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Study on the Hard Water Softening Treatment and Its Mechanism Based on the Solubility Product

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ABSTRACT

The paper was based on the knowledge of solubility product(Ksp) which is applied to softening treatment of hard water, and emphatically analyzed the mechanism of transforming permanent hard water into temporary hard water by using Ksp principle. Then the following conclusion were drawn: The transformation of the permanent hardness which belong to the same type is suitable for the conversion of CaSO_4 to CaCO_3 in hard water, and the transformation of different types of permanent hardness is suitable for the transformation of CaCl_2 , MgCl_2 and MgSO_4 in hard water. In this paper, the conversion efficiency of CaSO_4 to CaCO_3 was studied by experiments, and the amount of transformation was predicted by linear regression equation. In the prediction, the maximum absolute error was 0.67, the maximum relative error was 0.1%, the average absolute error was 0.073, and the average relative error was 0.028%. Therefore, the prediction accuracy is high and reliable.

1. Introduction

The rapid development of science and technology, promoting the development of industry, improving the quality of people's life. As an important part of industrial production and daily life, water is also getting more and more attention. The problems of hard water not only affect the industrial production, often bring security risks, but also affect people's health in a certain extent. How to use the simple way to make the concentration of calcium, magnesium ion concentration decrease in hard water, become a topic of our concern.

1.1. The Concept of Hard Water

The hard water is the water which containing much soluble calcium and magnesium ions, for example well water and spring water. The hardness of water is the content of salt in the water, that is, the content of calcium salt and magnesium salt. Groundwater such as well water and spring water contain much salt, belongs to hard water. In hard water, the Ca and Mg exist in the form of carbonate, bicarbonate, chloride and nitrate etc. The water contain more salt, the greater the hardness is, and vice versa[1].

1.2. The Classification of Hard Water

According to the content of calcium carbonate and magnesium carbonate in water(To couched in the forms of mg/L or ppm), the hardness of water is divided into four grades: soft water, 0-60ppm, a little hard water, 60-120ppm, hard water, 120-180ppm, the extremely hard water, 181ppm or more. The hard water also can be divided into temporary hard water and permanent hard water. The temporary hard water is the acid saline solution formed by Ca and Mg carbonate. The salt solution containing calcium bicarbonate and magnesium bicarbonate, the salt can be removed by boiling. Permanent hard water is the salt solution formed by the oxides of Ca, Mg sulfate salt solution containing calcium sulfate, sulfuric acid magnesium or calcium chloride, magnesium chloride salt solution. The heating method cannot translate the permanent hard water into soft water by salt precipitation[2].

1.3. The Harm of Hard Water

Hard water does not cause direct harm to human health. The hard water

quality of drinking water is rich in mineral elements needed for human body. It is a significant channel for people to supplement trace elements such as Ca, Mg, etc. But for the infant, infant's gut has not yet fully developed, if we use high hardness hard water to brewing infant formula which contains protein and mineral nutrients, excessive intake of mineral elements can cause indigestion.

In daily life, drinking hard water will have a certain impact on human health. People never drinking hard water before drinking it occasionally, can cause gastrointestinal dysfunction, the so-called "not yet acclimated to the new place". Use hard water to cook fish and vegetables will destroy or reduce the nutritional value of food for not easy to cook. Use hard water to brew up tea will change it's color, flavor and taste.

More specific, use hard water to wipe mirror would make it full of water stains. Washing clothes with hard water will reduce the washing efficiency of the soap and detergent. It also will cause water heaters, humidifiers and other equipment's pipe blocking, flow reduced, life expectancy shortened. Long-term use of hard water washing will not only make the white bathtub yellowing and on the surface of water using appliances is covered with scale plaque. It will cause human's skin become dry, rough and itching. The hair washed by hard water will dry, knotted and not easy to comb[3].

