

Synthesis of Carbonate Nano-particles from Concentrated Brine by CO₂ Fine Bubble Injection under Ultrasonic Irradiation, and Conversion to Inorganic Phosphor

Masakazu Matsumoto, Shinnosuke Kamei

College of Industrial Technology, Nihon University

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 brine discharge of a salt manufacturer in Japan was examined. From a salt solubility viewpoint, the synthesis of carbonate such as CaCO₃ and dolomite (CaMg(CO₃)₂) by reactive crystallization between the dissolved Ca²⁺ and Mg²⁺ ions in concentrated brine and CO₂ can be considered as an effective separation/recovery method. CaCO₃ has three crystal structures (polymorphs): stable calcite, metastable aragonite, and unstable vaterite, and the physicochemical properties (e.g., thermal stability, solubility, and density) depend on the polymorphs. In addition, it is necessary to not only uniform polymorph but also downsizing of particles in order to achieve high functionality in each industrial application. On the other hand, CaMg(CO₃)₂, which is the double salt of CaCO₃ and MgCO₃, has a crystal structure that is derived from the structure of the calcite of CaCO₃ by replacement of Ca²⁺ in the calcite to Mg²⁺, and it is widely used in various industrial fields. Furthermore, if the increase in Mg/Ca ratio and micronization of CaMg(CO₃)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, we used minute gas–liquid interfaces around CO₂ fine bubbles activated by ultrasonic (US) irradiation as new reaction fields and developed a crystallization technique to produce the carbonate nanoparticles from the concentrated brine. At the minute gas–liquid interfaces, local supersaturation is generated because of the acceleration of CO₂ mass transfer and the accumulation of Ca²⁺ caused by minimizing the bubble diameter, and because of the increment of local temperature caused by the pressure oscillations with US irradiation. When the addition of ion exchanged water containing CO₂ fine bubbles and US irradiation to the concentrated brine with adjusted Ca/Mg ratio, aragonite was obtained at Ca/Mg ratio of 0.33–0.4 and the carbonate yield was increased by US irradiation regardless of Ca/Mg ratio. Additionally, by increasing the residence number of CO₂ fine bubbles, CaMg(CO₃)₂ nanoparticles with a Mg/Ca ratio of 0.83 and an average size of 120 nm were obtained from the concentrated brine. Moreover, the obtained carbonate from the concentrated brine was converted to an inorganic phosphor by immersing it into a TbCl₃/CeCl₃ mixed solution at 298 K for 60 min. Consequently, CaMg(CO₃)₂ was better than aragonite for the synthesis of green inorganic phosphor with a high emission intensity, and the emission intensity of CaMg(CO₃)₂ phosphor increased with decreasing the average size of CaMg(CO₃)₂ as a mother crystal.