

Numerical Simulation of Thermal Energy Storage Unit Using $\text{CaCl}_2\text{-NH}_3$ System

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SUMMARY

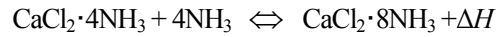
In order to develop one of thermal storage system using $\text{CaCl}_2 \cdot n\text{NH}_3$ system, the numerical simulation model for the above reaction system (Deammoniation reaction) is proposed and the simulation results were compared with the experimental results in this study. It was found that the end time of the reaction of this simulation model was shorter than that of the experiment, and its comparison of calculated value with experimental one on the end time of reaction indicated the error of approximately 15 %. In the simulation results of the reaction ratio on radius direction, the end time of reaction on the inner wall was approximately 30 % shorter than that on the central point. However, the temperature of the experiment rose earlier than that of the simulation on the operating time, and the reaction end time was shorter than that of experiment. Regarding the difference in the result of the simulation and the experimental, it was seemed that the thermodynamics properties and parameters were influenced. It was found that this simulation model was useful for the optimum design of this thermal energy storage unit.

KEY WORDS: thermal storage system, numerical simulation, ammoniated salts, ammine complex, calcium chloride, ammonia

1. INTRODUCTION

Recently, the possibility of significant global warming resulting from emissions of greenhouse gases by fossil fuel combustion has become an important concern within the international community. In the energy sector, energy utilization technologies in many industries are expected to develop high efficiency and high performance. For thermal energy storage systems utilizing a low heat source as solar energy or hot effluent (approximately 353~373 K), the processes using the chemical reaction of anhydrous salt with NH_3 have been proposed and discussed for its practicably^{1~6)}. For example, some prototypes of energy storage unit using $\text{CaCl}_2 \cdot n\text{NH}_3$ system have been designed and measured these performances^{3~6)}.

The reaction products from anhydrous salts and ammonia are referred to as ammoniated salts or ammine complexes and the state is either solid or liquid. The reaction is similar to hydration of anhydrous salts. In this study, the chemical reaction of $\text{CaCl}_2 \cdot 4\text{NH}_3$ with 4NH_3 was chosen here for the thermal energy storage system (see the following reversible chemical reaction: Ammoniation/Deammoniation), since this reaction can be driven by using low temperature heat sources. In this reversible reaction, ΔH (enthalpy change) is 43.8 kJ/mol-NH_3 at 0.1 MPa , 304 K ¹⁾, the value of which is considerably higher than the latent heat of vaporization of liquid NH_3 , 23.4 kJ/mol-NH_3 at 0.1 MPa , 240 K ²⁾.



Furthermore, this chemical reaction is well known as higher energy density system as compared with other reaction systems for energy storage system, and the salt is low cost and easy to supply.

In the author's previous work⁶⁾, the prototype of the horizontal thermal storage unit was already designed for the examination of heat transfer rate of the above ammoniated salt, and its performance was well discussed from the view point of the activation of chemical reaction on repeated runs (Ammoniation/Deammoniation).

In this study, in order to develop the thermal energy storage system using $\text{CaCl}_2 \cdot n\text{NH}_3$ system, the numerical simulation model for the above reaction system (Deammoniation reaction) was proposed, and the simulation results were compared with the experimental results⁶⁾.

2. SIMULATION METHOD / NUMERICAL ANALYSIS

2.1 Simulation model of heat conduction for one dimensional cylindrical coordinate system

Figure 1 shows a simulation model for one dimensional cylindrical coordinate system for a horizontal cylindrical reactor in this study. In radius R direction, the radius R is divided into small each element (Δr). The elements are defined as

