Utilization and Application of Kurion Mobile Processing System in Remediation of Radioactively Contaminated Water – 16370

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ABSTRACT

Kurion® Mobile Processing Systems (KMPS) were deployed in Fukushima as first-of-a-kind at-tank isotope removal systems to remediate Sr from reverse osmosis concentrated salt water. The systems were successful in their efforts and achieved their decontamination and availability goals. The use of KMPS has been considered for other applications where a modular system is of benefit. The use of different Kurion Ion Specific Media (ISM) allows for precision removal of hazardous ions from a variety of waste streams. This paper describes a range of projects in which KMPS modularity will benefit the nuclear industry. The KMPS is a flexible system that can be deployed quickly and efficiently.

One treatment system option being considered is the utilization of a KMPS for the removal of contamination from groundwater. Similar to its use in Japan, the KMPS can be sent to remote locations for the direct treatment of ground water. In particular, there are several sites across the world where uranium contamination is a problem.

Uranium treatability testing was performed on collected groundwater samples from a radiologically contaminated site. The tests were used to help provide designs for KMPS modifications. These designs included the addition of chemical treatment module for the control of pH and other chemistry, the addition of an ultraviolet module for the destruction of biological material, among others.

The tests determined the loading capacities of uranium capture resins (UCR) and media (UCM) for this specific waste stream.

Based on uranium loading capacities of 37.3 mg/L (end of test $C/C_0 = 0.5$) and 54.6 mg/L (extrapolated to $C/C_0 = 0.98$), and the longevity of the resin (45,911 BV for $C/C_0 = 0.5$, and 80,556 BV for $C/C_0 = 0.98$) UCR-1 was selected as the media/resin to be proposed for a uranium treatment system.

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INTRODUCTION

KMPS Background:

Since April of 2011, Kurion, Inc. has contracted with the Tokyo Electric Power Company (TEPCO) treat the cooling water of Fukushima Daiichi's reactors using Ion Specific Media (ISM) [1-3] targeting radio-cesium (Cs^+). The effluent of the Cs^+-sorption systems was 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.

The accumulated RO reject water had significant ^{90}Sr contamination as well as other radionuclides. The number of filled RO Reject water tanks has been growing at a rate of one new 1,000 m^3 tank every 3-4 days. To address the growing water storage situation, reduce the dose rates from Bremsstrahlung radiation, minimize the risk from inadvertent leaks or spills, and prepare for final disposition, TEPCO contracted Kurion to develop a system, the Kurion Mobile Processing System (KMPS) (Fig. 1) to target ^{90}Sr removal in the tanks. The KMPS uses a dual treatment mode: powder batch contact with filtration followed by a series of ion-exchange vessels. In October 2014, the KMPS began processing the $^{90}Sr^{2+}$ contaminated water at the Fukushima tanks; it was joined in February 2015 by a second KMPS unit. Both KMPS units operated successfully through June 2015. The operation of these systems has led to the continued reduction of dose at the Fukushima Daiichi Nuclear Power Plant and improved radioactive waste management.

New Uses and Case Study:

A variety of configurations and wastewater treatment modes are possible with the modularity and interoperability KMPS. These systems and media can be applied to other difficult wastewater problems involving high levels of contaminants and moderate salinity. One treatment system option being developed is the utilization of a modified KMPS for the removal of uranium contamination from groundwater. This process has potential applications at to several former nuclear fuels production facilities and U.S. government cleanup sites located in the U.S.

With modifications depending on the waste stream and the conditions, the KMPS can be used to treat many difficult problems. As a modular, mobile system, the KMPS was built to nuclear standards, reducing and even eliminating the need to build a separate facility for containment. In remote locations where power and supplies may be a problem, additional modifications can be utilized, reducing the dependency on external power and utility sources.

Fig. 1. KMPS Skid 5, a 4 vessel Ion-Exchange System

For this paper, the focused case study will be on uranium removal. The development of a uranium treatment system involves proof of principal laboratory testing (treatability tests), and development of a treatment process which includes a skid mounted system design, system fabrication, testing, operational procedures, startup and ultimately, operational support. The results of the treatability tests and applications for the design and operation of a treatment system are discussed in the following sections.

URANIUM TREATABILITY TESTS

Treatability tests using uranium-contaminated water were conducted. The objectives of the uranium treatability testing were to:

- Select uranium sorption ion-exchange media to be used in the treatment system.
- Evaluate methods to prevent calcium carbonate fouling of the uranium sorption ion-exchange vessels.
- Incorporate test results into a 60% uranium treatment system design.

