

QUANTITATIVE DETERMINATION OF DIFFERENT FORMS OF CALCIUM SULFATE BY POWDER X-RAY DIFFRACTOMETRY

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1. Introduction

Almost edible salt in Japan are produced by the manufacturing method with ion exchange membrane. In this method, seawater is concentrated by using ion exchange membrane electrodialyzer, and obtained brine crystallized through crystallization process. In brine, there are relatively large amounts of impurities such as magnesium, calcium and sulfate ions which are included in seawater. In these impurities, calcium and sulfate ions separate out during crystallization process, turning into calcium sulfates. In some cases, calcium sulfates attached to walls of equipment and heat transmission tube, causing operation problems. In addition, fine crystals of calcium sulfates may contaminate

into the products, bringing down the qualities of the products. For those reasons, it is important to clarify deposition behavior of calcium sulfates.

There are three different forms of calcium sulfates; dihydrate, hemihydrate and anhydrate. In salt production, the forms of calcium sulfate vary depending on temperature conditions and compositions of mother liquor. Moreover, because the transition phenomenon is caused, three kinds of hydrates are seen to exist together in the mother liquor as a suspension. Thus a method of X-ray diffraction analysis which can measure different forms of calcium sulfates simultaneously even in mixtures of three different types of hydrates was studied.

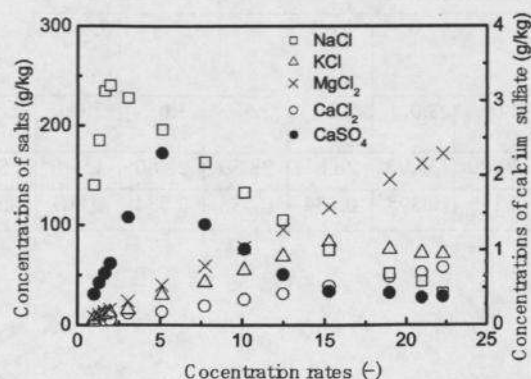


Figure1 Concentration characteristics of brine of the ion exchange membrane method

2. Concentrated characteristic of brine obtained by ion exchange membrane method. An example of condensation characteristics of brine obtained by the ion exchange membrane method is shown in Figure 1. When brine is concentrated, sodium chloride is separated out first and as further concentration occurs, solubility of sodium chloride decreases as calcium chloride and potassium chloride are concentrated and their concentrations increase. The compositions of mother liquor change during crystallization process as impurities become concentrated. In the manufacturing method with ion exchange membrane, separate of sodium chloride is

completed before potassium chloride is deposited and mother liquor at this stage is discharged as bittern.

On the other hand, calcium sulfates start to deposit almost at the same time as sodium chloride, beconcluded that high purity hydrates were successfully generated for each forms. Also from this figure, the largest angles of X-ray diffraction intensity specific to each form, 11.6° for dihydrates, 29.7° for hemihydrates and 25.5° for anhydrites were selected and those peaks were used for quantitative determination.

Table1 Composition of prepared sample

Mass concentration ratio(-)		
Dihydrates	Hemihydrates	Anhydrites
9	1	0
3	1	0
3	2	0
1	1	0
2	3	0
7	13	0
3	7	0
1	4	0
1	9	0
0	1	4
0	1	1
0	4	1
0	9	1
4	0	1
1	0	1
1	0	4
1	1	1
2	1	1
1	2	1
1	1	2
1	2	2
2	1	2
2	2	1
8	1	1
1	8	1
1	1	8

however they have tendencies to separate out in an order of dihydrate, hemihydrate and anhydrate as impurities in mother liquor increase and temperatures rise. As vacuum multiple-effect pan system is used in the ion exchange membrane method, the forms of calcium sulfates differ as temperature conditions and compositions of mother liquor in every crystallizer.

3. Experiments

Each form of calcium sulfates was prepared by the following method.

1) Dihydrates ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)

19wt% sodium sulfate aqueous solution and 21wt% calcium chloride aqueous solution were mixed at a temperature condition of 298K to generate precipitation. The precipitation that was isolated by filtration under reduced pressure and cleansed by purified water was dried for one day in a drying apparatus kept at 313K.

2) Hemihydrates ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$)

The obtained dihydrates at 1) was left sitting for 8 hours in the drying apparatus maintained in 423K.

3) Anhydrites (CaSO_4)

Dihydrates obtained at 1) was left sitting for 8 hours in an electric furnace kept at 1073K.

