Pretreatment Process for Performance Improvement of SIES at Kori Unit 2 in Korea

Sang-Jin Lee, Ho-Yeon Yang, Sang-Woon Shin and Myung-Jae Song
P.O.Box 149, Yuseong, Daejeon, Korea
Nuclear Environment Technology Institute,
Korea Hydro & Nuclear Power Co., Ltd.
*sgjrhee@khnp.co.kr

SUMMARY

Pretreatment process consisted of submerged hollow-fiber microfiltration(HMF) membrane and spiral-wound nanofiltration(SNF) membrane has been develcped by NETEC, KHNP for the purpose of improving the impurities of liquid radioactive waste before entering Selective Ion Exchange System(SIES). The lab-scale combined system was installed at Kori NPP #2 nuclear power plant and demonstration tests using actual liquid radioactive waste were carried out to verify the performance of the combined system. The submerged HMF membrane was adopted for removal of suspended solid in liquid radioactive waste and the SNF membrane was used for removal of particulate radioisotope such as, Ag-110m and oily waste because ion exchange resin can not remove particulate radioisotopes. The liquid waste in Waste Holdup Tank (WHT) was processed with HMF and SNF membrane, and SIES. The initial SS concentration and total activity of actual waste were 38,000ppb and 1.534×10^{-3} μCi/cc, respectively. The SS concentration and total activity of permeate were 30ppb and lower than LLD(Lower Limit of Detection), respectively.

INTRODUCTION

Liquid radioactive waste generated from the nuclear power plant is divided into the equipment drain waste, floor drain waste, chemical waste, and laundry waste, etc. There are 16 PWRs either operating or under construction and are 4 PHWRs operating in Korea. Evaporation system for liquid radioactive waste treatment has been used 12 PWR nuclear power plants. The new liquid waste processing system which combines centrifuge with ion exchanger has been introduced 4 PWR NPP(Yonggwang Unit 5&6, Ulchin Unit 5&6). The evaporator has achieved satisfactory decontamination and volume reduction capability. However, chemicals and impurities contained in liquid radioactive waste cause problems such as corrosion, scaling, and foaming during evaporation. These problems may markedly decrease the ability of decontamination and reduce the evaporator lifetime and increase maintenance expense higher.

To overcome these difficulties, Selective Ion Exchange System (SIES) has been introduced at Kori Unit 2 as a substitute of waste evaporator in 1999. The SIES was immediately fouled by oil& grease, high total dissolved solids (TDS) concentrations and boric acid contained in the liquid radwaste streams. The presence of high organics and contaminations in the waste stream resulted in high radionuclide concentrations in the product water making it rarely acceptable for release.

Since the SIES requires the pretreatment of impurities such as suspended solid (SS), organics and oily waste usually contained in the liquid radioactive waste, it has been studied in respect to minimization of secondary waste, cost effectiveness and ease of maintenance.

As a part of the project above, the lab scale unit processes such as, the microfiltration (MF) membrane, nanofiltration (NF) membrane, and Selective Ion Exchange System (SIES), has been installed at Kori Unit 2 and the demonstration tests of the unit process were carried out with actual waste in the plant to verify the effects of SS removal for MF and SS and particulate nuclide removal such as Ag-110m for NF, and ionic radionuclide removal for SIES, respectively. A series of experiments for determining the optimum arrangement of unit process was also performed. Based on the results of optimum arrangement experiments, long-term test of the combined process was carried out. In the present paper, the result of demonstration experiment using lab scale combined process with actual waste at Kori Unit 2 is discussed.

SYSTEM DESCRIPTION

The pretreatment module consists of the submerged hollow fiber type MF membrane and the spiral wound type NF membrane processes. MF membrane used in the experiment is a SuperMAK, which is manufactured by ENE Co. in Korea. The purpose of the MF membranes is to remove coarse suspended particulate contained in the waste stream before feeding the NF membrane process, and NF membrane is a NF90-2540 which is manufactured by Film Tech. Co in USA and used to remove fine suspended solid and oily waste in the permeate of MF membrane process. Since Pretreatment module is to allow most of the chemical contaminants to pass; much of the dissolved activity, i.e. cesium, iodine, and a portion of cobalt, remains in the process stream after this stage. Decontamination Factors (DF) is inversely proportional to the solubility of a given impurity. This is seen in the relatively low DFs observed for the highly soluble cesium.

