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RADIOACTIVE LAUNDRY WASTE TREATMENT SYSTEM WITHOUT SECONDARY WASTE GENERATION

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ABSTRACT

A new treatment system for the laundry liquid radwaste generated from nuclear power plant has been developed. The system is composed of a RO membrane module and a UV photo-oxidation reactor. It is designed with the flow rate, 1 ton/hr, and the volume reduction factor, more than 100. The DF(Decontamination Factor) over 100 is expected for the radioactive cobalt and cesium respectively. The best advantage is that there is almost no secondary waste generation from this system. In the present paper, the analysis on the liquid laundry radwaste property and the experiment for pretreatment of the laundry waste are discussed. The result of the demonstration test in the plant using radioactive and non-radioactive liquid waste is also discussed. The variable combination test using UV, H₂O₂, and O₃ is carried out for the design of the pretreatment process which will be a key technology of the system. The detergent removal capacity and technicality of the process are mainly described and evaluated.

INTRODUCTION

Radioactive liquid laundry waste is generating from decontamination of equipment, washing water of contaminated cloths and shower in the nuclear power plant. The radioactivity of the laundry waste is ranged between 10⁻⁷~10⁻⁴ μCi/cc but its total radioactivity can not be disregarded because its yearly generation volume is approximately 4000 ton per every reactor in Korean NPP, which covers large portion of the whole radioactive liquid waste. Korea Electric Power Corporation has developing the effective and safe treatment process for laundry liquid radwaste for the purpose of Zero-Release of radioactivity to the environment [1].

Presently, the liquid radwaste of the NPP is treated with the evaporator. The concentrated wastewater is dried in the CWDS (Concentrate Waste Drying System) and is solidified with paraffin for final disposal. However because the laundry radwaste contains non-degradable detergent, to treat it with evaporator is difficult, therefore the waste is discharged to the environment after dilution with lower limit of acceptance. Because of this fact, the safe and effective treatment process of liquid laundry waste is highly required. The present paper is to report the RO treatment process developed by KEPCO, which can separate radionuclides and detergent from the waste without phase change.

The characteristics and properties of detergent were analyzed. To improve RO effectiveness, the particles and detergent contained in the waste have to be removed. For this reason the experiments for development of pretreatment process were carried out. The experiments were mainly focused on the detergent removal that is the most problematic in the process of liquid laundry radwaste treatment. Activated carbon process, Advanced Oxidation Process such as O₃/H₂O₂ injection process and UV/ H₂O₂ photo-oxidation process were studied and compared each other in their own advantages based on the experimental results. In the Advanced Oxidation Process, the detergent removal rate depending on O₃ or H₂O₂ injection volume was measured. The effect of UV/H₂O₂ combination and pH influence was also studied.

The pilot system was finally decided in combination with pretreatment process and RO process of treatment capacity, 1ton/h, Decontamination Factor (DF) more than 100 and volume reduction rate more than 100. This system is placed in Younggwang NPP #4. Using this system, detergent removal unit and RO unit were tested and the industrial system design data were yielded. The pilot system was composed of tank module, RO module and UV/H₂O₂ photo-oxidation process module as a detergent removal process. The RO modules are composed of 4 of low-pressured BW (Brackish Water) and 4 of high-pressured SW (Sea Water) modules.

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The detergent removal rate was found to be very influenced by H₂O₂ injection volume. The H₂O₂ injection tests were carried out under the pulse and continuous mode. The continuous and concentration operations of the RO modules were carried out with the real radwaste to verify the effects of each module. The DFs for radioactive cobalt and cesium were measured.

MATERIAL AND METHOD

Detergent Analysis

The properties of laundry radwaste were analyzed in the physical, chemical and radioactive nuclides. The samples were collected at Kori NPP #2. The detergent using in the NPP generally contains anion surfactant and non-ion surfactant. The detergent was analyzed as below. The analyzing items, equipment and the methods were described as follows.

Physical and chemical analysis

- ◆ TS, TSS : 2520B and 2520C Standard Method (18th ed.), samples were dried at 103-105^oC.
- ◆ Conductivity: Conductivity TDS Meter (Orion 124)
- ◆ Surface Tension: NIMA Surface-Tensiometer
- ◆ Viscosity: Portable Viscometer Rion VT-03
- ◆ COD: measured COD_{CR} by MERCK photometer SQ118
- ◆ Anion surfactant: 5540C standard method (18th ed.) (Anionic Surfactants as MBAS)
Standard reagent; sodium dodecyl sulfate (NaO₃SO(CH₂)₁₁CH₃, 288.38)
- ◆ Non-ionic surfactant: 5540D Standard Method (18th ed. (Nonionic Surfactants as CTAS),
Standard reagent; C₁₂₋₁₈E₁₁
- ◆ Particle Size Analysis:
Particle Size Analyzer MALVERN PCS4700
 - Angle: 90^o
 - Wavelength: 480nm
 - Temperature: 20 °C
 - Dispersant: 3-distilled water (Refractive Index 1.33)

Radioactivity Analysis

- ◆ γ -ray Detector (CANBERRA)
 - Relative measurement effect: 50%

Pretreatment Process Test for Detergent Removal

Activated Carbon Adsorption Process

Activated carbon (SamchullyTM LS-100) was used for detergent removal. This carbon was made of coconut, and in granular type. The particle size was ranged in between 8~12 mesh. Another activated carbon type DT-10 (Diversified Technology) was used for detergent removal and additionally for radionuclide removal. The simulants were filtered by 0.45 μ m filter (Ministart, Sartorius Co.). The COD and the radioactivity of Cs and Co were measured from the permeates.

