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# The Effect of Different Parameters on the Efficiency of the Catalytic Reduction of Dissolved Oxygen

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Additional information is available at the end of the chapter

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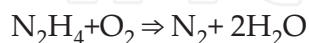
## 1. Introduction

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].

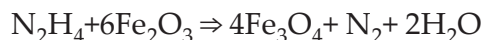
Dissolved Oxygen can be removed from water using a variety of methods broadly grouped into chemical, physical and hybrid systems, which make use of a combination of these methods. Physical methods used including thermal degassing, vacuum degassing or nitrogen bubble deaerations are traditionally carried 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  $\mu\text{g/L}$  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,  $\beta$ -ketoglucuronate, 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 faces two problems. At first, the consumption of this agent increase solids in the circulating boiler system where the controlling of this parameter at proper range is more 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 ( $N_2H_4$ ) 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, 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 is 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, was investigated. Also the operation condition such as temperature, pressure, flow rate of water, contact time and inlet dissolved Oxygen concentration was studied on the efficiency of the catalytic reduction of dissolved Oxygen. The part of the results of this work has been published in International Journal of MEJSR [11].

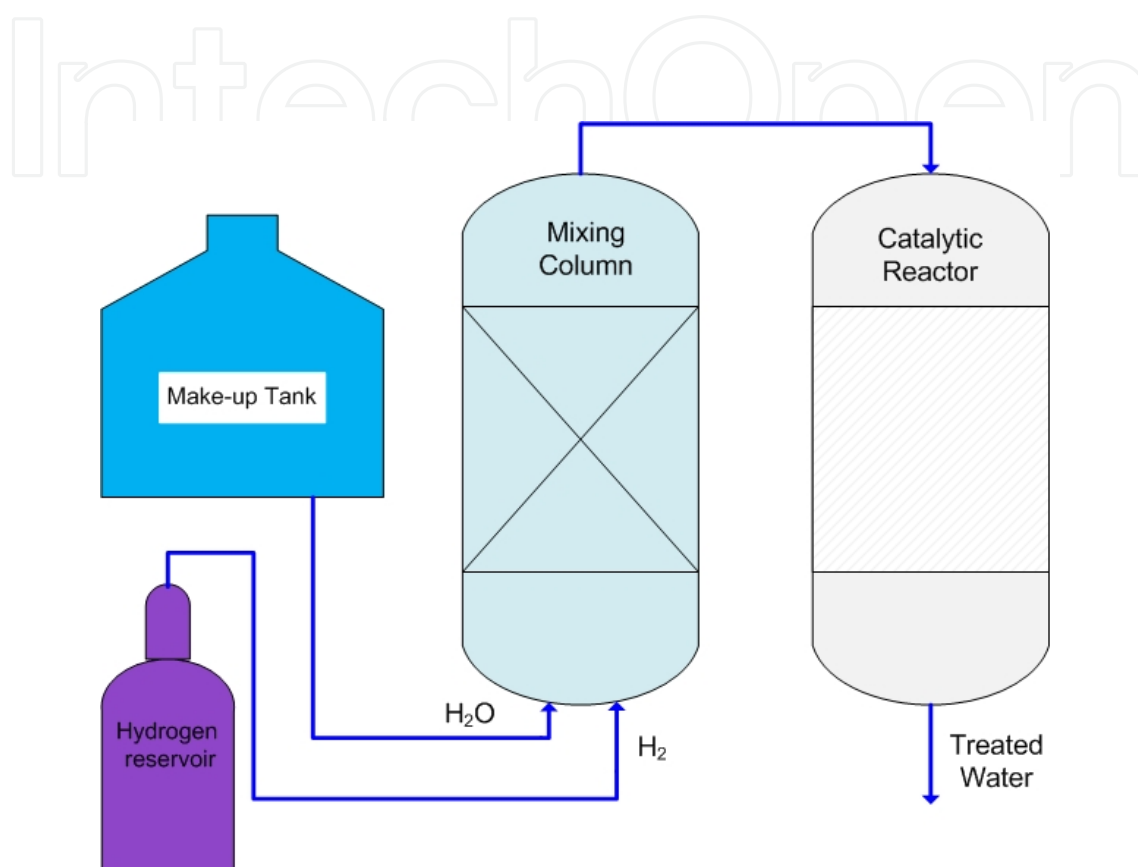
## 2. Catalytic reduction of dissolved oxygen

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. [12]). 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

### 3. Results and discussion

#### 3.1. Effect of temperature and pressure

In order to achieve optimum operation condition, various experimental is implemented at different pressures and temperatures. As shown in 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.

