

# Research on The Removal of Scale Ions from Circulating Cooling Wastewater by Chemical Coagulation Process

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**Abstract:** In this paper, the circulating cooling wastewater was treated by chemical coagulation process through adding NaOH/Na<sub>2</sub>CO<sub>3</sub>. The effect of NaOH and Na<sub>2</sub>CO<sub>3</sub> dose on removal of scale ions, such as Ca<sup>2+</sup>、Mg<sup>2+</sup>、Ba<sup>2+</sup>、Sr<sup>2+</sup>、SiO<sub>2</sub>, was studied and the removal mechanism was discussed. The results showed that the increase of NaOH dose was beneficial to the removal of above-mentioned scale ions. When NaOH was only added, the removal efficiency of Ca<sup>2+</sup>、Mg<sup>2+</sup>、Ba<sup>2+</sup>、Sr<sup>2+</sup>、SiO<sub>2</sub> was 86.3%, 91.6%, 86.5%, 58.1%, 84.2%, respectively. When 680 mg/L of NaOH and 300 mg/L of Na<sub>2</sub>CO<sub>3</sub> were added, and the effluent pH was above 11.2, the removal efficiency of Ca<sup>2+</sup>、Mg<sup>2+</sup> was 95.8% and 89.4%, respectively, and the concentration of Ca<sup>2+</sup> and Mg<sup>2+</sup> was below 20 mg/L, which met the target of wastewater treatment. Finally the possible removal mechanism of Ca<sup>2+</sup>、Mg<sup>2+</sup>、Ba<sup>2+</sup>、Sr<sup>2+</sup> and SiO<sub>2</sub> was discussed.

## 1 Introduction

A power plant was designed to apply technology of reverse osmosis membrane to treat its circulating cooling water. And the treated water would be completely reused instead of being discharged. However the high hardness of water impacted the process of reverse osmosis, which had to be soft by a pre-treatment process. Conventional softening methods include chemical coagulation and ion exchange [1-3]. And as the most widely used method, chemical coagulation include several subentry, such as lime softening method, lime-sodium carbonate softening method, sodium hydroxide-sodium carbonate softening method[4-5]. Enterprise prefer sodium hydroxide soften method to lime softening, because it show less material-consumption, lower secondary-pollution and more simply operated [6].

The current literature about chemical coagulation soften methods mainly focus on removing conventional scaling ions such as Ca<sup>2+</sup> and Mg<sup>2+</sup>, and research on removal of unconventional scaling ions, such as Ba<sup>2+</sup>, Sr<sup>2+</sup> and SiO<sub>2</sub> was not many[7-9]. Though applying “NaOH+Na<sub>2</sub>CO<sub>3</sub>” soften method to treat circulating cooling water of the power plant, this paper studied the removal efficacy of scaling ions, such as Ca<sup>2+</sup>, Mg<sup>2+</sup>, Ba<sup>2+</sup>, Sr<sup>2+</sup> and SiO<sub>2</sub>. The related reaction mechanism was deduced.

## 2 Material and methods

### 2.1 Quality of experimental water

**Table 1** Circulating cooling water quality of the power plant  
unit: mg/L (except pH)

| Item               | Value |
|--------------------|-------|
| pH                 | 8.5   |
| Ca <sup>+</sup>    | 254   |
| Mg <sup>2+</sup>   | 140   |
| Ba <sup>2+</sup>   | 0.267 |
| Sr <sup>2+</sup>   | 2.65  |
| SiO <sub>2</sub>   | 37.7  |
| ALK                | 324   |
| COD <sub>Cr</sub>  | 59.5  |
| NH <sub>3</sub> -N | 0.69  |

### 2.2 Experimental material and instrument

Experimental material: Sodium hydroxide, sodium carbonate, polymeric ferric sulfate (PFS), anionic polyacrylamide (PAM, molecular weight: 12 million), and all were solid state. Before being used, these materials would be configured to solution, the mass fraction respectively are 30%, 5%, 1% and 0.1%.

Experimental instrument: quadruple electric mixer (JJ-4A, Jiangsu Jintankexi instrument co., LTD), pH meter (FE20, Mettler Toledo).