$$r = r_0, r_1, \dots, r_{n-1}, r_n.$$

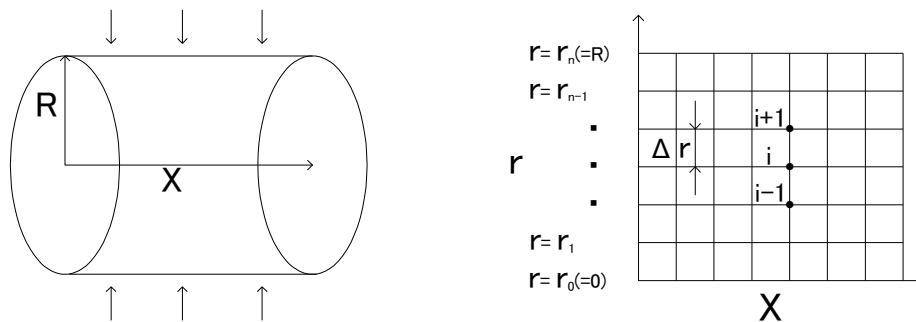


Figure 1. Simulation model.

The heat conduction with the thermochemical reaction for one dimensional cylindrical coordinate system is expressed by the following equation.

$$\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} - \frac{1}{\lambda} \bar{R} \Delta H = \frac{1}{\alpha} \frac{\partial T}{\partial t} \quad (1)$$

where r , λ , α , \bar{R} and ΔH are the distance of radius direction, the effective thermal conductivity, the effective thermal diffusivity, the mean reaction rate and the enthalpy change (reaction heat energy) of CaCl₂·nNH₃ reaction system, respectively. Here the mean reaction rate \bar{R} can be expressed by the following equation.

$$\bar{R} = k(t) \left(1 - \frac{P}{P_e} \right) \quad (2)$$

where $k(t)$, P and P_e are the reaction rate constant, the operating pressure and the equilibrium pressure of CaCl₂·nNH₃ reaction system, respectively.

Regarding $k(t)$, it is given by the Arrhenius equation.

$$k(t) = s \cdot \exp\left(-\frac{\Delta E}{RT}\right) \quad (3)$$

where s , ΔE , R and T are the frequency factor, the activation energy of CaCl₂·nNH₃ reaction system, universal gas constant and reaction temperature, respectively.

Regarding P_e of the above chemical reaction system, it is given as the generalized exponential function.

$$P_e = \exp\left(A + \frac{B}{T}\right) \quad (4)$$

where A and B are the constants of equilibrium pressure, respectively.

Regarding the boundary conditions (B.C.),

B.C. 1: at $r = 0$ in all time,

$$\left(\frac{\partial T}{\partial r}\right)_{r=0} = 0 \quad (5)$$

B.C. 2: at $r = r_n$ in all time,

$$\left(\frac{\partial T}{\partial r}\right)_{r=r_n} = -\frac{U}{\lambda} (T_{r=r_n} - T_w) \quad (6)$$

where U and T_w are the overall heat transfer coefficient on the basis of radius r_n and the temperature of outer wall, respectively.

In this study, in order to solve the partial differential equation (1), Crank-Nicolson's implicit method was adopted as the solution method, and the numerical results are given by calculating the following difference equations.

$$T_{0,j+1}^{(x+1)} = \left(\frac{1}{1+\beta}\right) \left\{ T_{1,j+1}^{(x)} - \frac{m}{2} \Delta r^2 \bar{R}^{(x)}_{0,j+1} \right\} + \left(\frac{1}{1+\beta}\right) \left\{ T_{1,j} - (1-\beta)T_{0,j} - \frac{m}{2} \Delta r^2 \bar{R}_{0,j} \right\} \quad (7)$$

$$T_{i,j+1}^{(x+1)} = \left\{ \frac{1}{2(1+\beta)} \right\} \left\{ \left(1 + \frac{1}{2i} \right) T_{i+1,j+1}^{(x)} + \left(1 - \frac{1}{2i} \right) T_{i-1,j+1}^{(x+1)} - m \Delta r^2 \bar{R}^{(x)}_{i,j+1} \right\} \\ + \left\{ \frac{1}{2(1+\beta)} \right\} \left\{ \left(1 + \frac{1}{2i} \right) T_{i+1,j} - 2(1-\beta)T_{i,j} + \left(1 - \frac{1}{2i} \right) T_{i-1,j} - m \Delta r^2 \bar{R}_{i,j} \right\} \quad (8)$$