The Kori Unit 2 SIES system, the Chem-Nuclear Advanced Liquid Processing System, consists of skid mounted vessels including two (2) deep bed Granular Activated Carbon(GAC) vessels (52 inch bed depth and 42 inch diameter), and four (4) ion exchange vessels (each 52 inch bed depth and 36 inch diameter) and all interconnecting piping.

GAC vessel provides filtration and removal of Total Organic Carbon (TOC) and one of ion exchange vessels is contained ion specific inorganic oxide based medium for removal of cesium with low specialty for sodium and lithium, because cesium in the waste was not perfectly rejected from NF membrane unit. Another vessel is contained a specialty grade cation resin utilized for hardness removal. The carbon and resin vessels are 36"EQUA*FLEX type ASME code pressure vessels and contain 40ft3 and 30ft3 of media, respectively.

First, liquid radwaste water passes through the pre-treatment module, which removes all impurities and particulate radionuclide (Ag-110m) to maintain the optimal performance of the SIES. The passed water is routed to the SIES modules for the removal of soluble species and then it is transferred to the monitor tank for sampling and analysis to determine if it should be released to the environment or recycled to the feed tank for the further processing.

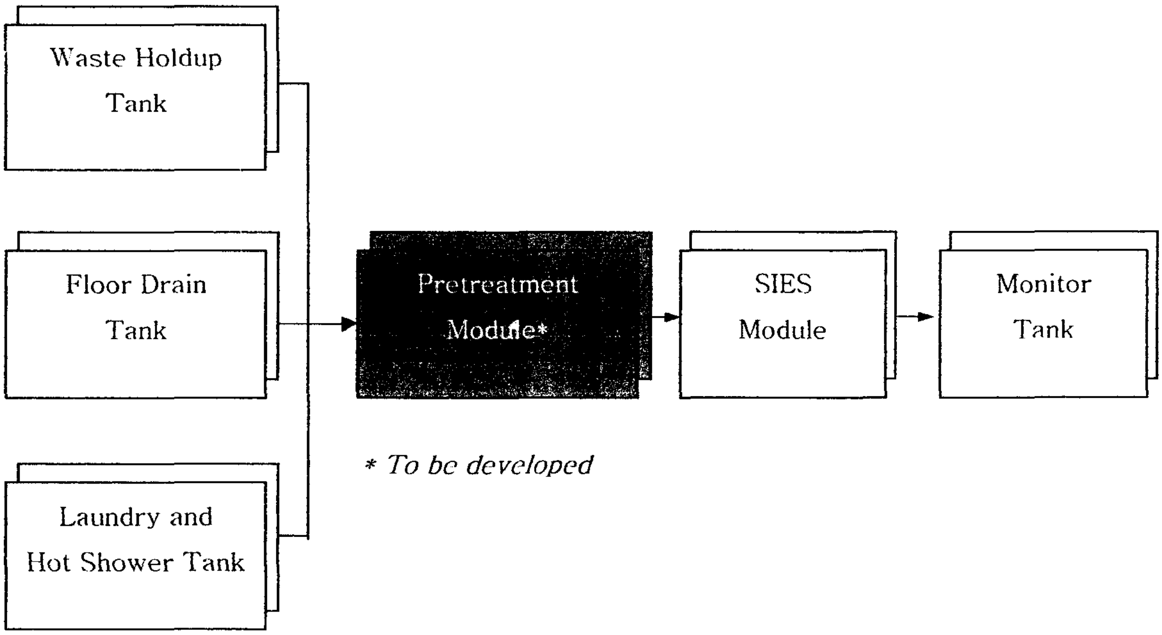

Figure 1. Flow Diagram of Lab. Scale Combined Process for Kori Unit 2

MATERIAL AND METHOD

Liquid Radioactive Waste

The physical and chemical properties of liquid radwaste were analyzed and the concentration of radionuclides contained in liquid radwaste was also measured. The samples were collected at Kori Unit 2. The characteristics and chemical & physical properties of liquid radwaste are shown in Table 1 and 2, respectively.