Three types of hydrates obtained in the above method were measured for the peak of X-ray diffraction using X-ray diffractometer (Mac Science, M03XHF22). However for measurement by X-ray diffractometer, X-ray target: Cu, Ni filter was used and measurement conditions were set at 40.0kV

tube voltage, 30.0mA tube current, 10.0~35.0deg measuring range and 5.0deg/min measuring speed.

The components of samples prepared by mixing calcium sulfate hydrates prepared as above are shown in Table 1. For those samples, the peak of X-ray diffraction was measured, setting the control conditions of X-ray diffractometer to be the same as the above.

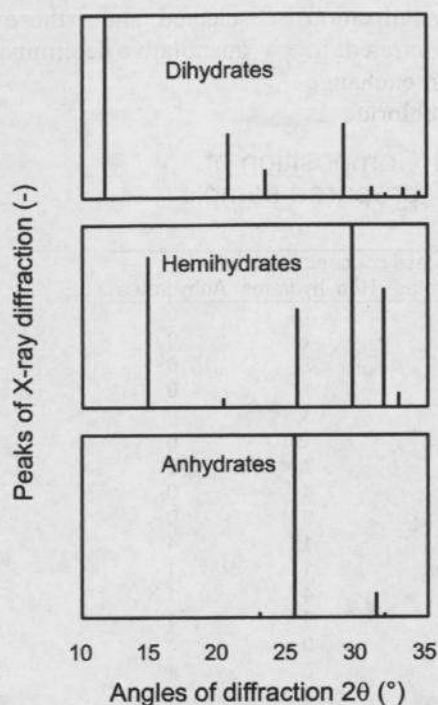


Figure2 Peaks of X-ray diffraction of each hydrates prepared

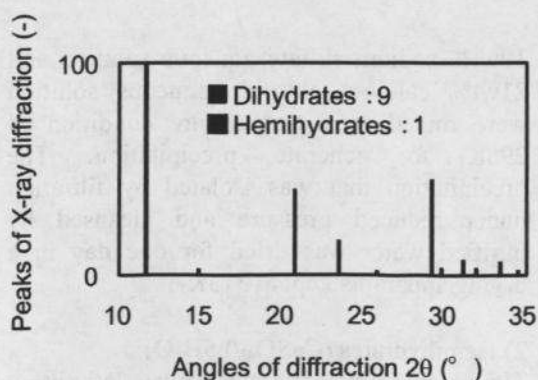


Figure3 The peaks of X-ray diffraction in samples with mixtures of two types of hydrates (mass concentration ratio dihydrates : hemihydrates = 9 : 1)

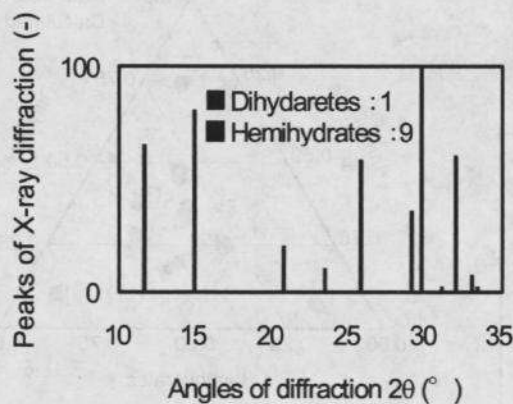


Figure4 The peaks of X-ray diffraction in samples with mixtures of two types of hydrates (mass concentration ratio dihydrates : hemihydrates = 1 : 9)

4.

Res

ults and discussion

4.1 The peaks of X-ray diffraction for each hydrate

Peaks of X-ray diffraction for each hydrates is shown in Figure 2. As each prepared samples shows an original pattern specific to each forms of hydrates in Figure 2, it can

4.2 Investigation of determination

be in proportion according to mass concentration ratio.

