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CHEMICAL FIXATION OF CARBON DIOXIDE USING SOLVENT EXTRACTION

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Abstract

Investigations were carried out to create a chemical fixation process, where carbon dioxide and sodium chloride solution are converted to sodium hydrogen carbonate and hydrochloric acid. Because the reaction has a large and positive free energy change, it does not proceed unless a suitable condition is established. The reaction is able to proceed if hydrochloric acid, which is one of the reaction products, is removed from the reaction system by extraction with amine. Stripping of hydrochloric acid from the organic phase containing amine hydrochloride is very difficult, due to the high chemical stability of amine hydrochloride. The stripping is accomplished by using a mixed aqueous-organic media as a stripping agent. This paper proposes both a total process and a process flow for the chemical fixation of carbon dioxide.

1. Introduction

Global warming caused by the increase in greenhouse effect gases is one of the most serious of environmental problems. Since the main component of greenhouse effect gases is carbon dioxide, reduction of carbon dioxide emission in environment is considered to be one of the counter measure against global warming¹⁾. At present, the suppression of consumption of fossil fuel that discharges carbon dioxide may result in delaying industrial development and lowering our standard of living. So, all over the world, technologies for absorption and fixation of carbon dioxide is being investigated.

In this paper, in order to chemically fix carbon dioxide, the production of hydrogen carbonates and inorganic acid from carbon dioxide and sea water was investigated using solvent extraction.

2. Theory

The reaction of carbon dioxide and sea water is expressed as follows^{2,3)}.



the reaction shown in eq. (1) produces strong acid and a salt of weak acid from weak acid and a salt of strong acid. Unless particular conditions are established, it cannot continue. If hydrochloric acid, which is one of the reaction products, is removed from this reaction system, the reaction can take place in spite of an extremely small equilibrium constant. The transfer of hydrochloric acid to the outside of the reaction system is accomplished by solvent extraction with amine. This reaction is expressed as follows:



Combining eqs. (1) and (2), we get eq. (3).



