# RESEARCH ON THE DESULFURIZATION TECHNOLOGY AND CALCIUM SULFATE PRODUCTION IN THE PROCESS OF EXTRACTING MAGNESIUM HYDROXIDE FROM BRINE

Zhou Xuejin Yuan Jianjun

College of Marine Science and Engineering,
Tianjin University of Science and Technology, Tianjin 300457, China

**Abstract**: The paper studied the desulfurization technique in the production of magnesium hydroxide using brine as raw material. Based on the analysis of the various factors whose effects were separately analyzed in several single-factor experiments, an orthogonal experiment was then conducted in order to get a proper set of operating parameters, and the results turned out to be ideal. Meanwhile, some experiments had also been carried out on the improvements of the quality of calcium sulphate dehydrate. The result reveals that both the purity and brightness has been improved quite a lot. The technique adopted here not only realizes the full utilization of the mother liquor of magnesium hydroxide, but also provides favorable conditions to the comprehensive utilization of sea water and brine, especially for the extraction of potassium chloride.

**Keywords**: brine; desulfurization technique; calcium sulphate dihydrate; orthogonal experiment; comprehensive utilization

## 1. PREFACE

Seawater is rich resources in magnesium and therefore is an important raw material for the production of high-purity magnesium compound. Magnesium compounds are the major chemical products of sea water utilization. The production capacity of magnesium compounds from sea water is about 100,000 tons in China. However, the product mainly is the magnesium chloride produced by evaporation technology, which has low value. We had successfully developed an innovative technology of producing magnesium hydroxide paste with brine and lime. The technology had been put into operation and obtained sound economic benefits. The schematic flow sheet used in this technology is shown in Figure 1.

At an early stage, calcium sulfate dehydrate produced in the process of extracting magnesium hydrate did not be used and to be stacked as a by product. At the same time, only a portion of the mother liquor of magnesium hydrate was used as precipitant. The rest of them were directly discharged into sea water, which more or less had some negative effects on environment. We had conducted further experiment in order to make the product of calcium sulfate so that the environment problem can be solved. Based on the experiment results, an industrial-scale production was developed and had been in operation, which put forward an innovative technology of comprehensive utilization of brine.

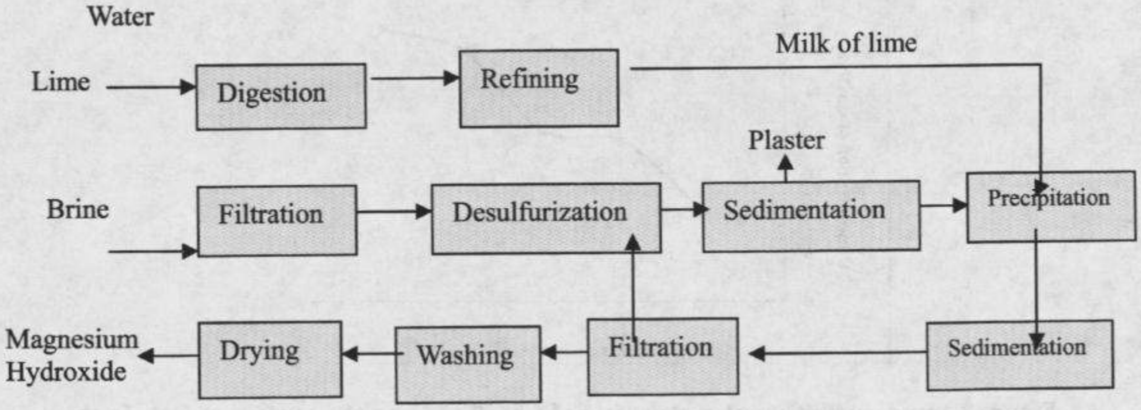


**Figure 1.Schematic flow sheet of producing magnesium hydrate with brine and lime**

## 2 . RESULTS AND DISCUSSION OF THE PROCESS OF DESULFURIZATION

According to the technical requirement of extracting magnesium from brine, the precipitant chosen here was the mother liquor of magnesium hydrate. When the mother liquor of magnesium hydroxide meets with the raw brine solution, precipitation reaction occurred as the following equation:

$CaCl_2+SO_4^{2-}=2Cl^-+CaSO_4\downarrow$

According to the precipitation crystallization theory, the factors influencing the desulfurization reaction and the quality of mother liquor were studied, respectively.

