

The Effect of Operation Condition on the Efficiency of the Catalytic Reduction of Dissolved Oxygen.

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ABSTRACT

In this paper, the catalytic reduction for removal of dissolved Oxygen in water has been performed to investigate the effect of operation condition on the efficiency of this method. Various experiments are implemented at different pressures, temperatures and flow rates of water to obtain the optimum conditions for the catalytic reduction. It is shown that the advantage of this process is its operation at moderate temperature and low pressure. Results show that increasing the water flow rate at low inlet oxygen levels, increases the efficiency of the process.

INTRODUCTION

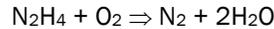
Many equipment, in particular steam generators of power reactors and water cooled stator windings in turbine generators, suffer from various forms of corrosion induced by the presence of dissolved Oxygen [1]. Removal of dissolved Oxygen (DO) from water is a necessary process in many industries including pharmaceutical, food, power and semiconductor. Acceptable levels of DO vary depending on the intended use of the water; in the power industry, for example, removal of DO is necessary to prevent corrosion in boilers and pipes, and levels of around 5 ppm are necessary. In comparison, ultrapure water, as used in the washing of silicon wafers in the semiconductor industry, is perhaps the most demanding in terms of DO level with some applications requiring extremely low DO levels of around 0.1 ppb [2, 3].

Dissolved Oxygen can be removed from water using a variety of methods broadly grouped into chemical, physical and hybrid systems, which make use of a combination of these methods. Physical methods used including thermal degassing, vacuum degassing or nitrogen bubble deaerations are traditionally carried out in packed towers. Disadvantages with these methods include high operating costs and a small surface area per unit volume. Using these physical methods, it is difficult to reduce the DO concentration from mg/L to µg/L levels. Physical methods have inherent deficiencies of being bulky, costly and inflexible in operation [4]. Recently, hollow fiber membrane contactor with high efficiency and some other advantages have been utilized to remove dissolved Oxygen but their use is still not common [5]. Chemical methods such as the use of sodium sulphite hydrazine, carbohydrazide, β-ketogluconate, and gallic acid or catalytic reduction offer a significant disadvantage in that a further, often toxic, impurity is introduced into the system [6, 7].

Sodium sulfite is another agent for Oxygen removal available in the industry which accounts for its use in low pressure systems. Using Sodium Sulfite at high pressure causes two problems. At first, the consumption of this agent

increases solids in the circulating boiler system where the controlling of this parameter at proper range is much important. Second, at high pressure boilers, Sodium sulfite breaks down to form Sulfur dioxide or Hydrogen Sulfide those both are corrosive gases which leave the boiler with steam resulting in low pH steam and condensate and cause the corrosion throughout the system.

Hydrazine (N₂H₄) is a powerful reducing agent that reacts with dissolved Oxygen to form nitrogen and water as follows:



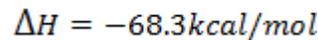
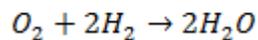
At high temperature and pressure, ammonia is also formed, which increases the feedwater pH level and reducing the risk of acidic corrosion. Hydrazine also reacts with soft haematite layers on the boiler tubes and forms a hard magnetite layer, which subsequently protects the boiler tubes from further corrosion. This occurs as a result of the chemical reaction:



Thus in order to reduce or remove the Ammonia, the injection of hydrazine should be reduced or stopped. Recently use of Hydrogen in the presence of catalyst becomes an attractive method; catalytically recombining the dissolved Oxygen with Hydrogen to form water is an attractive method, as it produces no byproduct [8,9]. Also, the catalytic method can reduce Oxygen levels below one part per billion [10]. In this study removal of dissolved Oxygen in water through reduction catalytic method, is investigated. Also the operation condition such as temperature, pressure and flow rate of water is studied on the efficiency of the catalytic reduction of dissolved Oxygen.

