Foreword

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Summary

The large-scale salt manufacturing process in Japan is called the salt making by ion exchange membrane method. The process can be divided into three stages: (1) The seawater collected from the sea is filtered, and "brine" with a high concentration of NaCl is produced by the electro-dialysis using ion exchange membrane system. (2) The "brine" is concentrated by several vacuum evaporators and the NaCl is crystallized. (3) Finally, the NaCl crystals are removed as a product by centrifugal drying. These salt manufacturing processes are ingenious in recovering heat energy to give inexpensive and high-grade NaCl. On the other hand, the technology to recover useful resources from a large amount of the effluent in electrodialysis and the separation and refinement of useful resources from the brine after removing NaCl crystals are required. The following five subjects were studied in this project researches science and technology.

(1) Development of novel nanofiltration membranes for separating Mg^{2+} and Ca^{2+} from effluent in electrodialysis (Kogakuin University, Kazuki AKAMATSU)

Novel nanofiltration (NF) membranes were developed for separating Mg^{2+} and Ca^{2+} from effluent in electrodialysis process to produce concentrated seawater from pretreated seawater, and a potential process using the developed membranes was discussed. Various preparation methods were tested to develop positively charged NF membranes as well as negatively charged ones. Throughout the research in this project, a novel negatively charged NF membrane having a high water permeability with a high ion selectivity was successfully developed. Separation tests using a practical effluent were also demonstrated with the developed NF membrane.

(2) Development of Morphology Control for Aggregated Particles of Mg and Ca Compounds in each Application (Doshisha University, Yoshiyuki SHIRAKAWA)

The sophistication of the method for synthesizing layered double hydroxides from residual Mg and Ca using removed K brine, which is obtained by removing potassium from bittern, and investigated the high-efficiency recovery of Mg and Ca was performed. In addition, in the formation of secondary particles of synthesized primary particles, a technology to aggregate them into a shape suitable for the application was also developed, and by controlling the type and concentration of coexisting impurity ions, they showed the effect of crystal habit modifier and it improved handling. It was found that it is possible to control the anion exchange ability.

(3) Production and Upgrading of Carbonates from K^{+} Removed Brine - Synthesis of Inorganic Phosphor Based

on Carbonate with Controlled Crystal Properties - (Nihon University, Masakazu MATSUMOTO)

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 seawater discharge of a salt manufacturer in Japan was examined. The production regions of the Ca and Mg carbonates were classified by solution pH and temperature during CO_2 fine bubble injection into three concentrated seawater samples, i.e., ED brine, concentrated ED brine, and removed KCl bittern. Additionally, to improve the crystal properties of $CaMg(CO_3)$, the average bubble diameter and CO_2 flow rate were varied in removed KCl bittern. The results indicated that minimizing the bubble diameter and the increase in F_{CO2} during CO_2 bubble injection into removed KCl bittern with a high Ca^{2+} and Mg^{2+} concentrations led to the high-yield crystallization of $CaMg(CO_3)_2$ fine-particles with higher Mg/Ca ratio. Furthermore, when the obtained $CaMg(CO_3)_2$ was converted to an inorganic phosphor by immersing it into $TbCl_3/CeCl_3$ mixed solution, $CaMg(CO_3)_2$ fine particles with a Mg/Ca ratio of approximately 0.5 were found to be suitable for the synthesis of green inorganic phosphor with a high emission intensity under the experimental conditions employed in this work.

(4) Utilization of Bromine in Seawater by Redox Reaction with Fine Bubble Supply and Application to Water Purification (Nihon University, Yoshinari Wada)

To create the utilization method of dissolved Br in the discharge concentrated bittern of salt manufactory in Japan, the production of Br oxyacid as an upgrading method for Br using O_3 fine bubbles, which enable the acceleration of OH• generation at the minute gas–liquid interfaces, was carried out. O_3 fine bubble injection into solution containing Br such as seawater led to the improvement of oxidation potential in the liquid phase, because oxyacids of Br such as hypobromous acid and bromate ion were generated by the selective oxidation of Br^- during the O_3 fine bubble injection into the NaBr solution. Additionally, when the organic compounds have different reactivities for each forms of Br oxyacids were degraded by Br oxyacids, it was cleared that the generation of hypobromous acid with O_3 fine bubble injection and Br coexistence is effective for achieving enhanced degradation of refractory organic compounds.

(5) Measurements of Physical Properties, which is the Key to the Separation Process Design and Optimization of Combined Process for an Advanced Recovery of Unused Seawater Resources (Nihon University, Toshihiko HIAKI)

A study was conducted to recover as much potassium chloride (KCl) and magnesium hydroxide ($Mg(OH)_2$) as possible from the concentrated brine of the by-products of the salt manufacturing process. In the cooling crystallization of the brine, the KCl crystals were precipitated at higher temperature and the amount of KCl recovered increased with the increase in the power required for stirring. On the other hand, the pH of the reaction field is important for the recovery of $Mg(OH)_2$ from removed-K brine by reaction crystallization. Three different precipitating agents were used in the experiments. It was found that the pH could be controlled by the reaction temperature and the concentration of removed-K brine, which inhibited the precipitation of $CaCO_3$ and selectively precipitated $Mg(OH)_2$.

These five research results are fruitful for the recovery of useful resources from the effluent of ion-exchange membrane electrodialysis, which is usually returned to the sea, and for the separation and refinement of useful resources from the brine after the removal of NaCl crystals. It is expected that these technologies will be used in the future as chemical products obtained from the salt manufacturing process.

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