### 2 .1 Impact of ratio of $Ca^{2+}/SO_4^{2-}$ on the desulfurization process

The main composition of mother liquor of magnesium hydroxide is calcium chloride and sodium chloride. The reaction happens when the ions of calcium in the mother liquor meet with the ions of sulfate in the brine. The crystal of calcium sulfate was formed. The ion of sulfate was precipitated from the brine. The experiment revealed that the ratio of $Ca^{2+}/SO_4^{2-}$ had obvious effects on the desulfurization process. Figure 2 shows the concentration change of $SO_4^{2-}$ in the mother liquor of desulfurization in response to different molar ratios of $Ca^{2+}/SO_4^{2-}$.

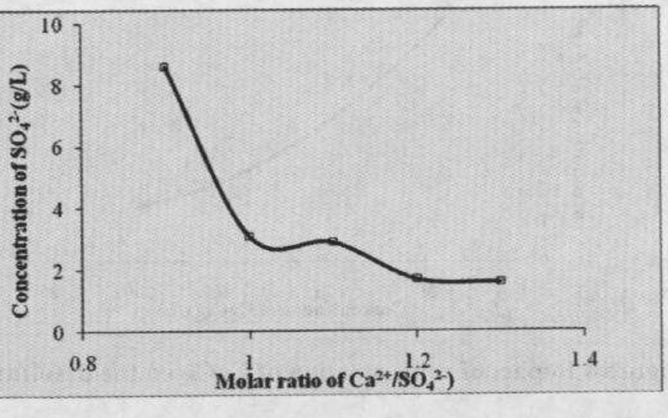


**Figure 2 Impact of molar ratio of $Ca^{2+}/SO_4^{2-}$ on the content of $SO_4^{2-}$ after desulfurization**

It can be seen from Figure 3 that the content of $SO_4^{2-}$ in brine was decreased with the molar ratio of $Ca^{2+}/SO_4^{2-}$ increased. It means that when the content of $SO_4^{2-}$ is a constant, the higher the concentration of $Ca^{2+}$ added, the better the desulfurization is. At the mean while, the content of $Ca^{2+}$ in the product was also increased. The high content of $Ca^{2+}$ reduced the purity of product. This condition is not good for producing high-purity magnesium hydrate.

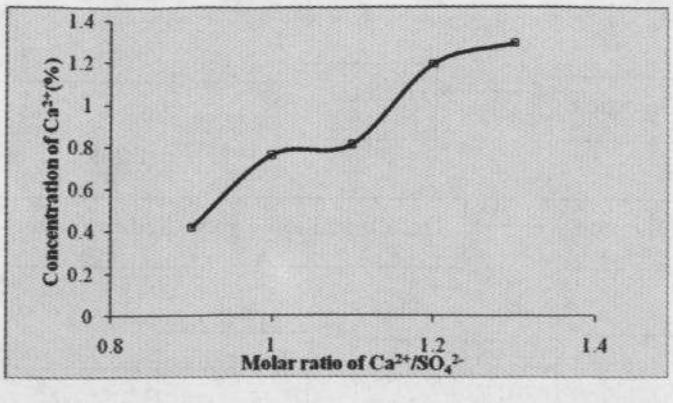


**Figure 3 Impact of different molar ratio of $Ca^{2+}/SO_4^{2-}$ on the content of $Ca^{2+}$ in the product**

**2. 2 Impact of the concentration of $CaCl_2$ in the mother liquor**

The experiment was carried out under the molar ratio of $Ca^{2+}/SO_4^{2-}$ equals to 1.2 by controlling the content of $CaCl_2$ in the mother liquor of the magnesium hydrate. The aim of the experiments is to find out the influence of concentration of $CaCl_2$ solution on the desulfurization process. Result of the experiment is shown in Figure 4.