MATERIALS AND METHODS

In the process of catalytic reduction of dissolved Oxygen, Hydrogen and Oxygen react in the presence of a catalyst to produce water:



The production of reaction is water that has no adverse effect on the system. An experimental setup was constructed to investigate the effective parameters in the catalytic reduction of dissolved Oxygen. Figure (1) shows the overview of this process. Water is pumped from the water tank to the Hydrogen/water mixer. The mixer is a concurrent gas-liquid upflow packed bed. The water saturated both with Oxygen and Hydrogen then enters the catalytic resin vessel where the Hydrogen and Oxygen react in presence of the catalyst. The reaction is catalyzed using 1.5 liter of K6333 resin catalyst (Lanxess Co. [11]). All results have been obtained under the following conditions:

- Operating pressure: 2- 3 bar
- For determination of remaining Oxygen in the product, used of ASTM D888-81
- Hydrogen gas with 99.99% purity

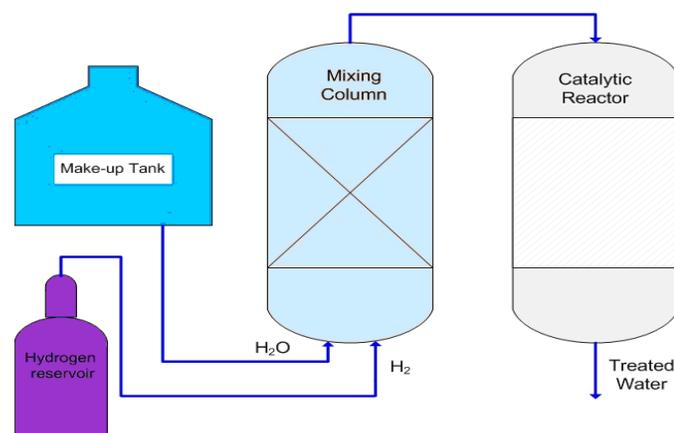


Figure 1: Overview catalytic process to remove dissolved Oxygen

RESULTS AND DISCUSSION

Effect of Temperature and Pressure

In order to achieve optimum operation condition, various experiments are implemented at different pressures and temperatures. As shown in Tables (1) and (2) and Figure (2) the proper temperature range for this system is between 10-50 °C. At temperature lower than 10 °C, the efficiency and the absorption of Oxygen would be reduced. This is due to the fact that at low temperature, the reaction between Oxygen and Hydrogen is no more possible and the catalyst is not able to accelerate this reaction. In other hand further increase in temperature upper than 50 °C may cause damage in the catalyst.

Table 1: remaining Oxygen at various temperatures

Efficiency %	Remaining dissolved Oxygen (ppb)	Water flow rate (lit/hr)	Hydrogen Injection Pressure (bar)	Mixing Column Pressure (bar)	Mixing Column Temperature (°c)	Catalytic Reactor Temperature (°c)	Inlet Dissolved Oxygen (ppm)	Sampling Time (min)
99	60	120	2.5	2	10	10	7.8	25
99.6	20	120	2.5	1.8	10	10	7.6	30
99.8	8	120	2.5	1.8	15	15	7.7	45
99.9	4	120	2.5	1.9	20	20	7.9	55
99.9	2	120	2.5	2.1	30	30	7.8	60
99.9	2	120	2.5	2	40	30	7.7	65

Table 2: Remaining Oxygen at moderate temperature (Residence time: 45s)

Efficiency %	Remaining dissolved Oxygen (ppb)	Water flow rate (lit/hr)	Hydrogen Injection Pressure (bar)	Mixing Column Pressure (bar)	Mixing Column Temperature (°c)	Catalytic Reactor Temperature (°c)	Inlet Dissolved Oxygen (ppm)	Sampling Time (min)
99.4	40	120	2.5	1.9	18	18	7.5	20
99.8	14	120	2.5	2	19	19	7.6	25
99.9	6	120	2.5	1.8	18	18	7.7	30
99.9	2	120	2.5	1.8	19	19	7.8	40
99.9	2	120	2.5	1.9	20	20	7.6	45
99.9	2	120	2.5	2	21	21	7.8	50

