## 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

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## Summary

The aim of this research project is to develop new separation technology and processes for natural resource acquisition using electrodialysis waste water and bittern in the salt production process as raw materials. The sub-theme 3 of this study, a process was developed to obtain KCl in high yield from concentrated brine by cooling crystallization. Furthermore, another process was investigated for efficiently collecting Mg(OH)<sub>2</sub> crystals from removed  $K^+$  brine by reactive crystallization.

In this study, the efficient recovery of KCl crystals by cooling crystallization using the concentrated brine obtained as a by-product in the final step of the salt manufacturing process was investigated. Furthermore, the recovery of  $Mg(OH)_2$  crystals with high quality by reaction crystallization using removed K<sup>+</sup> brine as the next raw material was investigated. A process was proposed for efficiently obtaining these two substances by making minor improvements to the current salt production process.

When recovering KCl from concentrated brine by cooling crystallization, it is expected that the recovery amount will be improved by narrowing the width of the metastable region between the saturated state and the supersaturated state where KCl crystals precipitate. Therefore, effect of mixing was studied. And all glass crystallization vessel with a triple-tube structure of an internal volume of 1 L was used for experiments. The temperature of vessel can be set by a chiller unit. As for the stirring conditions, two types of stirring blades and one to four baffle plates were installed. The torque was measured at a stirring speed of 150 to 500 rpm, and the required power for stirring was calculated. As a result, it was confirmed that the crystal precipitation temperature increased as the required power for stirring increased. Precipitation of KCl crystals at high temperature and a decrease in supercooling are considered to increase the amount of KCl recovered in a short time.

On the other hand, continuing from the past one year, investigated for efficiently collecting  $Mg(OH)_2$  crystals from removed K<sup>+</sup> brine by reactive crystallization. The pH of the aqueous solution is important for precipitating  $Mg(OH)_2$  crystals from removed K<sup>+</sup> brine. The removed K<sup>+</sup> brine concentration was adjusted by diluting it with water, and the pH was adjusted by adding NaOH. As a result, the pH of the aqueous solution became constant immediately when the concentration of  $Mg^{2+}$  in the removed K<sup>+</sup> brine was high. It is speculated that this is because the nucleation rate of  $Mg(OH)_2$  increases when the  $Mg^{2+}$  concentration in the aqueous solution is high. The pH of the aqueous solution after the reaction decreased as the concentration of  $Mg^{2+}$  in the removed K<sup>+</sup> brine decreased. The effect of the reaction temperature was that the pH decreased after the reaction when the temperature was high. Furthermore, it was shown that  $CaCO_3$  precipitation was suppressed and Mg  $(OH)_2$  was selectively precipitated by changing the reaction temperature and the composition of removed K<sup>+</sup> brine. The effects of different precipitants were investigated for NaOH, KOH and Ca(OH)<sub>2</sub>. Although Mg(OH)<sub>2</sub> was confirmed in all the precipitants, product of NaCl was confirmed when NaOH was used, and product of KCl was confirmed when KOH was used. In addition, it was found from the SEM image of the product that NaCl on the Mg(OH)<sub>2</sub> surface was dissolved and removed by washing the product with water.