Table 1. Typical characteristics of the liquid radioactive waste generated from Korean NPPs

Liquid waste	Treatment method	Characteristics
High TDS Borated waste	Evaporator	- obtain High DF, achieve zero-release - hold the discharge of boron - detergent and oily waste within liquid radwaste decrease the capability of evaporator - need the large cost of initial investment and maintenance
Low TDS Borated waste	Organic Ion Exchanger	- increase spent resin by adsorption of non-radioactive ions - difficult for the achievement of zero-release - difficult for the solidification of spent resins
Laundry waste	-	- discharge if satisfied with the release criteria - difficult for the achievement of zero-release - possible for contamination of environment by detergents
Lab. Chemical waste	Organic Ion Exchanger	- possible to discharge heavy metals into environment - difficult for the solidification of spent resins

Table 2. Chemical & physical properties of the liquid radwaste in Kori Unit 2

	Properties	Range	Properties	Range
Chemical & Physical Properties	PH	5.85 – 8.91	Cl-(ppm)	13 – 25
	COD(ppm)	16 – 141	NO^{2-}(ppm)	0.5 – 4.5
	Na^{+}(ppm)	10 – 15	$SO4^{2+}$(ppm)	6.8 – 8.8
	K^{+}(ppm)	0.2 – 1.4	SS(ppm)	75 – 155
	Ma^{2+}(ppm)	1 – 2	Non-ionic	(<10μm)
	Ca^{2+}(ppm)	3.4 – 60	Surfactant(ppm)	65 - 153
Specific Activity	Co-58(μCi/ml)	2.69E-5 – 5.99E-3	Cs-134(μCi/ml)	1.80E-5 – 4.58E-2
	Co-60(μCi/ml)	1.92E-5 – 2.91E-3	Cs-137(μCi/ml)	2.42E-5 – 5.63E-2

Lab Unit

The lab scale combined process consists of the MF membrane process and NF membrane process and selective ion exchange beds. MF membrane and NF membrane process were designed with 600 l/hr and 100 l/hr of permeate capacity, respectively. The flow rate of Selective Ion Exchange System was also designed 60 l/h for enough retention time in the column.

The MF process consists of MF module, waste feed pump, backwashing pump and control box, scaled 600 liters/hr. The module type of MF process is hollow fiber and the material of MF membrane is made of ploysulfone.

The Thin Film Composite (TFC) polyamide NF membrane in spiral wound type were used. Table 3 and 4 show the characteristics of the two membrane processes, respectively and Table 6 also shows the operation conditions in laboratory.

The Lab scale SIES consists of 5 columns in 5 liter volume and treats the permeate of MF or NF processes as a flow rate of 60 l/hr.

Table 3. The characteristics of microfiltration(MF) membrane used

Item		Characteristics
Module Type		Hollow Fiber
Operation Type		Submerged
Pore Size		0.2μm
Specification	Model	SuperMAK, ENE Co., Korea
	Fitting Size	1/2" PT
	Membrane Area	10m2
	Top	100(W) x 400(L) mm
	Bottom	250(W) x 400(L) mm
	Height	710 mm
Material	Head	ABS
	Core Tube	PVC
	Bonding	Urethane & Epoxy Resin

Table 4. The characteristics of nanofiltration(NF) membrane used

Item	Characteristics
Module Type	Spiral Wound
Model	NF90-2540
Nominal Active Surface Area (m2)	2.6
Product Permeability (m3/d)	2.3
Permeate (L/hr)	100
Max. Feed Flow (m3/hr)	1.4
Driving Pressure (kgf/cm2)	< 15
Recovery (%)	< 15
Conc. Ratio (%)	80 - 90

Table 5. Operation conditions of each pretreatment process

Item	Operation Conditions	
	MF Process	NF Process, Film Tech. Co, USA
Pressure	-50cmHg	8kgf/cm2
PH range	2-12	2-11
Temperature	0-40	< 40
Permeate (L/hr)	600	100
Turbidity (NTU)	-	1