$$T_{n,j+1}^{(x+1)} = \left\{ (1 + \beta) + \left(1 + \frac{1}{2i} \right) \frac{U\Delta r}{\lambda} \right\}^{-1} \times \left\{ T_{n-1,j+1}^{(x+1)} - \frac{m}{2} \Delta r^2 \bar{R}_{i,j+1}^{(x)} \right\} - \left\{ (1 - \beta) + \left(1 + \frac{1}{2i} \right) \frac{U\Delta r}{\lambda} \right\}^{-1} \\ \times \left[\left\{ (1 - \beta) + \left(1 + \frac{1}{2i} \right) \frac{U\Delta r}{\lambda} \right\} T_{n,j} - T_{n-1,j} + \frac{m}{2} \Delta r^2 \bar{R}_{n,j} - \frac{U\Delta r}{\lambda} \left(1 + \frac{1}{2i} \right) (T_{w,j+1} + T_{w,j}) \right] \quad (9)$$

where β and m are expressed as following equations, and Δt is time interval. The superscripts (x) and $(x+1)$ are the approximation of x and $x+1$ - order in the above difference equations.

$$\beta = \frac{\Delta r^2}{\alpha_e \cdot \Delta t} \quad (10)$$

$$m = \frac{\Delta H}{\lambda} \quad (11)$$

The error between the calculated value and the experimental one was defined by the following equation.

$$Error = \frac{V_{\text{exp}} - V_{\text{sim}}}{V_{\text{exp}}} \times 100 \quad [\%] \quad (12)$$

2.2 Thermodynamics properties and parameters

The thermodynamics properties and parameters^{2,4,6,7)} were adopted in this simulation are listed in Table 1.

Table 1. Thermodynamics properties of $\text{CaCl}_2 \cdot \text{NH}_3$ system

Symbol	Value	Unit
λ	0.116	W/m·K
α	4.17×10^{-8}	m ² /s
ΔH	42.1	kJ/mol-NH ₃
U	6.98	W/m ² ·K
T_w	353	K
s	2.99×10^{-7}	s ⁻¹
ΔE	35,020	kJ/mol-NH ₃
R	8.314	J/mol·K
A	23.33	-
B	-50.6×10^2	-
P	0.45	MPa

The simulation results for the deammoniation process obtained by above equations were compared with the experiment data⁶⁾.