The treatability tests included the following:

- Groundwater pH Adjustment Test: Used to determine the minimum amount

of hydrochloric acid (HCl) to be added to the groundwater to prevent calcium scaling.
- Equilibrium Batch Tests: Used to provide a basis for the down-selection of the inorganic media and organic resins.
- Dynamic Column Treatability Tests: Used to determine the ion-exchange performance for three media/resins down-selected during the equilibrium batch tests.

The treatability tests were performed using natural groundwater samples. The uranium concentrations ranged from around 400 to 1100 µg/L. The general characteristics of the water are provided in TABLE 1.

TABLE 1.   Groundwater Chemical Characteristics

Median Metals Concentrations				
Ca^{2+} (µg/L)	Mg^{2+} (µg/L)	K^+ (µg/L)	Na^+ (µg/L)	U (µg/L)
120000	63500	1800	42000	650
Median Anions Concentrations, Total Alkalinity, TDS and TSS				
NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Total Alkalinity (mg/L)	TDS (mg/L)	TSS (mg/L)
0.26	190	420	750	2.55

pH Adjustment Test

For the KMPS, an evaluation for the need of a pH adjustment module was contemplated. pH adjustment of feed water is commonly used to avoid calcium carbonate scaling in industrial and municipal water ion-exchange systems. Additionally, depending on the end goal for the client, pH adjustment can significantly change how the waste would be treated. So the speciation of uranium had to be evaluated.

In these particular water concentrations, uranium exists in the form of uranyl carbonate (Figure 2). In order for an inorganic media to be used to remove cationic uranyl (UO_2^{2+}), a pH adjustment module would be needed to reduce the pH below 5.5 to allow an inorganic media to be used. Above a pH of 5, an anion exchange resin is needed to remove the uranium complex. However, at higher pH's (7.5 or higher) calcium carbonate scaling may become an issue.

Potential Uranium Species in Groundwater
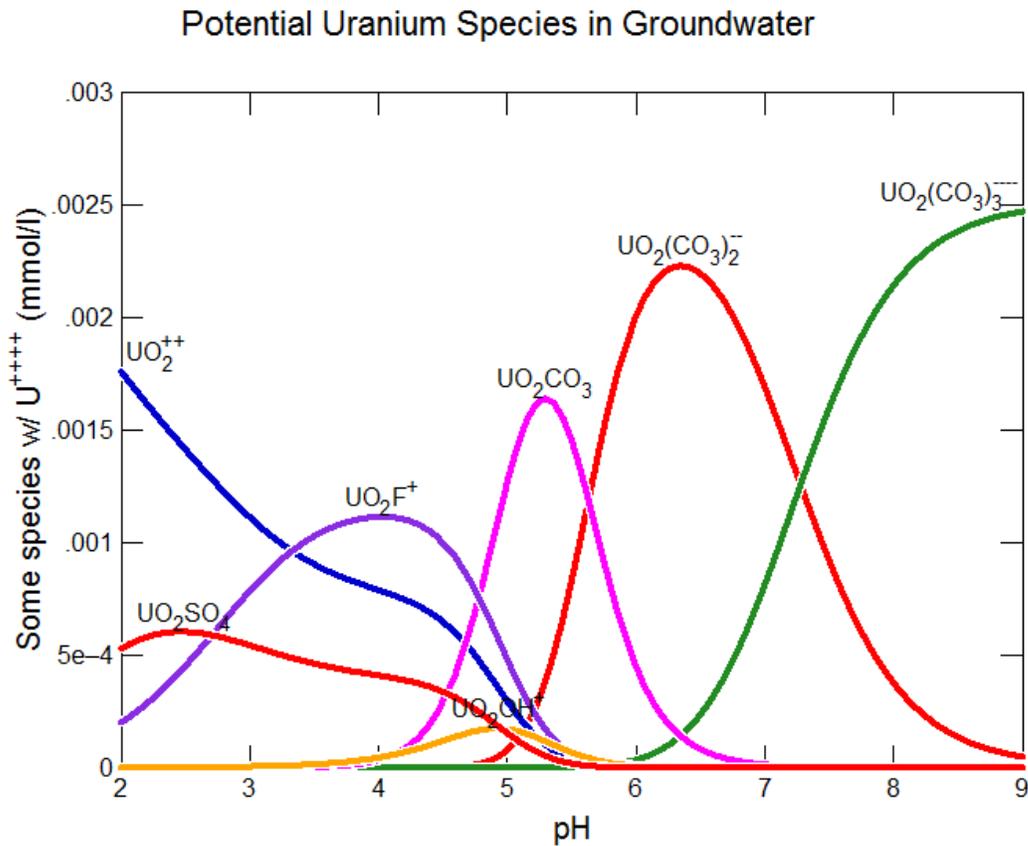
Figure 2. Uranium speciation in groundwater.