And in industrial production, Use boiler boiling hard water in long-term will form a pot of scale, hind the heater conduct heat. When the pot scale is too thick, it will cause the local overheating of the boiler, even cause the boiler cracked and explosion accident. At the same time, because the hard water problem, in industry, it cost tens millions of money each year due to equipment, pipeline's repair and replacement[3].

2. The Conventional Treatment Method of Hard Water

2.1. Electromagnetic Method

In water, with a certain electric or magnetic field to change the characteristics of the ion, even change deposition rate of CaCO_3 or MgCO_3 and physical characteristics during the deposition to prevent the form of hard water scale. Its main function is to affect the physical properties of the scale within a certain range. So the use of water after the treatment has a certain limitations in use time and scope. Mainly used for commercial circulation cooling water treatment, for instance, central air-

conditioning[4].

2.2. Ion Exchange Method

Many new synthetic ion exchange agents can be used to exchange Ca^{2+} , Mg^{2+} , etc. in the water. The Na^+ in the resin can remove the Ca^{2+} and Mg^{2+} in water by ion exchange. The saturated resin can be regenerated by 5%-8% NaCl solution. After the resin's softening, the Ca^{2+} and Mg^{2+} in the water can be replaced by Na^+ , which can be cause water hardening. But the salt content of the treated water will not be reduced[5].

2.3. Boiling Method

When the Hard water boiled, the water contains $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$ will be decomposed into insoluble CaCO_3 and Slightly soluble MgCO_3 . The MgCO_3 can react with water to produce more soluble $\text{Mg}(\text{OH})_2$ under the condition of further heating. But this method applies only to temporary hard water[4]. The chemical reaction equation is as follows.

2.4. Chemical Deposition Method

For permanent hard water, because of Ca^{2+} and Mg^{2+} exist in sulfate or chloride formation, boiling method can not achieve the softening result. It can be remove by milk of lime and soda ash[6].

For permanent hard water, we can use Na_3PO_4 or Na_2HPO_4 as precipitating agent to react with Ca^{2+} , Mg^{2+} and generated $\text{Ca}_3(\text{PO}_4)_2$ and $\text{Mg}_3(\text{PO}_4)_2$. Do not need to filter, because the precipitation is loose and stable, it will not produce scale. So the water with nitrate precipitation can be sent to the boiler for use[7].

Common water softener: sodium phosphate, six sodium hexametaphosphate, amine derivatives(EDTA).

3. The Transformation Mechanism of Permanent Hardness to Temporary Hardness by K_{sp} and S

3.1. Transformation of Permanent Hardness of the Same Type

For the transformation of permanent hardness of the same type, it is suitable for CaSO_4 transformation in hard water.

Hypothesis: $\text{CaSO}_4(\text{s}) + \text{CO}_3^{2-}(\text{aq}) \rightleftharpoons \text{CaCO}_3(\text{s}) + \text{SO}_4^{2-}(\text{aq})$

$$\text{So: } K^{\theta} = \frac{[\text{SO}_4^{2-}][\text{CaCO}_3]}{[\text{CO}_3^{2-}][\text{CaSO}_4]} = \frac{[\text{SO}_4^{2-}]}{[\text{CO}_3^{2-}]} \times \frac{[\text{Ca}^{2+}]}{[\text{Ca}^{2+}]} = K^{\theta}_{\text{SP}}(\text{CaSO}_4) / K^{\theta}_{\text{SP}}(\text{CaCO}_3)$$

According to the related form. $K^{\theta}_{\text{SP}}(\text{CaSO}_4) = 2.45 \times 10^{-5}$, $K^{\theta}_{\text{SP}}(\text{CaCO}_3) = 8.7 \times 10^{-9}$, so $K^{\theta} = 2.8 \times 10^3$. Because the K^{θ} indicates the extent of a reaction in this equation $K^{\theta} = 2.8 \times 10^3$. So the value of K is large. Precipitation transformation is quite completely. This equation is right. Thus, for the same type of precipitation, the precipitates with large solubility product (K_{SP}) can be easily transformed into the less solubility product (K_{SP}) precipitation[8].

