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The effect of HCl and H_2SO_4 injection to reverse osmosis on TDS and LSI for reducing fouling

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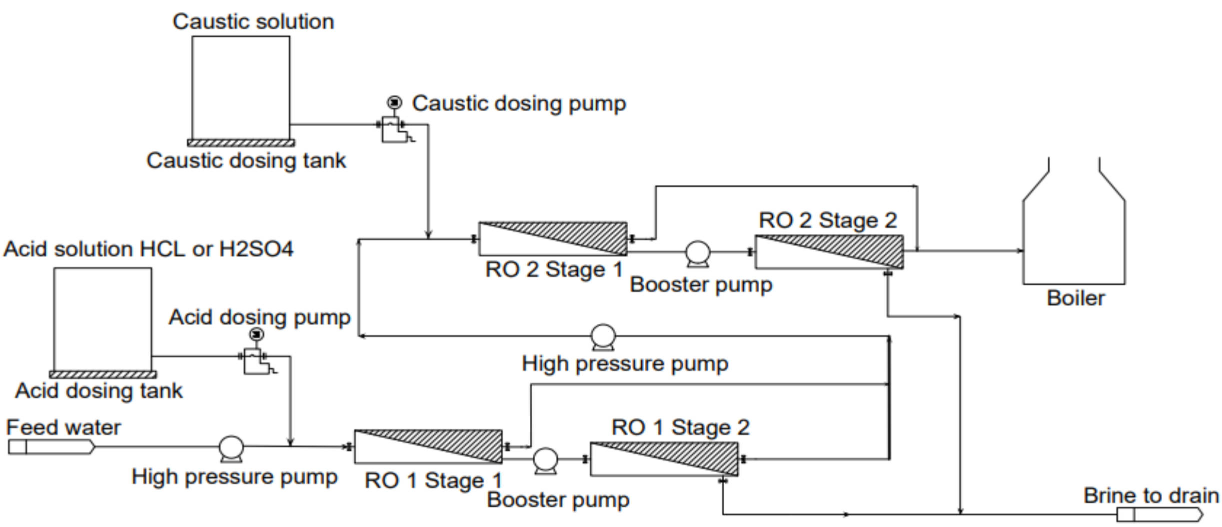
GRAPHICAL ABSTRACT



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ABSTRACT

Due to the quality of the water entering the water purifiers, sometimes the amount of solutes and hardness in the water is so high that after a short time, these systems become clogged or full. To solve this problem. Several methods have been proposed in this study, acid injection and its effect on reverse osmosis system by wave software have been investigated. To ensure the condition and accuracy of the incoming water, the necessary tests were performed through the laboratory and the condition of the water and the number of ions and its salts were reported. By injecting acid into the inlet water, the pH value was reduced from 7.58, which is the normal pH of the water, to 5 by micrograph in 0.2 intervals, and after examination, the following results were obtained: With decreasing pH, the LSI number has a suitable decrease, so that at pH 6.1 and lower, the LSI number is negative and this indicates the lack of premature fouling. However, with this reduction, the acidic property of the treated water increases and the possibility of chemical corrosion of the industrial equipment used increases, on the other hand, by injecting acid and lowering the pH, the amount of TDS increased, which should be tried in different ways to minimize this amount. In comparison between injections of two acids performed under the same conditions, the amount of TDS at the time of H_2SO_4 injection at the pH limit was 10% less than the time of HCl injection.

1. Introduction

Given the water crisis in the arid regions of the world, of Iran is no exception, using different desalination methods and efficiency of different water treatment systems, the effect of different methods and membranes on the performance of direct osmosis and reverse osmosis systems in all human societies has also been considered and each group has made an effort to optimize these methods or identify its advantages and disadvantages since the progress and health of any society depends on this divine blessing, the use of these experiences and their optimization to achieve suitable drinking water and industry is very important. In one study, different classifications of membrane sediments were organic and biological, during which polysaccharide and protein sediments were introduced as problematic sediments. Using pretreatment and coagulation systems, an attempt was made to reduce organic sediments (Amy. 2008) and then to evaluate the membrane performance in the reverse osmosis system and also to improve the membrane performance in terms of sedimentation by

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considering the amount of water, the modules were passed (Amiri and Samiei. 2007).