Since significant acids would be needed to lower the pH considerable for the use of inorganic media, pH adjustments below 5.5 were not considered. The remaining technical challenge would be scaling.

The pH adjustment tests were used to determine the minimal amount of HCl that yields a neutral or negative Langelier saturation index (LSI) [4], thereby avoiding calcium carbonate ($CaCO_3$) scaling. Based on the calculated pH_s, the target pH of 6.8 (LSI = 0) was selected as the operating pH for the batch and column tests. Test feed-waters were adjusted from the natural pH (around 7.2) to a pH of 6.8 using approximately 25 mL of 1 M HCl for every 18.9 L groundwater. Following experimental observation during the column tests revealing no visible signs of $CaCO_3$ scaling and no calcium, (Ca) loss through the column test system, based on analytical measurements. The operational pH range was determined to be between 6.8 and 7.0.

Equilibrium Batch Tests

The KMPS currently uses Kurion TS-G at Fukushima Daiichi. However, under these conditions, uranium removal by an inorganic media is unlikely. A selection of resins and one inorganic media were chosen to be tested in for this case study.

The objective of the Equilibrium Batch Tests was to provide a basis for the down-selection of the inorganic media and organic resins listed in Table 2. This was accomplished by performing equilibrium 3-point isotherm batch tests on the six media/resins, then evaluating the ion-exchange performance to determine the best three media/resins in terms of uranium loading capacity. The intent was to select up to three media/resins to be used in the column tests. The batch tests were performed with groundwater acidified to a pH of 6.8.

The batch tests were conducted by placing a weighed mass of media/resin (m) in a flat bottom container with a set volume of groundwater (V). Three data points were measured for each media/resin - each point in the tests representing a different volume to mass ratio (V/m). The three V/m ratios included:

- 1000 mL/g (e.g., 200 mL solution/0.2 g sample)
- 200 mL/g (e.g., 200 mL solution/1.0 g sample)
- 100 mL/g (e.g., 200 mL solution/2.0 g sample)

The mixtures were agitated on a shaker table for approximately 24 hours. All tests concluded with the analysis of water via ICP-MS for U, Ca, Mg, K, and Na.

After the batch tests were performed, the ion-exchange capacities, q, were calculated with the following equation [5]:

$$q = \frac{V}{m}(C_0 - C_e) \qquad \text{(Eq. 1)}$$

Where:
    q = ion-exchange capacity, µg/g
    C_0 = initial concentration, µg/L
    C_e = final equilibrium concentration, µg/L
    V = volume of liquid used in the batch test, L
    m = mass of ION-EXCHANGE material, g

To assess the initial concentration, C_0, a precursor sample was obtained from the same groundwater used to conduct the batch tests and was analyzed for the same analytes as the batch tests samples. The uranium concentration measured in the batch test precursor sample was 490 µg/L, which represented C_0.

Table 2. Media and resins used in testing.

Media ID	Properties
UCR-1	A strong base organic anion exchange resin in the chloride form.
UCR-2	A high efficiency, large bead, strong base organic anion exchange resin for mineral processing.
UCR-3	Modified GAC designed for metal recovery in mining applications.
UCR-4	Polystyrene – polymer structure
UCR-5	Polystyrene – polymer structure
UCM-1	A specialized sorbent with demonstrated the capability to remove uranium.

