The control of the $\text{Ca}^{2+}$ concentration in the water treatment of the central air conditioner

Min Chen, Mian Xue, Huiwu Xu, Xiaoguang Zhang
Energy Research Institute, Henan Academy of Science, Zhengzhou 450008, China

Abstract. This paper introduced the relationship between the $\text{Ca}^{2+}$ concentration and the fouling, so that the efficiency of central air conditioning to achieve the best. Through the experiment and long-term site test data, we can know that should control the $\text{Ca}^{2+}$ concentration between 160 and 180 mg/L.

1. Introduction
The central air conditioning water system consists of two parts of the cooling water system and freezing water system. [1] The cooling water system always is the open system, but the refrigerant plenty of water is the closed system. Not only wastes a large amount of energy, but also the normal operation of the air conditioning system can be bring a lot of harm. Conversely, we treat the water system. It will bring many benefits. First, energy conservation. Second, extend the service life of system piping and equipment. Third, ensure the normal operation of central air conditioning unit stability, reduce the failure rate and reduce maintenance costs, better to create a stable and comfortable working and living environment, serve the society.

In this paper, we mainly discuss between scale and $\text{Ca}^{2+}$ concentration. As we all know,[2] Prompted the formation of carbonate precipitation, calcium carbonate deposition on the surface of heat exchanger, the formation of the density of calcium carbonate scale, its thermal performance is very poor, so as to reduce the heat transfer efficiency of heat exchanger, serious when they make any blockage.

2. Scale formation mechanism and the mechanism of the water quality stabilizer

2.1. The mechanism of scale formation
In dilute solution solute ions, complex ion and single molecules and single molecular states exist, but in a supersaturated solution, generated by several dozens of molecular aggregation and crystal nucleus. The speed of crystal growth from the solute in the solution to the diffusion velocity of the crystal surface, and the solute on the surface of the crystal surface precipitation rate decision. Diffusion force is crystal on the surface of the solute concentration and concentration in the solution, the difference between the factors related to the diffusion velocity is the velocity, temperature, solution viscosity, etc. Kossel model proposed by the earlier that the adsorption of solutes on the crystal surface, for surface diffusion is called Kink lattice defects parts move, and crystallization.

2.2. The mechanism of the water quality stabilizer
By above knowable, to prevent the generation scale, can adopt the following three methods: prevent
generated crystal nucleus or critical nucleus; Prevent crystal growth; Scattered crystals.

In supersaturated solution, in order to prevent scaling, you can use the scale inhibitor, usually can use of scale inhibitors have polyphosphate, phosphoric acid salt and carboxyl group of low molecular weight polymer electrolytes. Scale inhibitor of functional group of scale of the components of the cation chelation. On the scale inhibition mechanism of chelating agent and different scale inhibitors, for chelating agent, to prevent the concentration of the scale, the relative concentration of cationic need equivalent concentration of chemical calculation. And for scale inhibitors, to prevent the concentration of the scale, with very small amounts, in contrast to the cation concentration, are equivalent concentration of chemical calculation.

If in the open system, cooling water system in the residence time is the critical crystal nucleus formation induction period, will not cause the scale formation. In the scale inhibitor is not used, however, because of in a very short time scale, therefore, in retention time long open cycle cooling water system, need to use the scale inhibitors.

3. A profile of circulating cooling water system in central air conditioning

3.1. The running parameters of circulating cooling water system

At present, for the most part of Zheng-Zhou hotel, restaurant, shopping malls, supermarkets and other service industries that are used in central air conditioning, such as steam boiler circulating water cooling system with tap water as make-up water. In this article we take the He-nan Zheng-Zhou international hotel Sofitel circulating cooling water system as an example, its various operation parameters see table 1 below.

| Item                              | Parameters |
|-----------------------------------|------------|
| Water recirculation rate/(m$^3$. h$^{-1}$) | 400        |
| Holding water quantity/(m$^3$)     | 45         |
| Splash quantity/(m$^3$. h$^{-1}$)  | 0.2        |

3.2. Circulating cooling water supplement water quality

The hotel make-up water for circulating water for tap water, the water quality are shown in table 2.

| The test items                              | Parameters |
|---------------------------------------------|------------|
| pH                                          | 6.50       |
| Electrical conductivity/( $\mu$S. cm$^{-1}$) | 814        |
| Hardness/( mmol. L$^{-1}$)                   | 3.13       |
| $\rho$(Ca$^{2+}$)/(mg. L$^{-1}$)             | 72.41      |
| $\rho$(Cl$^{-}$)/(mg. L$^{-1}$)              | 121.40     |
| Alkalinity/(mg. L$^{-1}$)                    | 207.45     |
| $\rho$(Fe$^{2+}$+Fe$^{3+}$)/(mg. L$^{-1}$)  | 0.5640     |
| Solid content/(mg. L$^{-1}$)                 | 626        |
| Total phosphorus content/(mg. L$^{-1}$)      | 0.1233     |

4. Field application

4.1. The determination methods of Ca$^{2+}$

Using EDTA titration method [4] to determine the concentration of Ca$^{2+}$, namely: take 10 ml Sofitel international hotel central air conditioning cooling water in the middle of 250 ml conical flask, add 3
drops of hydrochloric acid (1 + 1), 20% potassium hydroxide 5 ml, plus 30 mg calcium flavin - phenolphthalein indicator, fluorescent yellow-green with EDTA titration to disappear, and red is the end (due to the instructions in the process of titration end point is not easy to see, we should be determined under the white light, and at the bottom of the conical flask while darker black leather cushion live on the other table, this facilitate our observation of titration end point). Calcium ion mass concentration calculated according to the formula (1),

$$\rho(Ca) = \frac{V(EDTA) \times \rho(EDTA) \times 40.08}{V(water)} \times 1000$$  \hspace{1cm} (1)

