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Removal of Dissolved Oxygen from the Make-up Water of NPP Using Membrane-based Oxygen Removal System

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Abstract

Corrosion control, in the end-shield cooling system of Wolsung Nuclear Power Plant, is directly related to the control of dissolved oxygen (DO). The current method, being used to deoxygenate the end-shield cooling water, is a chemical treatment by addition of reducing agent, hydrazine, to react with DO. This method has several limitations including high reaction temperature of hydrazine, unwanted explosive hydrogen gas production, and its intrinsic harmful property. A new approach to remove DO using a membrane-based oxygen removal system (MORS) was tried to overcome limitations of the hydrazine treatment. The DO removal efficiency of the MORS was found to be in the range 87% to 98%: The higher vacuum, the lower water flow rate and the higher water temperature tend to increase the DO removal efficiency.

Key Words : dissolved oxygen, corrosion, hydrazine, membrane-based oxygen removal system, deoxygenation

1. Introduction

Dissolved oxygen, which causes corrosion on the surface of the materials, is one of the items that should be carefully monitored and controled in nuclear power plants. For corroding metals, the metal is oxidized by the anodic reaction to form soluble metal ion. The cathodic reduction reactions significant to corrosion are few in number: The reduction of hydrogen ions in acid solution, the reduction of an oxidized ion and the reduction of dissolved oxygen in solution. The principles and mechanisms of corrosion are described in details [1]. The current methods for DO control are either chemical or mechanical treatments [2]. The hydrazine treatment is one of the chemical methods and being used to remove DO from the end-shield cooling water. Hydrazine reacts with dissolved oxygen to form water and nitrogen and further unreacted hydrazine decomposes to produce ammonia, nitrogen and hydrogen at high temperature. The advantage of using hydrazine is its inert reaction products of water, nitrogen and the useful decomposition product ammonia which raises the pH in the coolants. However, Hydrazine has limitations due to slow reaction with oxygen at low temperature, unwanted explosive hydrogen gas production by decomposition and its intrinsic harmful property [3]. Although the catalytic oxygen removal method [4-6] has been also widely used, it uses explosive hydrogen gas or hazardous hydrazine as reducing agent too. This system has been installed at Kori Nuclear Power Plant and effectively removed DO from the make-up water [6].

The membrane-based oxygen removal method is a new technology for removing DO from the water and has been adopted to prepare the deoxygenated water used in the semiconductor and power plant. The membrane contactors work under the same principles as the conventional vacuum towers. However the membrane contactor has an order of magnitude greater surface area compared to vacuum towers, which means smaller size of the membrane contactor [7-10]. The MORS has some advantages including its modular design, high efficiency, ease of operation, minimal space requirement, no chemicals requirement and low instrumentation cost.

An experimental LOOP system was designed based on this new technology and the oxygen removal efficiency of the membrane contactor was measured as a function of water flow rate, temperature, degree of vacuum and degassing time. The MORS based on the experimental results was designed for the removal of DO from the make-up water of the end-shield cooling system of Wolsung unit #1. In this paper the data obtained on the experimental LOOP system and the performance test of the MORS are presented.

2. Experimental

The oxygen removal efficiency of the membrane contactor (Hoechst Celanese Corp.)