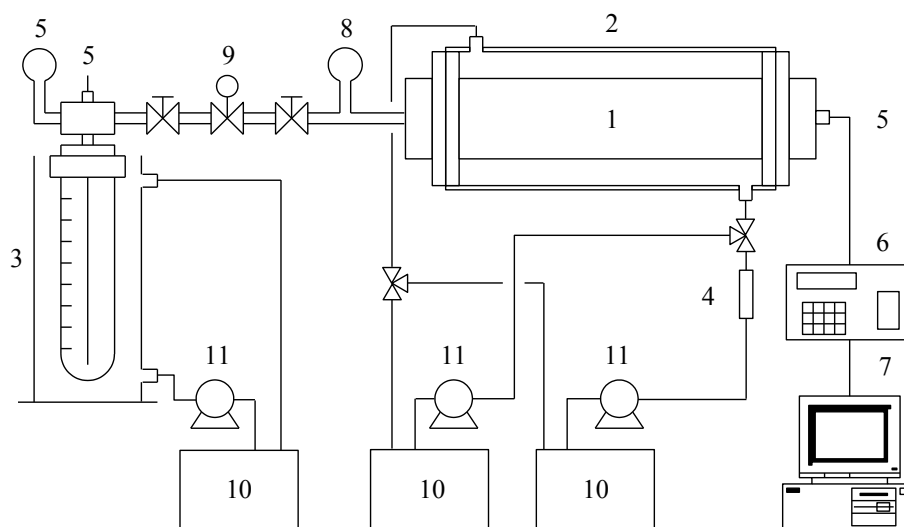
3. EXPERIMENTAL SECTION

3.1. Materials

CaCl₂ (Calcium chloride) used in the experiment is produced by Wako Pure Chemical Industries, Ltd. Japan. It is guaranteed reagent grade, and it is specified as the pure grade having minimum purity of 95.0 %. CaCl₂ is used without further purification. The powdered crystal of CaCl₂ is dried at 773 K and stored over silica gel in a desiccator. NH₃ (Ammonia) gas of 99.99 % purity is provided from Seitetsu Kagaku Co. Ltd.

3.2. Experimental apparatus

Figure 2 schematically shows the horizontal energy storage unit. This unit consists of the horizontal stainless steel reactor, the NH₃ glass vessel, the pressure regulator valve, pressure gauges, thermocouples and constant temperature water baths. The volume of stainless reactor is approximately $1.25 \times 10^{-3} \text{ m}^3$ (I.D. 44.6 mm) and it is covered with water jacket, which can control the temperature in the horizontal reactor. The NH₃ vessel is pressure resistant glass vessel, which volume is $0.3 \times 10^{-3} \text{ m}^3$, (up to 2.0 MPa), and the volume of the liquid NH₃ is measured by the microscope with an accuracy of $\pm 0.05 \%$ of full volume ($0.5 \times 10^{-3} \text{ m}^3$).



1: Reactor, 2: Water jacket, 3: Pyrex glass vessel, 4: Flow meter, 5: Thermocouple, 6: Digital thermometer, 7: Micro Computer, 8: Pressure gauge, 9: Pressure regulator valve, 10: Constant temperature bath, 11: Pump

Figure 2. Schematic diagram of horizontal thermal energy storage unit.

In order to insulate the horizontal stainless reactor from surroundings, the apparatus is wrapped by foamed polystyrol. The temperature in this apparatus is measured by using C-A (Chromel-Alumerl) thermocouples corrected by a digital thermometer, which is in the stainless pipe of 2 mm diameter.

The amount of liquid NH₃ transferred to the reactor from the NH₃ vessel can be measured by the microscope. The temperature of this reactor and the NH₃ vessel are controlled by using constant temperature water bath having minimum accuracy within ±0.1 K separately. The pressure in these vessels is measured by Bourdon gauge, which accuracy is ±0.1 % of full scale (up to 2.0 MPa). The pressure control in the horizontal stainless reactor is carried out using the pressure regulator valve. The temperature in this unit is measured by using C-A type thermocouples by the digital thermometer, and the temperature data as the digital signal (change of mV) is transferred to the micro computer and stored.

3.3. Experimental Procedure

3.3.1. Ammoniation ($\text{CaCl}_2 \Rightarrow \text{CaCl}_2 \cdot 8\text{NH}_3$)

CaCl₂ of 1 mole (approximately 110 g) was crushed below size of 200 JIS mesh and was dried at 773 K approximately for 5 hours by an oven. A dried powder sample was placed in this reactor. It was sealed, and worked by the vacuum pump in order to remove the air and any water from this system.

The NH₃ vessel was also evacuated for 2 hours and NH₃ gas was introduced from the cylinder into the NH₃ vessel, which was kept at constant temperature (273 K) by the cooling liquid. After liquid NH₃ was charged in it, its volume was measured by the microscope rapidly and recorded. Then this reactor was connected with the NH₃ vessel shown in Fig. 3. NH₃ gas moved to the reactor through the pressure regulator valve keeping constant pressure (0.5 MPa) during the reaction. The level of liquid NH₃ in the NH₃ vessel was measured by reading the scale of the NH₃ vessel using the microscope, and mole number of NH₃ absorbed to pure CaCl₂ was calculated from this volume change. The horizontal temperature distribution in detail was measured at the some points of horizontal axis in this reactor. The distance between the measuring point and next one was 0.05 m, and the temperature distributions at the center point were measured using thermocouples at the same time. The temperature of the reactor and each vessel was separately controlled by using the constant temperature water baths throughout the experiment.