It can be seen from Figure 4 that the content of $SO_4^{2-}$ in mother liquor after desulfurization is decreased with the concentration of $CaCl_2$ increased in feed. When the content of $SO_4^{2-}$ is a constant, the higher the concentration of $CaCl_2$ is, the better the desulfurization process is. This is due to the fact that the content of $CaCl_2$ reflects the actual concentration of total salt in the mother liquor of magnesium hydroxide. The high concentration of the salt in the solution reduces the solubility of $CaSO_4$. The concentration of $CaCl_2$ has a limitation in practical operation. Therefore, appropriate operation parameters should be selected.

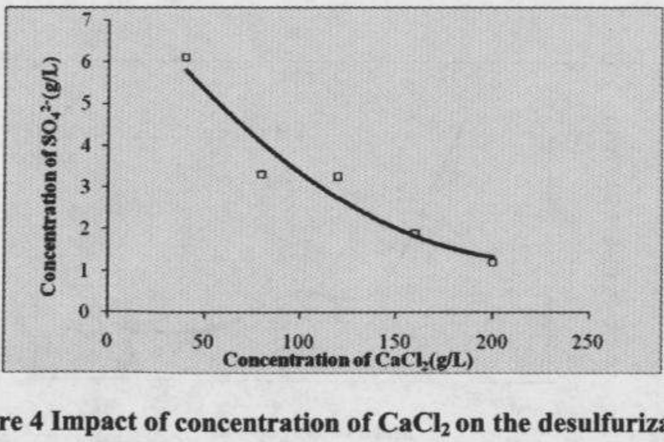


**Figure 4 Impact of concentration of $CaCl_2$ on the desulfurization**

**2.3 Impact of feed rate on the desulfurization**

The experiment was carried out by altering the feed rate of the mother liquor of magnesium hydroxide in precipitation process. It was found that feed rate has significant effect on the generation of $CaSO_4$. The lower the feed rate is, the lower content of $SO_4^{2-}$ in mother liquor after precipitation is, which is shown in Figure 5. The feed rate of the precipitant influences the degree of supersaturation directly. The degree of supersaturation can be kept at a low level with a slow feed rate, which is favorable in controlling the rate of nucleation and crystal growth and thus to obtain a larger size crystal. The properties of filtration of the crystals can be improved so that the high quality of the product could be expected,

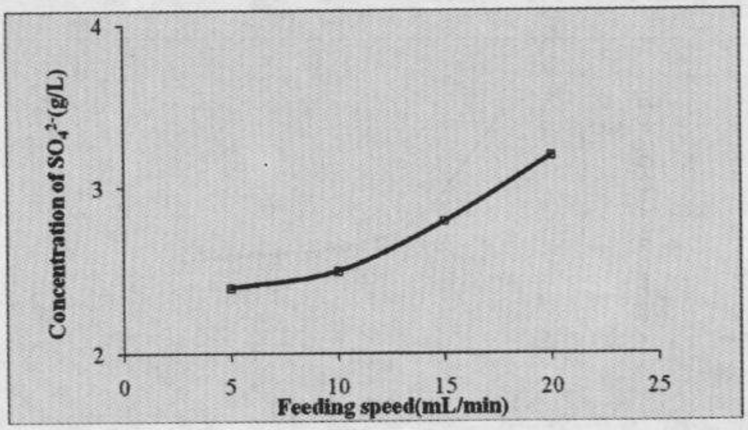


**Figure 5 Impact of feeding speed on the effect of desulfurization**

## 2.4 Impact of stirred speed on desulfurization

The mixing intensity has a strong impact on the crystallization process. The metastable zone becomes narrow and the rate of secondary nucleation will be increased with a fast stirred speed, which will produce a small crystal size. However, if the mixing intensity is too small, the crystal can not be suspended well. The suitable mixing intensity can be that the stirred speed enables a sufficient mixing to make the degree of supersaturation uniform. The result is shown in Figure 6