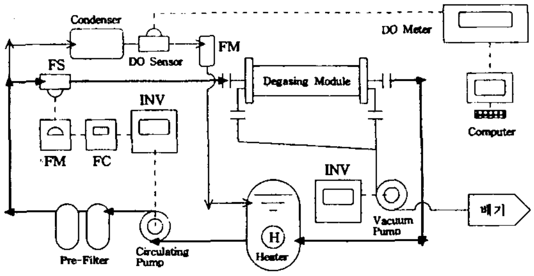

Fig. 1. Schematic Diagram of an Experimental LOOP System

was measured by changing water flow rate, temperature, degree of vacuum and degassing time using an experimental LOOP system shown in Figure 1. The membrane contactor used is approximately 4 inches in diameter and 28 inches in length. The maximum capacity of the 4-inch-diameter contactor is about 114 l /min [8,9]. The water flow rate was controled at 10, 20 and 30 l /min by changing the speed of a feed pump connected to a controller (KONICS EC-5500) coupled to a flow sensor (SIGNET 3-2533-PO). The LOOP experiments were conducted at 20, 30, 40 and 50℃. The degree of vacuum was changed from 0 to -740 mmHg using a liquid ring pump (NIKUNI 20SKSD-04). The dissolved oxygen concentration was measured using an on-line monitoring electrochemical sensor coupled to a digital DO analyzer (Orbisphere Model 3600). The sample is introduced at 200ml/min to the sensor by means of 1/4″ stainless steel tubing leading into flow chamber. The temperature of sample was kept constant at *ca.* 20℃ by a condenser equipped with an chiller (JEIO TECH, RBC-10) before introducing to the sensor. The measuring data were transferred to a computer via RS-232 output and further analyzed. The storage tank of the LOOP system has 130 l of deionized water and was under nitrogen gas atmosphere.

In the performance test of the MORS, the storage tank has 100 *l* of deionized water and was opened in atmosphere. The water was circulated at the flow rate of 5 and 12 m^3/hr by a feed pump (GROUNDFOS CRN8-20). The dissolved oxygen concentration in the tank was kept constant in the amount of equilibrium value which was carried out by being dissolved from atmosphere and by being removed from the membrane contactor. The equilibrium values were dependent on the circulating flow rate. The untreated DO concentration, which is the same with the equilibrium value, was measured before the membrane contactor and the treated DO right after the membrane contactor.

3. Results and Discussion

3.1. Efficiency Tests of the Experimental LOOP System

The details of the principles of DO removal by the membrane contactor were described else where [7-11]. The membrane contactor possesses thousands of hydrophobic hollow fiber tubules which have small pores (0.03㎛) on the wall. At these pores, the gaseous phase will be in direct contact with the liquid phase without dispersing one phase into the other. The dissolved oxygen can be removed from the water by lowering the partial pressure of oxygen in the gas phase in contact with the liquid phase [12]. These can be achieved by appling the vacuum to the gas phase of the membrane (vacuum mode) or by introducing nitrogen gas into the gas phase (sweep gas mode). In this work, the vacuum mode was used.

The oxygen removal efficiency was calculated by equation (1) with the untreated oxygen concentration ($[DO]_{in}$) which was measured before introducing into the membrane contactor and with the treated oxygen concentration ($[DO]_{out}$) which

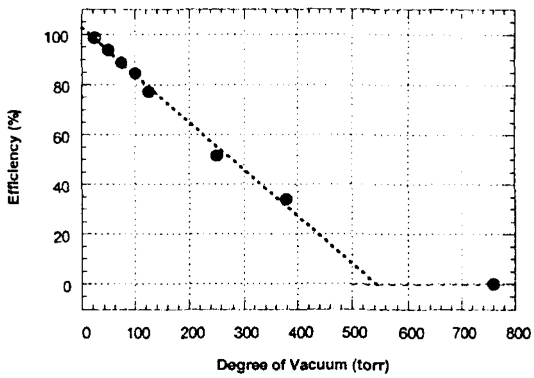

Fig. 2. Plot Showing the Effect of Degree of Vacuum on the DO Removal Efficiency: Water Flow Rate = 15 *l* /min and Water Temperature = 20℃

was measured right after the membrane contactor.

$$\mathrm{Eff.}(\%) = ([DO]_{in} - [DO]_{out}) \times 100/[DO]_{in} \quad (1)$$

Figure 2 shows the effects of vacuum on the efficiency of the membrane contactor. This was carried out at constant water flow rate and temperature of 15 *l* /min and 20℃, respectively. There was a linear relationship between the vacuum and DO removal efficiency. The minimum practically achievable vacuum pressure using the experimental LOOP system was 20 mmHg absolute and the DO removal efficiency was 99.7% at this vacuum. The higher degree of vacuum, the more increased DO removal efficiency. This plot demonstrates that small leakage from the atmosphere may deeply influence on the efficiency. Therefore, it is recommended that specially designed vacuum fittings or flanged connections be used in vacuum piping connection.