The simulants were made with tap water and detergent, AT (as in Table 1) and radionuclides, cesium and cobalt. Their radioactivity was adjusted in 10⁻⁴ μ Ci/cc, and the detergent in 0~200ppm of COD. Cesium-137 and cobalt-60 (\leq 99% in purity) from 0.1M of CsCl and CoCl₂ (of Du Pont) respectively were used.

Ozone/H₂O₂ Process

This process for detergent removal was already introduced in Kim *et al*, 1998[4], and was composed of ozone generator and ozone chamber. The ozone chamber was made of acrylic material, cylinder type (2cm H x ϕ 15cm ID), and the ozone generator has 50g/hr of ozone generating capacity (OZONIA, Model: OZAT CF-0B).

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The simulants were composed of non-ionic detergent (0.7 l), softener 'Shafran'(0.2 l) and bleach 'Laks' (0.1l) with 500 l of tap water, which were resulted in about 85ppm TOC. Of the simulants, twenty liter of the waste was pumped into the ozone chamber under pH adjustment and hydrogen peroxide injection for both continuous and batch tests. For the continuous test, the waste path was arranged from the top of the ozone chamber and to down for maximizing the reaction with ozone bubble that was generating from the diffuser located at the chamber base. The flow rate was 100 l/h for keeping 20 liters of the waste volume in the ozone chamber. The detergent foam generated by ozone bubble was led into the foam removal system and was destroyed by hot air. The redundant ozone was discharged to the environment, and the concentrated water was recycled to the ozone chamber.

Ozone/UV Process

For this test, the UV reactor was added to the ozone chamber. The waste discharged from the bottom of the ozone chamber was flowed to the UV reactor and to the ozone chamber again.

The experimental methods were the same as explained in the Ozone/H₂O₂ Process. The flow rate for the batch test was 7 liter/m for enough retention time in the UV reactor. Ozone injection volume was 1000ppm/h. Three 65W UV lamps with 254nm wavelength radiated in direct current were used. Thus the UV reactor had waste treatment capacity of 20 liters with 9.75W/liter.

UV/H₂O₂ Process

The UV/H₂O₂ process system [12] was composed of 15W UV lamp (General Electric), and cylinder-type glass reactor (22cm H x ϕ 4cm ID). During the tests (continuous or batch), 125ml of the waste in the reactor was used. H₂O₂ and pH controllers (NaOH or HCl) were added directly in the waste tank. This waste was injected to the reactor by peristaltic pump. The system was equipped for recirculation with the flow rate of 100l/h. The surface of the glass reactor was wrapped by aluminum foil for protection from UV radiation.

Demonstration Test for the Pilot Plant

Based on the experiment results from the pretreatment test, the pilot system was designed and placed in Younggwang NPP #4. The system consisted a tank module, a UV reactor module and a RO module. The system was designed with 1 ton/h of treatment capacity, volume reduction ≥ 100 and decontamination factor ≥ 100 .

Tank Module

The tank module consisted of 1000 liters capacity of waste tank for BW RO membrane, 200 liters of SW RO membrane and a chiller for tank waste. The actual laundry radwaste was offered from the chemical drain tank to the BW tank. The 25 μ m filter was placed in front of the BW tank for particle filtration of the waste. This filter discharges the particles when the ΔP was reached to the certain value. The BW tank reserved 10 times concentrated waste by the BW membrane, and the SW tank reserved waste concentrated 10 times again by the SW membrane. The chiller was used for chilling the waste heated up from the UV reactor.

RO Module

The RO module was composed of a micro filter, a feeding pump, an activated carbon bed, a carbon filter, a high pressure pump, a RO membrane and a pressure control valve, etc. The RO membranes possess 4 of low and 4 of high-pressure membranes. The micro filter of 5 μ m pore size was placed for particle removal like solid colloids to prevent frequent RO fouling. The feeding pump was operating by 3~4kg/cm². The high-pressure pump was controlled 15kg/cm² for BW membrane and 55kg/cm² for SW membrane. The pressure control valve was needle type. The activated carbon bed or activated carbon filter was placed to remove the remained organic material.

UV Reactor Module

One of 15kW/h UV lamp was placed in the middle of the cylindrical reactor. The UV reactor had about 30 liters of capacity with 4 ton/h in maximum flow rate. The reactor was designed to be able to connect with both the BW tank and SW tank. In front of the reactor, the chemical injection valve was placed for hydrogen peroxide injection.

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UV/H₂O₂ Reactor Test

Since the real laundry waste from Younggwang NPP #4 had no foam and below LLD in radioactivity when the reactor test was carried out, the waste was simulated in severe condition. The commercial detergent such as PF (commercial non-ionic detergent, 14% and supplementary agents 86%) was used for it. Radionuclides were also used for. The surfactant consists of Lauryl Alcohol-9(LA-9), 13.9% and Alcohol Ethoxylate (Softanol 90), 1.5%. The hydrogen peroxide, 30wt% was used as an oxidizer.