### 2.3 Experimental approach

The soften coagulation experiment was carried out in a beaker [10]. To add NaOH (or NaOH and Na<sub>2</sub>CO<sub>3</sub>, 30% purity) into 500ml water to regulate pH with 200r/min stirring for 5 minutes. Then add the polymeric ferric

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sulfate (PFS) with 200r/min stirring for 2 minutes. Next step is adding 1mg/L anionic polyacrylamide (PAM, molecular weight: 12 million) with 50r/min stirring for 20 minutes. After 30 minutes standing, the water was made into simple and analyzed. This paper treated concentration of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{SiO}_2$  as evaluation index to analyse the experimental result.



**Fig.1** Experimental process

## 2.4 The analytical approach of water quality

**Table 2** Analytical approach of water quality

| Monitoring program                  | Monitoring Approach   |
|-------------------------------------|---|
| $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ | Water quality-Determination of calcium and magnesium-Atomic absorption spectrophotometric method (GB 11905-89)  |
| $\text{Ba}^{2+}$                    | Water quality-Determination of barium-graphite furnace atomic absorption spectrophotometry (HJ 602-2011)        |
| $\text{Sr}^{2+}$                    | Water quality-Determination of 32 elements-Inductive coupled plasma optical emission spectrometry (HJ 776-2015) |
| $\text{SiO}_2$                      | Determination of silica (dissolved) (Heteropoly blue method)(SL 91.2-1994)                                      |
| pH                                  | Water quality-Determination of pH value – Glass electrode method  |

## 3 Results and discussion

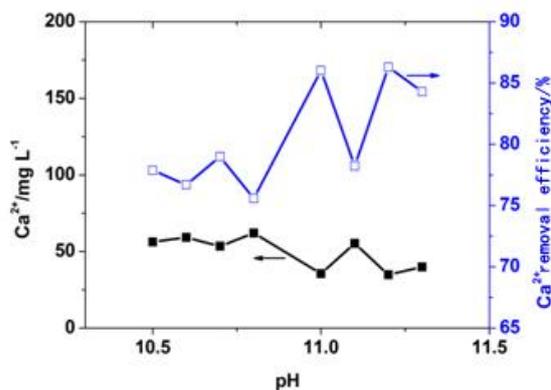
### 3.1 The Influence of Dosing Quantity of NaOH on Removing $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$

Only adding NaOH without  $\text{Na}_2\text{CO}_3$ , the dosage of PFS was kept as 100mg/L with the gradual increase in NaOH ranging from 400 to 720 mg/L. The pH ranged from 10.5-11.3m, and the change about concentration of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  was shown in Table 3, Figure 2 and Figure 3. Table 3 demonstrated that the concentration of  $\text{Ca}^{2+}$  trend down with increasing of pH, the concentration of  $\text{Ca}^{2+}$  of raw water was 254mg/L, when pH raise from 10.5 to 11.3, the concentration of  $\text{Ca}^{2+}$

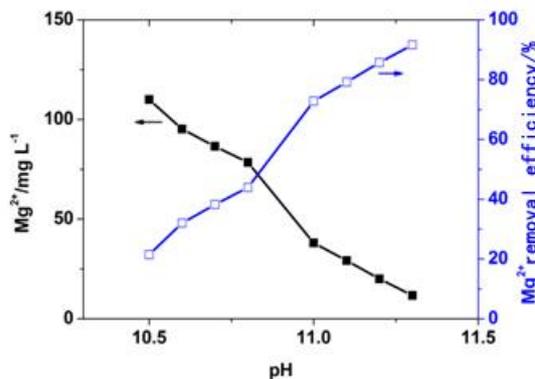
declined from 56.2mg/L to 39.9mg/L, and the removal efficiency went up from 77.9% to 86%. Similarly, Table 2 shows that the concentration of  $\text{Mg}^{2+}$  gradually decreased with increasing of pH, the concentration of  $\text{Mg}^{2+}$  of raw water was 140mg/L, when pH raise from 10.5 to 11.3, the concentration of  $\text{Mg}^{2+}$  declined from 110mg/L to 11.7mg/L, and the removal efficiency went up from 21.4% to 91.6%. When pH was greater than 7.5, the removal efficiency of  $\text{Ca}^{2+}$  was greater than 75%. However, the removal efficiency of  $\text{Mg}^{2+}$  was able to exceed 75 when pH raising to 11.1. It states that comparing with  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  was able to be removed in lower alkalinity condition. The pH should be greater than 11 when  $\text{Mg}^{2+}$  forming to  $\text{Mg}(\text{OH})_2$ [11].