In another study, the reversibility of sediment and the cleaning of FO direct osmosis and reverse osmosis RO membranes without the use of chemicals were investigated. The effect of hydraulic pressure on cleaning in both cases and the rate of return of water flux (discharge) in direct and reverse systems after cleaning were investigated (Mi and Elimelech. 2010). In another study, different types of sedimentation phenomena in membrane technologies were investigated and the main sediment phenomena and their effects on blockage of membrane systems were reviewed and the problems of membranes and refining processes and their practical applications were addressed (Guo et al. 2012). In a systematic study of colloidal organic sediments in FO forward osmosis systems under chemical conditions (pH and calcium ion concentration) was investigated by applying hydraulic pressure to the feed side and finally, after comparing RO and FO systems, researchers observed less sedimentation tendency in FO systems (Kim Y et al.2014). In a study using four stages of work, Stillwell SA and Webber ME were able to achieve 95% recovery and optimal water quality for drinking (Stillwell and Webber. 2016). Using the reverse osmosis method and simulation by HYDRANAUTICS software, Aghababaei N. tried to purify the Persian Gulf water for drinking in Bandar Abbas city, which achieved the following parameters by RO system efficiency at 1.2MPa pressure SO_4^{2-}=88.49%, TDS=61.42%, CL^-=70.34 and Na^+=50.85 (Aghababaei. 2017).

In another article, researchers examined the effect of TDS on the taste of drinking water. They with different tests performed with different TDS of water and special mineral compounds to change the amount of TDS on different people. Therfore the relationship between people's favorite water taste and TDS was discussed (Devesa and Dietrich. 2018). Yao W and et al discussed the effect of water quality used in fumigation systems (air humidification) on the amount of mass and sediment created in the human respiratory system at different ages. They find that the use of purified water in these devices is more suitable for the human body (Yao et al.2020).

In another study, water purification and desalination were investigated using the reverse osmosis method, this study and simulation were performed by ROSA - 72 software, which succeeded in purifying raw groundwater with TDS 1570-2910 mg/lit and its specific characteristics to drinking water with TDS 39.41 mg/lit, in this paper, the pressure is 7.91 bar and the membrane surface is 2.6 m^2 with 15% recovery (Abbas and Ahmed.2020).

Another study in Southern California examined the removal of TDS from tap water by boiling water, the addition of sodium bicarbonate, and electrolysis, which reduced TDS and provided the right flavored drinking water (Wang. 2021). In a new research about boiler feed water treatment using reverse osmosis and ion exchange which led to the proper supply of water to the boilers (Asadi et al. 2021).

In the present study, the effect of injection of HCL and H_2SO_4 acids in the pH range of the inlet water under test to pH5 with 0.2 micrograph of the reverse osmosis water treatment process on the amount of module fouling (by examining the LSI parameter) and TDS of the outlet water Its construction for operation in various industries with an emphasis on use in boilers and boilers. In this study, WAVE software has been used to simulate the desired reverse osmosis system.

2. Materials and methods

Due to the existence of many problems in RO systems such as blockages or foulings, in this study, an attempt has been made to solve this problem by using HCL and H_2SO_4 acids, due to the addition of acid to water, we face the problem of increasing the TDS of water when the problem of providing pristine water or water with very low difficulty is raised, this increase in TDS, although insignificant, is of vital importance, so in this study, the rate of increase in TDS when using acids and the problem of fouling of RO systems will be controlled, therefore, first, the types of possible foulings in the RO system are described and the ways to solve this problem are initially suggested, and then the use of acid in these systems is specifically addressed and examined.

Types of fouling in the RO system are, fouling by colloidal and organic compounds: This fouling contains the basic elements, the origin of this fouling is TSS and NTU. fouling by mineral compounds (scaling): This fouling involves the end elements and is caused by uncontrolled hardness entering the RO system. Biological fouling: This type of fouling accidentally engages the elements and can occur on any of the elements, it is mostly observed on the primary elements. Its source is the presence of microorganisms in drinking water. Due to the ability of microorganisms to multiply, if there is a small amount in the incoming water, it can cause many problems in our elements.

