New Standards in Liquid Waste Treatment at Fukushima Dai-ichi – 13134

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ABSTRACT

The earthquake and tsunami on March 11, 2011 severely damaged the Fukushima Dai-ichi nuclear plant leading to the most severe nuclear incident since Chernobyl. Ongoing operations to cool the damaged reactors at the site have led to the generation of highly radioactive coolant water. This is currently mainly treated to remove Cs-137 and Cs-134 and passed through a reverse osmosis (RO) unit to reduce the salinity before being cycled back to the reactors. Because only the Cs isotopes are removed, the RO reject water still contains many radioactive isotopes and this has led to the accumulation of over 200,000 cubic meters (52 million gallons) of extremely contaminated water which is currently stored on site in tanks. Energy*Solutions,* in partnership with Toshiba, were contracted to develop a system to reduce 62 isotopes in this waste down to allowable levels. This was a significant technical challenge given the high background salt content of the wastewater, the variation in aqueous chemistry of the radioactive isotopes and the presence of non-active competing ions (e.g. Ca and Mg) which inhibit the removal of isotopes such as Sr-89 and Sr-90.

Extensive testing was performed to design a suitable system that could meet the required decontamination goals. These tests were performed over a 6 month period at facilities available in the nearby Fukushima Dai-ni laboratory using actual waste samples. This data was then utilized to design a Multi Radioactive Nuclides Removal System (MRRS) for Fukushima which is a modified version of Energy*Solutions'* proprietary Advanced Liquid Processing System (ALPS)'. The stored tank waste is fed into a preliminary precipitation system where iron flocculation is performed to remove a number of isotopes, including Sb-125, Ru-106, Mn-54 and Co-60. The supernatant is then fed into a second precipitation tank where the pH is adjusted and the bulk of the Mg, Ca and Sr precipitated out as carbonates and hydroxides. After passing through a cross-flow ultrafiltration membrane, the permeate then goes through a total of 14 fixed ion exchange and adsorbent columns followed by a disposable polishing column to polish the residual isotopes down to allowable levels. At the end of the system, the effluent is filtered for a final time to removal any particulates that may have been picked up from the media columns and then stored prior to analysis.

INTRODUCTION

The Fukushima Dai-ichi Nuclear Power plant is located on the Eastern coast of Japan and consists of six boiling water reactors (BWRs). A massive earthquake on March 11, 2011 severed

off-site power to the plant and triggered the automatic shutdown of the three operating reactors - Units 1, 2, and 3. The control rods in those units were successfully inserted into the reactor cores, ending the fission chain reaction. The remaining reactors - Units 4, 5, and 6 - had previously been shut down for routine maintenance purposes. When the offsite power was cut, backup diesel generators began providing electricity to pumps circulating coolant to the six reactors. As a result of the earthquake, a tsunami occurred which broke the reactors' connection to the power grid and also resulted in flooding of the rooms containing the emergency generators. Consequently those generators ceased working causing power loss to the pumps that circulate coolant water in the reactor. This caused the reactors to overheat due to the high decay heat that normally continues for a short time even after a nuclear reactor shut down. After the loss of power, sea water was pumped into the reactor to maintain cooling. This water was exposed to the reactor core as well as other damaged reactor components resulting in the generation of a large volume of radioactively-contaminated wastewater [1]. To date, this water has just been treated to remove Cs-137 and Cs-134 and passed through a Reverse Osmosis (RO) system to reduce the total dissolved solids (TDS) content. The reject from this RO treatment is now stored on site in tanks at the Dai-ichi site and requires treatment. The current Cs-134/137 removal system is incapable of removing the other nuclides present, necessitating the development of a completely separate plant to reduce the levels of up to 62 radionuclides to, or below, the allowable limit. Additional waste water is continually being generated as a result of the on-going core cooling activities.

SCOPE OF THE PROJECT

The RO reject wastes currently stored at the Dai-ichi site are variable in composition but in general have the following characteristics:

- Close to neutral pH.

- The major isotopes responsible for the bulk of the radioactivity are Sr-89 and Sr-90/Y-90, but multiple other radioisotopes are present at lower levels.

- The wastes have a high TDS content (~ 20,000 mg/l), primarily NaCl, as a result of the RO treatment process.

- Concentrations of Ca and Mg are at levels measured in hundreds of mg/l, complicating Sr-89/90 removal.

In addition to the Sr-89/90, there are multiple other radioisotopes (both fission and activation products) that have been detected in the wastes that need to be removed by the treatment system. An analysis of one of the actual wastes used in preliminary laboratory testing in late 2011 is given below in Table 1.