To simulate the wastewater, 150 l of tap water was firstly filled in the SW tank, and for TOC 85ppm the detergent PF 75g(0.5g/l) was solved in. The volume of 100~5000ppm of hydrogen peroxide was injected using either the pulse mode or the continuous mode.

The piping was arranged for the simulants flow from the SW tank to the UV reactor and again to the SW tank. After the simulants filled in the UV reactor, the flow rate was adjusted using the back valve under the frontal valve fully opened. And then the reactor was operating about 5 minutes and then sampled 100ml for the first time in the frontal sampling port. The sampling was carried out every 10 minutes for an hour in the frontal and back sampling ports of the reactor. Sampling from the back port was done after 1 minute from the frontal sampling.

For the hydrogen peroxide injection, the injection pump was operated before the reactor switched on in a pulse mode. On the last stage of the UV reaction, the hydrogen peroxide injection pump was stopped after the last sampling and switched off the reactor. TOC and H₂O₂ were measured from the samples. H₂O₂ was titrated by KMnO₄ method. TOC was analyzed by TOC meter, ASI-5000A, Shimadzu.

Integrated Demonstration Test

The integrated demonstration test had carried out on the basis of the operation and experiment results of UV reactor test. For the first stage, the test was carried out on the simulants with addition of radionuclides, and for the second stage, the actual radwaste was used. This test was already reported in the other paper written by the present author, Park *et al*, 1999[11]. However the method is introduced here again.

(1) Test with simulants

The liquid waste in BW(Brackish Water) tank was processed with UV reactor and RO membrane through the two different flow paths. One flow path was connected in circulation mode from the BW tank to the UV reactor, or vice versa. The other one was from the BW tank to BW RO module. The wastewater in BW tank flow passed through the micro filter and to the BW module after bypassed the activated carbon bed and carbon filter.

The test was carried out with simulants composed of tap water, 800 l, and detergent, 400g, of which TOC concentration was equivalent to 100 ppm. The simulants were filled in BW waste tank. Radionuclides, cobalt and cesium, were added into the simulants to be 10⁻⁵ μCi/cc each in radioactivity. Hydrogen peroxide of 2000 ppm was added in the BW tank in bulk mode. The concentration operation in the BW module was carried out with the permeate flow rate of 10~12 LPM and with the feeding water pressure of 15 kg/cm². The operation was continued until 800 l of wastewater were reduced to 200 l. One liter of permeate was sampled from time to time for measurement of decontamination factor. The concentrated 200 l of waste were sent to the SW RO module for volume reduction since feeding valve was closed. The operation under the closed condition was continued until the water was reduced to 50 l. For this test, hydrogen peroxide was added continuously under the adjustment in maximum or at 7.0 of the pump control nod of chemical injection kit.

(2) Test with actual radwaste

All the lines were connected as same as the simulants test except the line-up for continuous feeding to BW tank from chemical waste tank. First of all the actual laundry radwaste, 800 l from the chemical waste tank, was filled in the BW module tank. The feeding valve was closed since the feeding water was filled in the tank. Radionuclides, Co-60 and Cs-137 of 10⁻⁵ μCi /cc respectively, were added as a tracer, into the tank. And then the UV reactor and BW membrane module were operated. At the same time the feeding valve was opened, and the flow rate of the feeding water was controlled at 10 LPM which was the same as that of permeate.

RESULTS

Detergent Analysis

Analysis Results

The detergent that was used in Kori NPP #4 before January '98 was analyzed for physical and chemical properties as shown in Table 1. After January '98, the detergent has been changed in LA as in Table 1, which was composed of non-ionic surfactant polyoxyethylene-nonylphenylether 7~8%, EDTA-4Na 5%, anti-foamier 1ppm and inhibitor (calcium lingot sulfonate) 3%. The physical, chemical properties and radioactive property of laundry radwaste of Kori NPP #4 were analyzed as shown in Table 2. Based on these data, the required factors for RO system such as RO membrane and pretreatment process were decided.

As shown in Tables 1 and 2 laundry radwaste contains very small amount of radioactive nuclides, surfactant, S.S and dissolved salts, etc. The dominant radionuclides were ^{58}Co , ^{60}Co , ^{134}Cs and ^{137}Cs . The surfactant is mainly nonionic. The dissolved salts and particles were generated from colloids compounds produced by metal hydro-oxides from chemical compounds having low solubility, such as CaSO_4 , CaCO_3 and $\text{Fe}(\text{OH})_3$. Inhibitor and EDTA were also contained in the detergent as a builder. The particle size was under $10\mu\text{m}$.

