

RO Concentrate Softening through Induced Crystallization in a Fluidized Bed Reactor

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Abstract. Induced crystallization technique was adopted in a fluidized bed reactor to remove scale-forming ions from RO concentrate in this paper, the result of which is as follows: the effluent of the fluidized bed reactor reached stability in two minutes after the operation started; the optimized consumption ratio of softener was 1, under the circumstances of which the removal rate of Ca^{2+} was 89.22%; the removal of Ca^{2+} was mainly completed at the position 20 centimeters above the bottom of the bed; the reflux rate had no influence on the removal of Ca^{2+} , but it had influence on the turbidity of effluent.

1 Introduction

Treating water with RO (Reverse Osmosis) process will produce RO concentrate. Especially when using RO to produce fresh water from brackish water, the concentrate yield may be higher than the fresh water yield [1]. At present, the total output of seawater desalination in China is $5 \times 10^5 \text{m}^3/\text{d}$ [2], while the recovery rate of RO when treating seawater is 30% to 40% [3]. That is to say, the daily fresh water output is $7.5 \times 10^5 \text{m}^3 \sim 1.17 \times 10^6 \text{m}^3$. Therefore, if RO concentrate is directly discharged without any recycling method, it would not only be a waste of water resources, but also affect the environment.

So far, the treatments of RO concentrate mainly include deep-well injection [4, 5], flush filters [6], boiler dedusting [7], salt manufacturing [8], electrolysis [9, 10], membrane distillation [11] and membrane crystallization [12]. The author proposed the method of softening RO concentrate through induced crystallization in a fluidized bed reactor and conducted relative experiments.

Induced crystallization means making oversaturated CaCO_3 and CaSO_4 grow on the added seed crystal to

achieve the goal of reducing the concentration of scale-forming ions in the solution. Induced crystallization coupling with a fluidized bed reactor means using fluidized bed packing as seed crystal and remove scale-forming ions during the process of oversaturated RO concentrate flowing from bottom to top in the fluidized bed reactor.

The crystallization process depends on the equilibrium relation between the solid and the solution. If the solution is already supersaturated when solid substance comes into contact with it, then the supersaturated portion of the substance in the solution will crystallize [13]. The crystallization process of RO concentrate can be divided into two parts, one is the formation of crystal nucleus and the other is the growth of crystals, which is the growing process of crystal nucleus [14]. And the mechanism of induced crystallization lies in adding crystal nucleus. Theoretically, induced crystallization can remove every substance that can precipitate as crystals from water solution [15].

Table 1. Experimental water quality

DD	pH	LSI	JD_m	YD	$1/2\text{Ca}^{2+}$	$1/2\text{Mg}^{2+}$	Cl^-	SO_4^{2-}
3587	7.89	1.813	21.84	36.90	27.95	8.954	350.64	308.8
Ba^{2+}	Sr^{2+}	SiO_2	TDS	K^+	Na^+	Fe^{3+}	F^-	
0.2210	1.690	39.65	2661	3.100	98.52	2.140	1.587	

Unit of measurement: DD: $\mu\text{S}/\text{cm}$; pH and LSI have no unit; JD_m , YD, $1/2\text{Ca}^{2+}$ and $1/2\text{Mg}^{2+}$: mmol/L ; other indicators: mg/L .

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2 Material and method

2.1 Experimental water

Prepare the experimental water based on the average water quality (as shown in Table 1) of the concentrate of two single-pass two-stage RO systems in Unit 3 and 4 of a power plant. The scale inhibitor (PTP-0100) content of the experimental water is 16mg/L.

2.2 Experimental facility

The experimental facility and process consists of a drug tank, a raw water tank, a dosing pump, a feed water pump, a fluidized bed, four sample connections, three flowmeters and other devices, as shown in Figure 1.