Ion-exchange material performance was determined by the maximum uranium capacity observed in the test or the maximum capacity (q_{max}) as derived from the Langmuir isotherm equation [5]:

$$q = \frac{q_{max}KC_e}{1 + KC_e}$$
(Eq. 2)

Where:

q = mass of sorbed solute per mass of adsorbent, µg/g or mg/g
C_e = effluent solute concentration, µg/L or mg/L
K = distribution coefficient, mL/g
q_{max} = mass of sorbed solute required to saturate completely a unit mass of adsorbent, µg/g or mg/g

The lower points were not used to form the Langmuir fits in all three cases, and when discarded, resulted in a Langmuir curve that fit the data very well, $R^2 > 0.9$. The R^2 value represents a fit between the calculated Langmuir isotherm curves and the batch test data points. Data analysis and development of Langmuir plots can be used to assess the relative equilibrium capacities, or q_{max}, for the three resins. The upper portion of the curve (right hand side) was not reached, indicating that tests with higher V/m ratios are required to reach the upper capacities. Although the upper capacities were not reached in the batch tests, the derived capacities can be used as a relative indicator of resin performance. The maximum uranium sorption capacities are for the top three performing media/resins are listed in TABLE 3 in order of performance. The three organic resins listed in TABLE 3 were tested in the Dynamic Column Tests.

TABLE 3.   Maximum Uranium Loading Capacities (q_{max})

Resin/Media	Maximum Uranium Sorption Capacity, q_{max} (µg/g)
UCR-2	345
UCR-1	314
UCR-5	259

Dynamic Column Tests

For the 60% design it is important to know what the utilization of the media would be. In particular the length and speed of the mass transfer zone as well as the capacity of the resin are key factors in design considerations. If the mass transfer zone is sharp, and the capacity is high, a lead-lag design would be considered. If the mass transfer zone is long, it will be more efficient to design a merry-go-round system, similar to how the KMPS currently operates. Dynamic treatability studies were performed to characterize the resins and better understand how a redesign would be needed depending on the ions removed from the solution.

The objective of the column treatability tests was to perform laboratory column tests on the three down-selected media/resins from the batch tests to determine uranium sorption properties (i.e., uranium loading capacity) to be applied in the design of the uranium ion-exchange treatment system. Dynamic column tests were performed with groundwater in the following manner:

1. UCR-1 – Tested with pH adjusted groundwater
2. UCR-2 – Tested with unaltered groundwater (i.e., no pH adjustment)
3. UCR-5 – Tested with pH adjusted groundwater

Because of the resin size and resulting increased fluid flow, UCR-2 was tested under non-acidified conditions (i.e., without pH adjustment) to provide a possible media/resin selection that could be used in the groundwater treatment system without pH adjustment.

The column test configuration is presented in Fig. 3. During the test the feed-water reservoir was filled with groundwater at regular intervals. The feed-water was acidified using HCl to adjust the pH to the target pH (6.8 – 7.0) for tests with UCR-1 and UCR-5.

 The column test configuration and flow parameters included:

- Two 5 mL bed volume (BV) columns in series with sample ports between columns – two sample ports.

- Optimum total column residence time RT: 5.5 min, scalable to a flow of 55 GPM used in the full-scale treatment system.
- Optimum Column #1 RT: 2.75 minutes.
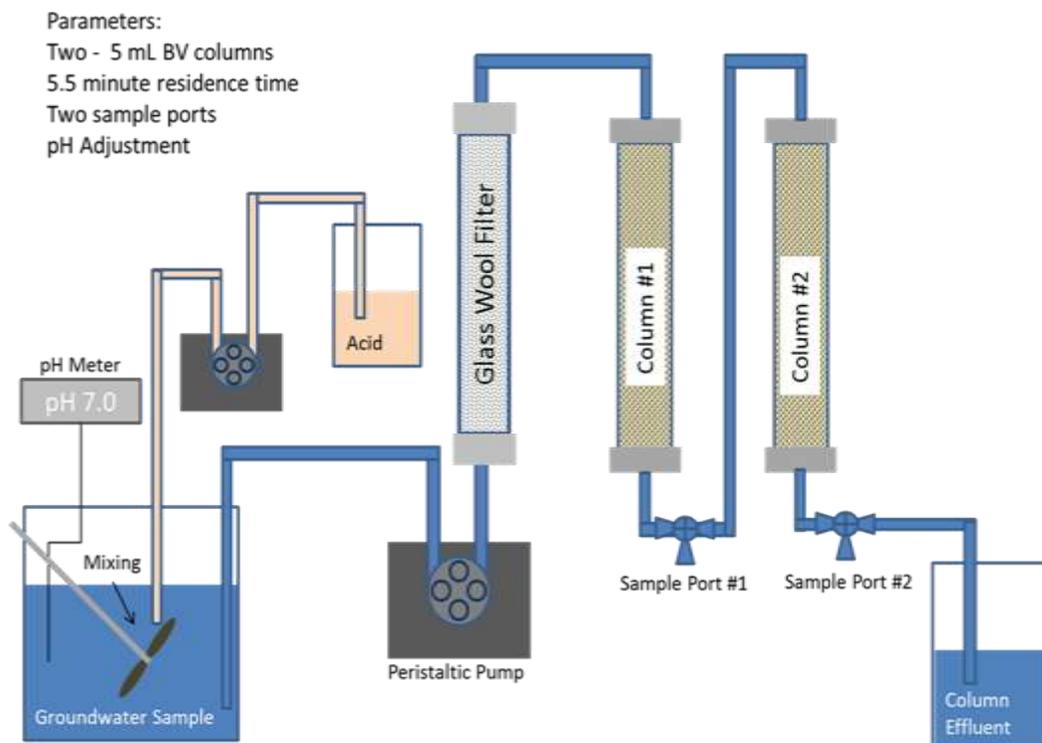
Fig. 3.   Column Treatability Test with pH Adjustment