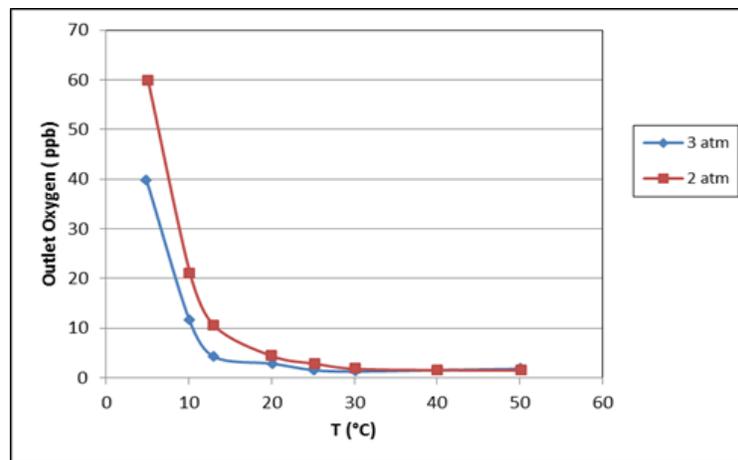


Figure 2: The effect of temperature on outlet Oxygen

Also as can be seen in Tables (3) and (4) and Figure (3), the appropriate pressure range for this process is between 1.7-3atm. As previously described the solution of Hydrogen in water is a function of the pressure based on Henry's law. The Henry constant for Hydrogen solution is ($7.07 \times 10^4 \text{ atm}\cdot\text{mol H}_2\text{O}/\text{mol H}_2$ (25 °C)), therefore the solution of this gas in water take places slowly, Indicating that the minimum pressure required to maintain the process in a liquid phase. These results also show that at upper temperatures, the pressure should be higher than that at low temperatures. Anyway the increase of Hydrogen solution with pressure results in the system efficiency improvement.

Table 3: Remaining Oxygen at 10 °C and different pressures (Residence time: 45s)

Efficiency %	Remaining dissolved Oxygen (ppb)	Water flow rate (lit/hr)	Hydrogen Injection Pressure (bar)	Mixing Column Pressure (bar)	Catalytic Reactor Pressure (°c) (bar)	Mixing Column Temperature (°c)	Catalytic Reactor Temperature (°c)	Inlet Dissolved Oxygen (ppm)	Sampling Time (min)
0	7900	120	1.5	1	1	10	10	7.9	0
73.7	2000	120	2	1.5	1.5	10	10	7.6	20
98.7	100	120	2.5	2	2	10	10	7.8	30
99.3	50	120	3	2.5	2.5	10	10	7.5	40
99.6	30	120	3.5	2	2	10	10	7.6	50
99.98	8	120	4	3.5	3.5	10	10	7.7	60

Table 4: Remaining Oxygen at 20 °C and different pressures (Residence time: 45s)

Efficiency %	Remaining dissolved Oxygen (ppb)	Water flow rate (lit/hr)	Hydrogen Injection Pressure (bar)	Mixing Column Pressure (bar)	Catalytic Reactor Pressure (°c) (bar)	Mixing Column Temperature (°c)	Catalytic Reactor Temperature (°c)	Inlet Dissolved Oxygen (ppm)	Sampling Time (min)
0	8000	120	1.5	1	1	20	20	8	0
98.7	100	120	2	1.5	1.5	20	20	7.7	20
99.8	8	120	2.5	2	2	20	20	7.7	30
99.9	4	120	3	2.5	2.5	20	20	7.9	40
99.97	2	120	3.5	3	3	20	20	7.8	50
99.97	2	120	4	3.5	3.5	20	20	7.8	60