3. Reagents and Experimental Method

Sodium chloride solution, sodium nitrate solution and magnesium chloride

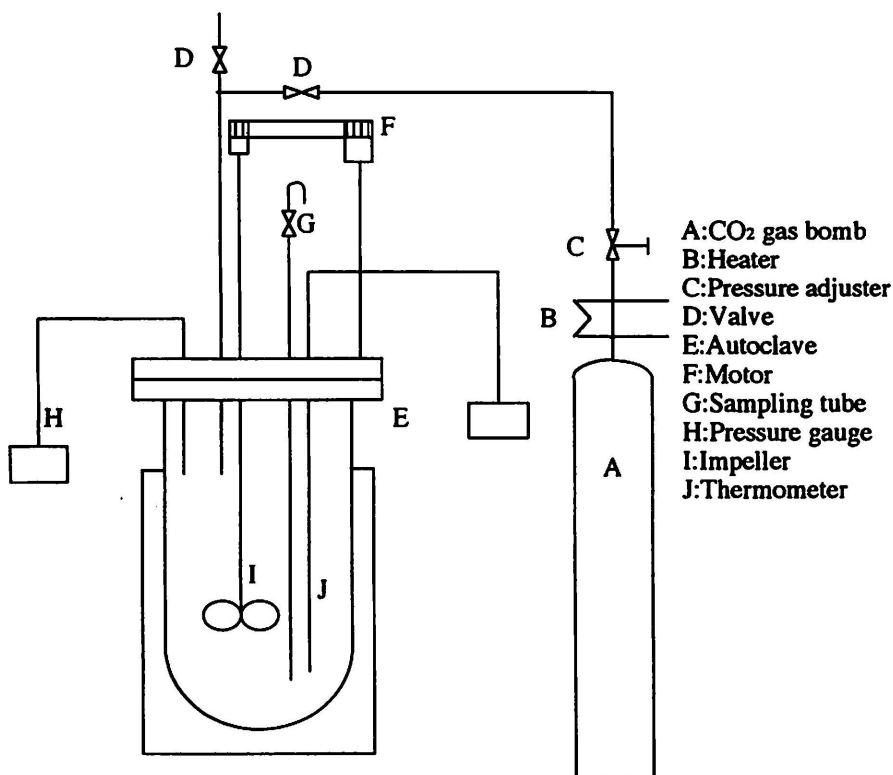


Fig. 1 Experimental apparatus

solution were used at various concentrations as aqueous phases. As an organic phase, either Priment JMT the trade name of primary amine, was used, or organic phases containing Priment JMT and various acidic extractants such as D2EHPA, PC-88A, Cyanex 272, and VA10, diluted in 1-butanol or n-hexane. For the stripping operation, water or non-aqueous solvent such as 1, 4-dioxane, acetonitrile, dimethylsulfoxide and N,N-dimethylformamide containing water were used, in order to recover hydrochloric acid from amine hydrochloride.

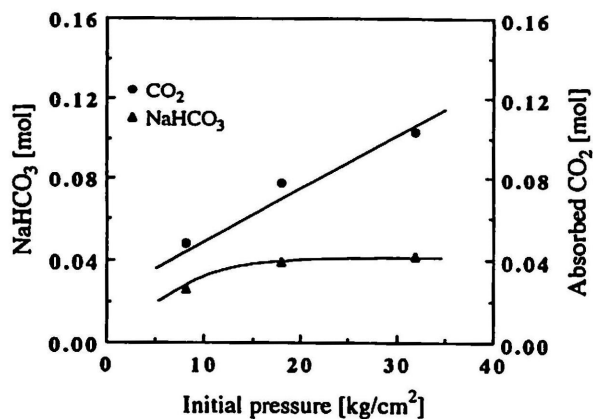
Figure 1 shows the experimental apparatus used. After introducing an aqueous and organic phase into an autoclave, it was filled with carbon dioxide at a constant pressure 10–30 kg/cm². Then, mixing commenced. Pressure was measured by means of a semiconductor pressure-voltage converter, and the decrease in pressure was recorded automatically. The concentration of hydrogen carbonates producing the aqueous phase was determined by a neutralization titration with hydrochloric acid. The amount of carbon dioxide absorbed was calculated from the decrease in pressure of gas phase. Hydrochloric acid was either stripped from the organic phase containing amine hydrochloride with water or recovered from a mixed aqueous-organic media. After the stripping operation, volume change in the organic phase was measured by means of a graduated cylinder. The concentration of hydrochloric acid in an aqueous phase after stripping was determined by a neutralization titration with sodium hydroxide solution.

4. Results and Discussion

4.1 Production of hydrogen carbonate

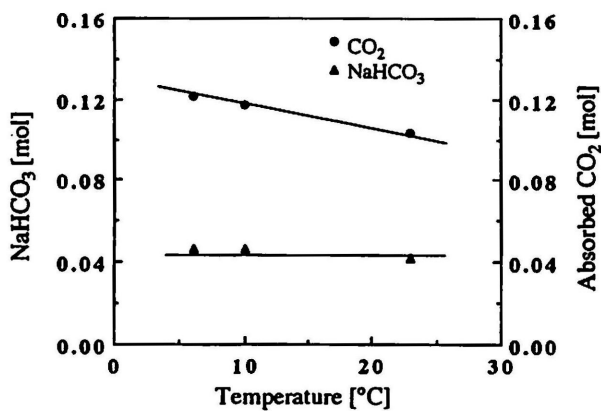
Figure 2 shows the amounts of absorbed carbon dioxide and sodium hydrogen carbonate produced as a function of the initial pressure of carbon dioxide. When the initial pressure increases, the amount of carbon dioxide physically absorbed increases linearly according to Henry's Law. In the reaction shown in eq. (3), the high initial pressure of carbon dioxide provides an excess amount of carbon dioxide. Since the composition of products depends on the initial amount of amine, a limiting the reactant, an increase in the initial pressure of carbon dioxide causes only a slight increase in production of sodium hydrogen carbonate. The reaction can proceed faster in the presence of an excess amount of carbon dioxide.