Scaling

Scaling is the same as the foulings obtained by mineral compounds in the system and usually involves the end elements. The source of this problem is the presence of uncontrolled water hardness in the feed water.

Measurement of scaling potential

Measurement of the concentration of precipitating compounds should be performed during the concentrate rejection of the RO system, the temperature of the feed water affects the intensity and potential of scaling. Due to the temperature difference of 10-15 8C during the year, if the antiscalant is used, the dose of antiscalant injection will change. Salinity (TDS) has a great effect on the scaling potential of the system. pH also has a strong effect on the scaling of the system.

In this study, water treatment systems are classified into two categories: SWRO (seawater treatment) and BWRO (flow water treatment in a BRAKISH WATER) system. It should be noted that in SWRO systems, due to the abundance of water and salinity and high ion concentration, purification systems with low recovery are used, in BWRO systems, due to the amount of water available and lower relative salinity than seawater, efforts are made to create higher recovery.

The compounds in seawater help reduce the intensity of scaling. If the recovery is not higher than 50% and the pH is not higher than 8.6, SW systems do not need to control the scaling (the scaling is so low that the CIP solves this problem every six months).

Scaling control methods are: Acid injection, antiscalant injection, hardening resin (IX), and nanofiltration (NF) which are not suitable for systems with TDS> 4000 or in other words not recommended for marine systems. It is also possible to reduce scaling by reducing the system recovery percentage.

One of the methods to control the skilling argument that will be examined in this study is the discussion of adding acid to the incoming water (FEED).

Acid injection

The most common surface water and groundwater are almost saturated concerning $CaCO_3$. The solubility of $CaCO_3$ depends on the pH and is observed by the following equation: (FILMTEC Reverse osmosis Membranes Technical Manual, version 8,2021).

$$\mathrm{Ca^{2+} + HCO_3^{2-} \rightarrow H^+ + CaCO_3} \quad (1)$$

Therefore, by adding H^+ as the acid in the equation, it can be tilted to the left and keep the calcium carbonate in a dissolved state. The acid used must be qualitatively suitable for use in eating and drinking (FOOD GRADE). Sulfuric acid is more readily available and more readily available than hydrochloric acid in many countries, but on the other hand, additive sulfate is added to the feed stream. This may put the sulfate deposit in a critical state.

Concentrated $CaCO_3$ in the sedimentation stream should have a tendency to dissolve, expressed by the Langelier Saturation Index (LSI) for brackish water and the Stability Index (S & DSI) for seawater. At saturated pH (pHs) water is in equilibrium with $CaCO_3$ The definition of LSI and S & DSL is as follows:

$$\mathrm{LSI = pH - pHs} \quad \text{(TDS<10000 mg/lit)} \quad (2)$$

$$S\&DSI = pH - pHsS\&DSI \quad \text{(TDS>10000 mg/lit)} \quad (3)$$

The pHs calculation methods are different for LSI and S & DSI.

To control the deposition of calcium carbonate should only be negative by adding acid, LSI, and S & DSI to the concentrated stream.

Adding acid is only useful for controlling carbonate deposition.

LSI parameter:(Langelier Saturation Index)

The problem occurs due to the calcium ions in the water that combine with HCO_3^- to form $CaCO_3$ and H^+ according to the following reaction

$$\mathrm{Ca^{2+} + HCO_3^{2-} \rightarrow H^+ + CaCO_3}$$

Equilibrium reactions occur when ions move from a low concentration to a high concentration when the concentration rises in one direction. If we want the reaction to go in such a way that the ions do not remain as ions and the $CaCO_3$ compound is formed, we have to increase the concentration to the right of the equation and one of these ways is to inject acid into the medium. One should always try to consider the LSI parameter negative.

$$LSI = pH - pHs$$

$$pHs = (9.3 + A + B) - (C + D) \quad (4)$$

pHs: The pH at which saturation occurs and calcium carbonate is formed and precipitated.

$$A = (\mathrm{Log10[TDS]} - 1)/10 \quad (5)$$

$$B = 13.12 * \mathrm{Log10}(°C + 273) + 34.55 \quad (6)$$

$$C = \mathrm{Log10}[Ca^{2+} \mathrm{as}\ CaCO_3] - 0.4 \quad (7)$$

$$D = Log10[alkalinity\ as\ CaCO_3] \quad (8)$$

This parameter is valid for TDS <4000 mg / L and is used for BW waters. This parameter is defined in SW waters as the Stiff & Davis Stability Index.