Table 1. Physical and Chemical Properties of Detergent used in Kori NPP

Physical Property	AT	LA	Chemical property (wt.%)	AT	LA
Ionic	Non-ionic	Non-ionic	H ₂ O	65	65
Boiling Temp.(.)	102	102	Alkyl amide (Conc.)	25	25
PH(at 21.)	4.28	7.12	Sodium alkyl sulfonate	3	3
Viscosity (at 21.)	3.26	3.48	High alcohol amine salt	3	3
Density (at 21.)	1.005	1.005	Mono ethylene glycol	1	1
Dilution Stability (1:1 v/v%)	none	none	Inhibitor	2	2
			EDTA	0.05(2Na)	0.05(4Na)

* AT : detergent for floor washing, LA : detergent for cloth washing

Table 2. Laundry Radwaste Characteristics of Kori NPP

Property		Property		Property	
PH	6.58~7.3	Anionic Surfactant (ppm)	ND	NO ₃ ⁻ (ppm)	0.47~4.5
Temperature(°C)	20.2~24.8	Nonionic Surfactant (ppm)	65~153	PO ₄ ⁻³ (ppm)	0
TS (ppm)	75~155	Na ⁺ (ppm)	10.0~14.89	SO ₄ ⁻² (ppm)	6.8~8.76
Conductivity (μS/cm)	67.5~130.3	NH ₄ ⁺ (ppm)	0	⁵⁴ Mn (μCi/cc)	0.9~1.1×10 ⁻⁸
Surface Tension (mN/m)	38.4~41.3	K ⁺ (ppm)	0~1.4	⁵⁸ Co (μCi/cc)	1.48~2.32×10 ⁻⁷
Viscosity (mPa·S)	1.0	Mg ⁺² (ppm)	1.09~2.0	⁶⁰ Co (μCi/cc)	3.52~3.81×10 ⁻⁷
Turbidity (NTU)	12~21	Ca ⁺² (ppm)	3.39~6.0	¹³⁴ Cs (μCi/cc)	1.3~1.9×10 ⁻⁸
COD(ppm)	50~141.3	Cl ⁻ (ppm)	13.32~25.0	¹³⁷ Cs (μCi/cc)	5.9~6.8×10 ⁻⁸

Pretreatment Process Test for Detergent Removal

Activated Carbon Adsorption Process

The isothermal adsorption and removal rate of detergent using activated carbon were observed using the simulants of COD, 65ppm that was controlled with detergent in the tap water 50ml. The activated carbons (LS-100 or DT-10), 20~200mg was used and stirred for 24hours at room temperature.

The experimental data obtained from the test were calculated in Freundlich equation. The adsorption coefficients, k and 1/n were -1.8283 and 0.3729 for the LS-100 and -7.06 and 5.5 for DT-10 respectively. These results were well accorded with the equation. Since the value 1/n for LS-100 was in between 0.1 and 0.5, it indicated that the adsorption of detergent in LS-100 is more effective than that in DT-10.

The detergent removal rate was more than 90% in LS-100 besides, it was lower than 60% in DT-10 under the same volume of detergent 100mg. This fact could be concluded that to use DT-10 for detergent removal is less effective than to use LS-100. However LS-100 produces more secondary waste than DT-10 in volume respect. To use the activated carbons, LS-100 or even DT-10 for detergent removal, another facility for recycling the activated carbon will be needed. In this respect, it was concluded that the activated carbon was not suitable for the radioactive laundry waste pretreatment process.

Ozone/H₂O₂ Process

The results from the test for the detergent removal, under the hydrogen peroxide and pH adjustment were as follows.

- 1) The detergent removal rate using only ozone without hydrogen peroxide injection was depending largely on pH effect. When the pH was higher, the detergent removal rate was larger.
- 2) When pH was 6.5, the detergent removal rate was increasing according to the volume of hydrogen peroxide injection getting large. However it was rather decreased above the certain volume of H₂O₂.
- 3) In the simulants of pH 9.5, as volume of hydrogen peroxide injection was increased, the detergent removal rate using ozone in fixed volume was decreased.

This process showed 99% of detergent removal rate under the optimum condition with pH 9.5, hydrogen peroxide 300ppm and 800ppm of ozone injection volume in the initial stage of simulants. The ozone injection took 40 minutes. This time can be reduced if a large scale of ozone generator would be used.

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Ozone/UV Process

This process showed 90% of detergent removal (TOC removal) on the batch test and 70% on the continuous test for an hour from the simulants with 300ppm of hydrogen peroxide but no pH adjusted.

It was resulted that for 1 ton/h treatment using by ozone generator, 1.5kg/h of ozone generator was required for obtaining 70% of detergent removal rate.

UV/H₂O₂ Process

The purpose of this experiment was to result in the optimum factors such as optimum waste volume upon UV lamp power for detergent removal, optimum retention time in the UV reactor, and optimum H₂O₂ injection volume, etc. It could be concluded as follows.

- 1) TOC removal rate was increased as H₂O₂ injection volume was increasing, but no more above the certain volume. The optimum H₂O₂ to treat waste of TOC, 85ppm was at about 600ppm.
- 2) The optimum TOC removal was at pH 9.5 but the removal rate was not always comparable to pH.
- 3) Among the dominant detergent compositions, non-ionic surfactant, PENPE (Polyoxy Ethylene Nonyl-Phenyl Ether) was the most easily degradable organic of detergent, on the other hand, EDTA was the most difficult organic to be degraded.
- 4) TOC removal was effective as the value 'n' of ethylene oxide of PENPE being larger. The TOC removal rate in LAS was higher than that in PENPE of $n=3$, but lower than that in PENPE of $n=5$.
- 5) The result of the UV radiation test on waste treatment volume showed that to remove TOC more than 85% for 1 ton of radwaste from the nuclear power plant, the UV lamp of 28.6kW at least would be required.