**Table 3** Change of Concentration of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  with influence of dosage of NaOH

| NaOH dosage(mg/L) | pH   | $\text{Ca}^{2+}$ (mg/L) | $\text{Mg}^{2+}$ (mg/L) | Removal efficiency of $\text{Ca}^{2+}$ (%) | Removal efficiency of $\text{Mg}^{2+}$ (%) |
|-------------------|------|-------------------------|-------------------------|--|--|
| 0(raw water)      | 8.5  | 254                     | 140                     | -  | -  |
| 400               | 10.5 | 56.2                    | 110                     | 77.9                                       | 21.4                                       |
| 480               | 10.6 | 59.2                    | 95.2                    | 76.7                                       | 32   |
| 520               | 10.7 | 53.4                    | 86.5                    | 79.0                                       | 38.2                                       |
| 560               | 10.8 | 62                      | 78.5                    | 75.6                                       | 43.9                                       |
| 600               | 11.0 | 35.5                    | 38.1                    | 86.0                                       | 72.8                                       |
| 640               | 11.1 | 55.3                    | 29.2                    | 78.2                                       | 79.1                                       |
| 680               | 11.2 | 34.8                    | 20                      | 86.3                                       | 85.7                                       |
| 720               | 11.3 | 39.9                    | 11.7                    | 84.3                                       | 91.6                                       |

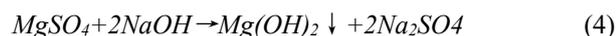
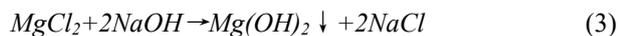
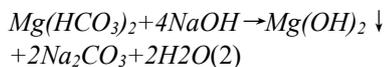


**Fig. 2** Variations in  $\text{Ca}^{2+}$  removal at different pH



**Fig. 3** Variations in Mg<sup>2+</sup> removal at different pH

According to the literature of Wang [12], Ca<sup>2+</sup> was mainly removed as CaCO<sub>3</sub>, and Mg<sup>2+</sup> was mainly removed as Mg(OH)<sub>2</sub>. It can be speculated that removing Ca<sup>2+</sup> and Mg<sup>2+</sup> according to following reactions:

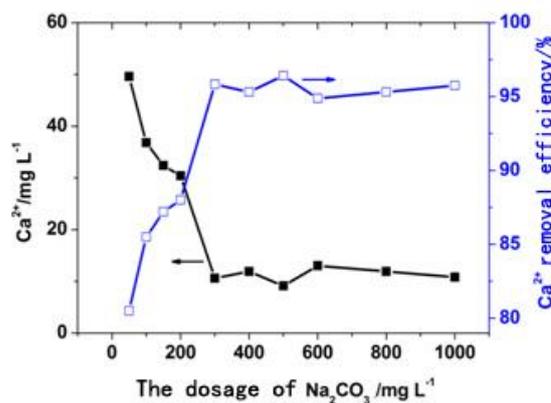


### 3.2 The Influence of dosing quantity of Na<sub>2</sub>CO<sub>3</sub> on removing Ca<sup>2+</sup> and Mg<sup>2+</sup>

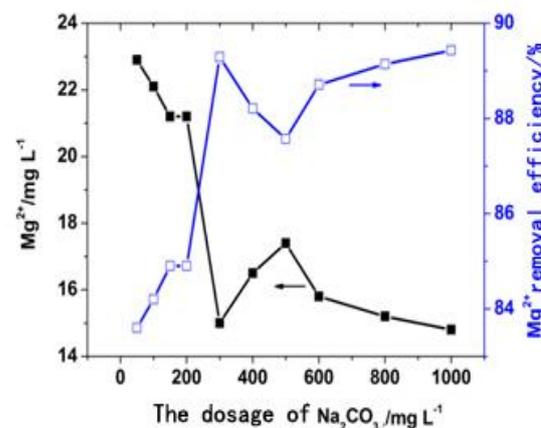
As mentioned earlier, adding NaOH could lead high removal efficiency of Ca<sup>2+</sup> and Mg<sup>2+</sup>. For higher removal efficiency and more reasonable dosage of NaOH, “NaOH+Na<sub>2</sub>CO<sub>3</sub>” dual-alkali soften method was applied in this research. The dosage of PFS was kept as 100mg/L, while NaOH was 680mg/L and pH was about 11.2. To regulate the dosage of Na<sub>2</sub>CO<sub>3</sub> and the change about concentration of Ca<sup>2+</sup> and Mg<sup>2+</sup> was shown in Table 3, Fig.2 and Fig.3. Fig.4 shows when the dosage of Na<sub>2</sub>CO<sub>3</sub> raised from 50mg/L to 300mg/L, Ca<sup>2+</sup> decreased from 49.6mg/L to 10.6mg/L, and removal efficiency increased from 80.5% to 95.8%. Though adding the dosage of Na<sub>2</sub>CO<sub>3</sub>, Ca<sup>2+</sup> was no longer change. It is because that CO<sub>3</sub><sup>2-</sup> and Ca<sup>2+</sup> reacted to form CaCO<sub>3</sub>, which leading to decrease of Ca<sup>2+</sup>. When CaCO<sub>3</sub> reaches solubility equilibrium, the concentration of Ca<sup>2+</sup> reaches its own equilibrium. Fig.5 states that when dosage of Na<sub>2</sub>CO<sub>3</sub> increased, the removal efficiency of Mg<sup>2+</sup> went up slightly. It is because that Mg<sup>2+</sup> was mainly removed as Mg(OH)<sub>2</sub>, the addition of CO<sub>3</sub><sup>2-</sup> made few contribution to pH.

**Table 4** Change of concentration of Ca<sup>2+</sup>, Mg<sup>2+</sup> with influence of dosage of Na<sub>2</sub>CO<sub>3</sub> (pH=11.2)

| NaOH dosage (mg/L) | Na <sub>2</sub> CO <sub>3</sub> dosage (mg/L) | Ca <sup>2+</sup> (mg/L) | Mg <sup>2+</sup> (mg/L) | Removal efficiency of Ca <sup>2+</sup> (%) | Removal efficiency of Mg <sup>2+</sup> (%) |
|--------------------|---|-------------------------|-------------------------|--|--|
| 0 (raw water)      | -   | 254                     | 140                     | -  | -  |
| 680                | 50  | 49.6                    | 22.9                    | 80.5                                       | 83.6                                       |
| 680                | 100   | 36.8                    | 22.1                    | 85.5                                       | 84.2                                       |
| 680                | 150   | 32.4                    | 21.2                    | 87.2                                       | 84.9                                       |
| 680                | 200   | 30.4                    | 21.2                    | 88.0                                       | 84.9                                       |
| 680                | 300   | 10.6                    | 15.0                    | 95.8                                       | 89.3                                       |
| 680                | 400   | 11.9                    | 16.5                    | 95.3                                       | 88.2                                       |
| 680                | 500   | 9.1                     | 17.4                    | 96.4                                       | 87.6                                       |
| 680                | 600   | 13.0                    | 15.8                    | 94.9                                       | 88.7                                       |
| 680                | 800   | 11.9                    | 15.2                    | 95.3                                       | 89.1                                       |
| 680                | 1000  | 10.8                    | 14.8                    | 95.8                                       | 89.4                                       |