Among them:
- $V(EDTA)$ — Determination of calcium ion concentration of the consumption of EDTA standard solution volume, mL;
- $\rho(EDTA)$ — The concentration of EDTA standard solution, mol/L;
- $V(water)$ — By taking the volume of cooling water, mL;
- 40.08 — With the 1.00 mL EDTA standard solution ($\rho(EDTA) = 1.000$ mol/L) is quite, to the quality of the calcium ions mg said.

4.2. The performance of the water quality stabilizer

Water quality stabilizer for palm red transparent clear solution, alkaline, shelf life for half a year, through the observation, after six months will be in the bottom crystal precipitation, precipitation is does not affect the use of the early, but if there is a large amount of precipitation will affect when used. The drug is mainly applied to cooling and circulating water system, and to the effects of anti-scaling gentle erosion. Each dosing quantity should calculate according to the test system of filling water to join.

4.3. Actual operation data and analysis

From May 2013 to October, the hotel the central air conditioning cooling water circulation for the laboratory test and water treatment, we take the typical measured below, in the table below for the hottest water quality analysis of the measured values, are shown in table 3 below.

| Sampling time | pH   | Temperature difference(℃) | $\rho(Ca^{2+})/(mg. L^{-1})$ | Solid content/(mg. L^{-1}) | S   | Treatment measures |
|---------------|------|---------------------------|-----------------------------|---------------------------|-----|-------------------|
| 20130709      | 8.2  | 3.3                       | 158.02                      | 3138                      | 5.70| 2.0L(W)           |
| 20130711      | 8.0  | 3.8                       | 162.78                      | 4936                      | 5.84| 2.3L(W)           |
| 20130714      | 8.0  | 2.8                       | 120.02                      | 4312                      | 5.28| 2.4L(W)           |
| 20130716      | 8.3  | 3.4                       | 125.28                      | 5392                      | 5.24| 2.1L(W)           |
| 20130718      | 8.0  | 4.6                       | 145.05                      | 5596                      | 5.62| 2.3L(W)           |
| 20130721      | 8.3  | 5.8                       | 190.20                      | 1920                      | 4.74| Sewage            |
| 20130723      | 8.0  | 3.6                       | 171.68                      | 7142                      | 6.06| 1.8L(W)           |
| 20130725      | 8.0  | 2.7                       | 178.23                      | 6614                      | 5.66| 1.9L(W)           |
| 20130728      | 7.8  | 1.7                       | 176.02                      | 2284                      | 6.02| 1.4L(W)           |
| 20130730      | 7.5  | 1.6                       | 169.43                      | 2178                      | 6.06| 2.1L(W)           |

Note: the "w" in the table refers to the water quality stabilizer

From the chart we can see when the $\rho(Ca^{2+})/(mg. L^{-1}) > 180$, we take the drainage measures; When the $\rho(Ca^{2+})/(mg. L^{-1}) > 180$, we add a certain amount of water quality stabilizer. S is the stability constant of the table, Ryzner pointed out [5], for inhibiting corrosion precipitate calcium
carbonate, instead of using saturation index, use stability index. Can use type (2) to predict corrosion or scaling.

\[ S = 2p - \text{pH} \]  \hspace{1cm} (2)

Judgment method is as follows:

- \( S = 6 \) Chemical equilibrium
- \( S > 6 \) Has a tendency to corrosion
- \( S < 6 \) Has a tendency to scale

In addition, we known from the literature [6] in the following Table 4,

| Stability index S | The tendency of water          |
|------------------|--------------------------------|
| 4.0~5.0          | Severe scaling                 |
| 5.0~6.0          | Mild scaling                   |
| 6.0~7.0          | Basically stable               |
| 7.0~7.5          | Slight corrosion               |
| 7.5~9.0          | Severe corrosion               |
| >9.0             | Extremely severe corrosion     |

We know from the above table, stability index should be controlled at about 6.0, can be achieved using the standard.

Watching our site processing of data, we are to control the stability index of 6.0 or so, and at the same time \( \rho \frac{(\text{Ca}^{2+})}{(\text{mg/L})} \) is controlled in 160.0~180.0, ensure air conditioning energy conservation and environmental protection of the normal operation, it shows that we are in the water treatment control the \( \text{Ca}^{2+} \) concentration in 160.0~180.0 mg/L is reasonable. In addition, we can also be found in clean air conditioning system, is on the inside of the water treatment scale are much less obvious.

5. Conclusion

By a large number of field experience, normally we should control the \( \rho \frac{(\text{Ca}^{2+})}{(\text{mg/L})} \) concentrations in 160.0~180.0, when the

- \( \text{Ca}^{2+} \) concentration is less than 160 mg/L, we add a certain amount of water quality stabilizer, when the \( \text{Ca}^{2+} \) concentration is higher than 180 mg/L, we will drain and add a certain amount of added water. Not only solve the problem of scale formation, and added water, also save the costs for cleaning at the same time, improve the economic benefits and environmental benefits.

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