The DO removal performance of the LOOP system was determined as a function of water flow rate at constant vacuum and temperature, and its result shown in Figure 3. The inlet DO

Table 1. The Data Obtained on the Performance Test of the MORS by Two Operational Conditions in a Series ($5m^3/h$) and a Parallel ($12m^3/h$) Configurations

25℃	$5m^3/h$	20 torr			25℃	$12\ m^3/h$	20 torr		
Test #	Eff.calc.	$[DO]_{in}$	$[DO]_{out}$	Eff.obsd.	Test #	Eff.calc.	$[DO]_{in}$	$[DO]_{out}$	Eff.obsd.
1		380	8.7	97.6	1		1620	211	87.0
2		350	9.2	97.4	2		1620	209	87.1
3	97.7±0.8	360	8.9	97.5	3	87.7±2.7	1620	205	87.3
4		360	8.6	97.6	4		1610	201	87.5
5		370	8.1	97.8	5		1610	202	87.5
Average				97.6±0.1	Average				87.3±0.2

49℃	$5\ m^3/h$	70 torr			49℃	$12\ m^3/h$	70 torr		
Test #	Eff.calc.	$[DO]_{in}$	$[DO]_{out}$	Eff.obsd.	Test #	Eff.calc.	$[DO]_{in}$	$[DO]_{out}$	Eff.obsd.
1		370	7.4	98.0	1		1200	76	93.7
2		400	8.1	98.0	2		1150	63	94.5
3	99.0±1.0	380	7.6	98.0	3	95.2±1.6	1200	59	95.1
4		395	7.5	98.1	4		1100	68	93.8
5		410	7.3	98.2	5		1150	65	94.3
Average				98.1±0.1	Average				94.3±0.6

where, Eff. obsd.(%) = $([DO]_{in} - [DO]_{out}) \times 100/[DO]_{in}$

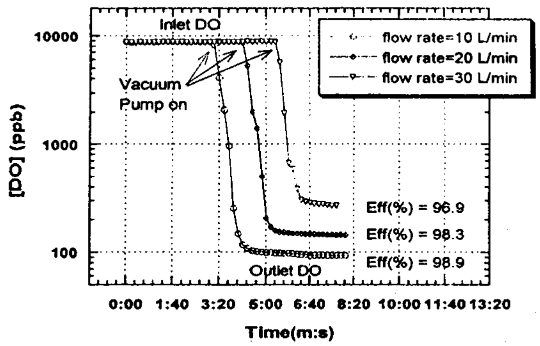

Fig. 3. Plots Showing the Effect of Water Flow Rate on the DO Removal Efficiency: Degree of Vacuum = 20 torr and Water Temperature = 20℃

was measured after membrane contactor under no vacuum for 3 to 5 min. and the outlet DO was measured as the same method but under 20 mmHg absolute pressure. The inlet DO of 7,300 ppb was removed up to 81 ppb by the membrane contactor at the water flow rate of 10 l /min, which means 98.9% DO removal efficiency. Figure 3 shows that the DO removal efficiency is increasing by lowering the water flow rate. This is accompanied by the increased mass transfer in the lowered flow rate [7-10]. This membrane contactor can approximately remove DO 87% in its design flow rate of 6 m^3/h (see Table 1).

The oxygen removal efficiency of the membrane contactor are deeply influenced on the water

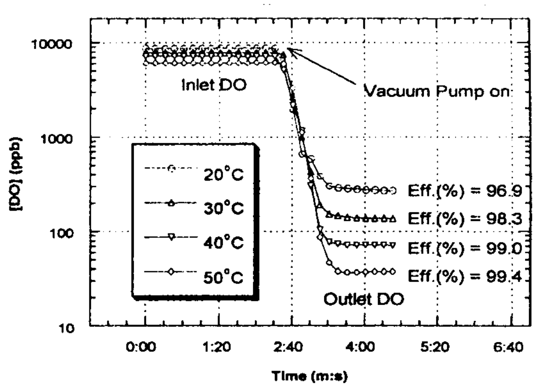

Fig. 4. Plots Showing the Effect of Water Temperature on the DO Removal Efficiency: Water Flow Rate = 30 *l* /min

