Study on concentrated seawater refining process by waste liquid in soda production

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Abstract. The concentrated seawater containing abundant salt components can be utilized as water resource in soda industry either to lower the production cost or prevent the environmental problems caused by excessive drainage. However, its application has been confined by the high contents of the scaling ions (Ca²⁺, Mg²⁺, SO₄²⁻) which probably cause production interruption and unnecessary energy consuming. Hence, this study has developed a process for concentrated seawater refining by the waste liquid from the soda production and investigated its optimum conditions: Ca(OH)₂/ Mg²⁺=1.0, pH ≥ 10.61, proportion of demonization waste liquid adding to 40% v/v, 10% w/v seed crystal input, and Ca²⁺/CO₃²⁻=1.1. The composition of refined liquid could satisfy the requirement of actual production.

1. Introduction

The capacity and scale of the seawater desalination projects are significantly growing in China recently since the rapid development of desalination technology that makes the desalinated seawater be an important alternative water resources, especially in the north-eastern coastal regions of China, short in the natural potable water resources. Meanwhile, the increasing amount of concentrated seawater, the byproduct in desalination process, also has aroused extensive attention, because its salt content is approximately double to nature seawater, the improper treatment and discharging would affect the local marine environment. Therefore, importing the concentrated seawater to the soda industry that the salt (majority of NaCl) acts as the main raw material, is a reasonable solution to utilize the resource of concentrated seawater as well as to increase the efficient and reduce the cost of soda production.

In spite of its beneficial aspects, the high concentrations of Ca²⁺, Mg²⁺, SO₄²⁻, regarded as the scaling ions that are apt to form insoluble crystals attached on the surface of equipment or pipes, probably resulting in a series problems, such as production interruption, unnecessary wash cost and energy consuming, etc. The methods of concentrated seawater refining that aim to removal the majority of scaling ions from the liquid before accessing to the production system, has been reported in several studies. Li caihong et al. [1], adopted chemical precipitation to soften the brine of salt lake, in which the lime milk was used to eliminate magnesium, and the calcium was precipitated by sodium carbonate subsequently. The impurity content of refined brine reached the requirement of soda production. Yuan junsheng et al. [2], used CO₂, the major component of flue gas, functioning as the...
precipitant to selectively remove the magnesium and calcium ions in seawater. The advantages were not only reducing the precipitant cost in the seawater refining process, but also partially clearing up the contamination of flue gas emission. Zhang ning et al. [3] developed the freezing technology, by which the removal rate of magnesium and calcium ions was 87.4%. The nan filtration technology, capable of providing better softening effect, was primarily applied on seawater pretreatment by SWCC Co., Ltd. in Saudi Arabia, of which the rejection coefficients of TDS, Ca\(^{2+}\), Mg\(^{2+}\), SO\(_4\)\(^{2-}\), were 37%, 80.67%, 88%, 93.56% respectively[4,5].

From the above research works, it can be concluded that the practical process of concentrated seawater refining should possess the following criteria: 1) high removal rate (≥80%); 2) relatively less energy and raw material consuming; 3) easy to operation and rare maintenance cost; 4) environment-friendly. The propose of this study is to explore a pretreat process of concentrated seawater softening, by which the content of Ca\(^{2+}\), Mg\(^{2+}\), SO\(_4\)\(^{2-}\) in the refined liquid is accessible to the soda production without the possibility of scaling. Moreover, the low price raw materials and even the waste liquid have been adopted in this process of that it not only lower the treatment cost, but also reduce the hazardous byproduct. To improve its applicability and efficiency, the optimum conditions and critical processing parameters are also investigated in this study.

2. Experimental section

2.1. Material and apparatus

The concentrated seawater was collected from a plan of seawater desalination project located in Caofeidian, HeBei province and the by-product waste liquid was collect from a plant of soda production in Tangshan Sanyou group Co., Ltd. The compositions were determined (as shown in Table 1) after being filtrated with medium-speed qualitative filter paper to remove the suspended matters. All the chemical reagents were of analytically pure level and deionized water was used during the tests. The refining treatment were performed in a 2 litre glass reactor, which was equipped with a mechanical agitator (as shown in Fig.1). The ion chromatography (Thermo fisher, ICS-900) was employed for ion contents determination and analysis.