Effluent from Sample Port #2 was collected via auto-sampler in 15 mL centrifuge tubes at regular intervals over the duration of the test. Effluent from Sample Port #1 was collected by hand at less frequent intervals than Sample Port #2. A subset of effluent samples were collected and shipped for laboratory analyses. In order to assess the representative concentration (initial concentration, C_0) of the feed-water entering the column test, precursor samples were obtained from the feed-water reservoir supplying the column test. The precursor samples were filtered, acidified, and analyzed for the same analytes as the column test samples. In order to maintain consistency between the inlet and effluent concentrations, the precursor samples were handled in the same manner as the column test samples. The uranium concentration for column test precursor samples ranged from around 400 to 900 µg/L, with an operating median of around 650 µg/L.

Effluent chemistry was monitored over the duration of the test, and was considered complete when $C/C_0 \geq 0.5$ for uranium in the Column #1 effluent, where C = effluent concentration at sample time (t_i), and C_0 = influent concentration (t_0). The measured effluent analytes included: U, Ca, K, Mg, and Na.

Column tests were completed in the following order:

- The UCR-2 column test ended with a C/C_0 equal to 0.84.
- The UCR-5 test ended with a C/C_0 equal to 0.66.
- The UCR-1 ended with a C/C_0 equal to 1.4, and the final data point used in the analysis was obtained with a C/C_0 equal to 0.5.

In all cases, the column tests were ended before reaching full breakthrough which was defined as $C/C_0 = 0.98$. In order to obtain the full column capacity through $C/C_0 = 0.98$, the breakthrough curves were extrapolated beyond the last column test data point using the Thomas modeling method [6]. In addition, the breakthrough curves and full Thomas model plots were compared. The linear form of the Thomas equation is shown in Equation 3 [5].

$$\ln\left(\frac{C_o}{C} - 1\right) = \frac{k_{th}q_{bed}M}{Q} - \frac{k_{th}C_oV}{Q} \qquad \text{(Eq. 3)}$$

Where:
    C = effluent solute concentration, mg/L
    C_0 = influent solute concentration, mg/L
    k_{th} = rate constant, L/hr-g
    q_{bed} (q_{max}) = maximum solid phase concentration of the sorbed solute, g/g (loading capacity)
    M = mass of adsorbent media, g
    V = throughput volume, L
    Q = flowrate, L/hr

As noted above, the final sample collected from UCR-1 Column resulted in a C/C_0 equal to 1.4 (i.e., > 1), which indicates the column had become saturated and was releasing uranium into the effluent before the last sample was collected. The spike in the effluent uranium concentration is likely caused by the fluctuation in the precursor (and groundwater) uranium concentrations. Prior to the collection of the final Column #1 sample, the precursor concentration increased from 530 µg/L to 920 µg/L.[1] The precursor concentration dropped to 650 µg/L in the last column test sample. Because of the premature spike in uranium concentration, the effective end of the UCR-1 column test was represented by the last sample before the uranium concentration spike where $C/C_0 = 0.5$.

The resulting uranium loading capacities for the three resins are listed in TABLE 4, and the combined breakthrough data and Thomas model fits are plotted in Fig. 4.

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[1] The ground water samples were not homogenous and were being received on a schedule. The concentration was found to have fluctuated several times during the experiment.