Comparative Evaluation between the Pretreatment Processes

To select the optimum pretreatment process for detergent removal, activated carbon adsorption process and Advanced Oxygen Process were compared each other in their experimental results. Comparison was firstly focused on the detergent removal rate in each process, secondly, was on the respects of capital cost, maintenance, operation and scale, particularly, on the minimum secondary waste generation. Each comparative item was summarized in Table 3, and each process is explained in detail as follows.

Activated Carbon Adsorption Process

The activated carbon, as known, was excellent for both organic (detergent) and cobalt removal. However the consumption of the carbon would be enormous, and thus it will produce large volume of secondary waste, which is required the other facility for carbon recycling. In this point of view, the activated carbon adsorption process is excluded for the pilot plant.

Ozone/H₂O₂ Process

As explained in **RESULTS**, Ozone/ H₂O₂ Process, the process showed 99% of detergent removal rate under the optimum condition with pH 9.5, hydrogen peroxide 300ppm. It also showed 90% removal rate under H₂O₂ 500ppm at pH 6.5, which was not described in the RESULT. To adjust pH in the waste, NaOH was usually used. In this case, considering the affect of Na⁺ to RO membrane, the high pH concentration was not desirable. Since the Ozone/hydrogen peroxide process showed the enough organic removal rate(90%) without pH control, the process could be advantageous in that respect, and also could contribute on minimization of secondary waste

Table 3. Comparison between the Processes for Detergent Removal

Process	System	Scale	Cost	Maintenance	Detergent Removal Rate
Ozone/H ₂ O ₂	Ozone generator, Oxygen generator, Ozone chamber, Ozone redundancy removal unit, Control box, H ₂ O ₂ injection unit	6.5m x 6.5m x 3m(H) for ozone generator and auxiliary facility + Φ 1.0 x 5.5 m (H) for ozone chamber	USD 275,000	Middle	99%
UV/ H ₂ O ₂	UV lamp, UV reactor, Control box, H ₂ O ₂ injection unit	1.5m x 1m x 1.5m	USD 84,000	High	90%
Ozone/UV/ H ₂ O ₂	Combined the above two processes	Combined the above two processes	USD 359,000	Low	85%

* Activated carbon process is excluded in the table, because of its large secondary waste generation.

* UV/H₂O₂ process can increase the detergent removal rate according to the reactor design method.

generation. However its disadvantage is still remained in many respects.

Firstly, disadvantage is in the huge facility scale, which will occupy large space. Ozone process is composed of ozone generator, oxygen generator, ozone chamber, destroying system for the ozone redundancy and control box. From the experiment results, the ozone facility was required at least 2.5kg/hr capacity of ozone generator in the case of 1ton/h waste treatment. The spaces of 6.5m x 6.5m x 3m(H) for auxiliary system and Φ1.0 x 5.5m(H) for the ozone chamber are additionally needed.

Secondly, the expenses for the maintenance and operation will be high due to the huge facility.

Thirdly, ozone facility will result in the high capital cost. "R class" of ozone facility will be spent approximately 4,200,000 USD.

Fourthly, considering ozone hazard, the ozone destroying system will be needed for the ozone redundancy.

Due to the above disadvantages, ozone process was disregarded in using for the laundry waste treatment process.

Ozone/UV Process

This process is expected synergy effect on to the ozone/hydrogen peroxide process. The detergent removal effect was quite high, but the problem was still remained in a huge facility scale and high capital cost as the ozone/hydrogen peroxide process was. Because of this fact, the matter of ozone and UV combined process will increase more of these problems.

UV/ H₂O₂ Process

According to the experiment results, 26.8W/□·h was needed for 85% of detergent removal. Namely, for 1ton/h of waste treatment, 28.6kW UV lamp was required. This high-pressure UV lamp is currently possible to be manufactured. The facility dimension is also small (1.5m x 1m x 1.5m) compared to that of the ozone system. The capital and maintenance cost are only 30% of the ozone process.

Hydrogen peroxide is rather cheap in price, and easy in storage and in handling. The lifetime of UV lamp is about 8000 hours. This fact makes easy in maintenance. Both the ozone process and the UV/H₂O₂ process have advantage to minimize the secondary waste generation, but in consideration of operation, scale and cost, UV/H₂O₂ process will be the most desirable pretreatment process.

Demonstration Test for Pilot Plant

UV/H₂O₂ Reactor Test

As shown in Fig. 1, the TOC removal rate was measured on the variation of H₂O₂ volume (100, 300, 600, 2000, 3000 and 5000ppm) in bulk mode. Using continuous mode for H₂O₂ injection, the TOC removal rate was also analyzed (See Fig. 2). The RPM number of H₂O₂ injection pump was adjusted at 2, 5 and 7 for injection, and after, the H₂O₂ of the sample was analyzed, because the H₂O₂ volume was hard to measure due to the short injection time interval. The RPM no. 2 was 0~25ppm of H₂O₂ from the frontal sample port, no. 5 was 50~200ppm and no. 7 was 200~500ppm. This fact seemed due to the sampling time that could not coincident to the injection time. This case, the H₂O₂ could be low in volume. The effect of H₂O₂ to RO membrane was not obvious but much foam generated in the waste tank as H₂O₂ volume high. This foam disturbed operation of the UV reactor and made RO fouling with foam intrusion. It was resulted in reduction of permeate velocity which could finally reduce the waste treatment capacity. On the other hand, high H₂O₂ volume reduced the organic removal capacity when using activated carbon filter or carbon bed. Therefore the high H₂O₂ volume is not desirable.

