

Development of Recovery and Upgrading Method of CO₂ Discharged from Salt Manufacturing Process –Arrangement of Crystallization Regions and Crystal Properties of Carbonates with Bubble Diameter and Solution Composition–

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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 CO₂ in boiler exhaust gas gases is desired. The reactive crystallization technique of carbonate (CaCO₃, MgCO₃, CaMg(CO₃)₂) using the bubble feeding of CO₂/O₂/N₂ gas with an exhaust gas composition is effective for a separation/recovery method of the dissolved Ca²⁺ and Mg²⁺ in the concentrated brine and capture/utilization method of CO₂, because the solubility of carbonate is lower than that of hydroxide at a pH range below 10.0. 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 carbonate. At the minute gas-liquid interfaces, Ca²⁺ and Mg²⁺ accumulate because of the negative electric charge on the fine bubble surface, and the concentration of CO₃²⁻ increases because of the acceleration of CO₂ mass transfer caused by minimizing the bubble diameter; hence, high-yield production of carbonate with high quality can be expected to achieve. At a reaction temperature of 298 K and reaction pH of 6.8, CO₂/O₂/N₂ bubbles with an average diameter (d_{bbi}) of 40 - 2000 μm were continuously supplied to three concentrated seawater samples, i.e., ED brine, concentrated brine, and removed-K brine, coming from salt manufacture discharge and carbonate was crystallized within the reaction time (t_r) of 90 min. Fine bubbles with a d_{bbi} of 40 μm 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_{bbi} of 200, 300, 800 or 2000 μm were obtained using a dispersing-type generator. The following results were obtained: 1) When CO₂/O₂/N₂ bubbles with d_{bbi} of 40 - 2000 μm were supplied into removed-K brine, the yield and Mg/Ca ratio of CaMg(CO₃)₂ increased obviously, and the particle size distribution shifted to smaller range with minimizing the bubble diameter. 2) Irrespective of [Mg²⁺]/[Ca²⁺] ratio in the bulk solution, minimizing the bubble diameter led to enhancement of carbonate yield based on CO₂, uniformation of crystal structure, and downsizing of carbonates. 3) In the case where [Mg²⁺]/[Ca²⁺] ratio in the bulk solution increased from 2.7 to 3.1 at d_{bbi} of 40 μm , the crystal structure of carbonate changed from aragonite CaCO₃ to CaMg(CO₃)₂ that has a crystal structure derived from the structure of calcite CaCO₃ by the ordered replacement of Ca²⁺ in calcite by Mg²⁺. 4) From the comparison with the obtained results in MgCl₂-CaCl₂ solution with different [Mg²⁺]/[Ca²⁺] values, the crystal structure of produced carbonates can be determined by d_{bbi} and [Mg²⁺]/[Ca²⁺].