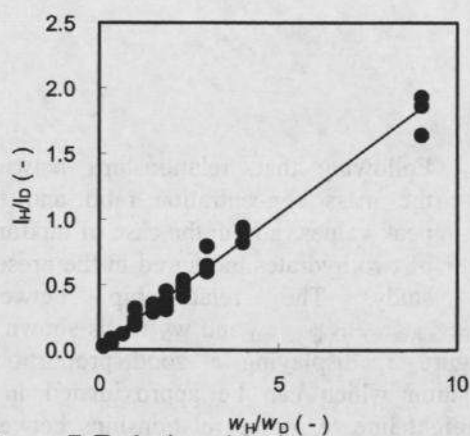


Figure5 Relationship between mass concentration ratio w_H/w_D and X-ray diffraction peak ratio I_H/I_D

Takashima et al.¹⁾ proposed determination of X-ray diffraction analysis subjecting samples with mixtures of two hydrates, reporting that

The peaks of X-ray diffraction when mass concentration ratio of hemihydrates and dihydrate were 1:9 and 9:1 respectively are shown in Figures 3 and 4. In the former case, the peak of hemihydrates is approximately 4 when the peak of dihydrates is fixed at 100. In the latter case, the peak of hemihydrates is 100 and the peak of dihydrates becomes approximately 55. When investigating all samples with mixtures of those two hydrates, their peak values were expected to

mass ratio of each hydrates can be shown as equation (1).

$$I_1/I_2 = k_{1/2} \times w_1/w_2 \quad (1)$$

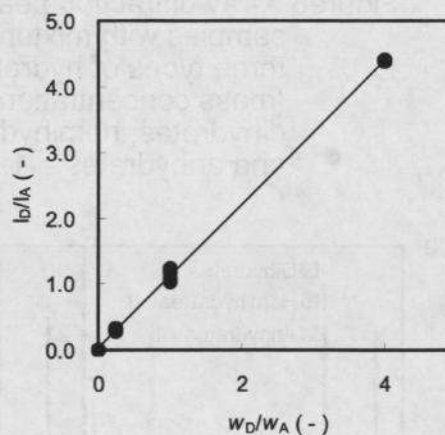


Figure7 Relationship between mass concentration ratio w_D/w_A and X-ray diffraction peak ratio I_D/I_A

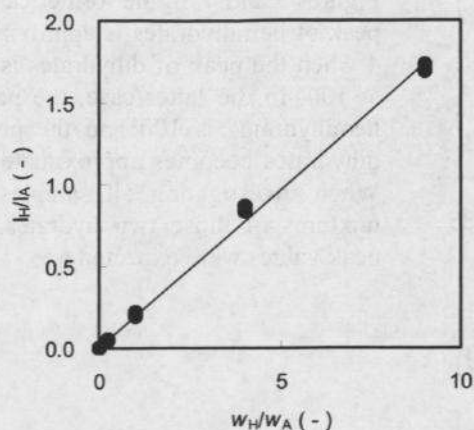


Figure 6 Relationship between mass concentration ratio w_H/w_A and X-ray diffraction peak ratio I_H/I_A

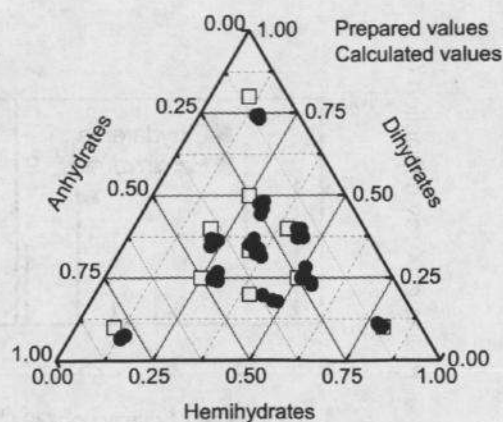


Figure 10 Relationships between the calculated mass concentrations by X-ray diffraction of samples with mixtures of three types

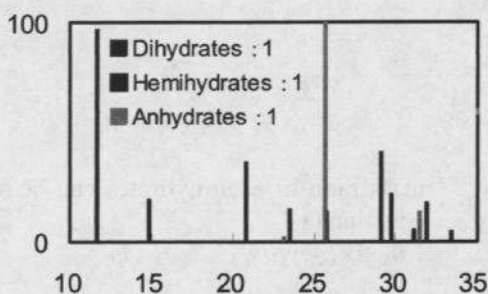


Figure 8 X-ray diffraction peaks samples with mixtures of three types of hydrates (mass concentration ratio of dihydrates, hemihydrates and anhydrites = 1:1:1)

