Development of Treatment Process for Radioactive Wastewater Generated from Molybdenum-99 Study – 16415

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ABSTRACT

Molybdenum-99 (Mo-99) high acidic waste solution was securely stored at INER for numerous years. Until 2004, the procedures of waste solution draw-out and pressure-release were accompanied, along with construction of treatment facilities. In 2009, after simulated solution and small volume Mo-99 waste solution tests, the treatment procedure was determined. Then batch-scale treatment facilities were set up. The waste solution was preserved using the instrument, along with modification of some facilities simultaneously. Ultimately all of 12 tanks of Mo-99 inorganic waste solution stored in Building 014 were finished on July, 2012. And residential 5 tanks of those solution served in Building 015B were also completed on September, 2014.

A practicable process has been developed for treating radioactive waste generated from Mo-99 study, and it can effectively remove radionuclides from a nitric acid solution. At first, after the waste was sucked from the bucket, the pH value was adjusted to about 10.0 through acid-alkali neutralization. Then, an adsorbent of natural zeolite powder was added to adsorb nuclides, and two adsorption columns filled with Cs-treat and Sr-treat adsorbents were used for removing nuclear species of Cs-137 and Sr-90. In this step, the nuclear species of Cs-137 and Sr-90 contained in the liquid waste are significantly reduced to a degree for manual operation allowable. Then, nitrate ion and mercury ion were removed through another procedure.

As a result, the operations were safer and more efficient than other conventional methods. Additionally, the hazard of accidental leakage caused by corrosion of the bucket after long period of storage can be effectively prevented and potential pollution threats are also eliminated.

INTRODUCTION

About 400 liters highly radioactive acidic liquid waste originating from Mo-99 production was stowed at INER over many years. In 2007, an examination of the waste solution showed that:

- The activity of Co-60 was decayed to a very low level,
- Significant Cs-137 and Sr-90 nuclides still exist,
- A risk of a spill exists due to the storage tank corrosion in the case of high pressure (as high as 5 kg/cm^2),
- The pH value of solution is negative.

A study on the treatment of the radioactive acidic liquid waste was conducted to solve the above problems, and allow for discharge of the liquid waste while avoiding environmental pollution. The first step of treatment is to neutralize the acidic liquid waste followed by nuclides removal (Phase I). Therefore, in the subsequent operation, the use of radiation shielding can be avoided. The above solution will then be treated to remove nitrate and mercury ions. Before discharging the liquid waste, the nitrate and mercury ions must be removed in the next step.

In Phase I of the treatment process, the bench tests were carried out by using simulated solutions, followed by real waste solutions. The results revealed that NaOH is the preferred solution to neutralize the high acidic waste solution and the pH of solution must be adjusted to 9~11 prior to the removal of nuclides. After pH adjustment and the separation of precipitate by filtration, the waste solution was ready for radionuclide removal. Two kinds of adsorbents were employed for Cs-137 removal, and a third was used for Sr-90 removal. Expensive inorganic selective ion exchange materials, Cs-Treat and Sr-Treat, can remove specific nuclides effectively. Another ion exchange material, DT-30A, is less effective than Cs-Treat for the removal of Cs-137, but much less expensive than Cs-Treat. Use of the three adsorbents in sequence significantly reduced the cost of the treatment process.

A 5-liter treatment system was set up to treat the radioactive liquid waste. This system includes a stirring reaction tank, a vacuum filter and adsorption columns. For personnel radiation protection, the reaction tank and filter were covered by lead frame with thickness of 30 mm and 5 mm respectively. Remote control and monitoring

systems were adopted based on the previous operation experience. In 2012, this treatment system has successfully treated all of the Mo-99 liquid waste, and reduced the activity of Cs-137 and Sr-90 from 2E+5 and 9E+5Bq/ml to 2 Bq/ml and less than LLD (Lower Limit of Detection) respectively.

WASTE SOLUTION PROPERTIES

Mo-99 is the mother nuclide of Tc-99m, which is often used as a nuclear medicine for organ analysis in cancer diagnosis. Several countries, such as Canada, Belgium, Netherlands, South Africa, Australia and the United States, have developed Mo-99 production technology.[1] Among them, Netherlands classified Mo-99 liquid waste into two categories, namely intermediate and low level, and then temporarily stored them in COVRA (Centrale Organisatie Voor Radioactief Afval), which is the central organization for the management of radioactive waste in the Netherlands.[2] A majority of countries have adopted this long-term storage approach for handling Mo-99 waste solutions.