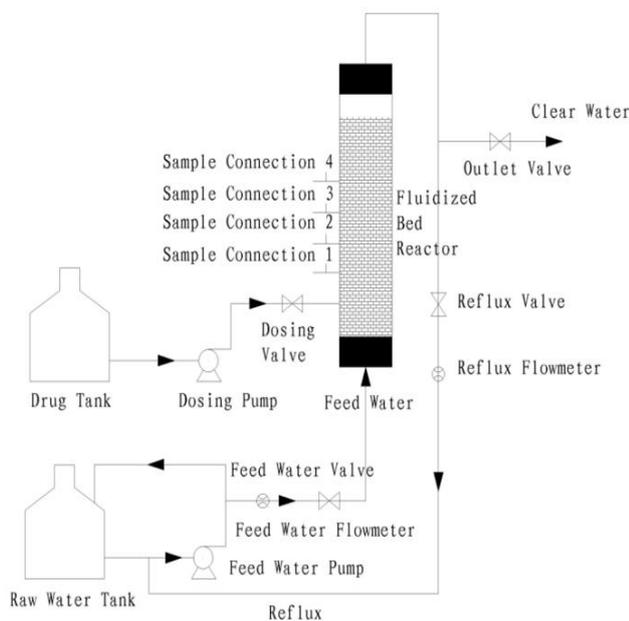


Figure 1. Process of induced crystallization in a fluidized bed reactor

The fluidized bed reactor is made of PMMA with the height of 100 centimeters and the inner diameter of 4 centimeters. A screen is installed inside the fluidized bed reactor to prevent the inducer from flowing out. The drug injection tube is introduced into the reactor 2 centimeters above the screen. Sample connections are installed 20 centimeters, 40 centimeters, 60 centimeters and 80 centimeters above the bottom of the reactor respectively. Limestone is used as fluidized bed packing, and the static bed height is 40 centimeters. Feed water flows into the reactor at the bottom of the bed and flows out from the outlet at the top of the reactor. The packing acts not only as the inducer but also as the sludge blanket in a clarification tank, which bear the functions of induced crystallization, clarification and filtration.

2.3 Experimental method

The operation process of the experimental facility is as follows: The experiment is conducted under room

temperature, and each experiment uses brand-new inducers. Turn on the feed water pump to start the experiment. Open the inlet and outlet valves and adjust the inlet flow to the set value. Test the turbidity of outlet water every 30 seconds. After the turbidity of outlet water is stabilized, open the dosing valve to add softener into the reactor. Promptly adjust the dosing flow to the set value, and the induced softening clarification process will be started. Then, test the Ca^{2+} of outlet water every 2 minutes, after the value of which is stabilized, test the Ca^{2+} , pH, hardness and turbidity of the outlet water from each sample connection. After that, turn on the reflux valve, and adjust the outlet valve until the reflux flow reaches the set value. Reduce the softener dosage according to the “feed water/concentrate” ratio. Test the Ca^{2+} and hardness of the outlet water every 2 minutes.

2.4 Fluidizing velocity

The necessary and sufficient condition for operating the fluidized bed reactor is: $u \in (u_{\min}, u_{\max}]$. Here, u , u_{\min} and u_{\max} respectively represent the flow rate, the minimum fluidizing velocity and the maximum fluidizing velocity of the fluidized bed reactor.

(1) u_{\min}

In order to ensure that the bed is fluidized, u must be higher than u_{\min} . u_{\min} is calculated by Formula 1 to 3 as follows.

Galileo Number (G_a):

$$G_a = \frac{d^3 \rho (\rho_p - \rho) g}{\mu^2} \quad (1)$$

where, d represents packing particle diameter (m); ρ represents water density, (1000kg/m^3); ρ_p represents packing density (kg/m^3); g represents gravitational acceleration, (9.81m/s^2); and μ represents water viscosity ($1.46 \times 10^{-3} \text{Pa}\cdot\text{s}$ under 7.0°C). Through measuring, d is 0.315 to 0.500mm and ρ_p is 2500kg/m^3 in this experiment.

Fluidization Reynolds Number (Re_{mf}):

$$Re_{mf} = \sqrt{33.7^2 + 0.0408 G_a} - 33.7 \quad (2)$$

Minimum Fluidizing Velocity (u_{\min}):

$$u_{\min} = \frac{Re_{mf} \mu}{\rho d} \quad (3)$$

Because it has to be ensured that inducers with the maximum particle diameter be in a state of suspension, d in Formula 1 to 3 must take the value of the maximum packing particle diameter, which is $0.500 \times 10^{-3} \text{m}$. Based on computation result, u_{\min} is 5.44m/h.