*NTU: Nephelometric Turbidity Unit

Methods

A series of experiments for determining the optimum arrangement of unit process was also performed. Two alternatives are MF-NF-SIES and MF-SIES-NF in order. In the experiments, Floor Drain Tank waste for MF-NF-SIES and Waste Holdup Tank waste for MF-SIES-NF were used respectively. The liquid waste is pumped into MF unit and then the permeate of MF unit goes to NF unit(or SIES unit), and finally the permeate of NF unit(or SIES unit) is treated by SIES unit(or NF unit). The membrane type of MF unit is a hollow fiber membrane, which is submerged in 200-liter container, and this unit is operated with the waste processing time of 6 min, backwashing of 10sec alternately. The permeate of MF unit is used as the water for backwashing. Based on the results of optimum arrangement experiments, long-term test of the combined process was carried out.

To evaluate the removal performance of unit process, turbidity, SS and total activity in the permeate are measured and the suction pressure of pump and the permeate rate are also monitored. Ca, Na, and Cl- ions are analyzed by Atomic Absorption Spectrophotometer (Thermo Jarrell Ash Co., Ltd., USA) and B, Si, Fe, Mg and Al ions are also measured by ICP. Total organic carbon is analyzed using by TOC analyzer (TOC-5000A, Shimadzu Co., Ltd., Japan) and SO42- ion by Ion Chromatography.

RESULTS

Optimum Arrangement Experiments

1. **MF-NF-SIES**

The 1.5m3 of FDT waste with the initial suspended solid 38,000ppb was treated in this experiment. Lab scale combined process is described in Figure 2. Turbidity and contents of suspended solid in the FDT wastewater and the processed water were measured and summarized in Table 6. As shown in Table 6, the removal efficiencies of Turbidity and SS in MF process were 98.7% and 98.1%, and 93.5% and 95.8% in NF process, respectively. Turbidity of the permeate in MF process remained below 1NTU and it was satisfying with the feeding condition of influent to NF process. Although Ag-110m could be removed by MF process in initial stage of the experiment, it was turned out that it ultimately passed MF process. So NF process was adopted for removal of Ag-110m contained in the permeate of MF process.

The 2nd column of SIES was packed a proprietary ion selective granular for cesium removal. This media has been used to process a wide variety of waste streams at PWR and at US DOE facilities and plays a very important role since cesium is particularly mobile and is not effectively removed by the previous process stages. The primary reason for its effectiveness in removing cesium is the ion selective nature of the media. Even though the ionic concentration of various non-radioactive impurities(salt, etc) is relatively high in the feed to the cesium removal stage, especially the boric acid and monovalent ions such as sodium, the media consistently shows the ability to remove all of the cesium to less than LLD level(1E-8 μCi/ml). The final column of the SIES is polishing using organic ion exchange resin. The purpose of this stage is to remove any residual ionic corrosion product activity.

Table 6. Characteristics of the FDT waste and the permeate of MF-NF-SIES process

Item	FDT Waste	Permeate of MF	Permeate of NF
PH	6.41	7.28	6.29
Turbidity (NTU)	58.9	0.77	0.05
SS(ppb)	38,000	720	30
Total Activity (μCi/cc)	1.543E-03	1.354E-03	2.067E-04

2. MF-SIES-NF

The WHT waste of 1.5m3 was used in MF-SIES-NF arrangement experiment. The characteristics of WHT waste and the permeate of MF and NF were summarized in Table 7. The MF process filtered more than 98.7% of turbidity of WHT waste. Suspended solid in MF passed waste was decreased roughly one twentieth that of WHT waste. SS in the permeate of NF process after passing SIES was removed as much as 99.12% that of MF permeate.

Since all of the suspended solids and all of the colloidal particulate in the wastewater are not effectively removed by MF process, ion exchange resins of SIES process were easily fouled in MF-SIES-NF combined process. So NF process was required for the removal of SS and turbidity contained in the wastewater prior to feeding SIES process.

From the results of experiment above, pretreatment process such as MF and NF processes for the removal of SS, turbidity and TOC is positively considered to maintain the treatment capacity of SIES process. And from a treatment effective point of view, MF-NF-SIES arrangement system was better than MF-SIES-NF one.