3.2. Transformation of Permanent Hardness of the Different Type

For the transformation of permanent hardness of the different type, it is suitable for CaCl_2 , MgCl_2 and MgSO_4 transformation in hard water.

Taking CaCl_2 as an example. It is known that solubility(S) of CaCl_2 is much larger than solubility(S) of CaCO_3 .

Hypothesis: $\text{Ca}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CaCO}_3(\text{s})$

$$\text{So: } K^{\theta} = 1 / [\text{Ca}^{2+}] \times [\text{CO}_3^{2-}] = 1 / [K^{\theta}_{\text{SP}}(\text{CaCO}_3)] = 1.1 \times 10^8$$

In this Equation, precipitation transformation is quite completely. Thus, for the different types of precipitation, the precipitates with large solubility(S) can be easily transformed into the less solubility(S) precipitation[8].

4. The Correlation Between CaSO_4 Content and Its Transformation

According to $3.1 \text{ CaSO}_4(\text{s}) + \text{CO}_3^{2-}(\text{aq}) \rightleftharpoons \text{CaCO}_3(\text{s}) + \text{SO}_4^{2-}(\text{aq})$, $K^{\theta} = 2.8 \times 10^3$, the value of K^{θ} is large, so precipitation transformation is quite completely. In order to further study the efficiency, the study finished the preparation of ten groups water with different content of CaSO_4 . Adding $1.06 \times 10^{-2} \text{ mg/L Na}_2\text{CO}_3$ solution, the amount of conversion was measured as shown in Table 1.

Table 1. The amount of conversion of CaSO_4 in different concentration

Serial number	Concentration of CaSO_4 (mg/L)	Amount of conversion of CaSO_4 (mg/L)
1	55	43.11
2	110	98.32
3	165	152.73
4	220	208.49
5	275	262.89
6	330	318.65
7	385	373.05
8	440	428.81
9	495	483.21
10	550	537.61

According to the data of table 1 set up the regression equation shown as Figure 1.

Figure 1. The correlation between the content of CaSO_4 in different concentration and the amount of conversion

So the regression relation between CaSO_4 content and the amount of its transformation is $y = 1.00x - 11.799$.

Error analysis of the content of CaSO_4 and its transformation as shown in Table 2.

Table 2. Error analysis of the amount of conversion of CaSO_4 in different concentration

Serial number	Concentration of CaSO_4 (mg/L)	Amount of conversion of CaSO_4 (mg/L)		Absolute error	Relative error (%)
		Measured value	Predictive value		
1	25	13.19	13.20	0.01	0.08
2	80	68.14	68.20	0.06	0.09
3	135	123.22	123.20	-0.02	-0.02
4	190	178.57	178.20	-0.37	-0.02
5	245	232.97	233.20	0.23	0.10
6	300	288.73	288.20	-0.53	-0.02
7	355	343.13	343.20	0.07	0.02
8	410	397.53	398.20	0.67	0.02
9	465	453.30	453.20	0.10	0.02
10	520	507.69	508.20	0.51	0.01
Average value				0.073	0.028

As shown in Table 2, between the measured and predicted values the maximum absolute error was 0.67, the maximum relative error was 0.1%, the average absolute error was 0.073, and the average relative error was 0.028%. Therefore, the prediction accuracy is high and reliable.

5. Conclusions

Suitable precipitation conversion agent can translate permanent hard water into temporary hard water effectively.

For the transformation of permanent hardness of the same type, it is

suitable for CaSO_4 transformation in hard water. For the transformation of permanent hardness of the different type, it is suitable for CaCl_2 , MgCl_2 and MgSO_4 transformation in hard water.

By linear regression equation, between the measured and predicted values the maximum absolute error was 0.67, the maximum relative error was 0.1%, the average absolute error was 0.073, and the average relative error was 0.028%. Therefore, the prediction accuracy is high and reliable.

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