The Mo-99 produced at INER in 1986 was from neutron irradiation of U-235. The process has been implemented 21 times, and each time produced 20 curies of Mo-99 products. After this process, the inorganic acidic and organic extracting solutions, which had been classified as GTCC (Greater-Than-Class-C) waste, were stored in lead-shielded tanks and heavy sand-shielded containers. The inorganic wastewater consisted of 10N nitric acid, mercury ion, and radioactive nuclides due to the nature of the production process. Chemical and radioactive analysis of the Mo-99 waste solution was performed in 1994 and the results are shown in Table I.

Table I. Chemical and radioactive analysis of Mo-99 waste solution in 1994

Solution	Co-60[a]	Cs-137[a]	Sr-90[a]	Gross α[a]	Gross β[a]
Inorganic	20.4~318[b]	2E+4~2E+5	<LLD[c]~9E+5	1E+1~2E+3	5E+4~1E+6
Organic	<LLD[c]~22	1E+2~1E	<LLD[c]~4E+	<LLD[c]	1E+3~2E

	.2	+3	3	~6E+3	+4

a. Unit：Bq/ml

b. Co-60 decayed to below LLD in 2006

c. LLD = lower limit of detection

All these Mo-99 waste solutions have been temporarily stored at INER for almost 20 years. During the storage period, the pressure of storage tanks increased to as large as 5kg/cm^2, which creates the risk of spill due to the corrosion of valves and tubes. [3] For long-term safe storage, the pressure must be released. In hope of releasing the pressure safely, analysis of the operational procedures, equipment design, radiation protection and operator's exposure dose must be conducted. During the pressure release and sampling process performed in 2005, it was noticed that the steel material of containers was corroded for those containing high concentration acids, but not for those containing washing water or organics. [4]

After long storage, the radioactivity of Co-60 nuclide in inorganic waste water was decayed significantly; however, the radioactivity of long half-life nuclides, such as Cs-137 and Sr-90, was still very high. In consideration of safe storage of wastewater, the inorganic waste solution, especially the one with high acidity, needs to be neutralized and the nuclides within it must be removed for the decommissioning of storage building and remediation of storage drums. Therefore, this article will focus on the treatment of acidic Mo-99 inorganic wastewater.

PROCESS FOR THE TREATMENT OF MO-99 INORGANIC WASTE SOLUTION

The flow diagram for the treatment Mo-99 inorganic liquid wastewater is shown in Fig. 1 Step 1 to 5 will be discussed in detail in the following paragraphs, and the Phase I is the most important part of this treatment process. Step 6 is the final step of the treatment process in which the wastewater can be completely discharged, however, this step is not the emphasis of this article. Before discharging the liquid waste, removal of nitrate and mercury is essential to comply with EPA regulations in Taiwan. In Step 1 to 4, the radioactivity of the wastewater was very high. Therefore, personnel need to be shielded by a lead frame for safe operation. After several operational trials

and adjustment of the treatment facilities, a remote control and monitoring system was incorporated to carry out the treatment process accurately. [5]