S & DSI parameter (Stiff & Davis Stability Inde):

$$S\&DSL = pH - PCa - PAlk - K \quad (9)$$

It should be noted that design software calculates these parameters and they can be used. These two parameters show only the deposition of calcium carbonate. It should be noted that these parameters should be negative to prevent calcium carbonate. In this study, using a reverse osmosis system that has two passes and each pass has two stages and its performance will be examined by simulated wave software, this system to supply water used in boilers or boilers Used, due to the amount of LSI in pass 1 at the time of design, which indicates fouling in the system performance, acid is injected into the incoming water to reduce this parameter and finally reduce it to reduce fouling. In this study, the injection of two acids, HCL (hydrochloric acid) and H_2SO_4 (sulfuric acid) is used and its effect and performance in each stage (each PASS) will be investigated. It should be noted that the injection dose was selected in such a way that the range 5 <pH <7.57 with a micrograph of 0.2 for the incoming water (FEED WATER) is obtained. This injection is done evenly by dousing pump.

3. Results and discussion

In this paper, the methods of water supply required for industrial systems such as boilers are investigated using WAVE software with acid injection method, The amount of water required for the boiler inlet in this study is 600 m^3/day, as well as the parameters and composition of the inlet water type of surface water, which has been reported by laboratory study as Table 1.

Table 1. Characteristics of feed water.

Parameter	Water	Unit
Electrical Conductivity (EC)	1.20	dS/m
pH	7.58	---
Total Dissolved Solids (TDS)	768	mg/lL
Non-Carbonate Alkalinity	0.30	meq/L
Carbonate Ion Concentration /co_3^{2-}/	0.0	meq/L
Bicarbonate Ion Concentration /HCO_3^-/	2.70	meq/L
Chloride Ion Concentration /Cl^-/	1.60	meq/L
Sulfate Ion Concentration /SO_4^{2-}/	8.71	meq/L
Calcium Ion Concentration /Ca^{2+}/	5.17	meq/L
Magnesium Ion Concentration /Mg^{2+}/	2.59	meq/L
Sodium Ion Concentration /Na^+/	5.51	meq/L
Potassium Ion Concentration /K^+/	0.04	meq/L
SAR	2.79	$(mmol/L)^{0.5}$
SSP	41.50	%
Total Hardness (TH)	386.17	mg/L
Residual Sodium Carbonate (RSC)	-4.76	me/L
Mg_{HAZ}	33.37	%
[Ca]/[Mg]	1.99	---

A system with the following specifications was obtained to design the reverse osmosis system, which was simulated by WAVE software to achieve the output water at the rate of 600m^3/day, its Schematic is in Fig. 1. In this system, two PASSs including two stages were used to achieve TDS<2 mg/L, This device is designed to supply water with standard IS: 10392-1982, which is suitable for operation in boilers. In the first pass, two stages were used; the first stage has five pressure vessels, each with a capacity of 6 modules. In the second stage, two pressure vessels were used with a capacity of 6 modules. PASS2 also consisted of two stages; the first stage consisting of two PVs with a capacity of 6 modules and the second stage consisting of a PV with a capacity of 6 modules were designed. It should be noted that the BW30-400 module is used in this system.