The amount of carbon dioxide absorbed and that of sodium hydrogen carbonate produced are shown as a function of temperature in Fig. 3. It is obvious from Fig. 3 that carbon dioxide is strongly absorbed at a low temperature. The amount of carbon dioxide physically absorbed increases as temperature decreases, while the sodium hydrogen carbonate produced scarcely changes. It was thus found that the reaction shown in eq. (3) is independent of temperature. The amounts of carbon dioxide absorbed and sodium hydrogen carbonate produced under various



Organic phase: 1.0mol/dm³ Priment JMT
 Aqueous phase: 5.0mol/dm³ NaCl
 Diluent: 1-butanol
 Phase ratio(A/O): 50cm³/50cm³

Fig. 2 Absorbed CO₂ and produced NaHCO₃ at various initial CO₂ pressures

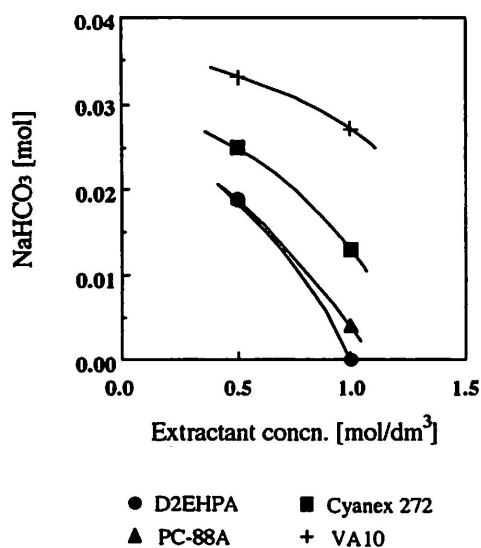


Organic phase: 1.0mol/dm³ Priment JMT
 Aqueous phase: 5.0mol/dm³ NaCl
 Diluent: 1-butanol
 Phase ratio(A/O): 50cm³/50cm³

Fig. 3 Absorbed CO₂ and produced NaHCO₃ at various temperatures

Table 1 Conversion of carbon dioxide to various hydrogen carbonates

Organic phase Diluent	Aqueous phase	Absorbed carbon dioxide [mol]	Hydrogen carbonates [mol]
1.0 mol/dm ³ Priment JMT 1-butanol	1.0 mol/dm ³ NaCl	0.110	0.0225
	3.0 mol/dm ³ NaCl	0.108	0.0359
	5.0 mol/dm ³ NaCl	0.103	0.0418
	5.0 mol/dm ³ NaNO ₃	0.104	0.0468
	0.24 mol/dm ³ MgCl ₂	0.111	0.0083



Organic phase: 1.0mol/dm³ Priment JMT
 and acidic extractant
 Aqueous phase: 5.0mol/dm³ NaCl
 Diluent: 1-butanol
 Phase ratio(A/O): 50cm³/50cm³

Fig. 4 Relationship between production of NaHCO₃ and acidic extractant concn.

experimental conditions are shown in Table 1. As the concentration of feed salts in an aqueous phase is high, the amount of sodium hydrogen carbonate produced increases, whereas the amount of carbon dioxide absorbed decreases. In the reaction shown in eq. (3), it is thought that physical absorption is the predominant factor in the absorption of carbon dioxide.

