

## Production of Carbonate from Concentrated Brine using Fine Bubbles of Boiler Exhaust Gases in Salt Manufacturing Process

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### Summary

During the salt manufacturing process in Japan, NaCl is manufactured by evaporative crystallization after concentrating seawater through electric dialysis membranes, and the concentrated brine and boiler exhaust gas are discharged. To build up an efficient salt manufacturing process that is adaptable to a carbon neutral society, the development of not only the recovery and upgrading method of Ca and Mg dissolved in concentrated brine discharged from salt manufacturing process but also the utilization method of CO<sub>2</sub> in boiler exhaust gas is essential. The reactive crystallization technique of carbonate using the bubble feeding of CO<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub> gas with an exhaust gas composition is effective for a separation/recovery method of the dissolved Ca<sup>2+</sup> and Mg<sup>2+</sup> in the concentrated brine, because the solubility of carbonate is lower than the solubility of hydroxide in the solution at a pH range below 8.0. Especially, dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>), which is double salt of calcium carbonate and magnesium carbonate, has numerous applications as the manufacture of refractories, as neutralizer of soil acidity in agriculture, as mineral supplement for food and drug, etc.. CaMg(CO<sub>3</sub>)<sub>2</sub> has crystal structure derived from that of calcite by ordered replacement Ca<sup>2+</sup> in calcite by Mg<sup>2+</sup>. To improve the functionality of crystal for the better CaMg(CO<sub>3</sub>)<sub>2</sub> utilization, it is essential to gain access to the Mg/Ca ratio of 1.0 and to reduce the particle size in the crystallization process. Generally, high concentrations of Ca<sup>2+</sup>, Mg<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> are necessary for the production of CaMg(CO<sub>3</sub>)<sub>2</sub> with a Mg/Ca ratio of 1.0, because the Mg/Ca ratio increases with increasing the supersolubility product in the bulk solution.

In this study, the micron-scale bubble formation technique that enables the generation of regions with a higher ion concentration around the minute gas-liquid interfaces was applied to the reactive crystallization of CaMg(CO<sub>3</sub>)<sub>2</sub>. In the regions near the minute gas-liquid interfaces, Ca<sup>2+</sup> and Mg<sup>2+</sup> accumulate because of the negative electric charge on the fine bubble surface, and the concentration of CO<sub>3</sub><sup>2-</sup> increases because of the acceleration of CO<sub>2</sub> mass transfer caused by minimizing the bubble diameter; hence, the fine particles of CaMg(CO<sub>3</sub>)<sub>2</sub> with a high Mg/Ca ratio can be expected to crystallize. At a reaction temperature of 298 K and reaction pH of 6.8, CO<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub> bubbles with an average diameter ( $d_{\text{bbi}}$ ) of 40 - 2000  $\mu\text{m}$  were continuously supplied to three concentrated seawater samples, i.e., ED brine, concentrated brine, and removed-K brine, coming from salt manufacture discharge and CaMg(CO<sub>3</sub>)<sub>2</sub> was crystallized within the reaction time ( $t_r$ ) of 120 min. Fine bubbles with a  $d_{\text{bbi}}$  of 40  $\mu\text{m}$  were generated using a self-supporting bubble generator by the shear of the impeller and a negative pressure owing to high-rotation. For comparison, the bubbles with a  $d_{\text{bbi}}$  of 200, 300, 800 or 2000  $\mu\text{m}$  were obtained using a dispersing-type generator.

Consequently, CO<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub> fine bubble injection into removed K brine with a higher Ca<sup>2+</sup> and Mg<sup>2+</sup> concentrations is effective for the high-yield crystallization of CaMg(CO<sub>3</sub>)<sub>2</sub> with a higher Mg/Ca ratio and downsizing of CaMg(CO<sub>3</sub>)<sub>2</sub> particles owing to the acceleration of crystal nucleation caused by the local increase in the supersaturation at the minute gas-liquid interfaces.