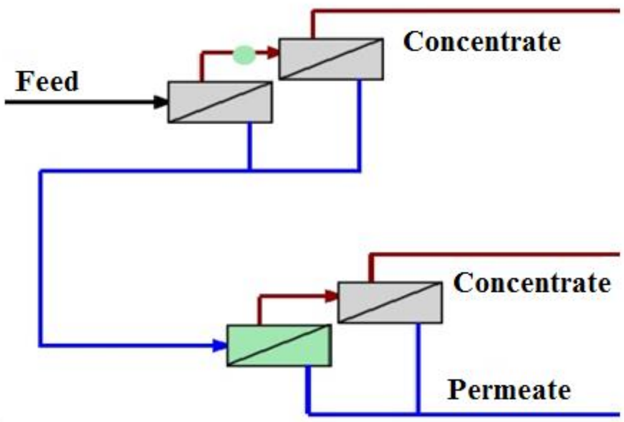


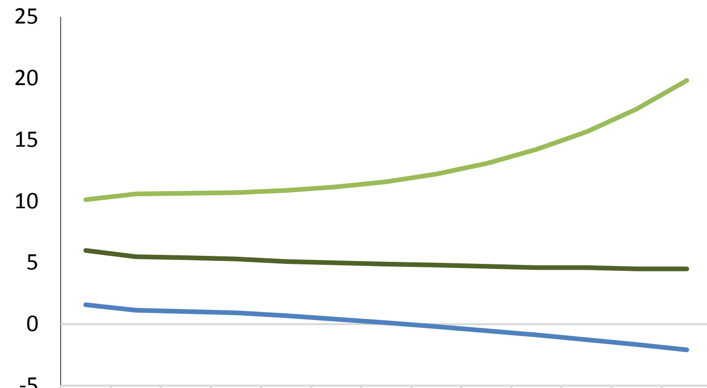
Fig. 1. Schematic of double RO system.

The simulation of the reverse osmosis system in wave software in the first step without injecting acid LSI = 1.58 in PASS1 and LSI = -2.86 in PASS2 indicates severe cramping in the not too distant future in the PASS1 reverse osmosis system (Table 2).

Table 2. Preliminary examination of RO system output without acid injection

	TDS	pH	LSI
PASS 1	10.13	6	1.58
PASS 2	0.82	5.3	-2.86

First, the injection of hydrochloric acid is investigated in this system: By injecting acid and reducing the pH of feed water, the amount of TDS, pH, and LSI parameters changes according to the following diagrams, and the horizontal axis is the pH of the incoming water.

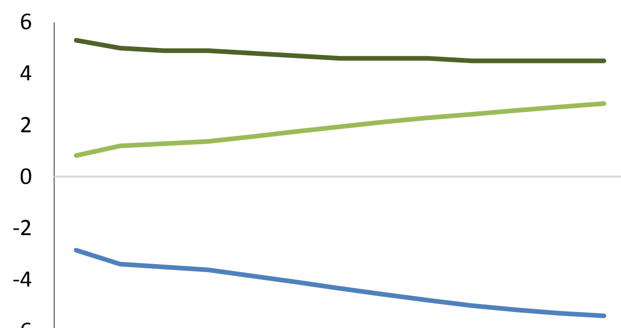


	7.57	7	6.9	6.8	6.6	6.4	6.2	6	5.8	5.6	5.4	5.2	5
LSI1	1.58	1.13	1.03	0.92	0.68	0.41	0.12	-0.19	-0.53	-0.88	-1.26	-1.66	-2.09
TDS PASS1	10.13	10.59	10.65	10.71	10.89	11.16	11.6	12.22	13.08	14.21	15.66	17.5	19.83
PH PASS 1	6	5.5	5.4	5.3	5.1	5	4.9	4.8	4.7	4.6	4.6	4.5	4.5

Fig. 2. Changes in LSI, TDS, pH parameters in PASS 1 due to HCL injection.

Fig. 2 shows PASS 1 of the RO treatment system, in which the LSI number is positive at the time of treatment by the RO system without acid injection at pH 7.57. This condition is the normal state of feed water and there are reports for values higher than 1, which gradually decreased with the injection of HCL acid and reduced fouling amount. When the pH of the inlet water drops to 6.1, the LSI value is reported as much as 0.

As the pH decreases, the LSI parameter becomes negative, which indicates less clogging and longer life of the modules. TDS increases in the opposite direction with increasing the acidity of the incoming water. Therefore, efforts should be made to maintain the optimal pH of the water due to the inverse numerical changes in the amount of TDS and LSI.