In the present test the maximum consumption of H₂O₂ in the UV reactor was about 700ppm. Thus in the case of high volume of H₂O₂ injected in bulk mode, it could cause various side effects, because a large volume of residual H₂O₂ could be intruded into the RO membrane module. The complete H₂O₂ exhaustion took half an hour in the reactor. Therefore H₂O₂ had to be injected every half an hour to the reactor in bulk mode.

Besides, the injected H₂O₂ into the reactor in continuous mode was exhausted all in the reactor. More effective operation would be expected if the continuous mode was chosen for H₂O₂ injection in routine flow rate. It would be desirable that the H₂O₂ volume was injected automatically according to the organic concentration and H₂O₂ consumption rate in the reactor. However this automatic system will be high in cost and maintenance. Accordingly, it would be the best solution if continuous injection of 300~500ppm of H₂O₂, which could exhaust completely in the reactor was possible.

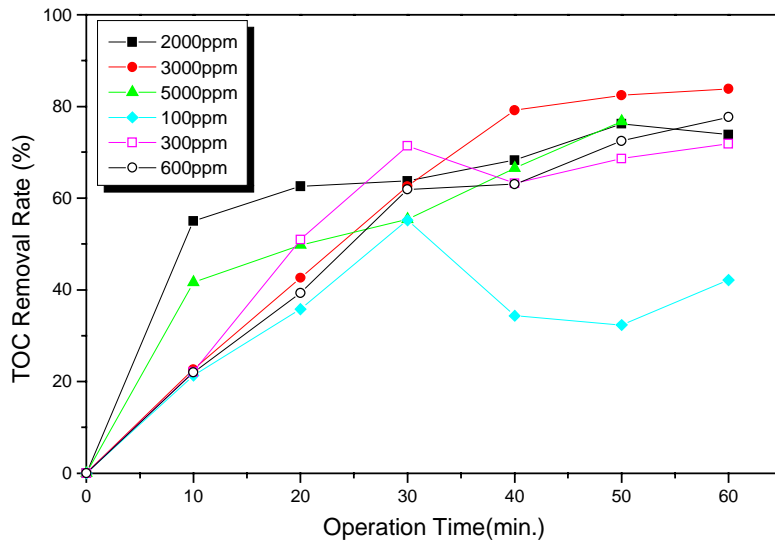


Figure 1. TOC Removal Rate upon H₂O₂ Volume Variation in Bulk Mode

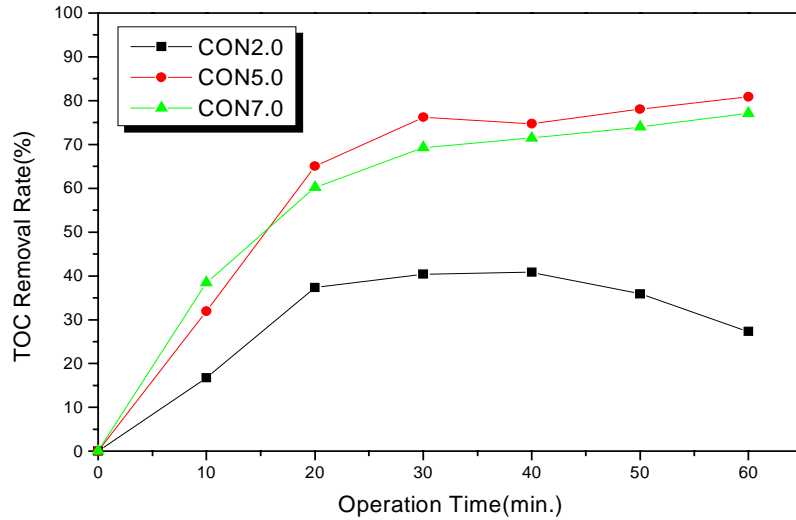


Figure 2. TOC Removal Rate upon H₂O₂ Volume Variation in Continuous Mode

Integrated Demonstration Test

(1) Demonstration test with simulants

The 800 of simulants with the initial TOC 73ppm was filled in the BW module tank for concentration operation. During the concentration of the radwaste water to 200, the samples for TOC measurement were taken every 10 minutes. Slight increase in the TOC from 73 to 78ppm was observed when the concentration operation was finished. Bearing in mind, it seems that the large portion of TOC was removed in the UV reactor, otherwise the final TOC after concentration should be about 290ppm.

The line with closed square in Figure 3 indicates the variation in TOC of the waste in the BW tank during the concentration operation. This figure shows that the TOC decreases for 40 minutes since operation started, and then it increases. This fact indicates that hydrogen peroxide injected in a pulse mode could be almost exhausted within 40 minutes and also indicates that the UV reactor was effective in reducing TOC.