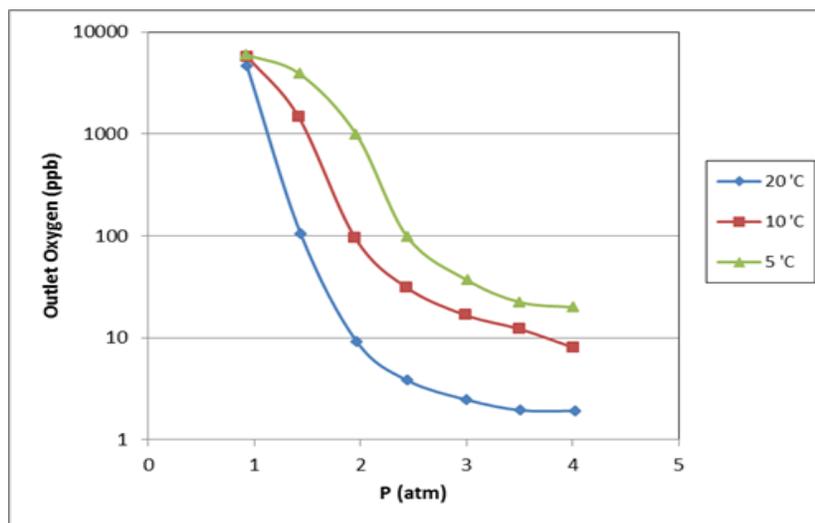


Figure 3: The effect of pressure on outlet Oxygen

Effect of water flow rate

Other experiments are implemented to illustrate the effect of water flow rate. At first, the inlet Oxygen level is reduced while other parameters are remained constant. The results shown in Table (5) indicate that in this case the remaining Oxygen is not upper than the limited level when the water flow rate is 120 lit/hr. In other experiment the water flow rate would be 240 lit/hr and other parameters are constant. In this condition as can be seen in Table (6), it is possible to reduce dissolved Oxygen by means of increasing the water flow rate at low inlet Oxygen level. In this condition the process would be more efficient.

Table 5: The performance of system at various values of inlet Oxygen

Remaining dissolved Oxygen (ppb)	Water flow rate (lit/hr)	Hydrogen Injection Pressure (bar)	Pressure (bar)		Temperature (°C)		Inlet Dissolved Oxygen (ppm)	Sampling Time (min)	Sample No.
			Catalytic Reactor	Mixing Column	Catalytic Reactor	Mixing Column			
8	120	2	1.5	1.5	23	22	7.2	35	1
6	120	2	1.5	1.5	23	22	6.9	40	2
5	120	2	1.5	1.5	23	22	6.2	45	3
4	120	2	1.5	1.5	23	22	5.8	50	4
4	120	2	1.5	1.5	23	22	5.2	55	5
4	120	2	1.5	1.5	23	22	4.6	60	6
3	120	2	1.5	1.5	24	22	4.1	65	7
2	120	2	1.5	1.5	24	22	3.5	80	8

Table 6: The effect of increasing of water flow rate

Remaining dissolved Oxygen (ppb)	Water flow rate (lit/hr)	Hydrogen Injection Pressure (bar)	Pressure (bar)		Temperature (°C)		Inlet Dissolved Oxygen (ppm)	Sampling Time (min)	Sample No.
			Catalytic Reactor	Mixing Column	Catalytic Reactor	Mixing Column			
28>	240	2	1.5	1.5	22	22	7.2	35	1
28>	240	2	1.5	1.5	23	23	6.8	40	2
28>	240	2	1.5	1.5	23	23	6.1	45	3
28>	240	2	1.5	1.5	23	23	5.8	50	4
24>	240	2	1.5	1.5	23	23	5.1	55	5
22	240	2	1.5	1.5	23	24	4.5	60	6
16	240	2	1.5	1.5	24	24	4	65	7
10	240	2	1.5	1.5	24	25	3.5	70	8