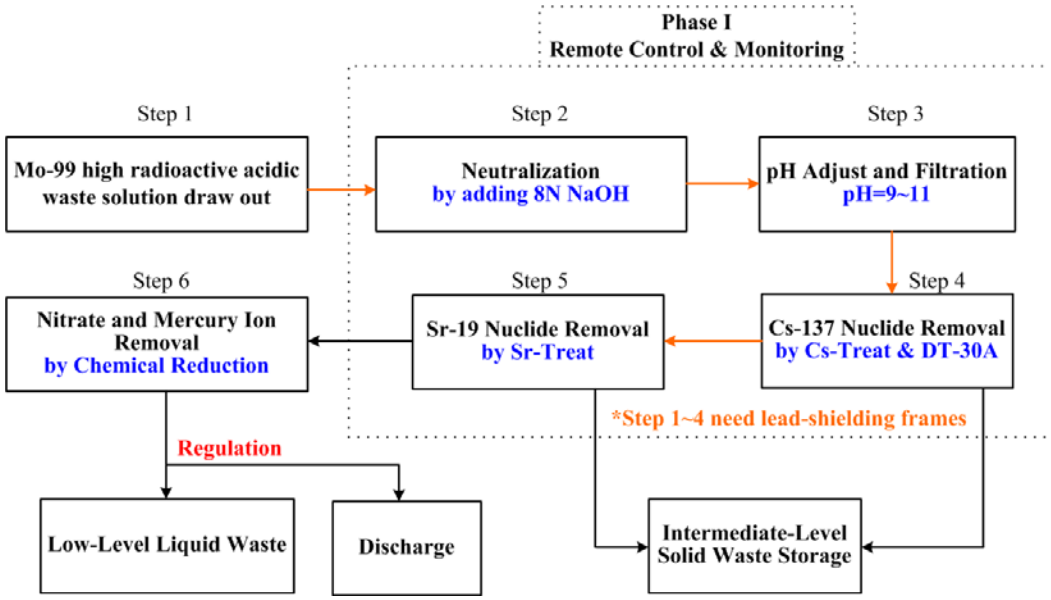


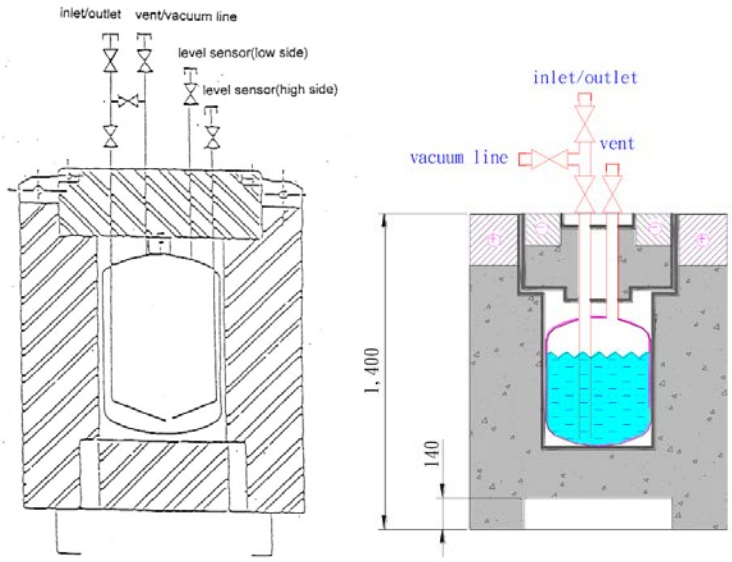
Fig. 1. Flow diagram for the treatment of Mo-99 liquid waste

Delivery from Storage Tank to Reaction Tank

Fig. 2 shows the structure of lead-shielded and heavy sand-shielded storage tanks, with a thickness of more than 16cm and 12.5cm, respectively. There were two kinds of inorganic waste water stored in the storage tanks, namely the raffinate and washing solution. Table II shows the specifications of these two kinds of storage tanks. By completing the connection between the storage tank and the reaction tank, as shown in Fig. 2 marked with “inlet/outlet”, the Mo-99 waste solution was pumped out by a diaphragm pump. The entire pipeline for connecting between the storage tank and the reaction tank was encased in a lead pipe with a thickness of 1.5 cm, which shielded the radioactivity of the waste solution.

The reaction tank was equipped with a mixer and was held in a steel framework with a load cell below. The load cell allowed the amount of waste solution entering the reaction tank to be accurately controlled. There was one level alarm detector attached at the top of the reaction tank to prevent overflow of the waste solution. The volume of the reaction tank is about 15 liters and three stainless baffles were attached inside the reaction tank, with equal distance between each other. A valve for the discharge of waste solution was set at the bottom of the reaction tank and was controlled by high-pressure air. The mixer in the reaction tank was a flat bade turbine made of stainless steel, same as the reaction tank. The mixer has a maximum rotation speed

of 300 rpm. A thermometer, pH meter and liquid level sensor were also installed in the reaction tank to monitor the temperature, pH, and level of waste solution.



(a) (b)

Fig. 2. Schematics of (a) lead-shielded and (b)heavy sand-shielded storage tanks

Table II. Specifications of storage tanks for Mo-99 waste solution

Waste solution	Capacity (liter)	Storage volume (liter)	Shielding & Thickness(cm)	Dimension (cm)	Dose rate μSv/h/ml
Raffinate	18	11	Lead, 16t	62Φ×120	15
Washing	50	33	Concrete, 12.5t	94Φ×120	10

Neutralization and Filtration

Once acid waste solution entered the reaction tank, 8 N sodium hydroxide solution was added into the tank to increase the pH of waste solution to around 9 to 11. The pH of solution was controlled carefully in order to match with the operation pH of the adsorbents. Since the acidic waste solution was 10N HNO_3, significant fume was generated by this process. To prevent overheating during the neutralization process, a water cooling system was employed to keep the temperature of waste solution in the range of 30~35℃.