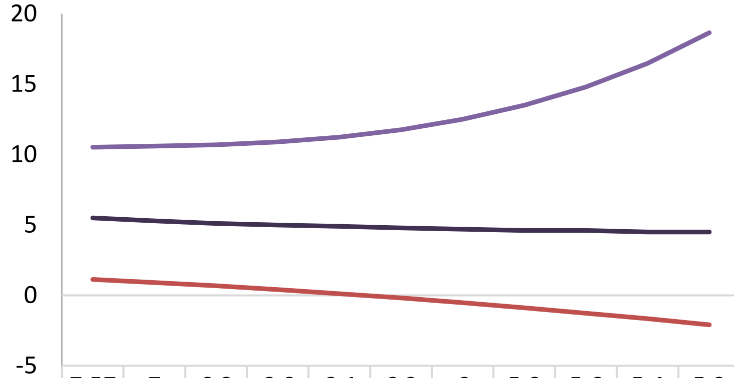


	7.57	7	6.9	6.8	6.6	6.4	6.2	6	5.8	5.6	5.4	5.2	5
LSI2	-2.86	-3.4	-3.51	-3.62	-3.86	-4.1	-4.34	-4.58	-4.8	-5.01	-5.18	-5.31	-5.41
TDS PASS2	0.82	1.2	1.28	1.37	1.56	1.75	1.94	2.12	2.29	2.43	2.57	2.71	2.84
PH PASS 2	5.3	5	4.9	4.9	4.8	4.7	4.6	4.6	4.6	4.5	4.5	4.5	4.5

Fig. 3. Changes in LSI, TDS, pH parameters in PASS2 due to HCL injection.

According to Fig. 3 in PASS2, since the water entering this stage of work is treated in PASS 1, the LSI is negative, indicating that the modules used in PASS2 are safe against clogging and fouling. At this stage, there is no need to add acid again, and when the pH of the treated water is required, the addition of NaOH before PASS2 can be used. The results of the stated reverse osmosis system with acid change and H_2SO_4 injection showed in Fig. 4 that when the pH of feed water decreases to approximately 6.3, the LSI parameter becomes zero. With the further decrease of pH, the decreasing trend, the negative LSI parameter is obtained, which indicates the absence or reduction of fouling. H_2SO_4 performed better than HCL by lowering the pH by 0.2 during H_2SO_4 acid utilization.

Fig. 2 represents that the numerical value of LSI is obtained by injecting chloric acid from the pH = 6.7 limit, but the TDS value increases with increasing the acidity and pH of the feed water, which reaches 12 mg/lit at the boundary point with pH6.7. The LSI decreases and the TDS increases by decreasing the pH of the feed water. Decreasing the LSI has a favorable effect and increasing the TDS has an adverse effect on the outlet water. These changes cause a sharp increase in the acidity of the outlet water, which is not appropriate and causes the chemical corrosion of devices and equipment by water, which should be prevented.

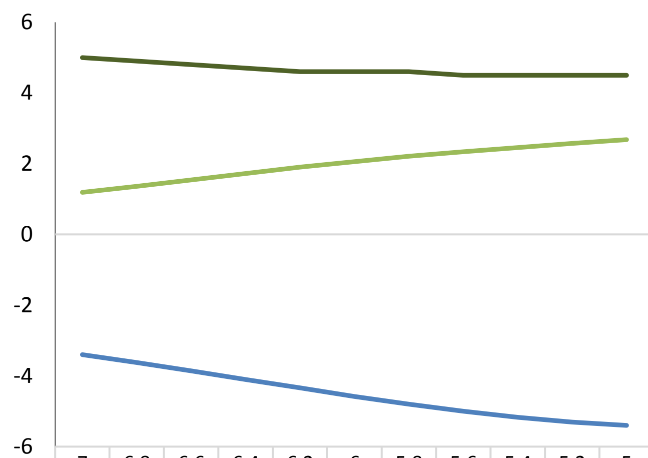


	7.57	7	6.8	6.6	6.4	6.2	6	5.8	5.6	5.4	5.2
LSI1	1.13	0.92	0.68	0.41	0.12	-0.19	-0.53	-0.88	-1.26	-1.66	-2.09
TDS PASS1	10.52	10.59	10.7	10.9	11.24	11.76	12.5	13.5	14.81	16.49	18.65
PH PASS 1	5.5	5.3	5.1	5	4.9	4.8	4.7	4.6	4.6	4.5	4.5

Fig. 4. Changes in LSI, TDS, and pH parameters in PASS1 due to H_2SO_4 injection.