The operation of SW RO module was performed after the 200 of concentrates was discharged from BW tank to SW tank. The line with closed circle in Figure 3 indicates TOC variation of the waste in the SW tank. Hydrogen peroxide was continuously added during the operation. While the operation was continued for an hour, TOC was decreased but evenly. This is the evidence for that the UV reactor could remove TOC under the above condition. Besides, the line with closed triangle indicates TOC variation during the concentration in the SW module under the closed condition, which means the feeding valve was closed. The TOC was decreased in linear pattern. This means that TOC can be nearly zero at the end of operation.

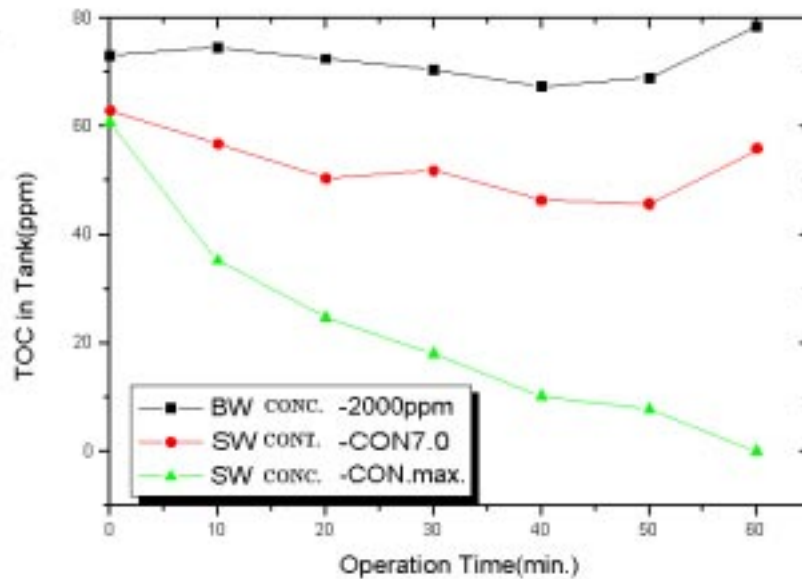


Figure 3. Result of Demonstration Test with Simulants (After Park *et al.* 1999)

(2) Demonstration test with actual radwaste

Figure 4 shows the TOC variation of the real laundry waste that was concentrated for 50 minutes in BW module. Before concentrated, 1.2ton of wastewater was treated in BW module under the continuous operation for 120 minutes with the flow rate, 10 LPM for both feeding and permeating. Contradictorily, the initial TOC was 23ppm when the concentration began, despite the initial TOC of radwaste preserved in the chemical waste tank was 5.5ppm. This difference could be occurred by the high concentration of residual TOC inside the pipes. The TOC in the figure was reducing in linear pattern. This tendency indicates that the UV reactor worked effectively for the TOC removal. During the BW RO operation, the fouling of the micro-filter was occurred frequently. This fact interrupted the smooth operation. Therefore, the micro-filter which can backwash during the operation is required to prevent the operational interruption.

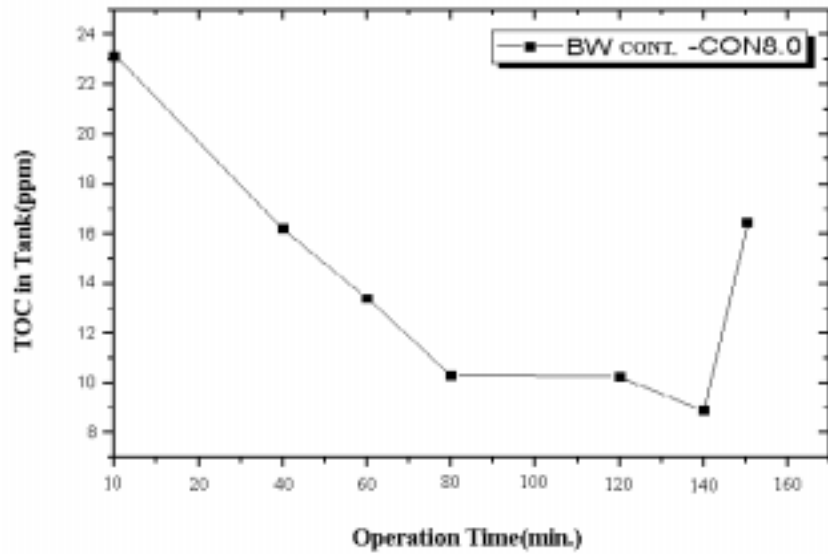


Figure 4. TOC Variation of Actual Waste in the BW Tank during Demonstration Test (After Park *et al.* 1999)

(3) Decontamination factors for radioactive cobalt and cesium [11]

Despite of the radioactivity of concentrate, 10^{-5} $\mu\text{Ci/cc}$, the activity of permeate was lower than LLD (Lower Limit of Detection). The DF was about 300. Table 4 shows the radioactivities and DFs of cobalt and cesium.