| Table 1. The main compositions of three liquid materials. |
|---------------------------------------------------------|
| **Concentrated seawater**                                |
| Ion content    | SO\(_4\)\(^{2-}\) | Ca\(^{2+}\) | Mg\(^{2+}\) | Cl\(^{-}\)    |
| kg/m\(^3\)     | 3.57           | 0.54       | 1.56       | 24.06        |
| Salt content   | MgSO\(_4\)     | CaSO\(_4\) | MgCl\(_2\) | NaCl         |
| kg/m\(^3\)     | 3.60           | 1.36       | 3.80       | 35.10        |
| **Deammoniation waste liquid**                           |
| Ion content    | SO\(_4\)\(^{2-}\) | Ca\(^{2+}\) | Mg\(^{2+}\) | Cl\(^{-}\)    |
| kg/m\(^3\)     | N/A            | 43.40      | N/A        | 107.14       |
| Salt content   | MgSO\(_4\)     | CaCl\(_2\) | MgCl\(_2\) | NaCl         |
| kg/m\(^3\)     | N/A            | 102.99     | N/A        | 49.14        |
| **Production recycling liquid**                          |
| Ion content    | Na\(^{+}\)     | HCO\(_3\) | CO\(_3\)\(^{2-}\) |
| kg/m\(^3\)     | 40.01          | 2.17      | 51.12      |
| Salt content   | Na\(_2\)CO\(_3\) | NaHCO\(_3\) |
| kg/m\(^3\)     | 90.31          | 2.99      |            |

2.2. Methods

2.2.1. Magnesium precipitation The main reaction of this step:

\[
Ca(OH)_2 + Mg^{2+} \rightarrow Mg(OH)_2 \downarrow + Ca^{2+}
\]

The amount of lime added into the solution was calculated as the following equation:
Where \( C(Mg^{2+}) \) was the concentration of magnesium ion in concentrated seawater; \( V \) was the volume of concentrated seawater; \( R \) was the molar ratio of \( Ca(OH)_{2}/Mg^{2+} \); and \( P \) was the mass fraction of \( Ca(OH)_{2} \) in lime. The lime was mixed with 500ml refined liquid under the agitation of magnetic stirring apparatus in 30min to make aqueous lime solution. The prepared aqueous lime solution was then pumped into the reactor by a peristaltic pump at a controlled rate to maintain steady pH and supersaturation for magnesium hydroxide crystallizing. The suspension liquid was aged in 30min at ambient temperature and then filtrated by medium-speed qualitative filter paper. The components of separated liquid phase were determined by ion chromatography.

**Figure 1.** The experimental reaction apparatus.

### 2.2.2. Sulfate precipitation

The main reaction of this step:

\[
SO_{4}^{2-} + Ca^{2+} \rightarrow CaSO_{4} \downarrow
\]

The volume of deammoniation waste liquid, of which the major composition was NaCl and CaCl2, added into the solution was calculated as the following equation:

\[
V_{2} = \frac{C_{1}(Ca^{2+}) - C(Ca^{2+})}{C_{2}(Ca^{2+}) - C_{1}(Ca^{2+})} \times V
\]

where \( C \) (Ca2+) , \( C_{1} \) (Ca2+) and \( C_{2} \) (Ca2+) were the concentration of calcium in the magnesium removed liquid, sulfate removed liquid and deammoniation waste liquid respectively; \( V \) were the volume of magnesium removed liquid. A certain mass of CaSO4 within the range of screened particle size, which performed as seed crystal was induced to the solution, and mixed 30min by the mechanical agitator. The deammoniation waste liquid dropped into the reactor at a controlled rate. The suspension liquid was aged in 30min at ambient temperature and then filtrated by medium-speed qualitative filter paper. The components of separated liquid phase were determined by ion chromatography.

### 2.2.3. Calcium precipitation

The main reaction of this step was.

\[
CO_{3}^{2-} + Ca^{2+} \rightarrow CaCO_{3} \downarrow
\]
2.3. The volume of production recycling liquid, drained from plants and equipment wash with high Na2CO3 content, was calculated as the following equation:

\[ V(Na_2CO_3) = \frac{C(Ca^{2+}) \times V}{40} \times R \times 106 \]

Where \( C(Ca^{2+}) \) and \( V \) respectively represented the content of calcium ion and the volume of the solution after sulfate removal; \( R \) was the molar ratio of \( Ca^{2+}/CO_3^{2-} \); \( C(Na2CO3) \) was the content of sodium carbonate in production recycling liquid. The production recycling liquid was dropped into the reactor at a controlled rate. The suspension liquid was aged in 30min at ambient temperature and then filtrated by medium-speed qualitative filter paper. The components of separated liquid phase were determined by ion chromatography.

3. Results and discussion

3.1. Magnesium removal

The magnesium removal proportions, compared to the original concentrated seawater, within various Ca(OH)2/Mg2+ ratios were listed in Table 2. The removal ratios of magnesium corresponding to different pH values were shown in Fig. 2.

| Experiment | Ca(OH)2/ Mg2+ | Mg2+ removal ratio | pH   |
|------------|---------------|--------------------|------|
| No.1       | 0.8           | 74.66%             | 10.55|
| No.2       | 0.9           | 80.15%             | 10.61|
| No.3       | 1.0           | 86.31%             | 10.70|
| No.4       | 1.1           | 94.70%             | 10.91|
| No.5       | 1.2           | 99.53%             | 11.27|

From the data in Table 2, it can be seen that with the incensement of Ca(OH)2/ Mg2+, from 0.8 to 1.2, the magnesium removal proportion has synchronously raised, from 74.66% to 99.53%. Considering with the precipitant consuming and the capacity of subsequent calcium elimination process, 1.0 was adopted as the optimum molar rate between Ca(OH)2 and Mg2+ in this step.