Isotope	Half Life	Concentration in RO Reject Bq/ml
Cs-134	2.07 years	2.50E+00
Cs-137	30.2 years	3.90E+00
Co-58	70.9 days	1.20E+00
Co-60	5.27 years	1.40E+01
Mn-54	312.1 days	4.50E+01
Ru-103	39.3 days	5.10E-01
Ru-106	1.02 years	7.80E+00
Sb-125	2.76 years	1.40E+02
Sr-89	50.52 days	1.10E+04
Sr-90	29.1 years	1.60E+04
Y-90	2.67 days	1.60E+04
Total beta	/	4.30E+04
Total alpha	/	4.60E-04

Table 1. Major Radioactive Isotopes in the Fukushima Waste Waters

Some of the shorter lived isotopes (e.g. Co-58, Ru-103) initially detect in the wastes during the preliminary trials have mostly decayed away and are currently present at much lower levels than indicated above.

LABORATORY TESTING

Prior to designing the treatment system, extensive testing was performed using actual waste samples from Fukushima Dai-ichi in order to identify suitable ion exchange media and adsorbents and to demonstrate the efficacy of the system design. During the testing, it soon because clear that pretreatment of the wastes was necessary to remove the bulk of the radioactivity and competing ions that would otherwise interfere with the performance of the ion exchange materials and adsorbents. Following the pretreatment stages, multiple ion exchange media were then used to polish the pretreated liquids to acceptable levels. The required activity levels in the final treated water were very challenging and were close to the limits of detection for many isotopes.

Pre-Treatment Stage 1

In order to reduce the activity of a large number of radionuclides, iron (III) chloride was added to the wastes to provide a source of iron for the generation of an iron (III) hydroxide floc in situ. The iron (III) chloride was added as a 40% solution, causing a drop in the pH and necessitating the addition of sodium hydroxide to raise the pH to near neutral. The floc was then filtered through a 0.45 μm filter in the laboratory (later testing used a laboratory-scale 20 nm ceramic cross-flow filtration system) and the aqueous phase passed to the second pretreatment stage. The addition of sodium hypochlorite was also found to enhance the removal of some radionuclides, especially Mn-54, presumably by generating higher oxidation state species more amenable for removal by co-precipitation with the iron hydroxide floc or adsorption on the surface of the floc particles. This treatment process is well known in the water treatment industry and forms the basis of the Enhanced Actinide Removal Plant (EARP) that has been operating successfully for over two decades at the Sellafield plant in the United Kingdom [2, 3].

This Stage 1 pretreatment was subjected to a large series of parametric experiments to evaluate the effects of iron dosing, hypochlorite dosing and final pH on isotope removal efficiencies. The final parameters selected represent a compromise between isotope removal efficiencies, chemical consumption and waste generation.

Pre-treatment Stage 2

The second pretreatment stage was designed to remove the bulk of the Ca, Mg and Sr ions that would otherwise impact any Sr-selective ion exchange media. Ion exchange media are most applicable to the removal of trace species from aqueous waste streams and the presence of hundreds of mg/l concentrations of competing ions will greatly impact media life and effectiveness leading to excessive media consumption. This latter issue is of particular importance when using Sr-selective ion exchange media since they tend to cost many times more than traditional ion exchange resins and other granular media.

Several approaches were considered to remove Ca, Mg and Sr from the wastes via the precipitation of insoluble salts. The solubilities of a number of salts of these metal ions are shown in Table 2 [4].

Metal Ion (M)	Solubility of salt (g per 100g of water)			
	MCO_3	MSO_4	$M(OH)_2$	$M_3(PO_4)_2$
Mg^{2+}	0.18	35.7	0.00069	0.00009
Ca^{2+}	0.00066	0.205	0.16	0.00012
Sr^{2+}	0.00034	0.0135	2.25	0.00001

Table 2. Solubility of Selected Metal Salts

Based upon the solubility data presented in Table 2, carbonate was selected as the anion to precipitate out the bulk of the Mg, Ca and Sr from the wastes. Sodium carbonate was added in excess of the stoichiometry of the combined Mg, Ca and Sr, and the pH raised using sodium hydroxide to ensure the presence of carbonate anions (CO_3^{2-}) rather than hydrogen carbonate (HCO_3^-) anions, thus minimizing residual alkaline earth metal concentrations. Using this approach, it was possible to reduce Mg and Ca levels from hundreds of mg/l to less than 5 mg/l and to remove in excess of 90% of the activity of Sr-89 and Sr-90. Phosphate was also considered but was eventually eliminated since excess phosphate could interfere with the removal of certain radionuclides, such as Sb-125, in the downstream adsorption system.

