Development of recovery technology of valuable metals from sea water

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Abstract. From the viewpoint of resource recovery, the characteristics of seawater can be expressed as “a multicomponent aqueous solution with a wide range of concentration distribution”. In salt production and desalination processes, production rates of recovery target components are calculated according to needs, and separation engineering of components based on membrane separation and crystallization operations are developed cleverly. The purpose of this study is to apply for changes in needs of valuable metals expected in the future. In order to recover valuable resources from brines, applied technologies considering for environmental conservation should be required. In this paper, we set up bivalent metal ions of Mg2+, Ca2+, Ba2+ and Sr2+ as the components to be recovered from seawater, and the systematic recovery method of bivalent metal ions using isothermal reactive crystallization of carbonate is proposed.

Keywords: Recovery Technology; Bivalent Metal Ion; Sea Water; Reactive Crystallization

1. Introduction

Seawater is a multicomponent aqueous solution with a wide range of concentration distribution. In the current salt recovery and desalination processes, sodium chloride and fresh water are produced from seawater using separation engineering based on membrane and crystallization. However, due to the change of lifestyle in the future, the demand for resources and consideration for environmental protection may change depending on the type and purity of valuable metals recovered from the seawater. Thus, it will be necessary to develop applied technologies for the transition of needs of valuable metals focusing environmental conservation. In this study, a method to systematically separate and recover divalent cations by reactive crystallization has developed. Using a simulated brine in which four types of divalent cations (Ca2+, Mg2+, Ba2+ and Sr2+ ions) coexist with three types of monovalent cations (Li+, K+ and Na+ ions) shown in Fig.1, the development of systematic separation and recovery of divalent cations by reactive crystallization is investigated. Expected uses of divalent cations are as follows.

![Figure 1. A simulated brine in which four types of divalent cations coexist with three types of monovalent cations](image)

Magnesium is widely used in aluminum sashes and cans. In recent years, the demand for magnesium as a light alloy material for automobiles has increased. In addition, applications of steel desulfurization...
agents, basic refractory bricks and rubber additives are expected. Barium is used in drilling fluids to assist in drilling drill holes into the ground, where barium sulfate is applied for the raw material of the weighting agent. On the other hand, strontium chloride and strontium nitrate are applied to fireworks and smoke cylinders using the red flame reaction. Strontium carbonate is added to ferrite magnets and cathode-ray tube glass.

2. Solubility of hydroxide and carbonate in Mg/Ca system

2.1. Comparison of hydroxide solubility

Figure 2 shows the solution pH dependence of hydroxide solubility in the Mg/Ca system. When magnesium or calcium concentration exceeds a straight line at a specific solution pH, hydroxide is precipitated. When both concentrations of magnesium ions (\(C_{\text{Mg}}\)) and calcium ions (\(C_{\text{Ca}}\)) are equal to 0.1 mol/l, selective crystallization of magnesium hydroxide [Mg(OH)\(_2\)] is possible in the solution pH between 9.2 to 11.8.

![Figure 2. Solution pH dependence of hydroxide solubility in Mg/Ca system](image)

2.2. Comparison of carbonate solubility

Figure 3 shows the relation between solution pH and concentration of \(\text{CO}_3^{2-}\) ions in carbonate system, where the total concentration of carbonic acid is 1.0 mol/l. The concentration of \(\text{CO}_3^{2-}\) ions increases with an increase in the solution pH.

![Figure 3. Relation between solution pH dependence and \(\text{CO}_3^{2-}\) ion concentration in carbonate system](image)

Figure 4 shows the solution pH dependence of carbonate solubility in the Mg/Ca system. In single-component aqueous solutions, an increasing of cation concentration lowers the solution pH at which carbonate crystallization appears. When both \(C_{\text{Mg}}\) and \(C_{\text{Ca}}\) are equal to 0.001 mol/l, selective crystallization of CaCO\(_3\) is possible in the basic region, where the solution pH is less than 8.5. Here, it
is necessary to consider the formation of complex salts in the crystallization process in the Mg/Ca system.

Figure 4. Solution pH dependence of carbonate solubility in Mg/Ca system

3. Experimental

3.1. Sample composition

Table 1 shows the component concentration used to prepare the brine, where $C_{[\text{mmol/kg}]}$ and $C_{[\text{mg/kg}]}$ represent molar and mass-based concentrations, respectively. Ion-exchange water was used as a solvent. In addition to magnesium, calcium, barium and strontium as divalent cations sodium ($\text{Na}^+$), potassium ($\text{K}^+$) and lithium ($\text{Li}^+$) ions are included as monovalent cations. Assuming the sample solution after removal of sulfate ion, chloride ions ($\text{Cl}^-$) are chosen as anions. The mass concentration of prepared brine ($\omega_0$) is set at 18.6 wt%.