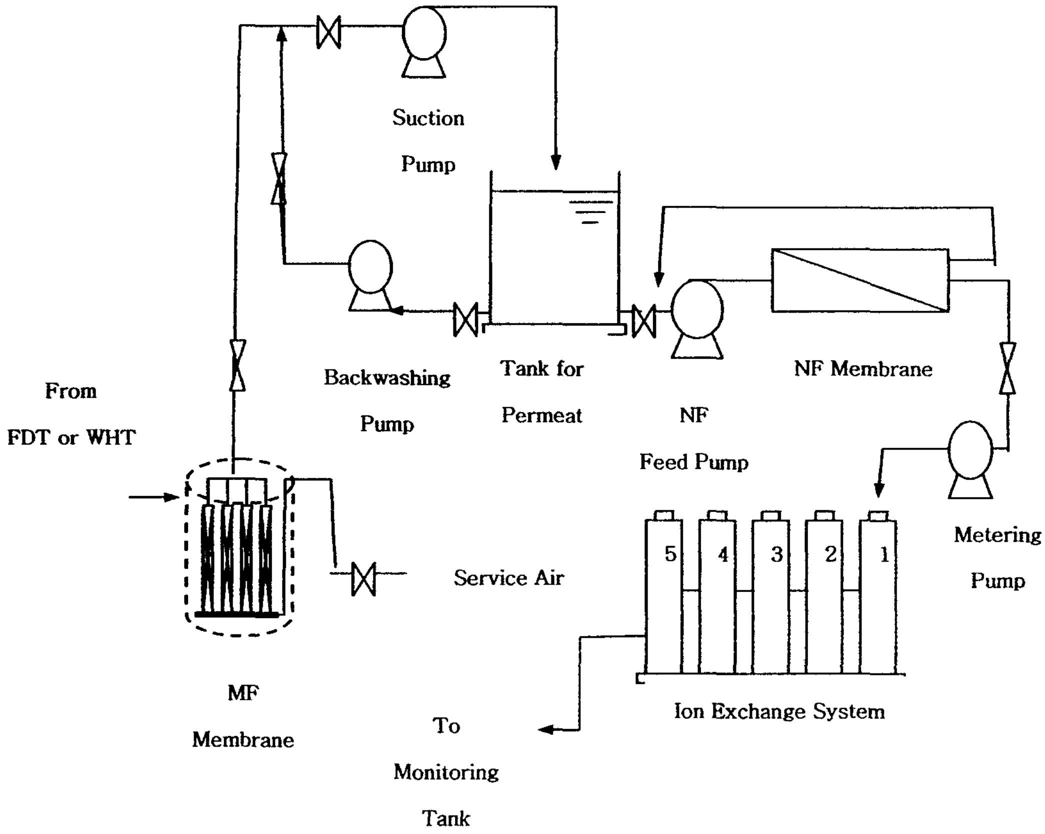

Figure 2. Schematic of Lab Scale Combined Process

Table 7. Characteristics of the WHT waste and the permeate of MF- SIES - NF process

Item	WHT Waste	Permeate of MF+SIES	Permeate of NF
PH	5.98	7.04	5.59
Turbidity(NTU)	42.6	0.55	0.05
SS(ppb)	23,000	1,140	10
Total Activity(μCi/cc)	2.499E-02	8.256E-03	1.9747E-06

Long-Term Field Test

From the results of experiment for determining the optimum arrangement of unit process, the MF-NF-SIES arrangement was selected for further long-term test due to its better efficiency in SS, turbidity and TOC removal. Approximately 24m3 of WHT wastewater was treated in this experiment. Turbidity, contents of suspended solid, and TOC in WHT wastewater and the permeate were measured and summarized in Table 8. As shown in Table 8, the Turbidity in the permeate of MF and NF process were 0.12NTU and 0.05NTU respectively. This result was similar to that of the MF-NF-SIES arrangement experiment. Turbidity of the permeate in MF process remained below 1NTU and it was satisfied with the feeding condition of influent to NF process. The removal efficiency of SS in MF and NF process were 97% and 60%, respectively. The removal efficiency of SS in MF process was in good agreement with that of the MF-NF-SIES arrangement experiment, whereas the removal efficiency of SS in NF process was quite different from that of the MF-NF-SIES arrangement experiment. The decrease of removal efficiency of SS in long-term test compared to the MF-NF-SIES arrangement experiment was affected by the degradation and plugging of NF membrane due to long-term experiment.