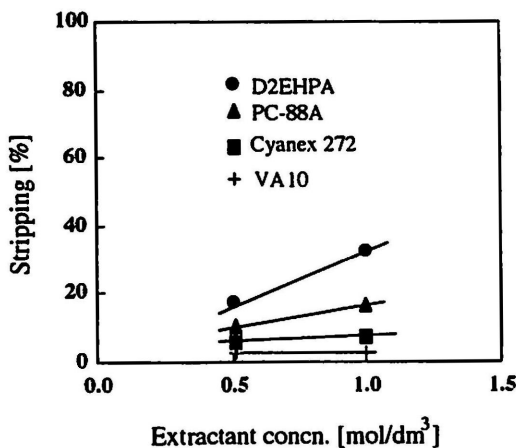
Figure 4 shows the amount of sodium hydrogen carbonate produced when a mixture of 1.0 mol/dm³ Priment JMT and various acidic extractants are used to

extract hydrochloric acid. Since the stronger acidity of acidic extractants leads to a stronger interaction with amine, the amount of sodium hydrogen carbonate produced decreases, because of the lack of extraction ability for hydrochloric acid.

4.2 Recovery of amine and hydrochloric acid from amine hydrochloride

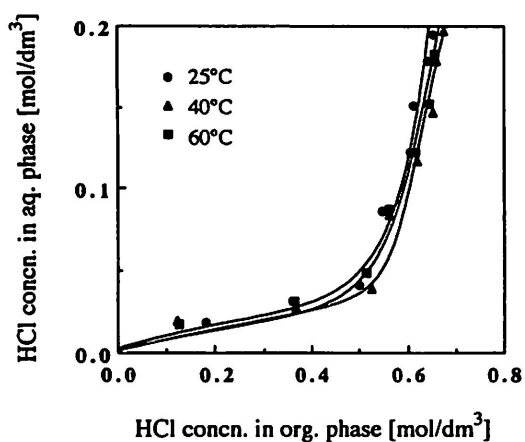
The stripping of hydrochloric acid with water from the organic phase is illustrated in Fig. 5. The organic phase was prepared by the reaction in eq. (3) using a mixture of Priment JMT and various acidic extractants diluted in n-hexane. When only amine or a mixture of amine and acidic extractants with a large dissociation constant, such as VA10 and Cyanex272 are used as an organic phase, hardly any hydrochloric acid is recovered at all. On the other hand, when an acidic extractant with a small dissociation constant, such as D2EHPA, is added to the organic phase containing amine, 20-30% hydrochloric acid can be recovered⁹⁾. The reaction in eq. (3) proceeds only about half the sodium hydrogen carbonate using a mixture of 1.0 mol/dm³ Priment JMT and 0.5 mol/dm³ D2EHPA, but the improvement in hydrochloric acid recovery may make it possible to operate a total production system.

Figure 6 shows the stripping isotherm of hydrochloric acid at various temperatures from 25°C to 60°C. The stripping of hydrochloric acid is independent of



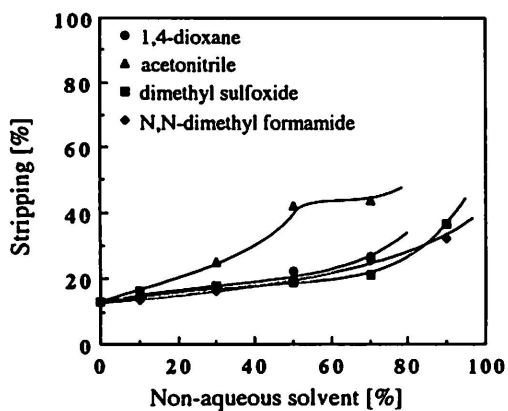
Organic phase: 1.0mol/dm³ Priment JMT
 and acidic extractant
 Aqueous phase: 5.0mol/dm³ NaCl
 Diluent: 1-butanol
 Phase ratio(A/O): 50cm³/50cm³

