

# Production and Upgrading of Carbonates from $K^+$ Removed Brine –Synthesis of Inorganic Phosphor Based on Carbonate with Controlled Crystal Properties–

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## Summary

To develop a utilization system for seawater resources based on the salt production process, a method for recovery and upgrading of Ca and Mg from the concentrated seawater discharge of a salt manufacturer in Japan was examined. From a salt solubility viewpoint, the synthesis of the carbonates by reactive crystallization between the dissolved  $Ca^{2+}$  and  $Mg^{2+}$  ions in concentrated seawater and  $CO_2$  can be considered as an effective separation/recovery method. In particular, dolomite ( $CaMg(CO_3)_2$ ), which is the double salt of  $CaCO_3$  and  $MgCO_3$ , has a crystal structure that is derived from the structure of the calcite form of  $CaCO_3$  by replacement of  $Ca^{2+}$  in the calcite to  $Mg^{2+}$ , and it is widely used in various industrial fields. Furthermore, if the increase in Mg/Ca ratio and micronization of  $CaMg(CO_3)_2$  can be achieved during the reactive crystallization process, applications as a mother crystal of inorganic phosphor with superior luminescent properties are expected. In this study, to synthesize dolomite ( $CaMg(CO_3)_2$ ) with desired crystal properties more effectively, the minute gas–liquid interfaces of  $CO_2$  fine bubbles were utilized as new crystallization regions where crystal nucleation is dominant. To classify the production regions of the Ca and Mg carbonates from concentrated seawater derived from salt manufacture discharge by solution pH and temperature ( $T_S$ ),  $CO_2$  fine bubbles with an average diameter ( $d_{bb1}$ ) of 40  $\mu m$  were continuously supplied to removed-K brine, and the Ca and Mg carbonates crystallized at the pH range 5.3 – 8.3 and  $T_S$  range 278 – 348 K. Consequently,  $CaMg(CO_3)_2$  with high selectivity was crystallized at the pH range 5.3 – 6.8 and  $T_S$  range 278 – 298 K, and aragonite form  $CaCO_3$  was preferentially produced at  $T_S > 333$  K and the pH values 5.3 and 6.0. Moreover, to select the suitable type of concentrated seawater discharge from the salt manufacturing process for the production of  $CaMg(CO_3)_2$  with a high Mg/Ca ratio during reactive crystallization,  $CO_2$  fine bubbles with a  $d_{bb1}$  of 40  $\mu m$  were continuously supplied to three concentrated seawater samples, i.e., ED brine, concentrated brine, and removed-K brine, at various  $CO_2$  flow rate ( $F_{CO_2}$ ) values at a solution pH of 6.8 and a  $T_S$  of 298 K, and  $CaMg(CO_3)_2$  was crystallized. These samples have different concentration products of  $Ca^{2+}$  and  $Mg^{2+}$  ( $[Ca^{2+}][Mg^{2+}]$ ). In the ED brine, the production of  $CaMg(CO_3)_2$  was confirmed, along with the production of aragonite  $CaCO_3$  as a by-product.  $CaMg(CO_3)_2$  was the dominant product crystallized from the concentrated brine and removed-K brine. The molar concentration of the produced  $CaMg(CO_3)_2$  and the Mg/Ca ratio of  $CaMg(CO_3)_2$  both increased with increasing  $[Ca^{2+}][Mg^{2+}]$  and  $F_{CO_2}$ . Additionally, to improve the crystal properties of  $CaMg(CO_3)_2$  such as Mg/Ca ratio and particle size,  $d_{bb1}$  and  $F_{CO_2}$  values were varied in removed-K brine at a solution pH of 6.8 and a  $T_S$  of 298 K. The results indicated that

minimizing the bubble diameter and the increase in  $F_{\text{CO}_2}$  led to the high-yield crystallization of  $\text{CaMg}(\text{CO}_3)_2$  fine-particles with higher Mg/Ca ratio. Furthermore, when the obtained  $\text{CaMg}(\text{CO}_3)_2$  was converted to an inorganic phosphor by immersing it into 0.10 mol/L of a  $\text{TbCl}_3/\text{CeCl}_3$  mixed solution at 298 K for 60 min,  $\text{CaMg}(\text{CO}_3)_2$  fine particles with an average size of 3 – 6  $\mu\text{m}$  and a Mg/Ca ratio of approximately 0.5 were found to be suitable for the synthesis of green inorganic phosphor with a high emission intensity under the experimental conditions employed in this study.