; thus, the term ‘basement water’ is sometimes used to refer to the water in this process loop. The ISMS used Kurion H media to remove Cs from June 2011 until July of 2013, where the media was switched to an enhanced H media (EH). A generalized flow sheet of the Fukushima process water loops is shown in Figure 1.

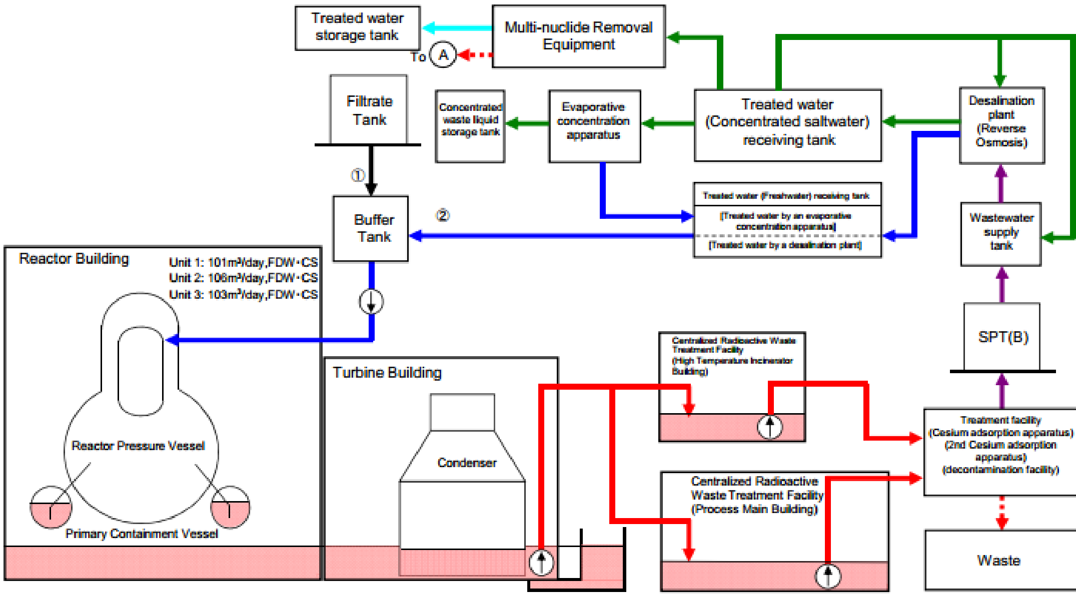


**Figure 1. The generalized flow sheet for water processing at Fukushima Daiichi Nuclear Power Plant (TEPCO [2]).**

The basement water passes through both the ISMS and the SARRY cesium removal systems and is routed into a reverse osmosis (RO) system. The permeate from the RO is recirculated back into the basements and forms the cooling loop for the cores. The rejected water from the RO is placed in carbon steel tanks (thus the term ‘tank water’ or ‘tank farm water’). Because Cs is the only species removed from the water using the Kurion ISMS, additional radionuclides (Sr, Co, etc) are sent to the Tank Farms in the RO concentrate. To address this ongoing issue, in December of 2013 Kurion was contracted to build a mobile processing system (KMPS) to treat 300 $m^3$/day of tank water to remove $^{90}$Sr and achieve a processing decontamination factor of 10 or greater. The decontamination factor (DF) is calculated by equation 1

$$DF = \frac{A_0}{A_f} \qquad \text{Equation 1.}$$

where $A_0$ is the initial activity into the system and $A_f$ is the final activity through the outlet of the system (final vessel). Because the DF is not linear with respect to percent removal and is different with respect to each column in the series, it is also advantageous to define the relationship between DF, percent removal, and percent breakthrough.

$$DF = \frac{1}{1-\%\,Removal} \qquad \text{Equation 2.}$$

$$\%\,Removal = 1 - \frac{1}{DF} \qquad \text{Equation 3.}$$

$$\%\,Breakthrough = \frac{1}{DF} \qquad \text{Equation 4.}$$

The ion specific media (ISM) for the KMPS were chosen to specifically remove $Sr^{2+}$ in the presence of $Ca^{2+}$ in a variety of conditions. The RO rejected water concentrated both the $Sr^{2+}$ and the $Ca^{2+}$ to quantities higher than expected. The media were evaluated based on distribution coefficient ($K_d$) from batch test reactions. To determine lifetime performance of the down-selected media, column tests were performed. Because of the specific nature of the testing, only selected examples are presented.