Also the performance of system is investigated at higher level of inlet Oxygen by providing other conditions for the results of Table (6). For example when the inlet Oxygen has value of 4.5 ppm, the remaining Oxygen level is upper than limited level (22 ppb). In this case the level of inlet Oxygen and the flow rate of water are maintained constant and other conditions have been effectively changed. As shown in Table (7), the performance of system has been improved with increasing both the pressure and temperature, so the remaining Oxygen level reaches lower than 20 ppb but these changes occurs gradually and slowly. This could be explained by the fact that the pressure increasing is effective only to a certain value and further increase after that only cause the further solution of Hydrogen without any effect on the system performance. In other hand, although the increase of temperature is effective for reaction of Hydrogen and Oxygen but the increase of temperature higher than 50 has an inverse effect on Hydrogen solution in water and any increase of temperature at constant pressure results in reduction of Hydrogen solution.

Table 7: The effect of other parameters on system performance (inlet Oxygen level: 4.5 ppm)

Remaining dissolved Oxygen (ppb)	Water flow rate (lit/hr)	Hydrogen Injection Pressure (bar)	Pressure (bar)		Temperature (°C)		Inlet Dissolved Oxygen (ppm)	Sampling Time (min)	Sample No.
			Catalytic Reactor	Mixing Column	Catalytic Reactor	Mixing Column			
26	240	2	1.5	1.5	24	24	4.5	40	1
22	240	2	1.6	1.6	26	26	4.6	45	2
20	240	2	1.7	1.7	28	28	4.5	50	3
18	240	2.1	1.8	1.8	30	30	4.6	55	4
17	240	2.2	1.8	1.8	32	32	4.5	60	5
15	240	2.3	2	2	34	34	4.5	65	6
13	240	2.4	2.1	2.1	36	36	4.6	70	7
12	240	2.5	2.2	2.2	40	40	4.5	75	8

The system performance in low level of inlet Oxygen and high water flow rate

In order to investigate the system performance in low level of inlet Oxygen and high water flow rates, another experiment is implemented with the value of 1ppm of inlet Oxygen and the water flow rate of 640 lit/hr. The results listed in Table (8) show the reduction of dissolved Oxygen with time. However the residence time is reduced in both Hydrogen and catalytic towers because of increasing in water flow rate. Thus under this condition, the time is not enough for complete solution of Hydrogen and reaction with Oxygen. For example after 75 min, the remaining Oxygen is 22 ppb while the sufficient time for this reduction has obtained almost 30 min before.

Table 8: The system performance in low level of inlet Oxygen and high water flow rate

Remaining dissolved Oxygen (ppb)	Water flow rate (lit/hr)	Hydrogen Injection Pressure (bar)	Pressure (bar)		Temperature (°C)		Inlet Dissolved Oxygen (ppm)	Sampling Time (min)	Sample No.
			Catalytic Reactor	Mixing Column	Catalytic Reactor	Mixing Column			
28>	640	2	1	1	24	24	1	40	1
28>	640	2	1.1	1.1	24	24	1.1	45	2
28>	640	2	1.2	1.2	25	25	1	50	3
28>	640	2	1.3	1.3	25	25	1.1	55	4
28>	640	2	1.4	1.4	26	26	1	60	5
28	640	2	1.5	1.5	27	27	1	70	6
26	640	2	1.6	1.6	27	27	1	80	7
22	640	2	1.7	1.7	28	28	1	90	8

CONCLUSION

The operation condition is one of the most important parameters that influence the efficiency of the catalytic reduction of dissolved Oxygen. The advantage of this process is its operation at moderate temperature and low pressure. The Hydrogen pressure helps its solution in the system and prevents the formation of two phase flow after the mixing column. As shown in this paper it is possible to reduce dissolved Oxygen by increasing the water flow rate at low inlet Oxygen levels. This condition would increase the process efficiency.

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