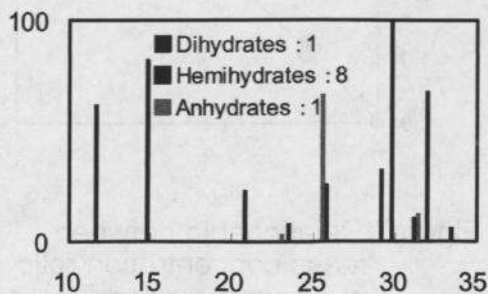


Figure 9 X-ray diffraction peaks samples with mixtures of three types of hydrates (mass concentration ratio of dihydrates, hemihydrates and anhydrites = 1:8:1)

Following that, relationships between the mass concentration ratio and the peak values ratio in the case of mixtures of two hydrates measured in the present study. The relationship between $I_{H(\text{hemihydrate})}/I_{D(\text{dihydrate})}$ and w_H/w_D is shown in Figure 5, displaying a good proportional relation which can be approximated in a straight line. Also the relationships between $I_{H/A(\text{anhydrate})}$ and w_H/w_A , $I_{D/A}$ and w_D/w_A are shown in Figures 6 and 7, displaying good proportional relations equal to that of Figure 5. Therefore, when two types of hydrates coexist, their respective coefficients $k_{H/D}$, $k_{H/A}$ and $k_{D/A}$ are 0.21, 0.19 and 1.1 respectively, and the mass concentration ratio can be

calculated by the equations (2), (3) and (4). In all combinations, the X-ray diffraction intensity and the mass concentration were in proportion. From this result, it can be shown that

$$I_H/I_D = k_{H/D} \times w_H/w_D \quad (2)$$

$$I_H/I_A = k_{H/A} \times w_H/w_A \quad (3)$$

$$I_D/I_A = k_{D/A} \times w_D/w_A \quad (4)$$

The peaks of X-ray diffraction measured in samples with mixtures of three types of hydrates were shown in Figures 8 and 9. In the former mass concentration ratio of dihydrates, hemihydrates and anhydrites is 1:1:1. In the latter mass concentration ratio of dihydrates, hemihydrates and anhydrate is 1:8:1. Just as samples with mixtures of two types of calcium sulfates, with the increase in the mass concentration of hemihydrates, the peak intensity also increased. The same tendencies were also observed in dihydrates and anhydrites.

If the equations (2) and (3) that were established between two hydrates could be applied to the samples with mixtures of three types of calcium sulfates, the following relationships are also expected to be valid.

$$I_H/I_D = k_{H/D} \times (w_H/w_D) \quad (2)$$

$$I_H/I_A = k_{H/A} \times (w_H/w_A) \quad (3)$$

$$w_H + w_D + w_A = 1 \quad (5)$$

When equations (2), (3) and (5) are adjusted accordingly to their mass concentrations, equations (6), (7) and (8) can be obtained.

$$w_H = 1/(k_{H/D} \cdot k_{H/A}) \times (I_H/I_D) \times (I_H/I_A)/A \quad (6)$$

$$w_D = 1/k_{H/D} \times (I_H/I_D)/A \quad (7)$$

$$w_A = 1/k_{H/A} \times (I_H/I_A)/A \quad (8)$$

In here, it can be defined that $A = 1/k_{H/D} \times (I_H/I_D) + 1/k_{H/A} \times (I_H/I_A) + 1/(k_{H/D} \cdot k_{H/A}) \times (I_H/I_D) \times (I_H/I_A)$. The relationships between the mass concentrations measured by X-ray diffraction method using equations (5), (6) and (7) and the actual mass concentration of each hydrate when actually prepared are shown in Figure 10. Though when the mass concentrations of hemihydrates are low, the measured figures have tendencies to be increased by around 5%, the concentration of each hydrate was excellently corresponding.

5. Conclusions

A simultaneous quantitative determination of calcium sulfates of different forms by X-ray diffraction method was investigated. When measuring substances including two types of calcium sulfates, the fixing proportional

constants $k_{H(\text{hemihydrate})/D(\text{dihydrate})}$, $k_{H/A(\text{anhydrate})}$ and $k_{D/A}$ from the relationships of X-ray diffraction intensity ratio and mass concentration ratio of each form of calcium sulfates was determined. In the cases of mixtures of three calcium sulfates, quantitative determination is possible for each form of mass concentrations, by using proportional constants $k_{H/D}$ and $k_{H/A}$.

We expect that it is possible to evaluate existing forms and implantation of calcium sulfates in solutions of salt manufacturing process by using the present method.

6. Reference

- 1) S. Takashima, G. Hashizume, T. Hagino, Nihon Shio Gakkaishi, Jpn., **10**, pp.178-182 (1956)