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Recovery and Upgrading of Calcium and Magnesium from Brine Solution −Synthesis of Carbonate and Hydroxyl Apatite−

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Summary

In order to build up a utilization system of seawater resources based on the desalination and salt production process and to prevent scaling in reverse osmosis and electrodialysis units, a recovery and upgrading method for calcium (Ca) and magnesium (Mg) from the discharge concentrated brine 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. As a solid products, calcium carbonate ($CaCO_3$), magnesium carbonate ($MgCO_3$), and dolomite ($CaMg(CO_3)_2$), which is double salt of $CaCO_3$ and $MgCO_3$, are expected to crystallize. Moreover, the obtained $CaCO_3$ is able to upgrade to hydroxyl apatite ($Ca_{10}(PO_4)_6(OH)_2$) by treatment of phosphoric acid and hydroxide.

In this paper, the synthesis of $CaCO_3$ by reactive crystallization between the dissolved Ca^{2+} in the brine solution and CO_2 bubbles and the conversion from obtained $CaCO_3$ to $Ca_{10}(PO_4)_6(OH)_2$ were examined. When CO_2 bubbles were continuously supplied to the brine solution, only $CaCO_3$ was crystallized, and the product yield of metastable aragonite $CaCO_3$ increased by minimizing bubble diameter. Furthermore, the suspended $CaCO_3$ particles in the solution were converted efficiently to $Ca_{10}(PO_4)_6(OH)_2$ and $Ca(PO_4)_2$ by treatment of phosphoric acid and hydroxide at reaction temperature of 333 K and pH of 7.0.

In addition, CO_2 fine-bubbles with an average bubble diameter of 40 μm were supplied to the concentrated brine coming from salt manufacture discharge using self-supporting bubble generator and dolomite ($CaMg(CO_3)_2$) was crystallized. The results indicated that the minimizing bubble diameter accelerated remarkably the crystallization of $CaMg(CO_3)_2$ fine particles with higher Mg/Ca ratio and reduced t_r necessary for the achievement of Mg/Ca ratio of 1.0.