Fig.3 illustrated the relationship between magnesium removal ratio and pH value of the solution. The result is consistent with the tendency of Ca(OH)2/ Mg2+ that the higher pH value could promote the removal of magnesium. When the solution pH value reached to 10.61 or above, more than 80% soluble magnesium in the concentrated seawater would be precipitated and separated from the liquid phase.

3.2. Sulfate removal

As the apparent of “salt effect” that the existence of high concentrated strong electrolyte (NaCl), significantly influence the solubility of weak electrolyte (CaSO4), its solubility product constant (Ksp) was obviously varied to theoretical value. The recent concentration of calcium was insufficient to precipitate the soluble sulfate ion. Therefore, adding the demonization waste liquid to a certain proportion was able to raise the concentration of calcium ion and promote CaSO4 formation. In Table 3, it showed that adding the waste liquid to 20% and 40% proportion, the sulfate removal ratio was 43.33% and 50.61% respectively.
Figure 2. The removal ratios of magnesium via different pH values.

The comparison of dosage of selected CaSO4 as seed crystal was demonstrated in Table 4. With the dosage proportion gradually raising from 5%, 15% to 20% to the volume of the treated liquid, the SO42- removal ratios varied from 74.24%, and 77.00% to 76.67%. The average removal ratios increased approx. 50% compared to the former tests without adding seed crystal. The results proved that 10% w/v should be considered as the optimal dosage proportion for CaSO4 seed crystal. Otherwise, the extra input (20%) rarely functions in this situation. Hence, the seed crystal could be regarded as another crucial factor for improving the sulfate removal.

Table 3. The data of sulfate removal experiment

| Demonization waste liquid proportion (v/v) | Ca\(^{2+}\) Content | SO\(_4^{2-}\) Content | SO\(_4^{2-}\) Removal ratio |
|-------------------------------------------|----------------------|----------------------|--------------------------|
| 20%                                       | 10.03g/L             | 1.87g/L              | 43.33%                   |
| 40%                                       | 17.20g/L             | 1.63g/L              | 50.61%                   |

Table 4. The data of various seed crystal proportions experiment*

| Seed crystal Proportion (w/v) | Ca\(^{2+}\) Content | SO\(_4^{2-}\) Content | SO\(_4^{2-}\) Removal ratio |
|-----------------------------|----------------------|----------------------|--------------------------|
| 5%                          | 16.27g/L             | 0.85g/L              | 74.24%                   |
| 10%                         | 15.64g/L             | 0.76g/L              | 77.00%                   |
| 20%                         | 16.45g/L             | 0.77g/L              | 76.67%                   |

*The experiment performed in 40% demonization waste liquid addition.

3.3. Calcium removal

The data of calcium removal conducted in different rate of Ca2+/CO32- was listed in Table 5. The calcium removal proportion enhanced from 70.89% to 99.95% with the increment of Ca2+/CO32- ratio, from 0.8 to 1.1, and pH value raised from 6.98 to 9.42. Therefore, Ca2+/CO32- ratio=1.1 was adopted as the optimal calcium removal condition since the total residue contents of scaling ions in refined liquid already satisfying the procedures of soda production.
4. Conclusion
The prerequisite of utilizing the concentrated seawater from the desalination project, as an alternative water resource in soda manufacturing, is the refining pretreatment that prevents the insoluble salt from scaling through the production procedures. This paper has carried out a new approach that using lime and waste liquid generated along with the soda production for concentrated seawater refining and investigated its critical factors and optimal conditions.

Through the results of experiment and data analysis, it can be concluded that when pH value ≥ 10.61, more than 80% soluble magnesiu in the concentrated seawater can be precipitated; the salt effect has a significant influence on sulfate ion precipitation and the addition of seed crystal could increase the removal ratio within 50%; and the calcium removal proportion is obviously relevant to the Ca2+/CO32- rate. The optimum concentrated seawater refining conditions are: Ca(OH)2/ Mg2+=1.0, pH≥10.61, proportion of demonization waste liquid adding to 40%/v/v, 10% w/v seed crystal input, and Ca2+/CO32-=1.1. At the least 30min ageing time and well stirring also improve the effect of softening. After the entire treatment, the contents of scaling ions remaining in the refined solution: Mg2+=0.01g/L, Ca2+=0.01g/L, and SO42--0.27g/L reaches the water quality request of soda production.

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