Chemical properties of the permeate was analyzed and summarized in Table 9. Boron in the waste is present as B(OH)2 with high solubility in water at pH below 5, but as pH increases, low soluble various anion species such as B(OH)4-, B3O3(OH)4- and B3O3(OH)52- are produced from the hydrolysis of B(OH)3. Accordingly, B(OH)3 under the low pH can permeate MF and NF membrane easily.

The liquid waste in FDT was processed with MF membrane, NF membrane, and SIES. Total activity of actual waste was 1.534E-3 μCi/cc and initial concentration of each nuclide was shown in Table 10. The activity of permeate was lower than LLD (Lower Limit of detection) and the decontamination factor (DF) was about 2,000 for the liquid radioactive with radioactivity 1.534E-3 μCi/cc.

Table 8. Characteristics of the WHT waste and the permeate in long-term field test

Item	WHT Waste	Permeate of MF	Permeate of NF
Turbidity (NTU)	45.65	0.12	0.05
SS (ppb)	20,300	722	279.5
TOC (ppm)	21.74	5.68	2.56
Total Activity (μCi/cc)	1.065E-01	5.461E-02	3.62E-02

Table 9. Chemical properties of the WHT wastes and the permeates of the long-term test

Elements	WHT Waste	MF permeate	NF permeate	Analyzer
B	1,240	1,210	1,260	ICP
Si	3.6	3.7	3.5	
Fe	1.2	0.12	0.01	
Mg	0.47	0.38	0.22	
Al	< 0.1	< 0.1	< 0.1	
Ca	2.3	1.6	0.75	AAS
Na	4.8	4.1	3.8	
Cl^-	-	-	ND	
$SO4^{2-}$	2.5	1.8	ND	IC

CONCLUSION

Demonstration tests using actual liquid radioactive waste were carried out to verify the performance of the lab-scale combined pretreatment system utilizing both the hollow-fiber microfiltration (HMF) membrane and the spiral-wound nanofiltration(SNF) membrane system at Kori Unit 2 NPP in Korea. The SS, turbidity and TOC removal using the combined pretreatment system met the feed condition of the SIES process.

Table 10. Data sheet of long-term test of the MF-NF-SIES

Isotope	FDT waste (μCi/cc)	MF		NF		SIES	
		Activity (μCi/cc)	DF	Activity (μCi/cc)	DF	Activity (μCi/cc)	DF
Mn-54	1.810E-5	1.347E-5	1.34	1.000E-8	134.70	1.000E-8	1
Co-57	5.880E-6	1.000E-8	588.00	1.000E-8	1	1.000E-8	1
Co-58	1.102E-3	9.772E-4	1.13	1.084E-5	90.14	1.000E-8	1
Co-60	5.608E-5	3.676E-5	1.38	1.000E-8	367.60	1.000E-8	1
Ag-110m	1.535E-5	1.236E-5	1.24	1.000E-8	123.60	1.000E-8	1
Cs-134	6.224E-5	6.743E-5		4.029E-5	1.67	1.000E-8	402.90-
Cs-137	2.743E-4	2.592E-4	1.06	1.556E-4	1.67	1.000E-8	1,556
SUM	1.534E-3	1.478E-3	1.04	2.067E-4	7.15	8.000E-8	2,076

NOTE: 1.00E-8 is used for minimum detectable activity (MDA) for calculating DF's

Through optimum arrangement experiments, the MF-NF-SIES arrangement system was proved as the preferable pretreatment system. Especially, more than 99% of Ag-110m contained in the permeate was removed by NF membrane process. The experiment results were used for design criteria for manufacturing the combined pretreatment process of SIES to be installed at Kori Unit 2.

For Kori Unit 2, floor space limitations were very restrictive; therefore, the combined pretreatment process was specially designed. All components are to be installed in an area that is approximately 280 x 530 cm in September 2003.

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