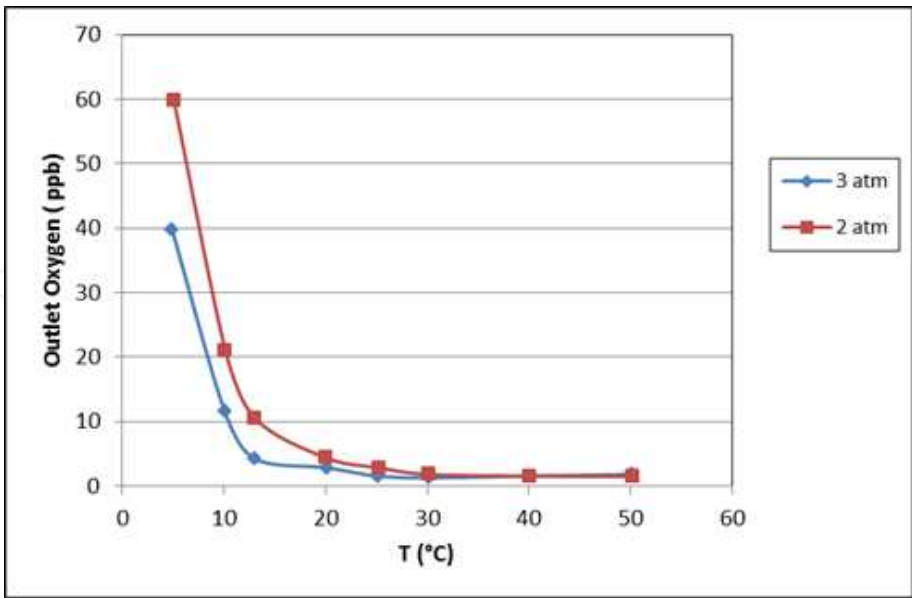


Figure 2. The effect of temperature on outlet Oxygen

Also as can be seen in Figure (3), the appropriate pressure range for this process is between 1.7-3 atm. 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 ( $7.07 \times 10^4$  atm.mo1 H<sub>2</sub>O/mo1H<sub>2</sub> (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.

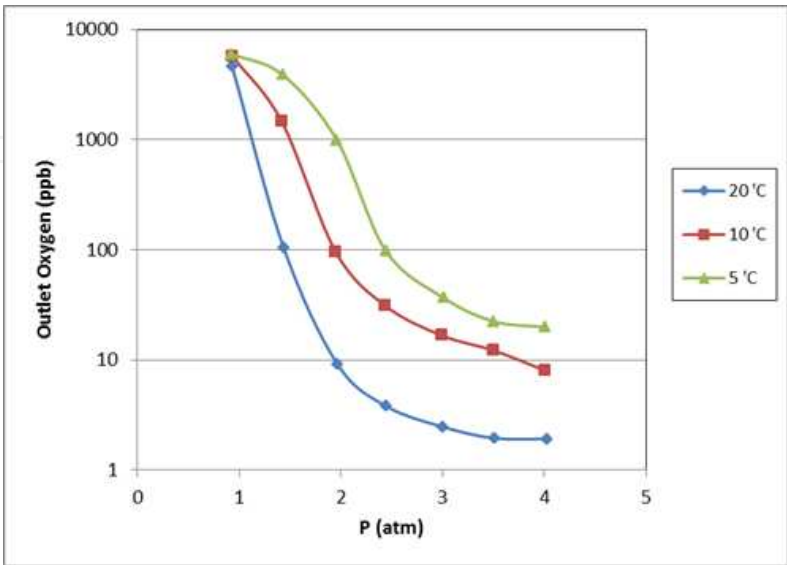


Figure 3. The effect of pressure on outlet Oxygen

### 3.2. 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 remain constant. The results shown in Table (1) 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 (2), 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.

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

**Table 1.** The performance of system at various values of inlet Oxygen

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

**Table 2.** The effect of increasing of water flow rate

Also the performance of system is investigated at higher level of inlet Oxygen by providing other condition for the results of Table (2). 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 condition have been effectively changed. As shown in Table (3), 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 occurred 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.

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

**Table 3.** The effect of other parameters on system performance (inlet Oxygen level: 4.5 ppm)

### 3.3. 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 (4) 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.