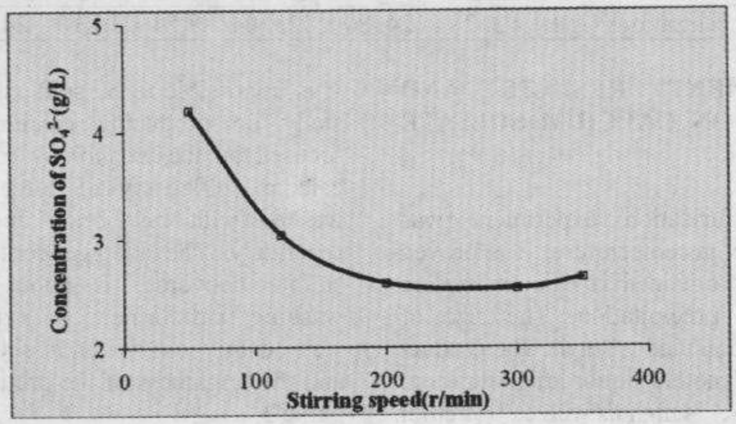


**Figure 6 Impact of stirred speed on the effect of desulfurization**

## 2.5 Impact of aging time on desulfurization

Under industrial equipment conditions, the degree of supersaturation in the precipitation is large, and the nucleation rate of calcium sulfate is quick. Large size crystals are hard to form. The crystal size could become larger after a certain time aging. The aging process is that the small crystal was dissolved while the large ones grew. Thus, the crystal becomes larger and more uniform comparing with before aging process. The aging process was carried out as that the mixing was still kept for a period after reaction. The results of effect of different aging times on the desulfurization are shown in Figure 7. The result revealed that the suitable aging time would be 2-3 hours in the precipitation of calcium sulfate.

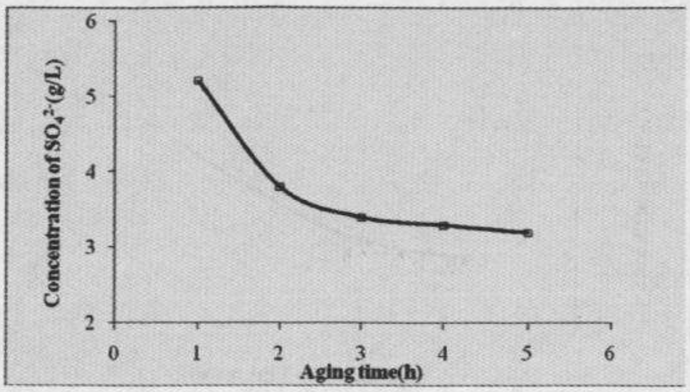


**Figure 7.Impact of aging time on the effect of desulfurization**

## 2.6 Results of the orthogonal experiment.

Based on results of the single-factor experiments, an orthogonal experiment was carried out by considering the main factors in the process. The main factors are molar ratio of $Ca^{2+}/SO_4^{2-}$, concentration of $CaCl_2$, feed rate of precipitant and stirred speed. According to the results of the orthogonal experiment the content of the mother liquor after desulfurization with the optimized operating parameters is given in Table 1.

**Table 1 Composition of mother liquor after desulfurization**

| Irons | $Ca^{2+}$ | $Mg^{2+}$ | $Cl^-$ | $K^+$ | $SO_4^{2-}$ | $Na^+$ |
|---|---|---|---|---|---|---|
| Concentrations ( g/L) | 3. 28 | 24. 80 | 123. 04 | 8.54 | 3.13 | 24.87 |

## 3. EXPERIMENT RESULTS AND DISCUSSION ON CALCIUM SULFATE PRODUCTION

The desulfurization experiment was carried out at room temperature. It is proved that the crystals obtained is calcium sulfate dehydrate after precipitation. The size of calcium sulfate obtained is small. The product contains a lot of mother liquor after filtration. The impurity level is high as well as bad color. It is impossible to be sold as a product. The study on producing calcium sulfate was focused on the technology of washing. The calcium sulfate crystals after filtration were washed with raw brine and fresh water, separately. The average content of calcium sulfate dehydrate is about 88.79% after washing with brine. The experiment result washed by fresh water is shown in Table 2 and the brightness of the product is shown as Table 3.