Analysis of the precipitate indicated that it consisted predominantly of magnesium hydroxide and calcium carbonate as opposed to solely the carbonates of these two cations. This was presumably due to the very low solubility of magnesium hydroxide in comparison to magnesium carbonate.

Ion Exchanger and Adsorbent Selection

Although the two pretreatment stages were found to remove in excess of 95% of the total radioactivity, a number of ion exchange media and adsorbents were still required to get the activity of many isotopes down to the required levels. The selection of ion exchange media was influenced by a number of factors including:

- Media availability. Although many selective ion exchange media have been described in the scientific literature, relatively few are commercially available in the quantities required for the treatment of the waste liquids stored at the Fukushima site.

- Selectivity. The RO waste streams requiring treatment contain high background levels of inactive ions such as sodium, chloride and sulfate. Suitable media must show a high selectivity of target radioisotopes over these background ions. Conventional strong acid cation exchange resins, strong base anion exchange resins and zeolites do not have sufficient selectivity to be of use. Several inorganic compounds are known to be suitable for Sr-89/90 under these conditions [5,6].

- Physical attributes. Any resin selected must have sufficient physical integrity to be used in column systems. Although polymeric ion exchange resins generally have good physical stability, many inorganic media exist as fine powders which are unsuitable for dynamic column operations. Only inorganic media available in pelletized or granular forms were considered for testing.

- Capacity. Frequent media change outs will generate excessive amounts of radioactive waste for disposal and will also cause system downtime resulting in a decreased waste throughput. Media with either a demonstrated high capacity for the isotope of interest or predicted high capacities were selected.

Media Testing

Media identified from the scientific literature and manufacturers' technical data sheets that appeared to offer some selectivity for the key isotopes in the waste solutions were extensively tested. This was achieved using simple batch techniques and small column experiments using the facilities of the nearby (but undamaged) Fukushima Dai-ni plant. A photograph showing part of the treatment column used in the preliminary testing is shown in Figure 1.

Figure 1. Column Trials used to Develop the Waste Treatment Process

Figure 1 shows part of the series of columns used to treat the wastes after the pretreatment steps had been performed. The data obtained from these preliminary trials was used to refine the selection of the media and parameters such as flow rate and pH optimized to maximize the performance of the media. Over the course of the testing, several iterations of columns were assessed before the final arrangement of media columns was selected. In the photograph, 50 ml ion exchange columns are being used for the testing and the water is passed through from left to right at a flow rate of approximately 10 bed volumes (BVs) per hour using a peristaltic pump.

SYSTEM ENGINEERING

Energy*Solutions* was responsible for conceptual design of the treatment system. This process, which would normally be done over 6 month time frame, was condensed down to a period of 6 weeks. The overall system design consists of three distinct engineering steps as discussed previously.

Stage 1 Pretreatment

The Stage 1 iron hydroxide floc pre-treatment consists of two conical-bottomed vessels for the ferric hydroxide precipitation and chemical feed tanks. These are operated in sequence with one vessel filling while the other undergoes the precipitation step followed by the solids liquid separation. Stage 1 pre-treatment operates in batch mode, but has to allow a net continuous throughput of 250 m^3/day (46 gpm) per train. This is the reason for the two large 26.25 m^3 (6,935 gallon) precipitation vessels. One vessel is filling over a period of 150 minutes while the effluent in the second vessel is being dosed, settled, decanted and finally filtered. This batch treatment cycle takes approximately 100 minutes to accomplish. After settling, the bulk of the clear supernatant is decanted and sent to the Stage 2 pretreatment while the settled precipitate is passed to the cross flow ultrafiltration (XUF) unit where it is concentrated and stored for ultimate disposal. Filtrate from the XUF unit is also passed to Stage 2.

Stage 2 Pretreatment

Stage 2 pre-treatment consists of a single precipitation vessel and the associated chemical feed tanks. Unlike Stage 1, Stage 2 pre-treatment operates in continuous mode with a throughput of 250 m^3/day (46 gpm) per train. Filtrate from Stage 1 pretreatment continuously flows into the precipitation vessel, where it is dosed with sodium carbonate and the pH raised to approximately 12 using sodium hydroxide. This vessel is vigorously agitated and has a residence time of

approximately 15 minutes. Slurry overflows out of this vessel continuously into a second ultrafiltration recirculation vessel, which feeds into the ultrafiltration recirculation loop. Concentrated slurry is intermittently discharged from this loop such that the dilute slurry inflow is matched by the filtrate and concentrated slurry outflow. Each stage 2 pre-treatment train is capable of processing a minimum of 250 m^3/day (46 gpm) in normal operation per train.