(2) u_{\max}

To ensure that the packing will not flow out of the reactor, u must not be higher than u_{max} . u_{max} is related with the height of the bed and the reactor, and needs to be determined by experiment. The experiment process is as follows: Turn on the feed water pump after evacuation of all the air inside the fluidized bed reactor. Open the inlet and outlet valves and adjust the inlet flow while observing the expansion height of the bed. When the bed is expanded to a place approximately 5 centimeters below the outlet, record the current inlet flow which is the maximum flow (Q_{max}) allowed in the reactor. Based on the experiment result, Q_{max} is 90L/h. And by calculation, u_{max} should be 71.66m/h.

2.5 Retention time

The retention time of concentrate in the bed (t) is calculated by Formula 4:

$$t = \frac{3.6(\frac{1}{4}\pi\Phi^2H - \frac{m}{\rho})}{Q} \quad (4)$$

where, t represents the retention time of concentrate in the bed (s); Φ represents the inner diameter of the reactor (cm); H represents the bed height during steady operation (cm); m represents the mass of inducer inside the reactor (g); ρ represents the inducer density (2.50g/cm³) and Q represents the inlet flow (L/h).

Based on the experiment result, H is 91cm under the condition when Q is 90L/h and m is 660g. Therefore, t is calculated to be 35.12s.

2.6 Softener

Based on the experimental water quality in Table 1, NaOH is selected as the softener. The amount of softener is expressed through the consumption ratio of softener (N), where N is defined as the molar ratio of NaOH to the experimental water alkalinity (JD_m). In order to ensure complete neutralization of NaOH and HCO_3^- , the theory value of N should be 1.0.

3. Results and Discussion

3.1 Induction time

In the light of The Test Method of Water Coagulation and Precipitation Test Cup (GB/T 16881-2008), induced precipitation time (hereinafter referred to as “induction time”) is determined under the temperature of 10°C with softener dosage of 16mg/L. The relation between the residual Ca^{2+} after the experimental water is softened by induced precipitation and the induction time is shown in Figure 2, where the value of N in curve a and c is 0.8, the inducer dosage is 0 and 30g/L, respectively; while the

value of N in curve b and d is 1.1, the inducer dosage is 0 and 30g/L, respectively.

During the crystallization process, inducer acts as the crystal seed, lowering down the energy barrier of the reaction. Therefore, under the same circumstance, adding inducer will accelerate the crystallization process and reduce the residual Ca^{2+} . As reflected in Figure 2, curve c is below curve a while curve d is below curve b.

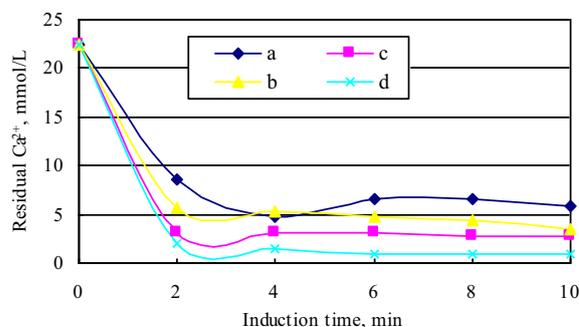


Figure 2. Relation between the residual Ca^{2+} and the induction time

3.2 Operation time

Reflux rate is defined as the percentage of reflux flow in the total inlet flow.

Using the experimental facility shown in Figure 1, the relation between the removal rate of Ca^{2+} and the operation time is shown in Figure 3, under the condition where the reflux rate is 50%, the water temperature is 19.3°C, u is 63.59m/h, t is 46.38s and N is 1.02. Here, the beginning of the operation is the time when softener starts to be added.

After the softener is added, the CO_3^{2-} level of the inlet flow will keep rising until a supersaturated solution of Ca^{2+} and CO_3^{2-} is formed. The supersaturated solution flows through the fluidized bed reactor and induces the crystallization process. The generated crystals will adhere to the surface of inducer particles, and the Ca^{2+} level will drop. This reaction process takes approximately 2 minutes according to Figure 3.

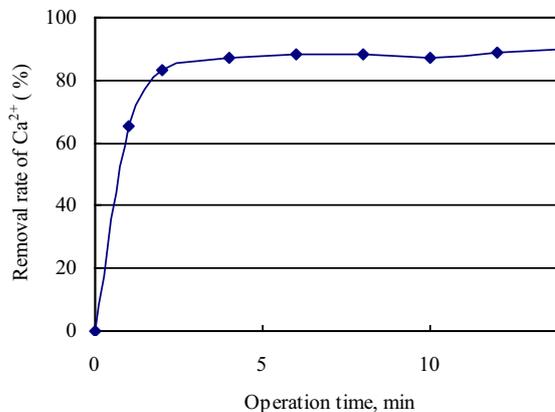


Figure 3. Relation between the removal rate of Ca^{2+} and the operation time

3.3 Softener dosage

Under the same condition as Section 2.2, the relation between the removal rate of Ca^{2+} and N is shown in Figure 4.