If too much NaOH solution is added, significant yellow-brown foam will be formed on the surface of the mixture, making it difficult to determine the volume of either NaOH or waste solution and the measurement of solution pH will be meaningless. In this case, it would take several hours to mix the solution until the foam disappeared. When the pH of solution was below 1.2, there would be no precipitate formed. However, when the value of pH exceeded 2, lots of fine precipitates were formed in the solution. If the pH value was controlled perfectly in the range of 9~11, the color of the waste solution would be green or brown, depending on the source of Mo-99 waste solution. Fig. 3(a) shows the reaction condition in the reaction tank. When the pH was too low, the waste solution would become transparent with less precipitate.

After mixing completely, the releasing valve at the bottom of the tank can be opened by using compressed air to allow the waste solution to go into the negative-pressure filter. The filter was equipped with a filter paper that has diameter of 40cm, and pore size of approximately 3μm. To prevent the spill of high radioactive waste solution, the filtration process was carried out under negative pressure of higher than 30in-Hg (i.e.76 cm-Hg), so that the waste solution could be sucked into the 18 liter lead storage tank. Fig. 3(b) shows the precipitate in the negative-pressure filter and the radioactivity was about 7.15μSv/hr. The most common problem in the filtration process is the blocking of pipe by coarse DT-30A particles. However, if DT-30A were grinded too fine, the filtered waste solution will contain those fine particulates with size smaller than 3μm. Therefore, the adsorption column would be blocked during the subsequent nuclides adsorption process.

(a) (b)

Fig. 3. (a)Neutralization of waste solution and (b) the filtered cake

Nuclide Adsorption

After pH adjustment and the separation of precipitate by filtration, the waste solution was ready for radionuclides removal. Several nuclide removal methods from the literature were assessed and the method of using inorganic adsorbents was selected for this purpose. [6-11] During nuclide adsorption, the waste solution was pumped from the lead storage tank to the fixed adsorption columns for Cs-137 and Sr-90 removal. The inorganic selective ion adsorbents, Cs-Treat and Sr-Treat, were employed for Cs-137 and Sr-90 removal, respectively. They were both commercial products purchased from Fortum Nuclear Services Ltd, Finland. The operating environment and characteristics of these adsorbents are shown in Table III.

Table III. Properties of Cs-Treat and Sr-Treat

Item	Cs-Treat	Sr-Treat
Operating pH	1~13	>10

Selectivity	$K_{Cs/Na}$=1,500,000	-
Total Ion Exchange Capacity	0.3~0.4 meq/g	4.5~5.5 meq/g
Color	Dark Brown/Black	White

The pH of waste solution must be adjusted in advance to meet the working pH of adsorbents. The selectivity of Cs-Treat was very high. Therefore, the adsorption efficiency of Cs-137 in the high-salt environment was very good. However, due to the high cost of Cs-Treat, an alternative, DT-30A, was selected for the preliminary treatment of waste solution. About 400 grams of DT-30A were added in the reaction tank, which held 12litersof waste solution, right after neutralization and filtration step. DT-30A was mixed thoroughly with waste solution and then filtrated by the same negative-pressure filter.

After three to four batch operations of DT-30A mentioned above, the radioactivity of the Mo-99 wastewater was reduced to 25μSv/hr per 100ml of solution. Afterward, the waste solution was pumped into the adsorption column filled with Cs-Treat and Sr-Treat adsorbents to further lower the radioactivity of wastewater contributing from Cs-137 and Sr-90 nuclides. When the radioactivity of Cs-137 adsorption column reached nearly 2000μSv/hr, the adsorption process was stopped and the column was refilled with fresh Cs-Treat adsorbent. The operators were shielded during the entire replacement procedure to comply with the radiation protection regulations. The spent Cs-Treat adsorbent was then stored in a reformed lead-shielded tank.