TABLE 4.   Column Test Uranium Loading Capacities

Resin	Test End/ Extrapolated	Loading Capacity (mg/g)	Total BVs	C/C_0
UCR-1	Test End	37.3	45,911	0.50
	Extrapolated	54.6	80,556	0.98
UCR-2	Test End	19.2	39,858	0.84
	Extrapolated	26.6	63,232	0.98
UCR-5	Test End	23.1	35,000	0.66
	Extrapolated	24.3	60,713	0.98
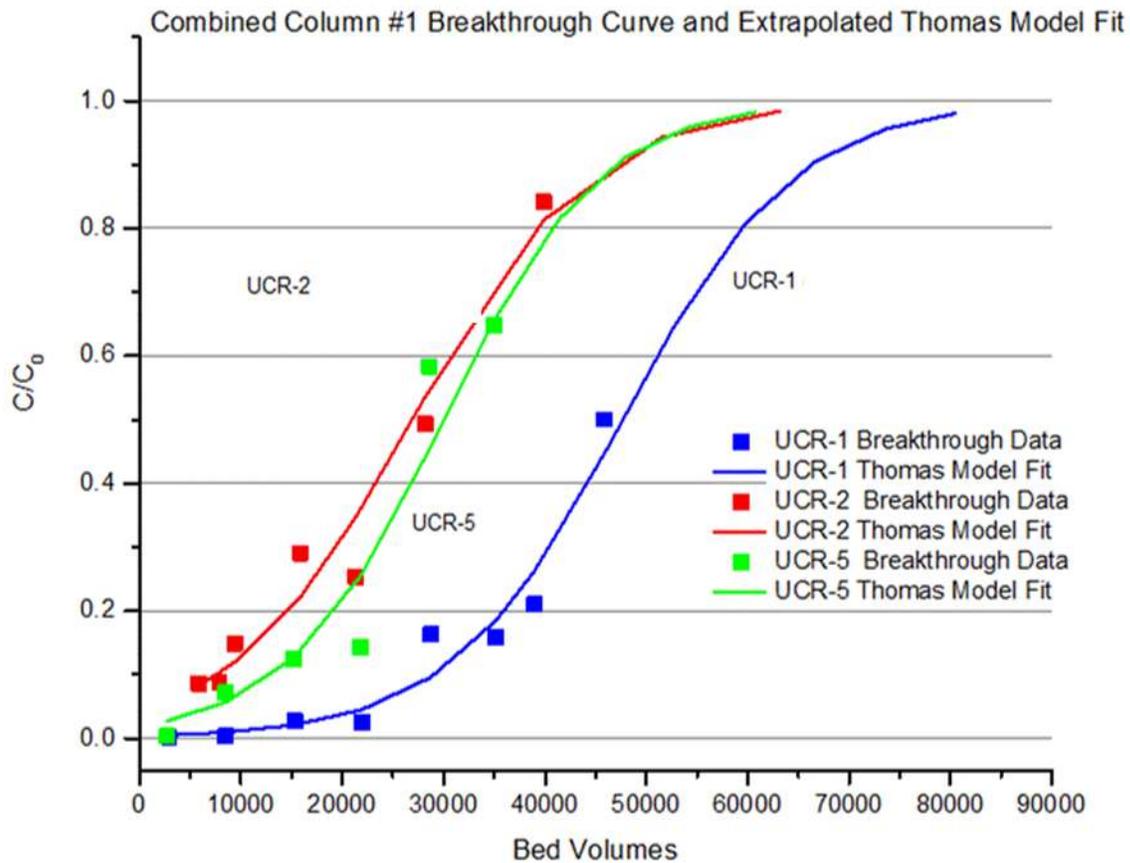
Fig. 4. Combined Breakthrough and Model Fits for UCR-1, UCR-2, and UCR-5

The column test breakthrough curves show the effluent concentration (C) divided by the feed-water concentration (initial concentration, C_0), for Column #1 over the

11

test duration. The column loading capacities were calculated based on breakthrough results, C/C_0 vs BVs from Column #1. Column tests are generally not run through completion (e.g., C/C_0 = 0.98 – 1.0) because sufficient data are gathered with a C/C_0 equal to 0.5 to extrapolate a breakthrough and calculate loading capacities, as shown in Fig. 4.