When $N < 1.0$, the CO_3^{2-} level rises with the value of N , and the solution goes through the stages of unsaturation, saturation and finally supersaturation. The removal rate of Ca^{2+} increases with the value of N until N reaches 1.0. When $N > 1.0$, there will be no HCO_3^- left in the inlet flow. And keep adding the value of N will no longer affect the CO_3^{2-} level, which means the supersaturated degree of the solution will not change, and the removal rate of Ca^{2+} will maintain at the level when N reaches 1.0.

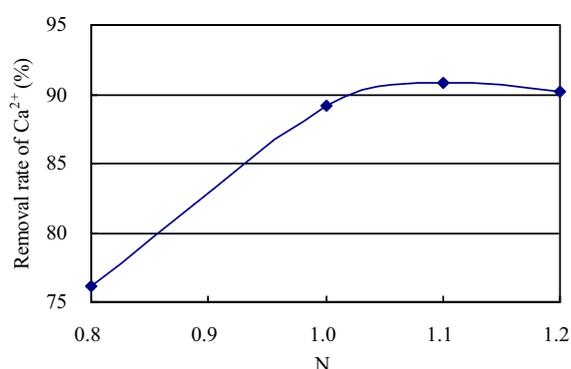


Figure 4. Relation between the removal rate of Ca^{2+} and N

3.4 Height of the fluidized bed reactor

Using the experimental facility shown in Figure 1, the relation between the removal rate of Ca^{2+} and the height of the reactor is shown in Figure 5, under the condition where the reflux rate is 50%, the water temperature is 19.6°C , u is 65.97m/h , t is 46.19s and N is 1.04 .

The taller the reactor is, the longer the inlet flow will be in contact with the inducer, and the higher the removal rate of Ca^{2+} will be. However, when the height of the reactor is enough to ensure adequate crystallization time, raising the height will have little effect on the removal rate of Ca^{2+} .

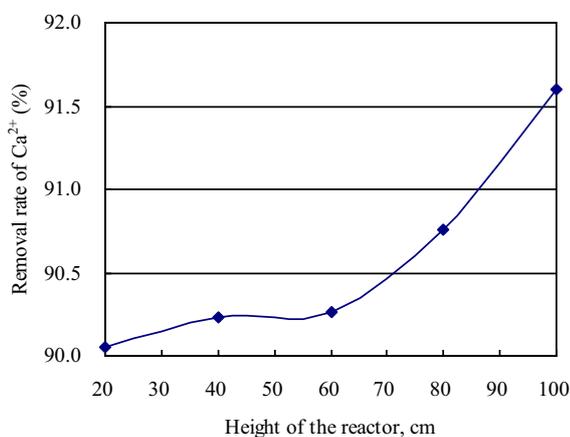


Figure 5. Relation between the removal rate of Ca^{2+} and the height of the reactor

3.5 Reflux rate

Using the experimental facility shown in Figure 1, the relation between the removal rate of Ca^{2+} , the effluent turbidity and the reflux rate is shown in Figure 6, under the condition where the water temperature is 19.6°C , u is 66.35m/h , t is 46.17s and N is 1.02 .

In the fluidized bed reactor, the inducer layer is acting as a filter bed. Therefore, higher reflux rate means longer filtering time of the inlet flow and lower effluent turbidity. Nevertheless, if the reflux rate is too high, the pore size of the filter bed will become larger and the filter bed will be less capable of intercepting suspended solids, resulting in higher effluent turbidity.