## METHODS

Traditional equilibrium contact batch tests [3] were used to qualify media for both the powder addition step used to condition the feed to the ion exchange vessels and the media in used in the vessels. These tests are conducted presuming that equilibrium between the solution and ion exchange media is reached within the specified contact time (typically 17 hours or more).

Then shortened contact batch tests (40 minutes) were performed on prospective media as part of the down-selection process for use in the KMPS powder addition step. Finally, column tests [3] were done under a number of precursor conditions to examine media performance in the ion exchange vessels under processing conditions similar to that at Fukushima.

### Equilibrium Batch Testing

Numerous media were tested for sorption performance in both parts of the KMPS. Equilibrium batch tests are a conventional method for ranking suitable ion exchange process materials. Distribution coefficients ($K_d$) results from batch test experiments are used to screen media performance before more accurate (and resource intensive) column tests are considered. Figure 2 presents the equilibrium batch test results of Kurion media. Equation 5 provides the calculation for $K_d$.

$$K_d = V/m*(C_o-C_e)/C_e\ (mL/g) \qquad \text{Equation 5.}$$

Where V is volume of treated liquid in mL, m is media mass in grams, $C_o$ is the ionic species of interest at its original concentration, $C_e$ is the ionic species of interest at its 'equilibrium' concentration (at time t, e.g. the end of the contact time). Among the assumptions implicit with the $K_d$ construct is [4]:

(1) only trace amounts of contaminants exist in the aqueous and solid phases,

(2) the relationship between the amount of contaminant in the solid and liquid phases is linear,

(3) equilibrium conditions exist,

(4) equally rapid adsorption and desorption kinetics exists,

(5) it describes contaminant partitioning between 1 sorbate (contaminant) and 1 sorbent (media), and

(6) all adsorption sites are accessible and have equal strength.

Once $K_d$ results are quantified, selections can be made regarding which media warrant more resource intensive column tests to define separation properties under process conditions.

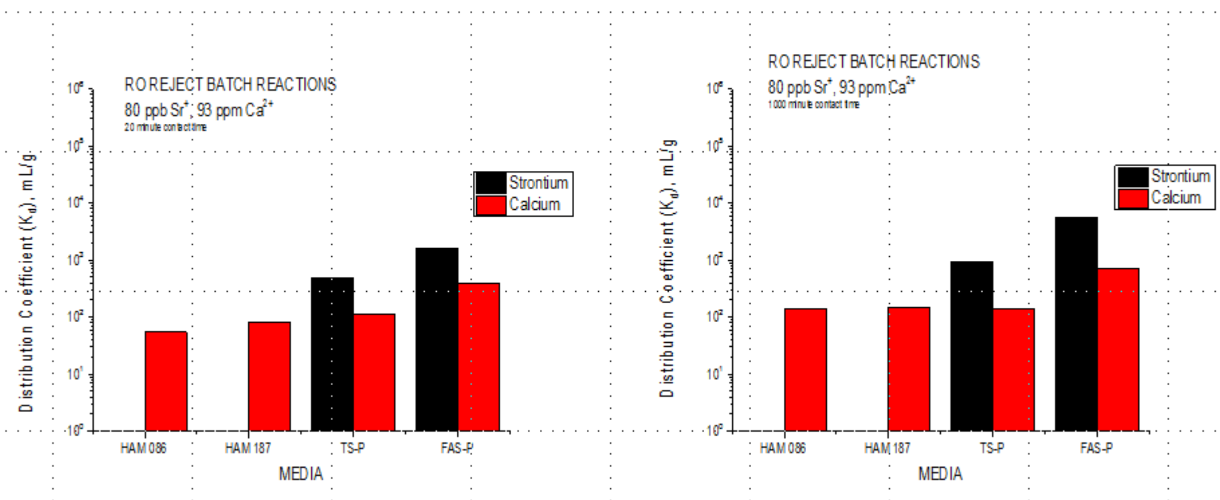


Figure 2: Equilibrium Batch Test vs Shortened Contact Time Batch Test (Kurion Media Example)