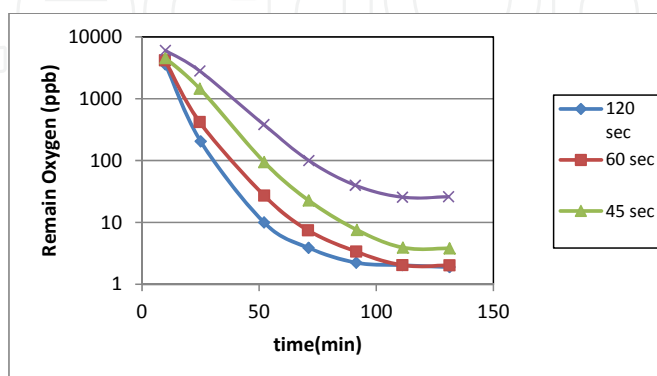
Sample No.	Sampling Time (min)	Inlet Dissolved Oxygen (ppm)	Temperature (°C)		Pressure (bar)		Hydrogen Injection Pressure (bar)	Water flow rate (lit/hr)	Remaining dissolved Oxygen (ppb)
			Mixing Column	Catalytic Reactor	Mixing Column	Catalytic Reactor			
1	40	1	24	24	1	1	2	640	28"/>
2	45	1.1	24	24	1.1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

**Table 4.** The system performance in low level of inlet Oxygen and high water flow rate

### 3.4. Effect of contact time

An important parameter to control the process is the contact time that influenced by column dimensions, volume of resin and the linear velocity of water. In fact the contact time is fluid residence time in the catalyst column in which DO on the catalyst surface reacts with Hydrogen. The results of experiments in different conditions are shown in Figure (4). In all conditions efficiency is the Oxygen absorption relative to the input of dissolved Oxygen in water.

As seen in Figure 4 in the contact time of less than 45 seconds, the decrease in dissolved Oxygen levels below 5 ppb is not possible. It is hard to reduce the dissolved Oxygen level of less than 10 ppb when the exposure time is less than 30 seconds. Therefore, the ideal time should be considered based on desired reduction of dissolved Oxygen. For use in steam power plants that dissolved Oxygen levels should be less than 5 ppb, time is at least about 45 seconds.

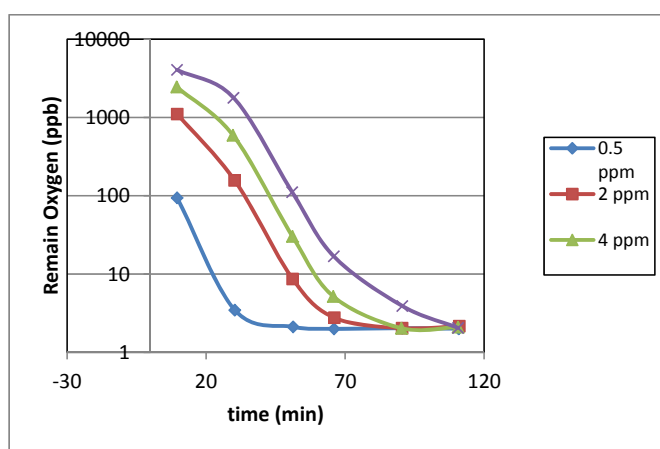


**Figure 4.** The effect of contact time on remaining Oxygen



### 3.5. Effect of inlet dissolved Oxygen concentration

The amount of dissolved Oxygen in the water inlet at the start time of the system is effective on the operating time. In other words, the time required to reach the limit concentration for the remaining Oxygen in the outlet water of the catalytic column, is influenced by the dissolved Oxygen in water input. In a fixed volume of catalyst, the less amount of dissolved Oxygen in water, a higher amount of the water flows through the catalyst bed. In this condition the desired results would be achieved and the Hydrogen injection rate would be lower. The results of experiments in different concentrations of dissolved Oxygen are shown in Figure (5). For example when the input of dissolved Oxygen is 0.5 ppm, the time needed to reach to the desired point of 5 ppb of remaining DO is short even at the contact time of 30 seconds.



**Figure 5.** The effect of different concentrations of dissolved Oxygen

## 4. Conclusion

The operation condition is one of the most important parameters that influence on the efficiency of the catalytic reduction of dissolved Oxygen. The advantage of this process is its operation at moderate temperature and low pressure. The role of pressure is helping for Hydrogen solution in the system. Also the Hydrogen pressure prevents the formation of two phase flow after the mixing column. 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.

Also, The contact time and Oxygen concentration are the most important parameters that influence on the efficiency of the catalytic reduction of dissolved Oxygen. In steam power plants that dissolved oxygen levels should be less than 5ppb, time is at least about 45 seconds. Also In a fixed volume of catalyst, at low amount of dissolved Oxygen in water inlet, it would be possible to increase water flow rate and decrease the Hydrogen injection and therefore reach to desired outlet Oxygen concentration.

## Author details

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