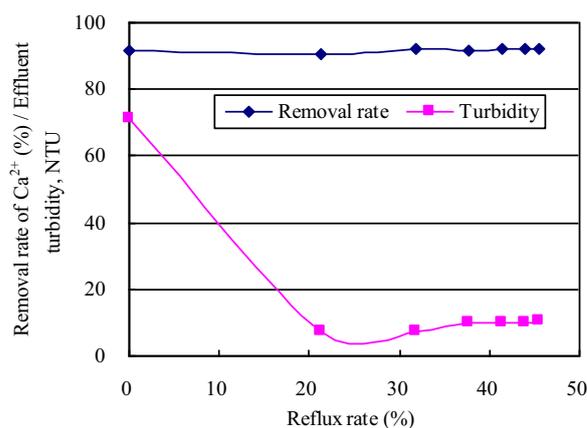


Figure 6. Relation between the removal rate of Ca^{2+} /effluent turbidity and the reflux rate

4. Conclusion

RO concentrate softening through induced crystallization in a fluidized bed reactor has the following characteristics:

(1) The start-up speed of the reactor is relatively fast. The effluent quality can reach stability in approximately 2 minutes after the operation starts, as shown in Figure 2 and 3.

(2) The optimized consumption ratio of softener is 1. When softener is inadequate ($N = 0.8$), the removal rate of Ca^{2+} merely reaches 76.18%. When softener is just enough to completely neutralize HCO_3^- ($N = 1.0$), the removal rate of Ca^{2+} can reach 89.22%. Keep adding softener would not improve the removal rate of Ca^{2+} obviously. As shown in Figure 2 and 4.

(3) The removal of Ca^{2+} was mainly completed at 20 centimeters above the bottom of the bed. For comparison, the removal rate of Ca^{2+} is 90.05% and 91.60% respectively at 20 centimeters and 100 centimeters above the bottom of the bed. The removal rate at the latter position is merely 1.72% higher than that at the former one, as shown in Figure 5.

(4) The reflux rate has no influence on the removal of Ca^{2+} , but it had great influence on effluent turbidity. When the reflux rate is higher than 20%, the effluent turbidity will be lower than 10.5 NTU, as shown in Figure 6.

References

1. Shi Weiping. Discussion and Countermeasure of the Comprehensive Utilization of RO Condensate [J], Energy Saving of Non-Ferrous Metallurgy (China), **21**, 15 (2004)
2. Li Guodong, Wang Wei, Li Fengjuan, et al. Study and Development of RO Membrane [J], Polymer Bulletin (China), **38** (2010)
3. Zhou Baiqing, Chen Zhihe. Water Treatment in Thermal Power Plant [M], China Electric Power Press, 177 (2009)
4. Wu Liancheng, Zheng Fei. Study of the Discharge and Utilization of RO Condensate [J], Henan Technology, **9**, 66 (2008)
5. Ning R Y, Tarquin A, Trzcinski M C, *et al.* Recovery optimization of RO concentrate from desert wells [J], Desalination, **201**, 315-322 (2006)
6. Zhang Sheng, Mao Yonghao, et al. Recycling of RO Condensate [J], Industrial Water & Wastewater, **38**, 56 (2007)
7. Song Sheling, Guo Lijun, Sun Xiufang. Recycling and Application of RO Wastewater [J], Energy Conservation, **6**, 39-40 (2005)
8. Zhang Deqiang, Qiao Baodong, Wei Bingju, et al. Study of Concentrated Seawater Salt Technology After Seawater Desalination [J], Journal of Salt and Chemical Industry, **6**, 4-9 (2007)
9. Yang Q F, Ma Z F, Hasson D, *et al.* Destruction of anti-scalants in RO concentrates by electrochemical oxidation [J], Journal of Chemical Industry and Engineering (China), **55**, 339-340 (2004)
10. Badruzzaman M, Oppenheimer J, Adham S, *et al.* Innovative beneficial reuse of reverse osmosis concentrate using bipolar membrane electro dialysis and electrochlorination process [J], Membr Sci, **326**, 392-399 (2009)
11. Wang Jun, Luan Zhaokun, *et al.* Study of Applying Hydrophobic Membrane Distillation Technology in RO Condensate Recycling [J], China Water & Wastewater, **23**, 1 (2007)
12. Drioli E, Macedonio F. New trends in membrane technology for water treatment and desalination[A]. 5th IWA Conference on Membranes for Water and Wastewater Treatment [C], Beijing: IWA-MTC 2009 Organising Committee (2009)
13. Ding Xuwei, Tan Qiu. Industrial Crystallization [M], Chemical Industry Press, **10**, 122-125 (1985)
14. Lu Jiufang. Separation Process Chemistry [M], Tsinghua University Press, 232 (1993)
15. Chen Ping. The study of water softening and fluorine removal through carrier-induced precipitation and crystallization [D], Xi'an University of Architecture and Technology, 7 (2004)