Most of the solutes in PASS 2 are absorbed by PASS 1 and less clogging and fouling occurs, with only a sharp decrease in the pH of the outlet water of the capture system. According to Fig. 4, the LSI number becomes negative by injecting H_2SO_4 from the approximate limit of pH 6.3 At this point, the pH of outlet water PASS 1 is approximately 4.85 and the number TDS is 11.5 mg/lit, which is decrease 0.5 mg/lit compared to the use of chloric acid. Fig. 5 shows the change of parameters in pass2 by changing the pH.

With an increase of water acidity Fig. 6 indicates that the amount of CO_2 dissolved in the outlet water increases as the acidity of the water increases, which should be eliminated using special methods and the addition of workstations. This amount of CO_2 production in both modes of acid injection is almost the same.



	7	6.8	6.6	6.4	6.2	6	5.8	5.6	5.4	5.2	5
LSI2	-3.4	-3.62	-3.86	-4.1	-4.34	-4.58	-4.8	-5	-5.17	-5.31	-5.4
TDS PASS2	1.19	1.36	1.54	1.72	1.9	2.06	2.21	2.34	2.46	2.57	2.68
PH PASS 2	5	4.9	4.8	4.7	4.6	4.6	4.6	4.5	4.5	4.5	4.5

Fig. 5. Changes in LSI, TDS, and pH parameters in PASS2 due to H_2SO_4 injection.

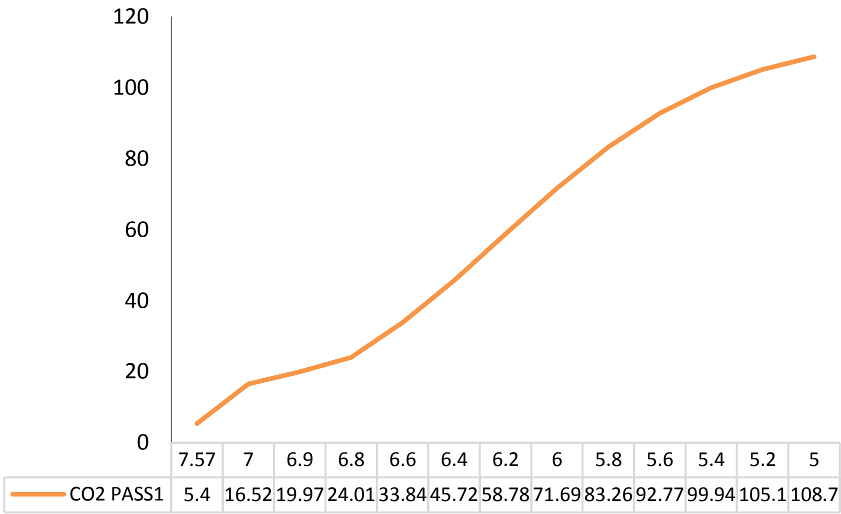


Fig. 6. Increase of CO_2 outlet water from PASS 1.

4. Conclusions

The following is achieved by injecting acid into the feed water: Significant reduction in LSI, which is a very favorable effect and significantly reduces the fouling number. Increasing the amount of TDS in outlet water by increasing the amount of acid injection, which is an adverse effect, especially when preparing pure water for use in boilers. Increasing the amount of CO_2 in the outlet water, which should be eliminated by other methods and create another workstation and other costs. Increasing the amount of acid injection sharply declines the pH of water output so that this acidic property of water increases the corrosion capability in industrial and mechanical systems and causes premature wear. NaOH injection can be used before PASS2 to solve this problem. A 10% decrease in TDS was observed at the boundary point in comparing HCL and H_2SO_4 acids when using H_2SO_4, which is considered as a positive effect of using this acid. It is recommended to use ION EXCHANGE or ULTRA FILTER systems along with the use of acid in water dehardening.

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