**Fig. 4** Variations in Ca<sup>2+</sup> removal at different Na<sub>2</sub>CO<sub>3</sub>



**Fig. 5** Variations in Mg<sup>2+</sup> removal at different Na<sub>2</sub>CO<sub>3</sub>

It can be speculated that “NaOH+Na<sub>2</sub>CO<sub>3</sub>” dual-alkali soften method not only involve in reaction (1) ~reaction (4), and there should be reaction (5):



Theoretical dosages of NaOH and Na<sub>2</sub>CO<sub>3</sub> can be estimated by following reactions



Hz—the hardness of carbonate in raw water, mmol/L;  
 HMg—the hardness of magnesium in raw water, mmol/L;  
 HCa—the hardness of calcium in raw water, mmol/L;  
 CO<sub>2</sub>—the content of carbon dioxide in raw water, mmol/L;  
 Fe—the content of iron in raw water, mmol/L;  
 K—the dosage of coagulant, 0.1-0.5mmol/L;  
 Ac—the excess alkalinity of NaOH, 0.2-0.4mmol/L;  
 β—the excess amount of Na<sub>2</sub>CO<sub>3</sub>, 1.0-1.4 mmol/L.

According to data of water quality, theoretical dosages of NaOH and Na<sub>2</sub>CO<sub>3</sub> are 380mg/L and 46mg/L respectively. However, experimental dosages of NaOH and Na<sub>2</sub>CO<sub>3</sub> are 680mg/L and 300mg/L respectively, greater than the theoretical value. The researcher Liu [14] agrees the point that the theoretical dosage is different

from that of experiment. Therefore the theoretical value should only be intended as a reference, and the optimum

dosage need to be ascertained by experiment.

**Table 5** Change of concentration of Ba<sup>2+</sup>, Sr<sup>2+</sup>, SiO<sub>2</sub> with influence of dosage of NaOH

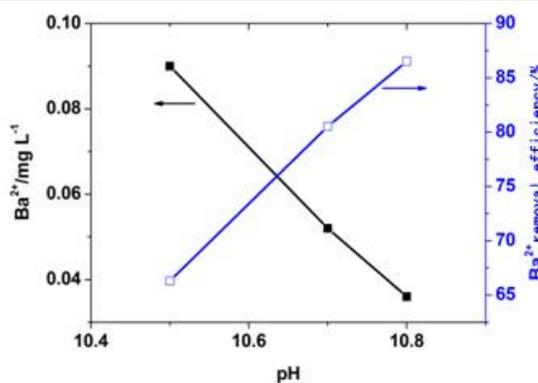
| NaOH dosage(mg/L) | pH   | Ba <sup>2+</sup> (mg/L) | Sr <sup>2+</sup> (mg/L) | SiO <sub>2</sub> (mg/L) | Removal efficiency of Ba <sup>2+</sup> (%) | Removal efficiency of Sr <sup>2+</sup> (%) | Removal efficiency of SiO <sub>2</sub> (%) |
|-------------------|------|-------------------------|-------------------------|-------------------------|--|--|--|
| 0(raw water)      | 8.5  | 0.267                   | 2.65                    | 37.7                    | -  | -  | -  |
| 400               | 10.5 | 0.09                    | 2.09                    | 27.6                    | 66.3                                       | 21.1                                       | 26.8                                       |
| 480               | 10.6 | -                       | 2.27                    | 17                      | -  | 14.3                                       | 54.9                                       |
| 520               | 10.7 | 0.052                   | 1.43                    | 5.74                    | 80.5                                       | 46   | 84.8                                       |
| 560               | 10.8 | 0.036                   | 1.11                    | 5.96                    | 86.5                                       | 58.1                                       | 84.2                                       |

