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Recovery and Upgrading of Calcium and Magnesium from Concentrated Brine -Control of $CaMg(CO_3)_2$ Crystal Properties Using CO_2 Fine Bubbles-

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Summary

In order to build up a utilization system of seawater resources based on the salt production process, a recovery and upgrading method for calcium (Ca) and magnesium (Mg) from the discharge concentrated brine (bittern) of salt manufactory in Japan was studied. From the viewpoint of solubility of salts, the synthesis of carbonate by reactive crystallization between the dissolved Ca^{2+} and Mg^{2+} in concentrated brine and carbon dioxide (CO_2) can be considered as an effective separation/recovery method. In this study, utilizing the minute gas-liquid interfaces around CO_2 fine bubbles as novel reaction fields where the crystal nucleation proceeds predominantly, a crystallization technique that enable the synthesis of dolomite ($CaMg(CO_3)_2$) fine-particles with a Mg/Ca ratio of 1.0 was developed. In the regions near the gas-liquid interfaces of CO_2 fine bubbles, the local increase in the concentrations of Ca^{2+}, Mg^{2+}, and CO_3^{2-} caused by the electric charge on fine bubble surface and the acceleration of CO_2 mass transfer owing to minimizing the bubble diameter. In the ranges of a reaction temperature (T_S) of 298 - 313 K and CO_2 flow rate (F_{CO2}) of 1.49 - 23.8 mmol/(l・min), CO_2 bubbles with an average diameter (d_{bbl}) of 40 - 2000 μm were continuously supplied to the concentrated brine coming from salt manufacture discharge and $CaMg(CO_3)_2$ was crystallized within the reaction time of 120 min. Fine bubbles with d_{bbl} of 40 μm were generated using a self-supporting bubble generator by increasing the impeller shear rate under reduced pressure. For comparison, the reactive crystallization with the injection of CO_2 bubbles at d_{bbl} of 300 or 2000 μm was performed using a dispersing-type bubble generator. The results indicated that the minimizing bubble diameter and the increase in F_{CO2} led to the high-yield crystallization of $CaMg(CO_3)_2$ fine-particles with higher Mg/Ca ratio.