

Recovery and Upgrading of Calcium and Magnesium for Scaling Prevention and Utilization of Seawater Resources

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Summary

In systems for utilizing seawater resources based on the desalination and salt production process, to prevent scaling in reverse osmosis (RO) and electrodialysis (ED) units, the calcium (Ca) and magnesium (Mg) recovery and upgrading method was studied. From the viewpoint of solubility of salts, the synthesis of calcium carbonate (CaCO_3) by reactive crystallization between the dissolved Ca^{2+} in seawater/brine and carbon dioxide (CO_2) can be considered as an effective separation/recovery method. The obtained CaCO_3 is able to upgrade to hydroxyl apatite (HAP) with treatment of phosphoric acid and hydroxide. Moreover, the remained Mg^{2+} ion can be recovered from the removed Ca^{2+} brine solution by using reactive crystallization of magnesium carbonate (MgCO_3).

In this paper, as a two-stage process of Ca^{2+} recovery, CaCO_3 generation using the dissolved Ca^{2+} ion in the brine solution and CO_2 bubbles, and conversion to HAP were examined. Additionally, in order to simplify and facilitate the process, the one-stage process of HAP generation, including treatment of phosphoric acid and hydroxide, was also investigated. The experimental results in a two-stage process were as follows: 1-1) when CO_2 bubbles were continuously supplied to the brine solution, only CaCO_3 was crystallized; 1-2) aragonite fine particles were produced by minimizing bubble size; and 1-3) the suspended CaCO_3 particles in the solution were almost converted to HAP with treatment of phosphoric acid and hydroxide at a solution pH of 7.0. Moreover, the following results were obtained by examination about one-stage process of HAP generation: 1-4) when the brine solution was treated with phosphoric acid and hydroxide, HAP was generated in the range over 4.7 of solution pH; and 5) the generation rate and crystallinity of HAP increased with an increase in solution pH. Furthermore, the effects of CO_3^{2-} feeding method, solution pH and temperature on reactive crystallization of MgCO_3 in the removed Ca^{2+} brine solution can be summarized as follows: 2-1) when CO_2 minute-bubbles were continuously supplied to the removed Ca^{2+} brine solution, the produced moles of basic magnesium carbonate ($4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) was higher than that obtained with milli-sized bubble method and solution mixing methods, and the selectivity of $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ reached to 100%; 2-2) nucleation and crystallization of $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ in minute-bubble method were enhanced with an increase in solution pH and temperature; and 2-3) the production of $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ fine crystals was accelerated by using minute-bubble method.