XUF Units

There are two XUF units associated with each treatment system. The first unit produces a ferric hydroxide slurry with a pH of around 8 whilst the second unit generates a calcium carbonate/magnesium hydroxide slurry with a pH of approximately 12. These wastes are discharged to separate containment vessels for storage. Both units use ceramic membranes with a nominal 20 nm pore size operated in recirculation mode.

Ion Exchange System

After the pretreatment stages, the liquid passes to the ALPS multi-media ion exchange train where it passes through a total of 14 one cubic meter ion exchange columns containing a series of media designed to remove specific isotopes of interest, followed by a three cubic meter disposable column for final polishing. The identification of the media used in the process is proprietary but includes inorganic media with high selectivities for Cs, Sr, Sb and other ions, granular activated carbons (GACs) for the removal of colloidal species and organics, chelating organic resins for the removal of polyvalent ions and transition metals, and a hybrid organic/inorganic media for final effluent polishing.

During the passage through the ion exchange system there is also a pH reduction, in order to optimize media performance, which is accomplished by controlled HCl addition. Two booster pumps are also required to maintain the required flow rates through the treatment train. A picture of the completed plant with some specific areas identified is shown in Figure 2.
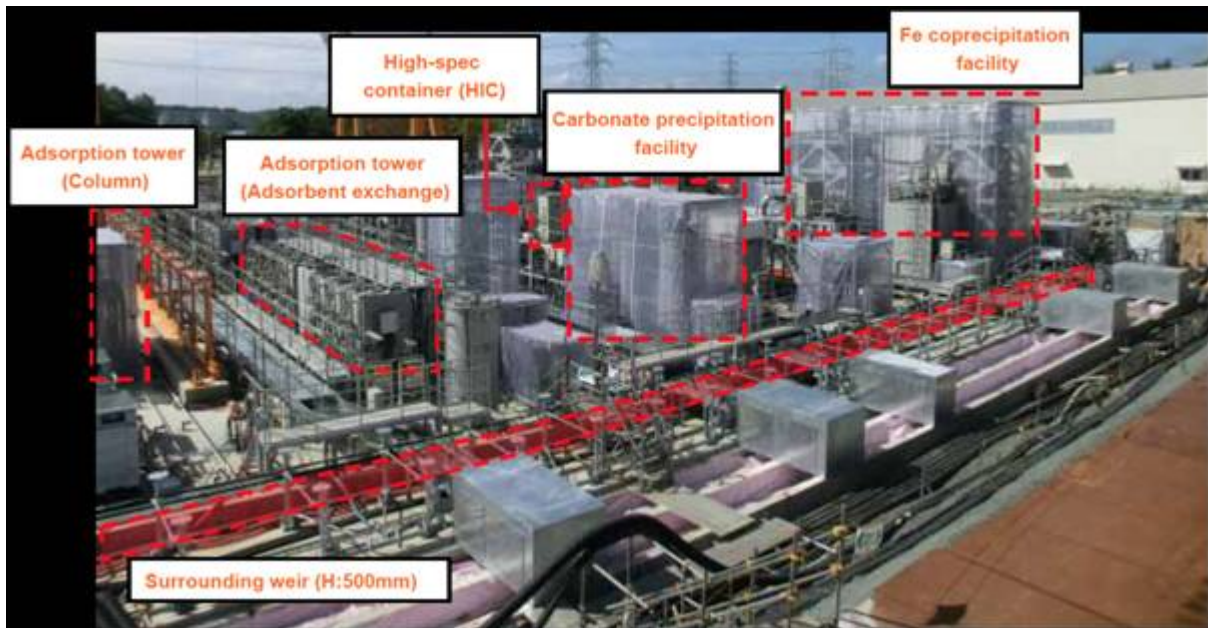
Figure 2. Photograph of the Fukushima Dai-ichi Coolant Water Treatment plant (supplied by TEPCO)

CONCLUSIONS

On a laboratory scale, stored wastes from the RO unit used to treat the cooling waters from the damaged Fukushima Dai-ichi reactors have been successfully decontaminated by a hybrid treatment process, consisting of multiple precipitation, ion exchange and adsorption steps, to reduce the activities of multiple radioactive isotopes from activities as high as 10E+04 Bq/ml down to levels below the allowable limit. These laboratory trials were then used to design and engineer a full scale system at the Fukushima Dai-ichi plant. Three separate treatment trains have been constructed at the Fukushima site with each capable of treating a flow rate of up to 250 m^3 (approximately 66,000 US gallons) of waste per day. The system is currently undergoing final testing and is expected to become operational in early 2013.

ACKNOWLEDGEMENTS

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