### 3.3 The influence of dosing quantity of NaOH on removing Sr<sup>2+</sup>, Mg<sup>2+</sup> and Ba<sup>2+</sup>

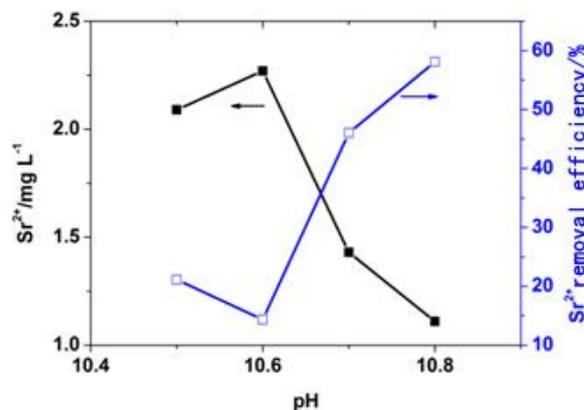
Only adding NaOH without Na<sub>2</sub>CO<sub>3</sub>, the dosage of PFS was kept as 100mg/L with the gradual increase in NaOH ranging from 400 to 560 mg/L. The pH ranged from 10.5-11.3m, and the change about concentrations of Ba<sup>2+</sup>, Sr<sup>2+</sup> and SiO<sub>2</sub> were shown in Table 5, Fig.6, Fig.7 and Fig.8. The result demonstrated that the concentrations of Ba<sup>2+</sup>, Sr<sup>2+</sup> and SiO<sub>2</sub> were gradually decreased with increasing of pH, which consistent with the literature [6]. When pH raise from 10.5 to 11.3, the concentration of Ba<sup>2+</sup> declined from 0.09mg/L to 0.036mg/L, and the removal efficiency went up from 66.3% to 86.5%; the concentration of Sr<sup>2+</sup> decreased from 2.09mg/L to 1.11mg/L, and the removal efficiency increased from 21.1% to 58.1%; the concentration of SiO<sub>2</sub> descend from 27.6mg/L to 5.96mg/L, and the removal efficiency raised from 26.8% to 84.2%.

The increase of removal efficiency of Ba<sup>2+</sup> and Sr<sup>2+</sup> may be caused by rising pH. When pH kept rising, HCO<sub>3</sub><sup>-</sup> continuously turned to CO<sub>3</sub><sup>2-</sup>, which further made Ba<sup>2+</sup> and Sr<sup>2+</sup> translated to BaCO<sub>3</sub> and SrCO<sub>3</sub> respectively (be removed as sediment). The rising pH also promoted the reaction that SiO<sub>2</sub> turned to SiO<sub>3</sub><sup>2-</sup>, and then the SiO<sub>3</sub><sup>2-</sup> reacting with Ca<sup>2+</sup>(Mg<sup>2+</sup>) to form CaCO<sub>3</sub> (MgCO<sub>3</sub>) [15-16].

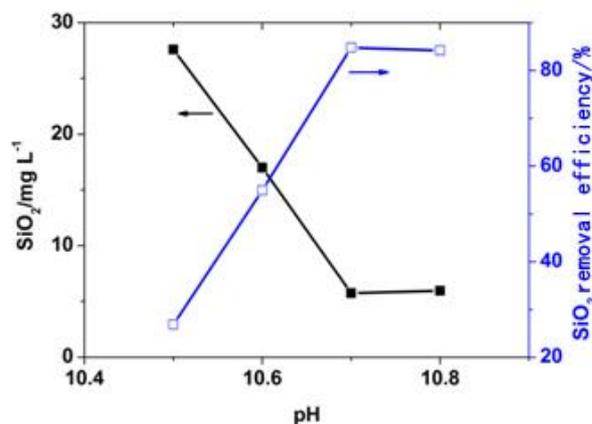
It can be speculated that using NaOH to remove Ba<sup>2+</sup>, Sr<sup>2+</sup> and SiO<sub>2</sub> should follow reactions below:



**Fig.6** Variations in Ba<sup>2+</sup> at different pH



**Fig. 7** Variations in Sr<sup>2+</sup> at different pH



**Fig. 8** Variations in SiO<sub>2</sub> at different pH

## 4 Conclusion

For preferable removal efficiency, the dosage of NaOH and Na<sub>2</sub>CO<sub>3</sub> should be regulated to 680mg/L and 380mg/L respectively, and the pH should be no less than 11.2. The predicting outcomes are that Both Ca<sup>2+</sup> and Mg<sup>2+</sup> will be no less than 20mg/L, which meet the target of wastewater treatment.