Remote Operation

Remote control and monitoring systems were adopted by learning from previous operating experience. The remote control system, including neutralization stirring unit and pump control for reagent feeding, was customized for the process. The monitoring system mainly improved the accuracy of neutralization process and prevented the overflow of waste solution. The monitoring system comprised radiation detectors and CCD cameras to overlook the progress of neutralization and adsorption. The remote control and monitoring systems were very useful for reducing personnel's exposure to radioactivity.

Fig. 4. Monitoring system of waste solution treatment facilities

Off-Gas System

Since the Mo-99 inorganic waste solutions contained high concentrations of nitric acid, the system needed to be ventilated and equipped with HEPA (High-Efficiency Particulate Air) filters to capture radioactive nuclides during treatment. The lead-shielded frame was connected to a scrubber through a two-inch outlet nozzle, and then to a movable HEPA filter as well as the building's HEPA filters for off-gas preliminary and final treatment. The scrubber was 180 cm in height, 30 cm in diameter and has a gas flow rate of 280 L/min. Weak NaOH solution was cycled in the scrubber for washing nitric acid gas, and used NaOH solution was employed as the base for neutralization. The scrubbed gas was then pumped into HEPAs with filter efficiency higher than 99.97% to capture nuclides.

Facilities

A 5-liter per batch system was set up for the treatment of Mo-99 radioactive waste solution. This system includes a stirring reaction tank, a vacuum filter, adsorption columns and off-gas HEPA etc. For personnel radiation protection, the reaction tank, filter and adsorption columns were covered by lead frame with the thickness of 30 mm, 5 mm and 3mm, respectively. All facilities were tested by pure water and simulation solution before real sample was treated. Fig.5. shows the panoramic view of whole treatment facilities at INER. The tank named WC-103contained that waste solution that was the first treated due to its lowest radioactivity and acidity. The

treatment results of WC-103 are shown in Table IV. The COD in the waste solution was reduced by using active charcoal powder in batch operation to the concentration of 76 mg/L. However, the remaining substance, such as nitrate, mercury, TOC and ABS, needs to be treated by other methods.

In 2012, this treatment system has successfully treated all of the Mo-99 liquid waste, and reduced the activity of Cs-137 and Sr-90 from 2E+5 and 9E+5Bq/ml to 2Bq/ml and less than LLD respectively.

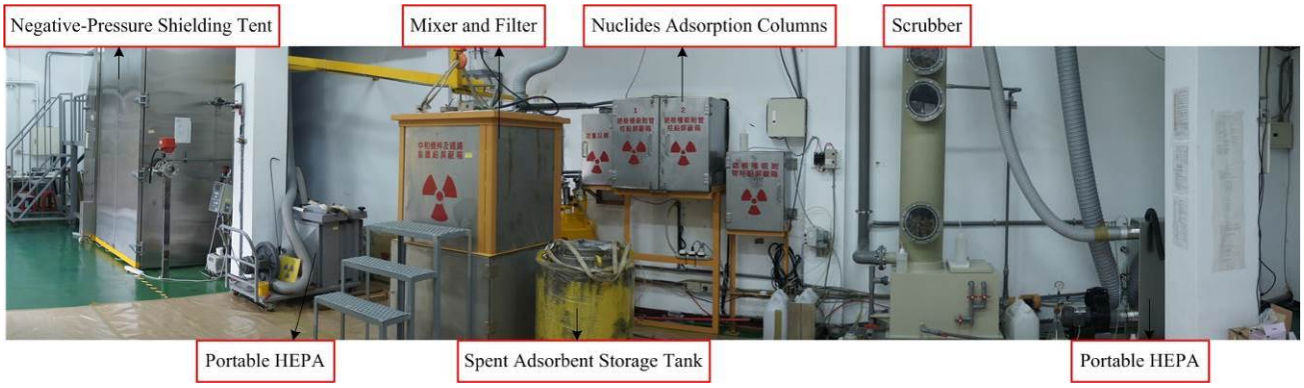


Fig. 5. Treatment facilities for Mo-99 waste solution at INER

Table IV. Treatment results for WC-103 liquid waste

Radioactivity Analysis	Before Treatment	After Treatment
Gross α	<1.07E-2 Bq/ml	<1.07E-2 Bq/ml
Gross β	2.49E+1 Bq/ml	3.8 Bq/ml
Radioactivity of Cs-137	3.99 Bq/ml	0.287 Bq/ml
Radioactivity of Sr-90	6.39E+2 Bq/ml	<1.64E-2 Bq/ml
Concentration(after radionuclides removal)		Regulation of EPA
Nitrate(NO_3^-)	93400 mg/L	50 mg/L
Mercury(Hg)	646 mg/L	0.005 mg/L
COD	536 mg/L	200 mg/L