Fig. 5 Relationship between stripping and acidic extractant concentration



Organic phase: 1.0mol/dm³ Priment JMT
 0.5mol/dm³ D2EHPA
 Diluent: 1-butanol

Fig. 6 Stripping isotherm of HCl with water at various temperatures

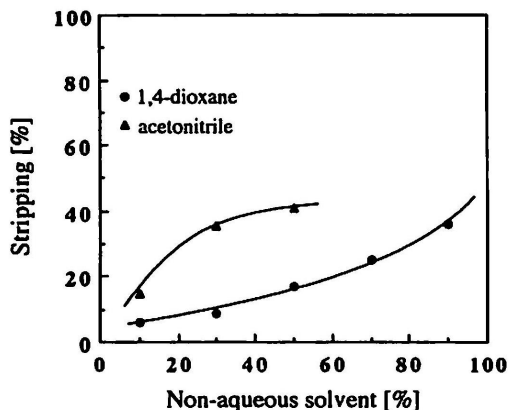


Organic phase: 1.0mol/dm³ Priment JMT
 0.5mol/dm³ D2EHPA
 Diluent: n-hexane

Fig. 7 Effect of non-aqueous solvent on the stripping of HCl from mixed extractant

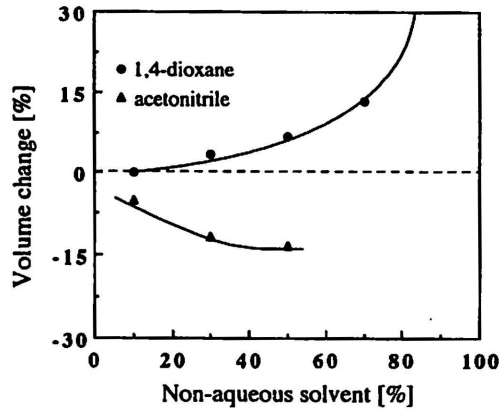
temperature, so the recovery is hardly improved. These results relate to the fact that the reaction in eq. (3) does not increase with an increase in temperature (see Fig. 3). The stripping operation of hydrochloric acid with mixed aqueous-organic media was investigated (see Fig. 7). Stripping increases in proportion to an increase in the ratio of non-aqueous solvent in a mixed aqueous-organic media. When acetonitrile is used as a mixed aqueous-organic media, hydrochloric acid is effectively stripped also from the organic phase. Stripping of hydrochloric acid by a mixed aqueous-organic media was also investigated when only amine was used as an organic phase. The relation between stripping of hydrochloric acid and a mixed aqueous-organic media is shown in Fig. 8. When a mixed aqueous-organic media is used for stripping, hydrochloric acid can be stripped, even if using only amine as an organic phase.

Volume change in organic phase after the stripping operation is illustrated in Fig. 9. The volume of the organic phase changes remarkably in accordance with an increase in the ratio of non-aqueous solvent in a mixed aqueous-organic media. It is thought that the volume change in the organic phase after stripping is caused by an inter-dissolution of non-aqueous solvent between a mixed aqueous-organic media and an organic phase. Thus the stripping of hydrochloric acid is promoted by reducing activity of extractants in an organic phase⁹. In the case of a stripping operation of hydrochloric acid from 1,4-dioxane-water media containing amine hydrochloride, the volume of organic phase increases. It is confirmed that when the organic phase and water are shaken after a stripping operation, 1,4-dioxane distributed in the organic phase is transferred to the water. If we set up a continu-



Organic phase: 1.0mol/dm³ Priment JMT
Diluent: n-hexane

Fig. 8 Effect of non-aqueous solvent on the stripping of HCl from Priment JMT



[Organic phase: 1.0mol/dm³ Priment JMT
Diluent: n-hexane]

Fig. 9 Volume change in organic phase after the stripping operation

ous stripping and recovering process for hydrochloric acid, amine in the organic phase can be regenerated and hydrochloric acid can be obtained.