**Table 2 Average content of $CaCl_2$ washed by fresh water**

| Product | Component | | | | | $CaSO_4{\cdot}2H_2O$ | |
|---|---|---|---|---|---|---|---|
| | $Ca^{2+}$ | $Mg^{2+}$ | $K^+$ | $Cl^-$ | $SO_4^{2-}$ | Wet Base | Dry Base |
| Plaster(Filtration) | 18.93 | 0.58 | - | 3.14 | 45.29 | 81.4 | 94.22 |
| Plaster (Washed once) | 19.68 | 0.22 | - | 0.84 | 47.61 | 84.62 | 97.16 |
| Plaster (Washed twice) | 20.19 | 0.13 | - | 0.39 | 48.62 | 86.82 | 98.54 |

**Table 3 Brightness of $CaCl_2$**

| Item | Sample | | | Commercial product |
|---|---|---|---|---|
| | Unwashed | Washed by brine | Washed by fresh water | |
| Brightness | 77.74 | 84.62 | 94.69 | 87.35 |

## 4 CONCLUSIONS

(1)Among the factors influencing the desulfurization, the molar ratio of $Ca^{2+}/SO_4^{2-}$, feed rate and the concentration of calcium chloride are significant. The suitable molar ratio $Ca^{2+}/SO_4^{2}$ is about 1 because of that a slightly high molar ratio will cause the reaction toward the direction of generating $CaSO_4$, but a higher molar ratio of $Ca^{2+}/SO_4^{2-}$ will lead to a rise of the concentration of $Ca^{2+}$ in the mother liquor, which may affect the quality of product. Feed rate can directly influence the supersaturation in the crystallization process. A low feed rate is favorable in obtaining large size calcium sulfate dehydrate. A long reaction time requires a large volume of reactor. The concentration of calcium chloride is the main factor affecting the total concentration of the liquid phase after crystallization and further influences the solubility of calcium sulfate. According to the requirement of the precipitation of magnesium hydroxide, the calcium concentration was restrained in the mother liquor of the magnesium hydroxide. High concentration of calcium will result in a high nucleation rate, which is not favorable for the crystallization of calcium sulfate.

(2) The purity and brightness of calcium sulfate were improved by adopting washing technology. The crystals can be considered as valuable chemical product.

(3) Because the calcium sulfate can be a product the mother liquor in the process of extracting magnesium hydroxide is now being adequately used. This technology creates favorable condition for the comprehensive utilization of brine. Base on this technology, a more comprehensive technology routine may be formed in the salt chemical industry.

Reference


[1] Jian-Hua Yuan. Summary of new technology on desulfurization in brine [J]. Chlorine-alkali industry. 2002, 2(2):10-13

[2] Cao Fengmin, Zheng Jun. Technology improvement on removal of sulfate in salt water purification process [J]. Chlorine-alkali industry, 2003,1 (1): 13-14,16

[3] Ding Xiufen, Zhao Shoujun. Research on making $CaSO4{\cdot}2H_2O$ form the waste of bromide soda making industry [J]. Sea-Lake Salt and Chemical Industry (now the " Journal of Salt and Chemical Industry"), 2001, 30 (2): 21 - 29.

[4] Wang Luming. Study on the determining of reaction condition of making magnesium form brine [J]. Sea-Lake Salt and Chemical Industry (now the " Journal of Salt and Chemical Industry").2000, 29 (1): 8 - 9.

[5] Zhang Shibin, and so on. Influence of the chemical composition of saturated salt brine on the crystallization process of sodium chloride [J]. Sea-Lake Salt and Chemical Industry (now the " Journal of Salt and Chemical Industry"), 1996, 25 (4): 27 - 30.

[6] Ye Tielin. Principles and application of crystallization process in chemical industry [M]. Beijing: Beijing University of Technology Press, 2006.4.

[7] GarsideJ, Davey RJ, JonesA C. Advancesin Industrial Crystallization. London: Butter worth Heinemann, 1991, 1 - 15.