**Shortened Contact Time Batch Testing**

Because the powder addition in the feed conditioning step is part of a continuous flow process, a second type of batch test, focused on the kinetic rate of the sorption, was performed. Figure 3 presents the results of this constrained batch testing between Kurion media and other vendors' media. In this case, the media with the best sorption behavior within 40 minutes was the down select candidate. An additional benefit of the selected media (FAS-P) was that not only did it sorb Sr from the feed; it also removes competing cations such as Ca, significantly improving media performance in the vessel trains.

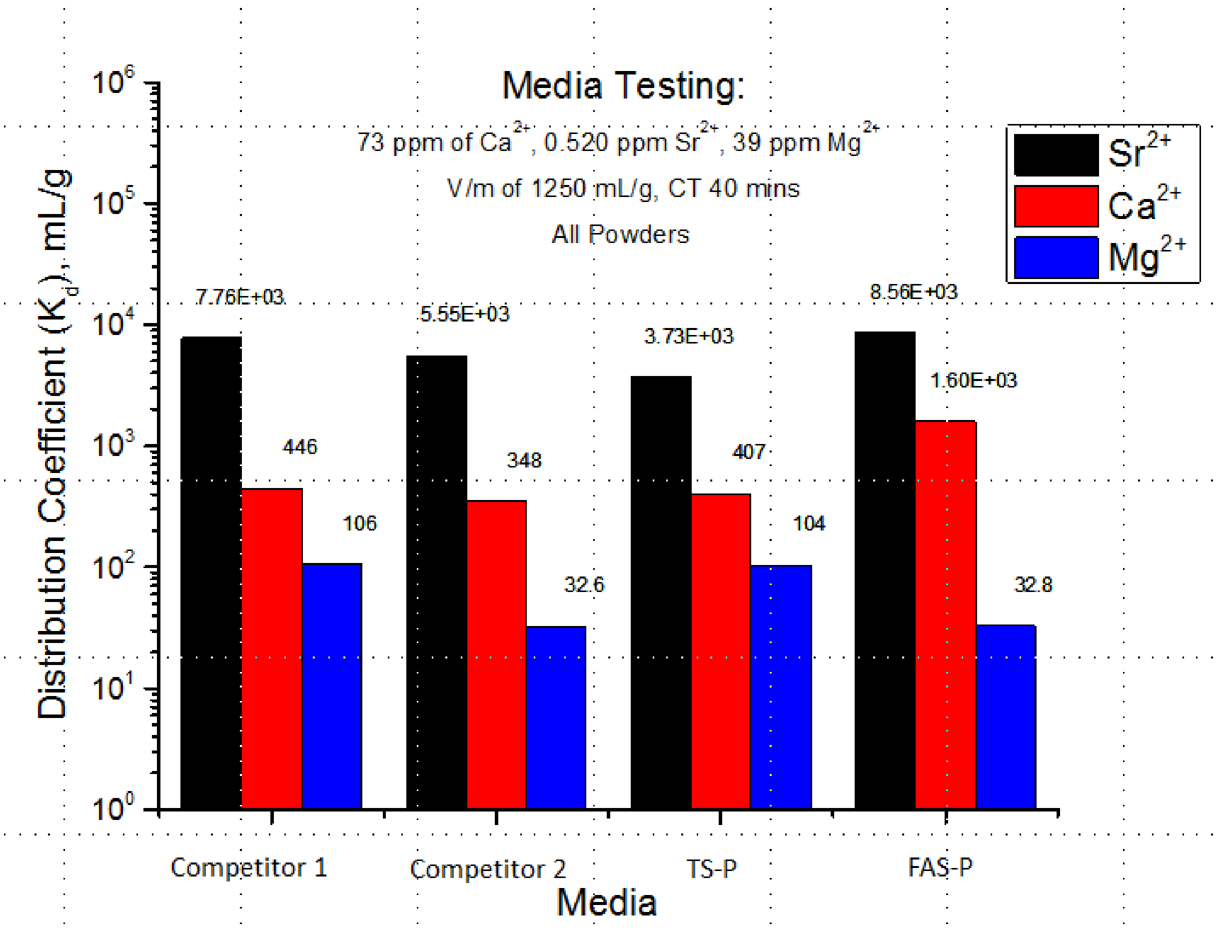


Figure 3: Shortened Contact Time Batch Test Comparison (Competition vs Kurion Media Example)

**Column Testing**

Batch tests determining equilibrium behavior or fast kinetics are only part of meeting the project goals. Column tests were performed to provide results that scaled to the field conditions at the Fukushima site and provided an analogous mass transport environment. In this case, a 5.4 minute residence time of the solution in the column was the basis for testing.

At Fukushima, this corresponds to roughly 55 gallons per minute through a vessel bed. In the Kurion column tests, the equivalent flowrate through the laboratory columns was 0.92 mL/min. The column bed volume was 5 mL. The size of the media (14 x 50 Mesh) was kept consistent and the columns were appropriately sized to minimize wall or channeling effects at both laboratory and production scale.

The process test that captures the current KMPS operation most closely is an 8 day rotation test (Figure 4), with nominal precursor compositions of 75 ppm Ca, 40 ppm Mg, and 0.5 ppm Sr. Table I shows the percent breakthrough for the system and for each column over the rotation period. At the scale of the laboratory test, new precursor solutions were prepared when columns were moved up in position or removed from the process train. This test demonstrated that an extended operational mode provided the same degree of contaminant removal over the previous 4 day rotation schedule. Operating the KMPS on a longer schedule allows TEPCO to improve vessel performance by maximizing media usage and reduces worker dose by optimizing change-out and maintenance times.