The total stripping of hydrochloric acid in a continuous countercurrent multistage stripping was constructed by means of computer simulation⁹. In order to analyze the behavior in each stage of the multistage extraction and stripping process, it is important to express extraction and stripping isotherms with a mathematical function. In our study, the stripping isotherms are represented by

$$C_A = \frac{C_0}{a + b \cdot C_0} \quad (4)$$

where C_A and C_0 denote the equilibrium concentration of hydrochloric acid in the aqueous and organic phase, and a and b are constants. The stripping data obtained in batch experiments if fitted to the above function by the least squares method, and then the constants are determined. A schematic diagram of a multistage countercurrent stripping process is illustrated in Fig. 10. In the figure, A , O , C_A and C_0 indicate, respectively, the flow rate of the aqueous phase, flow rate of the organic phase, the hydrochloric acid concentration in aqueous phase and hydrochloric acid concentration in the organic phase. Subscript F represents the feed solution, and the figures in parentheses denote the stage number of stripping operations. The distribution ratio D is defined as follows:

$$D = \frac{C_0}{C_A} \quad (5)$$

When the stripping isotherm, feed concentrations of both phases, flow rates of both phases, and the number of stages are fixed, the concentrations in the aqueous

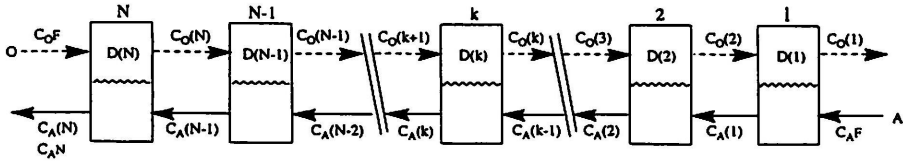


Fig. 10 Schematic diagram for countercurrent multistage stripping

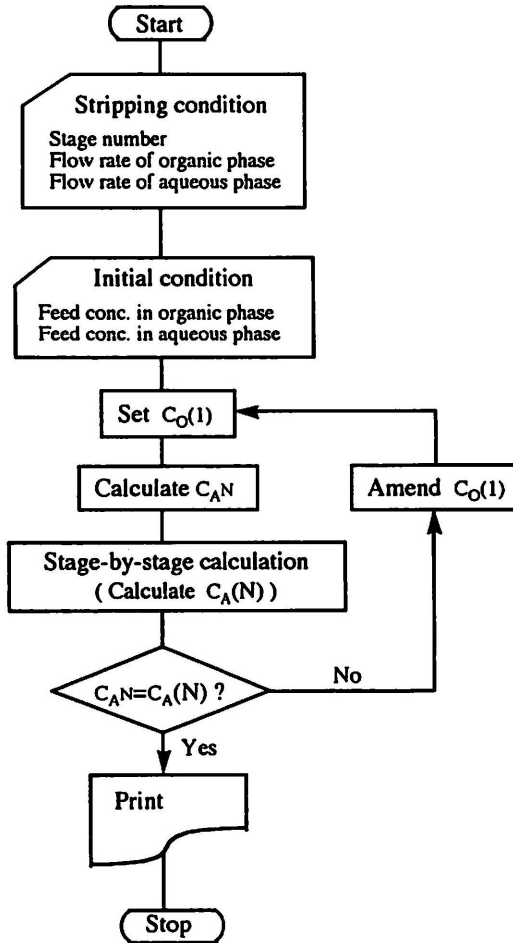


Fig. 11 Algorithm of computer simulation for multistage countercurrent stripping process

and organic phase in each stage will remain unknown. Then, if the final outlet concentration in organic phase $C_O(1)$ is assumed to be of a certain value, the other unknown values are calculated by the trial and error method using the following procedures. The algorithm of the computer calculation is shown in Fig. 11.

