**Reactive crystallization of dolomite by CO2 fine bubble injection from concentrated brine and conversion to inorganic phosphor**

Taichi Kimura1, Yoshinari Wada1, Shinnosuke Kamei1, Koji Masaoka1, 2,

Toshihiko Hiaki1, Masakazu Matsumoto1\*

*1 College of Industrial Technology, Nihon University, 1-2-1 Izumi-cho Narashino, Japan;*

*2 Research Institute of Salt and Sea Water Science, The salt Industry Center, 4-13-20 Sakawa, Odawara, Japan*

*\*Corresponding author: matsumoto.masakazu@nihon-u.ac.jp*

**Highlights**

* Minimizing bubble size increased produced weight and Mg/Ca ratio of CaMg(CO3)2.
* Mg/Ca ratio of CaMg(CO3)2 increased with an increase in crystallization time.
* Emission intensity of CaMg(CO3)2 phosphor increased with increasing the immerse time.

**1. Introduction** During the salt manufacturing process in Japan, NaCl is manufactured by evaporative crystallization after concentrating seawater through electric dialysis membranes, and the concentrated brine which contains ions such as K+, Ca2+ and Mg2+ with high concentration is discharged. To build a utilization system for seawater resources based on the salt production process, a recovery and upgrading method for Ca2+ and Mg2+ from the concentrated brine is demanded. From the viewpoint of solubility of salts, the synthesis of carbonate by reactive crystallization between the dissolved Ca2+ and Mg2+ in the concentrated brine and CO2 can be considered an effective separation/recovery method, as the solubility of carbonate of Ca2+ and Mg2+ is lower than the solubility of hydroxide in the solution at a pH range below 8.0. In particular, dolomite (CaMg(CO3)2), which is the double salt derived from the structure of calcite by the ordered replacement of Ca2+ and Mg2+, is used in various industrial fields. To improve the functionality of CaMg(CO3), it is essential to gain access to the Mg/Ca ratio of 1.0. Generally, high concentrations of Ca2+, Mg2+ and CO32- are necessary for synthesis of CaMg(CO3)2 with a high Mg/Ca ratio [1]. In this study, the fine bubble formation technique that enables the generation of regions with a higher ion concentration near the gas-liquid interfaces was applied to the reactive crystallization of CaMg(CO3)2 from the concentrated brine. Furthermore, CaMg(CO3)2 with a high Mg/Ca ratio can be converted to phosphor which is superior to emission intensity and quantum efficiency, because Mg2+ ions in crystal structure of CaMg(CO3)2 are arrayed more regularly than solid solution. In this paper, we report the effects of CO2 fine bubble injection on the produced weight of CaMg(CO3)2 (*W*dolomite) and the Mg/Ca ratio during reactive crystallization of CaMg(CO3)2 from concentrated brine, and the effects of immerse time on emission intensity of phosphor converted from the obtained CaMg(CO3)2.

**2. Experimental**

**2.1 Reactive crystallization of CaMg(CO3)2 from the concentrated brine by fine bubble injection**

The concentrated brine that is removed K+ by cooling crystallization of KCl after NaCl production in salt manufacturing process was used. The major components of the concentrated brine are MgCl2, NaCl and CaCl2 which have the concentrations of 2.1, 0.8 and 0.7 mol/L, respectively. Fine bubbles with an average bubble diameter (*d*bbl) of 40 µm were generated using a self-supporting bubble generator by shear of impeller and a negative pressure owing to high-rotation, with the rotation rate maintained at 1500 min-1 and the CO2 flow rate controlled at 11.9 mmol/(L·min). For comparison, the bubbles with *d*bbl of 2000 µm were obtained using a dispersing-type generator. At 298 K, CO2 bubbles were continuously supplied to 300 mL of concentrated brine, and CaMg(CO3)2 was crystallized within a crystallization time (*t*c) of 60 min. The solution pH during crystallization was maintained constant at 6.8 by adding 8.0 mol/L-NaOH aqueous solution. The Mg/Ca ratio of CaMg(CO3)2 was estimated from the amount of peak shift from calcite CaCO3 to CaMg(CO3)2 [2].

**2.2 Conversion to phosphor from the CaMg(CO3)2 obtained by CO2 fine bubble injection**

10.0 g/L of the obtained CaMg(CO3)2 at *t*c of 60 min were immersed into mixed solution of 0.1 mol/L TbCl3 and 0.1 mol/L CeCl3 at 298 K. The immerse time (*t*i) is controlled in the range of 0 – 24 h. Fluorescence spectra of the CaMg(CO3)2 phosphor were measured by fluorescence spectrometer.

**3. Results and discussion**

**3.1 Effects of CO2 fine bubble formation on the reactive crystallization of CaMg(CO3)2**

The reactive crystallization of CaMg(CO3)2 from the concentrated brine was performed at *d*bbl of 40 or 2000 µm. *W*dolomiteand the Mg/Ca ratio at *d*bbl of 40 µm was obviously higher than the 2000 µm at all values of *t*c, and the Mg/Ca ratio at *d*bbl of 40 µm reached 0.86 with 60 min crystallization. The results indicate that generation high concentration of Ca2+, Mg2+ and CO32- probably because of the acceleration of CO2 absorption and the electrification of the fine bubble surface caused by minimization of the bubble diameter.

**3.2 Conversion to phosphor from obtained CaMg(CO3)2**

The obtained CaMg(CO3)2 with a Mg/Ca ratio of 0.86 crystallized by fine bubble injection at *d*bbl of 40 µm was converted to phosphor. The fluorescence spectra of the CaMg(CO2)3 phosphor are shown in **Figure 1**. Under light irradiation at wavelength of 254 nm, the green emission was observed in visual at all *t*i values and the emission peak intensities at 489, 544, 548 and 621 nm increased with an increase in *t*i. This is caused that the replacement of Mg2+ in CaMg(CO3)2 to Tb3+ acting as an emission center and Ce3+ acting as a sensitizer proceeded with increasing *t*i.

**4. Conclusions**  Using the CO2 bubbles with different *d*bbl values, the reactive crystallization of CaMg(CO3)2 from the concentrated brine was carried out. The results indicate that the minimization of *d*bbl led to the increase in *W*dolomite and Mg/Ca ratio. Additionally, when the obtained CaMg(CO3)2 with Mg/Ca ratio of 0.86 converted to phosphor by immersing into 0.1 mol/L TbCl3 and CeCl3 solution, the emission intensity of CaMg(CO3)2 phosphor increased with increasing *t*i.

**Acknowledgements** This work was financially supported by the Salt Science Research Foundation (No. 17A3), Japan. We also acknowledge the Naikai Salt Industry Co., Ltd for provision of Bittern.

**References**

1. T. Oomori, K. Kaneshima, T. Taira, Y. Kitano, Geochem. J. 17 (1983) 327-336.
2. H. Mitsusio, H. Nishizawa, K. Matsuoka, Res. Res. Kochi Univ. Nat. Sci. 32 (1983) 327-334.