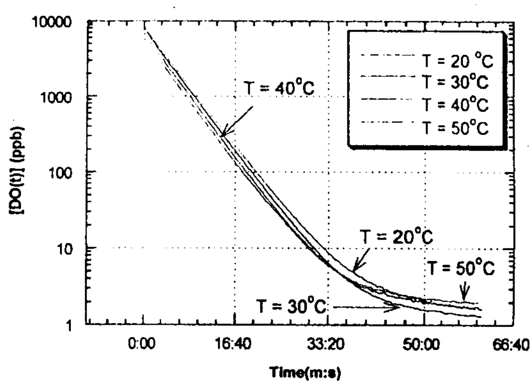

Fig. 5. Plots Showing the Change of DO Concentration with the Treated Time: Water Flow Rate = 30 *l* /min and Water Temperature = 20, 30, 40 and 50℃

temperature. The dissolved oxygen can be effectively removed when the vacuum level approaches near the vapor pressure of water, which depends on the water temperature. The mobility of oxygen in water is more increased at higher temperature. Oxygen removal performance is given in Figure 4 at various temperature. The degree of the vacuum was decreased from 20 to 60 mmHg when the water temperature was increased from 20 to 50℃. However the DO removal efficiency is increased from 96.9% to 99.4% even in lowered degree of vacuum. It may be explained by lowered partial pressure of oxygen in the gas phase caused by increased water vapour pressure. In the condition temperature of 50℃ which is similar to the end-shield cooling water of Wolsung NPP, the inlet DO of 6,100 ppb was treated up to 38 ppb. The DO removal efficiency was calculated to be 99.4% by equation (1). It is recommended that the liquid ring vacuum pump be used due to the water vapour carryover into the vacuum line. The vacuum pump size, which will depend on the water temperature, vacuum level and water flow rate, must also be considered in the system design.

For the purpose of predicting the variation of DO in the end-shield cooling system which is a closed LOOP, the dissolved oxygen concentration was measured as a function of the treated time using the experimental LOOP system. The result are given in Figure 5. In the closed system, the dissolved oxygen concentration can be calculated by equation (2),

$$[DO]_t = [DO]_0 \times \exp\{-(W/V) \times Eff. \times t\} \quad (2)$$

where $[DO]_0$ and $[DO]_t$ are the dissolved oxygen concentration at time zero and t respectively, W is a water flow rate, V is a total volume of water and Eff. is a DO removal efficiency. The observed dissolved oxygen concentrations seem to be quite similar to the theoretical value calculated by equation (2) in the range 7,000 ppb to 100 ppb. However, large discrepancies were observed in the range 100 ppb to 1 ppb. It may be caused by leakage from the atmosphere and insufficient vacuum pump size for the large vapour load.

3.2. Performance Tests of the MORS

For the purpose of removing the DO from the make-up water of the end-shield cooling system, the MORS was designed based on the experience obtained on the experimental LOOP system. The MORS consists of two membrane contactors and can be operated in a two series configuration or a two in parallel configuration. The plant's make-up water can be deoxygenated at the water flow rate up to 6 m^3/h in a series operation and 12 m^3/h in a parallel operation using this MORS. The performance test of the MORS was carried out with the end-shield cooling water of Wolsung NPP. The test was conducted each five times at the water temperature of 25 ± 2℃ and 50 ± 2℃ and the water flow rate of 5 m^3/h and 12 m^3/h. The results are shown in Table 1. In a series operation at 50℃, the inlet untreated DO of 400 ppb was removed to 8 ppb which gives to 98% of DO removal efficiency. In a parallel operation at 50℃, the inlet untreated DO of 1,150 ppb was lowered to 65 ppb which corresponds to 94% of DO removal efficiency. The better DO removal requirement, the more membrane contactors in series are needed. The result were found to be in good agreement with those of the experimental LOOP test and the theoretical values calculated by the Liqui-Cel® contactor sizing program for oxygen removal.

4. Conclusions

The membrane-based oxygen removal system was applied to remove dissolved oxygen from the plant's make-up water. The oxygen removal efficiency was affected by the vacuum, the water flow rate and the water temperature. The MORS for removal of DO from the make-up water of NPP can be operated in a series and parallel configurations with two membrane contactors. The DO removal efficiency was found to be in the range 87% to 98% at various experimental conditions. Based on the equation (2) including the input parameter of 98% DO removal efficiency, an initial DO 8,500 ppb, the water flow rate of 5 m^3/hr and the total volume of 5 m^3, the DO of 25 ppb will be obtained after about 6 hours. In order to remove dissolved oxygen from the end-shield cooling water of Wolsung NPP which its total volume is 567 m^3, the high flow rate MORS is needed. Such system is being designed and will be installed in near future.

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