(1) Firstly, the final outlet concentration of organic phase $C_O (1)$ is assumed to have a certain value. The value is voluntary and it exists between zero (complete stripping) and $(C_{AF} \cdot A + C_{OF} \cdot O) / O$ (no stripping). If $C_O (1)$ is assumed to be a given value, the final outlet concentration of aqueous phase C_{AN} is calculated from the material balance of overall stages.

$$C_{AN} = (C_{AF} \cdot A + C_{OF} \cdot O - C_O (1) \cdot O) / A \quad (6)$$

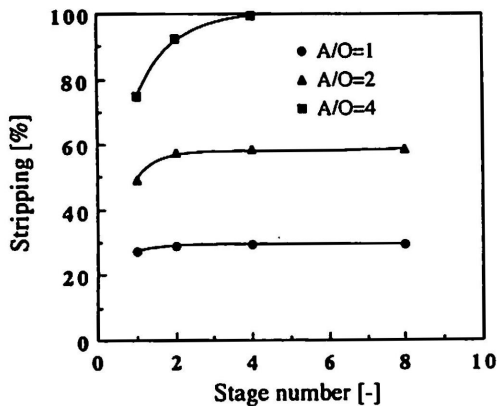
(2) If $C_O (1)$ is assumed to be a given value, $C_A (1)$ is calculated from the mathematical function for the stripping isotherm. If $C_A (1)$ is determined, $C_O (2)$ is calculated from the material balance at the first stage.

$$C_O (2) = (C_A (1) \cdot A + C_O (1) \cdot O - C_{AF} \cdot A) / O \quad (7)$$

(3) If $C_O (2)$ is determined, $C_A (2)$ and $C_O (3)$ are calculated from the mathematical function and the material balance, respectively. In the same manner, the calculation proceeds to the n -th stage, and then final outlet concentration of the aqueous phase $C_A (N)$ is obtained.

(4) If C_{AN} is in good agreement with $C_A (N)$ within the value $|C_{AN} - C_A (N)| < 10^{-5}$ mol/dm³, the assumed value $C_O (1)$ is regarded as correct. Next, the equilibrium state at all stages in the countercurrent stripping process is determined. The above calculation is repeated by amending $C_O (1)$ according to the magnitude of $|C_{AN} - C_A (N)|$ until the value of $|C_{AN} - C_A (N)|$ approaches a value less than 10^{-5} mol/dm³.

The simulation results are shown in Fig. 12 as the relation between stripping



Organic phase: 1.0mol/dm³ Priment JMT
Diluent: n-hexane

Fig. 12 Simulation for stripping of HCl using 70 vol% 1,4-dioxane solution

percentage and stripping stage at various phase ratios. In the calculation, 70 vol% 1, 4-dioxane-water was used as a stripping agent to strip hydrochloric acid from the organic phase comprising 1.0 mol/dm^3 Priment JMT diluted in n-hexane. When the phase ratio (A/O) is increased from 1 to 4 and the stage number is increased, stripping increases remarkably. If a phase ratio of 4 is used, 100% stripping can be obtained in 4 stage stripping. The phase ratios of 1 and 2 result in 32% and 60% stripping, respectively, in 4 stage stripping.

4.3 Fixation process of carbon dioxide

We investigated the chemical fixation process for carbon dioxide (see Fig. 13)⁴⁾. Firstly, carbon dioxide will be converted to sodium hydrogen carbonate by the reaction outlined in eq. (3). The conversion of carbon dioxide to sodium hydrogen carbonate makes it possible to store at smaller volume as compared with carbon dioxide itself. Sodium hydrogen carbonate may be used as a raw material.

If potassium chloride or sodium nitrate are used as starting materials, other hydrogen carbonates and nitric acid can be produced.

If hydrochloric acid, a by-product of this process can be stripped from the organic phase containing amine hydrochloride, amine can be recycled to this process and hydrochloric acid can be utilized as a raw material. The phase separation between the organic and aqueous phases is then carried out. Sodium hydrogen carbonate is recovered from the separated aqueous phase, while the organic phase is moved to a regeneration operation. The mixed aqueous-organic media (containing 1, 4-dioxane) can more effectively strip hydrochloric acid from the organic phase than can water. Since the stripped hydrochloric acid and 1, 4-dioxane are dissolved