Table 4. Radioactivity and Decontamination Factor in Concentrate and Permeate (After Park *et al.* 1999)

Radioactive Co			Radioactive Cs		
Concentrate	Permeate	DF	Concentrate	Permeate	DF
1.46×10^{-5} $\mu\text{Ci/cc}$	4.98×10^{-8} $\mu\text{Ci/cc}$	292	5.23×10^{-5} $\mu\text{Ci/cc}$	1.67×10^{-7} $\mu\text{Ci/cc}$	313
1.01×10^{-5} $\mu\text{Ci/cc}$	3.57×10^{-8} $\mu\text{Ci/cc}$	282	4.11×10^{-5} $\mu\text{Ci/cc}$	1.36×10^{-7} $\mu\text{Ci/cc}$	302

CONCLUSION

Yearly generation of the liquid laundry radwaste was approximately 4,000 ton per every reactor. The dominant radionuclides were cobalt and cesium. Its total radioactivity was ranged between $10^{-7} \sim 10^{-4}$ $\mu\text{Ci/cc}$. Due to using the tap water for washing contaminated cloths, there was no particular component which affects to RO membrane apart from detergent, various particles and laundry debris. The detergent using in the NPP was liquid type, and was composed of various organic material such as 15 ~ 20% of non-ionic surfactant and 75 ~ 80% of supplementary additives, EDTA and zeolite, etc. These micro particles showed various in volumes according to each NPP and it could cause disturbance on the fluent operation of the RO membrane system. Therefore pretreatment system was required for the effective removal of the detergent particles.

Of various pretreatment processes, such as the activated carbon, ozone/ H_2O_2 oxidation and UV/ H_2O_2 photo-oxidation, the UV/ H_2O_2 photo-oxidation was proved to be the most desirable process by the comparative experiment

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in the present study. This process is easy to maintain, and convenient in purchasing, storage and handling of H₂O₂. The organic removal rate more than 70% per once passed through the reactor was achieved in this study under the reasonable application of reactor design and operational factor. Since this process could remove the detergent foam completely, it was applicable as a pretreatment process for laundry waste before evaporation process too.

The reduction of flow rate due to H₂O₂ injection could be improved with continuous injection mode rather than bulk mode. UV/H₂O₂ photo-oxidation process is proved to be very effective for detergent removal. The UV/H₂O₂ process equipped in the pilot system was effective under the continuous injection mode with 300~500ppm of H₂O₂ in front of the reactor. The reactor was excellent in removal of foam but TOC removal rate was below 50% when the wastewater passed once through the reactor. Since the 5 μ m micro-filter was fouled frequently, automatic backwash filter was required for fluent operation of the system. The design criterion of the pilot system on volume reduction more than 100 was achievable. The DF was 300 for cesium and cobalt respectively of the waste with radioactivity about 10⁻⁵ μ Ci/cc.

The RO module operation in 0.6 ton/h was more effective and advantageous than in 1ton/h, which was aimed in the beginning, for membrane life extension. It was also concluded that using only 8 of the low-pressure RO was more cost effective than using both high-pressure and low-pressure RO.

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REFERENCES

1. Yong Kwang Nuclear Power Plant I, "Scheme of Management Improvement on Radioactive Liquid Laundry Waste" (1994).
2. M. Kikuchi, Y. Sugimoto, H. Yusa and K. Ebara, "Development of a Laundry Waste Treatment System", *Nuc. Eng. and Des.*, 44, pp. 413~420 (1977).
3. J. B. Kim and S. M. Park, "Study on Radioactive Laundry Waste Treatment Process", '98 Spring-term Symposium Proceeding of Nuclear Society, pp. 421-426 (1998).
4. J. B. Kim, J. K. Park, S. M. Park, H. J. Ahn and M. J. Song, "Development of a Laundry Radwaste Treatment System", *RECOD 98, Proceedings, Vol. 1*, pp. 224-229 (1998).
5. IAEA, "Treatment of Low- and Intermediate-Level Liquid Radioactive Wastes", Technical Report Series No. 236, IAEA, pp 91~113 (1984).
6. F. T. Teng and C. J. Shih, "Treatment of Laundry Wastewater from a Nuclear Power Plant by R.O.", *Proc. Ind. Waste Conf.*, 39, pp.281~(1985).
7. M. Okazaki, S. Kimura, "Selective Transport Mechanism Through the Reverse Osmosis Membrane", *J. of Chem. Eng. of Japan*, Vol. 17, 192 (1984).
8. Zahid Amjad, "RO Membrane Technology, Water Chemistry, and Industrial Applications", Van Nostrand Reinhold, NY (1992).
9. G. A. Fitchett, N. J. Ray, C. H. de Whalley, "Reverse Osmosis for Water Purification", *CEGB Res.*, 35 (1981).
10. O. Legrini, E. Oliveros, and A. M. Braun, Photochemical processes for Water Treatment, *Chem. Rev.*, 93(2), pp. 671~698 (1993).
11. Se-Moon Park, Jong-Kil Park, Jong-Bin Kim, Sang-Woon Shin, and Myung-Chan Lee, "Development of the Pilot System for Radioactive Laundry Waste Treatment Using UV Photo-Oxidation Process and Reverse Osmosis Membrane", *J. Korean Nuc. Soc.*, Vol. 31, No. 5, pp.506-511 (1999).
12. Se-Moon Park, Jong-Bin Kim, Eun-Jung Park, and Myung-Chan Lee, "Comparative Study on the Organic Removal Effect in Liquid Radwaste between the Two Different Type of UV Lamps for UV Photo-Oxidation Degradation Process", *Proceedings of International Symposium on Radiation Safety Management '99*, pp. 359-367 (1999).