This paper deducts the removal mechanism: scale ions are mainly removed by translated to sediment. Ca<sup>2+</sup> is translated to CaCO<sub>3</sub>; Mg<sup>2+</sup> is turned to Mg(OH)<sub>2</sub>; Ba<sup>2+</sup> and Sr<sup>2+</sup> become BaCO<sub>3</sub> and SrCO<sub>3</sub> respectively; SiO<sub>2</sub> may be formed as CaSiO<sub>3</sub> and MgSiO<sub>3</sub>.

## References

1. S.U. Yan, X.U. Zhen, Z. Wang, J. Wang. Application of zero wastewater discharging system in a power plant with air-cooled units situated in northern china. *Thermal Power Generation*, 40(10), 74-77 (2011).
2. X.U. Yiming, H.E. Qingfeng, J. Huang, L.I. Pingli, Y. Chen, W.U. Haoyun, et al. Influence of pretreatment of reverse osmosis concentrate on performance of air gap membrane distillation process. *Membrane Sci. Technol.* 34(3): 86-91 (2014).
3. H. Zhang, L. Cui, B. Wu. Present situation of the research on water hardness removal. *Ind. Water Treat.* 31(12), 5-8 (2011).
4. J.T. Zhang, J. Dong. Comparative analysis of recycling technology of circulating sewage treatment of thermal power plant. *Technol. Water Treat.* 38(8), 124-127 (2012).
5. Z.Y. Xiao, Y. Chen, W.Q. Kang. Leakage test of rare earth tailings dam treated by lime softening - precipitation filtration - reverse osmosis. *Technol. Water Treat.* 38(9), 96-99 (2012).
6. R.Z. Hu, Y.L. Huang, S.Y. Yang. Comparison hardness removal of underground water resource by lime and sodium hydroxide. *Water & Wastewater Eng.* 42(7), 29-35 (2016)
7. L. Tian, Y. Qi, N. Yang. Research on the removal of scale ions from RO concentrated water by chemical coagulation process. *Ind. Water Treat.* 34(2), 43-46 (2014).
8. F.I. Gong, Y.Q. Wang, M.J. Shan, et al. To treat the hardness of reverse osmosis concentrate brine by lime softening method. *Environ. Sci. & Technol.*, 37, 154-157 (2014).
9. L. L. Jing, W.U. Song, L. Wang, et al. Study on the Advanced Treatment of Groundwater with High Concentration of Hardness and Sulfate. *J Chongqing Normal Univ.* 31(6), 153-158 (2014).
10. F. Duan, W.G. Dong, L.F. Tian. Research on the removal of organic compounds from high salinity wastewater from coal chemical industry. *J. Coal Processing & Comprehensive Utilization.* (4), 21-24 (2016).
11. T.L. Ye, X.J. Wang, L. Reng. Advanced treatment and reuse of Printing RO concentrated water, *Chinese J Environ. Engin.* 9(2), 781-786 (2015).
12. Q.G. Wang, C. Le, P.F. Fu, W.L. Jiang, Y. Han, R.F. Zhuo. Study on the treatment of nanofiltration concentrated liquor of landfill leachate by the coagulation-coagulation-coagulating sedimentation-electrochemical oxidation process. *Environ. Sci. & Technol.* 27(3), 27-30 (2014).
13. East China architectural design institute co. LTD. Water supply and drainage design manual(Book 4: Industrial water treatment) 2nd edition. [M]. Beijing: China architecture & building press. (2002)
14. Yuhua L, Haiyang D. Study on the removal hardness of circulating cooling water of power plant. *J. Refining & Chem. Ind.* 23(12), 11-13 (2012).
15. Jing W, Zhengjiang W, Baohong Y. Experimental study on the pretreatment process of the terminal wastewater of coal-fired power plant. *Thermal Power Generation.* 39(10), 55-59 (2010).
16. R.F. Jin, D. Wang, J.T. Zhou, L.M. Teng, J. Su. Experimental study on the treatment of silicate wastewater by coagulation method. *Ind. Water Treat.* 23(1), 42-44 (2003).