TOC	284.2 mg/L	100 mg/L
ABS	4686 mg/L	10 mg/L

LESSON LEARNED

Fine precipitate particles still existed in filtered waste solution, and those particles would block the adsorption column, therefore, the Cs-137 adsorption treatment can't be operated effectively. High acidity would also lower the efficiency of Cs-Treat and made the adsorbent to dissolve. By using self-developed treatment process and equipment, the treatment costs were significantly reduced, particularly when DT-30A batch adsorption was adopted prior to Cs-Treat column operation. Most of the radioactivity of Mo-99 waste solution was removed, however, the contaminants such as nitrate, mercury, as well as α nuclide in solution still need to be treated, which could be removed by chemical reaction and membrane filtration. In such operation, lead shielding is not required any more.

CONCLUSIONS

The acidic Mo-99 radioactive waste liquid was treated by a compacted process, and facilities which were simple, feasible and easy to operate. After the neutralization, filtration and nuclides adsorption processes, the treated Mo-99 inorganic waste solution met the criteria for discharge. The Cs-137 and Sr-90 nuclide adsorption columns were in parallel, which shortened the treatment time. The expensive Cs-Treat and cheap DT-30A adsorbents were used in turn to lower the operational cost. Treatment capacity is limited to about 5 liters, which is safe for operators from a radiation protection perspective. The process generated a small amount of filter cake and spent adsorbents, and they were categorized as low-level waste. The solid waste was stored in the reformed, empty shielded tanks which were originally used to store the Mo-99 solutions.

REFERENCES

1. IAEA, Management of radioactive waste from ^{99}Mo production, IAEA-TECDOC-1051, November, 1998.

2. Rozé.M. van Kleef, COVRA NV, Radioactive waste treatment from Mo-99 production facility in the Netherlands, WM'01 Conference, February 25-March 1, 2001, Tucson, USA.
3. Pen Ben-Li, Ma Yung-Kuang, Chiu Chin-Lee, Tsao Kuo-Hoa, Safety analysis of pressure releasing and sampling of the shielded Mo-99 liquid waste drums at INER, INER-OM-0711R, 2005, Taiwan (In Chinese).
4. Pen Ben-Li, Tsao Kuo-Hao, Chu Yeong-Ton, The pressure discharge and sampling of 014B's Mo-99 drums, INER-SOP-0050, 2006, Taiwan (In Chinese).
5. Pen Ben-Li, Tsao Kuo-Hao, Shih-Yi Lee, Hsiao Hsien-Ming, Chemical equipment design and performance test for Mo-99 waste treatment, INER-7489R, 2010, Taiwan (In Chinese).
6. L.I. Rudenko and V.E. Khan; "Membrane methods for treating liquid radioactive wastes from the shelter to remove transuranic elements" Radiochemistry, Vol.47, No.1, pp.89-92, Russia, 2005.
7. V.N.Kosyakov, I. E. Veleshko,N. G. Yakovlev,V. N. Chernetskii, and N. E. Nifant'ev, Water-soluble chitosans as flocculants for deactivation of liquid radioactive, Radiochemistry, Vol.45, No.4, pp.403-407, Russia, 2003.
8. J. Kamenik and F Sebesta, Comparison of some commercial and laboratory prepared cesium ion-exchangers, Czech Technical University in Prague, Department of Nuclear Chemistry, Czechoslovak Journal of Physics, Vol. 53, Supplement 1, pp. A571-A576, Czech Republic, 2003.
9. Dmitry V Marinina and Garrett N Brownb, Studies of sorbent/ion-exchange materials for the removal of radioactive strontium from liquid radioactive waste and high hardness ground waters, Waste Management, Vol. 20, Issue 7, pp. 545–553, USA, 2000.
10. Paul Sylvester and Abraham Clearfield, The removal of strontium and cesium from simulated Hanford groundwater using inorganic ion exchange materials, Solvent Extraction and Ion Exchange, Vol. 16, Issue 6, pp. 1527 – 1539, USA, 1998.
11. E. Tusa, Use of nuclide removal system (NURES) for clean-up of different waste liquids, Fortum Engineering Ltd, Finland.

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