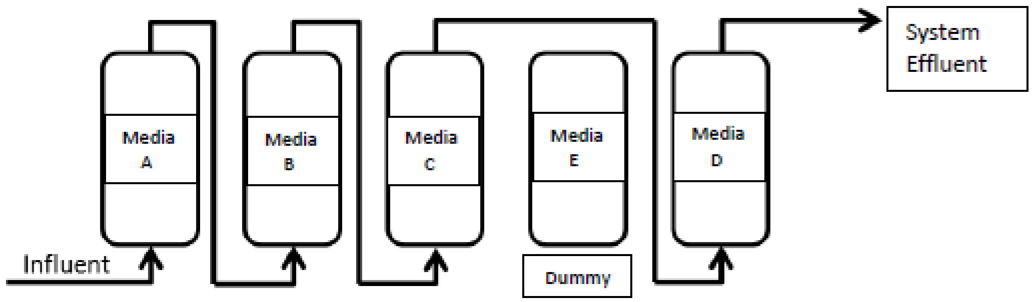


Figure 4: KMPS 8 Day Column Rotation Configuration for TS-G

TABLE I. Vessel performance in eight day rotation

| | | Column Position | | | | |
|---|---|---|---|---|---|---|
| **Rotation** | | 1 | 2 | 3 | DUMMY | 4 |
| **0** | Column Name | A | B | C | E | D |
| | Effluent Sr | 120 | ND | ND | NA | ND |
| | % Breakthrough | 25.50% | | | NA | |
| **1** | Name | B | C | E | D | F |
| | Effluent Sr | 180 | ND | ND | NA | ND |
| | % Breakthrough | 42.90% | | | NA | |
| **2** | Name | C | E | D | F | G |
| | Effluent Sr | 330 | 8.2 | ND | NA | ND |
| | % Breakthrough | 67.30% | 1.67% | | NA | |
| **3** | Name | E | D | F | G | H |
| | Effluent Sr | 210 | 8.1 | ND | NA | ND |
| | % Breakthrough | 42.90% | 1.65% | | NA | |
| **4** | Name | D | F | G | H | I |
| | Effluent Sr | 220 | 5.8 | ND | NA | ND |
| | % Breakthrough | 41.50% | 1.09% | | NA | |
| **5** | Name | F | G | H | I | J |
| | Effluent Sr | 260 | 7.7 | ND | NA | ND |
| | % Breakthrough | 50.00% | 1.48% | | NA | |

**All values listed in ppb**
**ND = Non Detectable. MDL was 0.15 ppb**
**RDL= Reportable Detectable Limit was 13 ppb**
**NA = Not Applicable. Dummy column is not online at the time of measurement.**

## DISCUSSION

Several extreme tank water environments with elevated Ca and Sr levels, as well as typical tank water compositions, and conditioned tank water (decreased Ca and Sr levels from the powder conditioning step) were also examined during testing to determine vessel longevity, operational optimization (column rotation intervals, mass transfer length), and potential dose constraints as Sr is sorbed. This series of tests narrowed the field for potential media that met the project constraints for powder conditioning and vessel processing substantially.

Although several media were observed to have very high $K_d$'s in the equilibrium batch tests, many of them did not perform their sorption quickly. Thus media with superior equilibrium performance were passed over in favor of those that were fast acting. Kurion's FAS-P, a zeolite with an affinity for Sr and Ca was found to have the best combination of species selectivity and speed.

Subsequent physical testing identified Kurion's TS-G media as having the most favorable combination of features for use in a vessel. It was found to have reasonably high selectivity for Sr, was stable under saline conditions because it did not use a binder; it does not thermally decompose or have adverse performance in a radiation field under the processing conditions. Furthermore, its sorption rate and capacity were well matched to the dose and shielding requirements set out by TEPCO in the system design.

## CONCLUSIONS

Kurion has demonstrated that two media (FAS-P and TS-G) can help to remove both $Ca^{2+}$ and $Sr^{2+}$ in the Tank water at Fukushima Daiichi. The project has been successful with a DF considerably higher than the targeted DF of 10. The system removes $Sr^{2+}$ as designed as well as the remaining $Cs^{+}$ from the $Cs^{+}$ sorption systems and other residual contaminants in the effluent. The work shows that the laboratory scale tests conducted are a good analog for the performance of the system and the media sorption in the Fukushima environment.

The success of the KMPS-1 unit at Fukushima Daiichi has helped to reduce worker dose and the dose at the site boundary. Trapping the $^{90}Sr$ on Kurion's ion exchange media and confining the spent media in secondary containers (or the KMPS vessels) reduces risk to the public by minimizing spread of contaminants. The data obtained from the laboratory and from the field allows Kurion to recommend the parameters to optimize the vessel life and improve the mass transfer zone performance. By increasing the vessel life recommendation, the number of contaminated vessels will be reduced.

## REFERENCES


1. M. S Denton, J. L. Mertz, and K. M. Morita, "Isotope Specific Remediation Media and Systems--13614," Waste Management Conference: International Collaboration and Continuous Improvement, Phoenix Convention Center, Phoenix, Arizona, US, February 24-28. Waste Management Symposia (2013)
2. Tokyo Electric Power Company website http://www.tepco.co.jp/en/press/corp-com/release/betu14_e/images/141105e0201.pdf
3. G. N. Eby, *Principles of Environmental Geochemistry*, pp. 221-223, K. Dodson, Editor, Brooks/Cole, Belmont, CA (2004)
4. United States Environmental Protection Agency website http://www.epa.gov/radiation/docs/kdreport/vol2/402-r-99-004b_ch2.pdf