Table 1. Component concentration of prepared brine (18.6 wt%)

| Component | $C_{[\text{mmol/kg}]}$ | Component | $C_{[\text{mg/kg}]}$ |
|-----------|------------------------|-----------|----------------------|
| NaCl      | 2990                   | Na        | 46300                |
| KCl       | 13.60                  | K         | 350                  |
| LiCl      | 0.45                   | Li        | 2                    |
| $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ | 10.94 | Mg | 180 |
| $\text{CaCl}_2$ | 24.70 | Ca | 660 |
| $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ | 0.89 | Ba | 81 |
| $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ | 0.96 | Sr | 56 |

3.2. Experimental method
After mixing the prepared brine and sodium carbonate at the specified mass ratio, hydrochloric acid or sodium hydroxide aqueous solution was added as a pH adjuster. The mass concentration $\omega$ of brine after adjusting the aqueous solution pH was set to 12.3 wt%. When precipitation was observed, the suspension was filtered and the components of the aqueous solution after solid-liquid separation were quantified. The temperature of the sample solution ($T$) is constant at 298 K.

### 3.3. Analysis

K$^+$ ions concentration of the sample solution was measured by flame spectroscopy, and the measurement of other cation concentrations were employed by ICP spectrophotometry. Furthermore, the precipitate after solid-liquid separation was dried under reduced pressure and XRD measurement was performed.

### 4. Results and discussion

#### 4.1. Separation of bivalent ions using reactive crystallization

When the solution pH of prepared brine was adjusted among 7-12 by adding only sodium hydroxide aqueous solution, concentrations of K$^+$, Li$^+$ and Br$^-$ ions within filtrate were the same as the prepared values. On the other hand, precipitation was observed when the solution pH was set to 10-12. Analysis of the filtrate after solid-liquid separation showed that the concentration of Mg$^{2+}$ ions decreased significantly in solution pH range among 11-12. In addition, the concentrations of Ca$^{2+}$ and Ba$^{2+}$ ions decreased slightly in solution pH at 12.

The ratio of the ion concentration when the aqueous solution pH is adjusted from 7 to 12 after adding the prepared amount of sodium carbonate to brine is shown in Fig. 5. Where $(C_i)_{0}$ and $C_i$ represent the prepared concentration of each component in the brine and the filtrate concentration after solution pH adjustment, respectively. In all basic regions, the concentrations of K$^+$ and Li$^+$ ions are consistent with the each prepared value, and no precipitation of monovalent cation carbonate was observed. On the other hand, Ca$^{2+}$ ions can be recovered as carbonates in the basic region. In particular in brine/OH$^-$/CO$_{3}^{2-}$ system, selective recovery of only Ca$^{2+}$ ions is possible in the solution pH range of 7-8. An idea of recovering Ba$^{2+}$ and Sr$^{2+}$ ions is considered to set the solution pH among 9-10 after recovering of Ca$^{2+}$ ions in solution pH at 7-8. In brine/OH$^-$/CO$_{3}^{2-}$ system, separation of Ba$^{2+}$ and Sr$^{2+}$ ions due to change in solution pH is difficult. A separating method between Sr$^{2+}$/Ba$^{2+}$ and Ca$^{2+}$ ions is conceivable using the difference in solubility of sulfate.

#### 4.2. Examination of continuous recovery method of divalent cations

The order of divalent ion recovery will be investigated using three anions (OH$^-$, CO$_{3}^{2-}$ and SO$_{4}^{2-}$). Focusing on the solution pH dependence of hydroxide and carbonate solubility, three groupings of (Ca$^{2+}$, Mg$^{2+}$ and Ba$^{2+}$/ Sr$^{2+}$) are performed. Figure 6 shows methods for continuous recovery of group ions, taking into account the anions and pH changes in the system. Three types (I-II, III-IV and V-VI) are the
methods for preferential recovery of Mg\textsuperscript{2+}, Ba\textsuperscript{2+}/Sr\textsuperscript{2+} and Ca\textsuperscript{2+}, respectively. In the example of method I, the operation for continuously collecting Mg\textsuperscript{2+}, Ca\textsuperscript{2+}, Ba\textsuperscript{2+}/Sr\textsuperscript{2+} ions is as follows.

Mg\textsuperscript{2+} ions are recovered as magnesium hydroxide in brine/OH\textsuperscript{-} system under solution pH at 11. After adding CO\textsubscript{3}\textsuperscript{2-} ions, the solution pH is lowered to 8, and Ca\textsuperscript{2+} ions are recovered as calcium carbonate. Increase of the solution pH up to 10 in the containing CO\textsubscript{3}\textsuperscript{2-} ion system, and recover of both Ba\textsuperscript{2+} and Sr\textsuperscript{2+} ions as carbonate are employed.

5. Conclusion
Adjusting the concentrations of hydroxide and carbonate ions, divalent cations can be selectively separated from aqueous solutions containing monovalent cations. Focusing on the solution pH dependence of hydroxide and carbonate solubility, three groupings of divalent cations (Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, Ba\textsuperscript{2+}/Sr\textsuperscript{2+}) are possible. Six recovery methods are proposed for continuous separation of three groupings of divalent cations.