TREATABILITY SYSTEM DESIGN CONSIDERATIONS

Uranium Loading Performance

UCR-1 showed breakthrough on Column #1 after around 8,500 BVs, and continued through around 45,911 BVs with an ending C/C_0 of 0.5. UCR-1 Column #2 appeared to show no breakthrough and ended with a C/C0 of 0.004 at around 40,700 BV. Based on the Column #1 uranium loading capacities of 37.3 mg/L (end of test C/C_0 = 0.5) and 54.6 mg/L (extrapolated to C/C_0 = 0.98), and the longevity of the resin (45,911 BV for C/C_0 = 0.5, and 80,556 BV for C/C_0 = 0.98) UCR-1 was selected as the media/resin to be used in the uranium treatment system. The UCR-1 breakthrough data and Thomas model fits for Column #1 and Column #2 are plotted in Fig. 5.
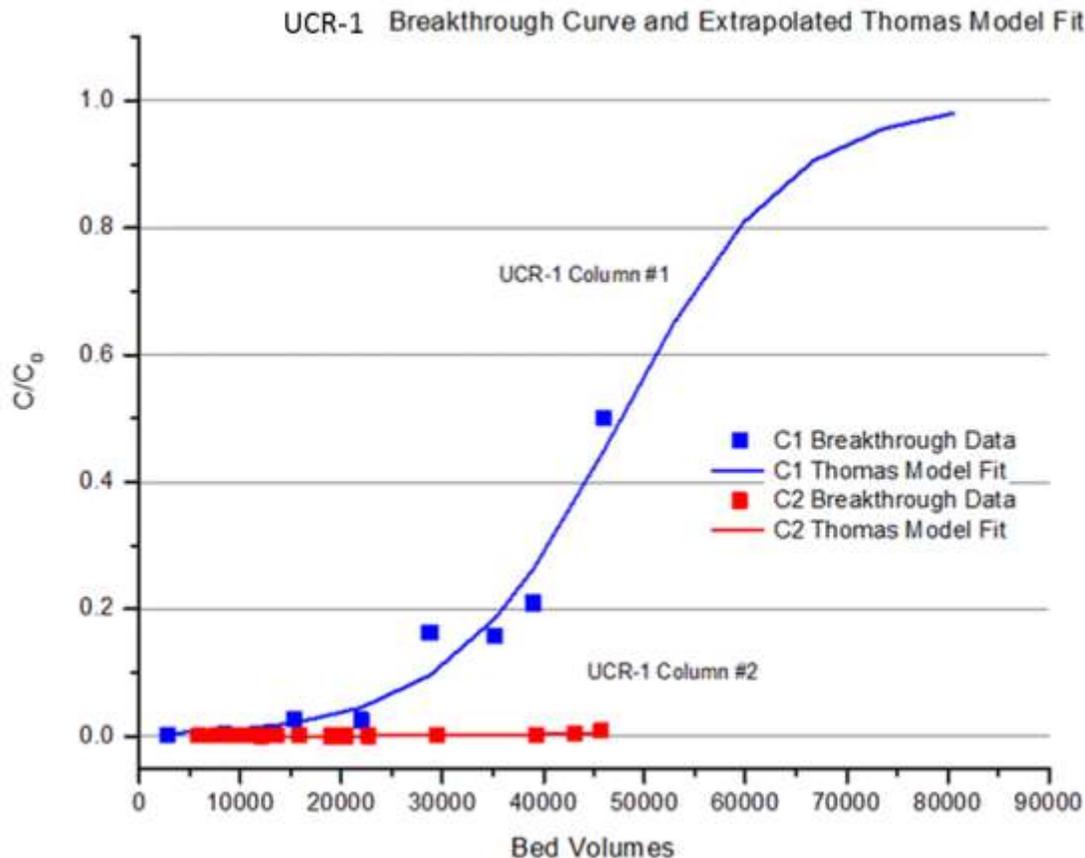
Fig. 5. UCR-1 Breakthrough and Thomas Model Fit for Column #1 and #2

Integration of the Column #1 Thomas Model curve in Fig. 5 and scaling analysis reveals that a full-scale ISM lead vessel (Column #1) filled with UCR-1 will last on the order of 278 days (73,800 BV) in a treatment system being fed groundwater with a median concentration of 650 μg/L. The lag ISM vessel (Column #2) will have reached about 4.7 % capacity at 278 days of operation.

Fluctuating Uranium Concentrations

The final sample collected from UCR-1 Column #1 resulted in a C/C_0 equal to 1.4, which indicates the column had become saturated and was releasing uranium into the effluent in the period prior to ending the test. The spike in the effluent uranium concentration is likely caused by the fluctuation in the precursor (groundwater sample) uranium concentrations.