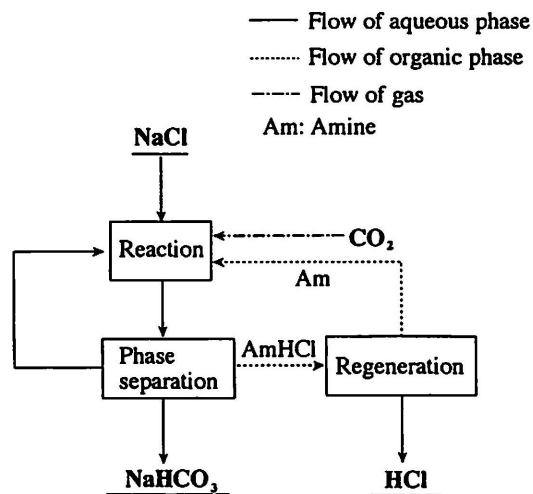


Fig. 13 Chemical fixation process of carbon dioxide

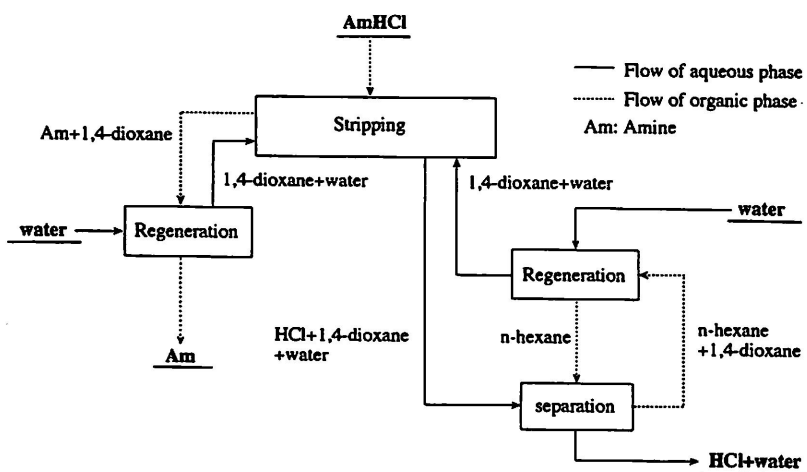


Fig. 14 Recovery process of HCl and amine from AmHCl

in a single phase, it is necessary to separate 1, 4-dioxane and hydrochloric acid.

The recovery process of amine and hydrochloric acid is given in detail in Fig. 14. At first, 1,4-dioxane-water mixed solvent is used to strip hydrochloric acid from the organic phase. The organic phase is moved from a stripping step to a regeneration step, where amine and 1, 4-dioxane are separated by adding water. 1, 4-dioxane-water mixed solvent is recycled to a stripping step. 1,4-dioxane-water mixed solvent from a stripping step is transferred to a separation step, and, there, by adding n-hexane 1, 4-dioxane and hydrochloric acid are separated. The hexane phase containing 1,4-dioxane is mixed with water in a regeneration step to obtain n-hexane and 1, 4-dioxane-water mixed solvent. One advantage of the process shown in Fig. 13 and 14 that it hardly requires a heating and cooling operations at all.

5. Conclusions

As a chemical fixation method of carbon dioxide, the reaction of carbon dioxide and sodium chloride, removing hydrochloric acid by solvent extraction, was investigated using the various organic phases containing amine and acidic extractants.

The main reaction for producing hydrogen carbonates and amine hydrochloride can easily proceed in the presence of amine organic solvent in an autoclave at the pressure of 10-30 kg/cm² carbon dioxide. The stripping of hydrochloric acid from the organic phase including amine hydrochloride is very difficult, because amine hydrochloride is chemically stable and must be decomposed into the original amine and hydrochloric acid. It was discovered that the stripping can be effected by the use of non-aqueous solvent such as 1, 4-dioxane. The process flow of the main reaction for a chemical fixation of carbon dioxide and the recovery step for amine

and hydrochloric acid were proposed on the basis of our investigation and experimental results.

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