There is a possibility for uranium to leach from the column during periods of extreme uranium concentration fluctuations, or periods of inactivity – i.e., no flow through column. These conditions will result in fluctuating equilibrium between sorbed uranium and the local water environment, which could result in desorption of uranium from the resin. Ion-exchange systems work best with consistent concentrations/feed-water conditions. Design considerations include:

- Controlling feed-water conditions upstream of the ion-exchange treatment system to prevent large fluctuations.
- Multiple ion-exchange vessels in series will prevent uranium from exiting the lag vessel if large fluctuations occur. In the UCR-1 column test, although a spike occurred in C1, the maximum C/C_0 in C2 was 0.034 (uranium = 22 μg/L) (see Fig. 5). In a three column system, the uranium effluent concentration would be well below 30 μg/L, the U.S. Environmental Protection Agency (EPA) Maximum Contaminant Level (MCL) [7].

Acidification to Prevent CaCO$_3$ Scaling

The acidification of the ion-exchange feed-water (groundwater) using HCl was discussed with regard to the prevention of $CaCO_3$ scaling. Based on the calculated pH_s given the target pH of 6.8 (LSI = 0) was selected for the pH adjustments. The column test feed-water for the UCR-1 column test was adjusted to a final pH of 7.0 based on observation of no observed $CaCO_3$ scaling, and analytical data showing no Ca loss through the column test system. In practice, the operating pH may be represented as a range instead of single value. The operating pH range will be based on the goal of maintaining the highest pH possible without increasing the scaling potential, thereby achieving the most efficient use of chemical additives. Based on the results of the LSI calculation and the column test results, the proposed operating pH range is 6.8 – 7.0. This range represents an initial operating parameter and is subject to adjustment as operating experience is gained.

CONCLUSIONS

The uranium treatability tests were conducted in two phases: (1) the Equilibrium Batch Tests to down-select a subset of media to be tested in the Dynamic Column Tests and (2) the Dynamic Column Tests with three media – UCR-1, UCR-2, and UCR-5. The results of the batch tests revealed the three top performing media resins as:

- UCR-2
- UCR-1
- UCR-5

The results of the column tests revealed that UCR-1 had the best performance of all the media/resins tested, and based on performance in the column tests, it is recommended that UCR-1 be used as the resin of choice in the uranium treatment system. The change in performance between the batch and column tests for UCR-1 (No. 2 in the batch test, and No. 1 in the column test) and UCR-2 (No. 1 in the batch test, and No. 2 in the column test) is likely a result of the difference in test conditions between the two tests. The ground water was acidified to a pH of 6.8 for the UCR-2 resin batch test, and not acidified for the column tests (natural pH of around 7.2).

Analysis of the extrapolated breakthrough curve for UCR-1 shows the lead ion-exchange vessel filled with UCR-1 will last approximately 278 days (73,800 BV), with second column being around 4.7 % utilized at the same time.

One other factor to consider as part of the treatment system operation is the relative differences in uranium concentration that will pass through the treatment system. The uranium concentrations in the as-received groundwater represents a potential range of working concentrations, and a potential range of uranium loading capacities. The following design approaches will be implemented in the uranium treatment system:

- Controlling feed-water conditions upstream of the ion-exchange treatment system to prevent large fluctuations.
- Multiple ion-exchange vessels in series will prevent uranium from exiting the lag vessel if large fluctuations occur.

Additionally, the uranium concentrations in the inlet water will decrease over time during the operation of the treatment system as uranium is removed from the local aquifer. Uranium loading capacities are related to the uranium concentration in that the loading capacities will decrease as the uranium concentrations decrease. In order to predict the amount of resin usage over the duration of the treatability system operation, a relationship between groundwater uranium concentrations and

expected loading capacities will be developed.

With modifications, the KMPS design can be used for multiple types of processes. The KMPS has worked in saline concentrations to remove Sr^{2+} from water in Fukushima, Japan. It can be also used to remove uranium from slightly acidic ground water. The selection of media can be completed within a matter of weeks, depending on the availability of simulants or actual water conditions. With the addition of a pH module, the water can be treated and if necessary, the ions can be tailored for removal by several types of media. For uranium, an adjustment into the lower pH range would allow inorganic ISM to be utilized, possibly making the way for the media itself to be stabilized by vitrification.

The use of KMPS has been considered for other applications where a modular system is of benefit. The use of different Kurion ISM allows for precision removal of hazardous ions from a variety of waste streams. The KMPS is a flexible system that can be deployed quickly and efficiently.

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