After the temperature of the reactor and ammonia vessel was stabilized, a needle valve was opened to keep the constant pressure using the regulator valve in this reactor. Operating temperature and pressure in the reactor were controlled to 303 K and 0.5 MPa, respectively. The amount of liquid NH₃ transferred to the reactor from NH₃ vessel was measured reading the scale of NH₃ vessel using the microscope. The NH₃ mole number absorbed to the CaCl₂ was calculated from the volume change of NH₃ vessel. When 8 moles of NH₃ was absorbed to the pure CaCl₂, the experiment of ammoniation was just finished.

3.3.2 Deammoniation ($\text{CaCl}_2 \cdot 8\text{NH}_3 \Rightarrow \text{CaCl}_2 \cdot 4\text{NH}_3$)

The deammoniation from the ammoniated salt (CaCl₂·8NH₃) was carried out by using the same experimental apparatus. In this case, the NH₃ vessel was kept at constant temperature of 293 K by circulating water from the constant temperature bath, and the horizontal reaction was heated to 353 K by heating water. The NH₃ mole number desorbed from the ammoniated salt was evaluated by the same method of 1st-Ammoniation. When 4 moles of NH₃ was desorbed from CaCl₂·8NH₃, this deammoniation process was ended.

4. RESULTS AND DISCUSSION

Figure 3 shows the relation between reaction ratio and operating (reaction) time. It was found that the end time of the reaction of this simulation model was shorter than that of the experiment, and the comparison of calculated value with experimental one on the end time of reaction indicated the error of approximately 15 %. Regarding the reason of the difference of the both results, it was seemed that the heat loss of the experimental apparatus was influenced. Therefore, it is necessary to analyze the influence of the heat loss the experimental apparatus.

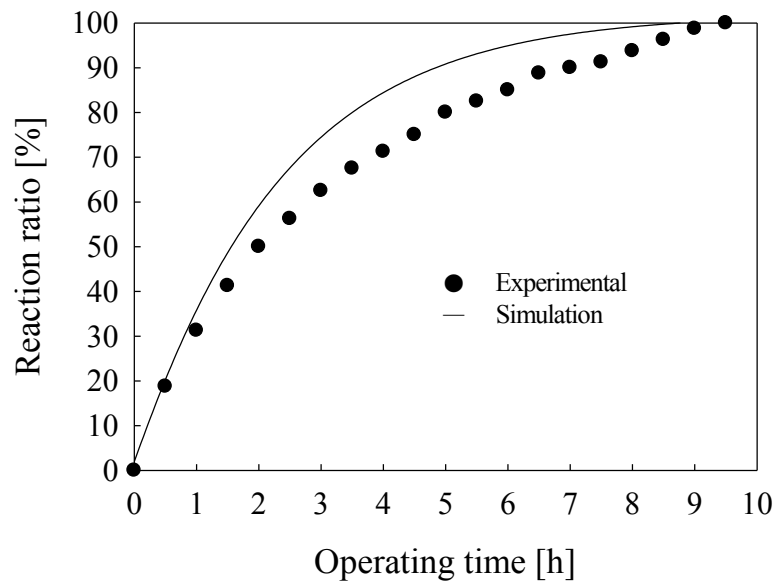


Figure 3. Relation between reaction ratio and operating time.

Figure 4 shows the relation between reaction ratio on the radius direction and operating (reaction) time. It was founded that the end time of reaction on the inner wall was shortest among those of other points, and the end time of reaction on the inner wall was approximately 30 % shorter than that on the central point. Regarding the difference in their tendencies, it is seemed that its reason is the low heat transfer rate (e.g. effective thermal conductivity λ , thermal diffusivity α and overall heat transfer coefficient U) on typical gas – solid phase reaction.

Figure 5 shows the relation between temperature change on the radius direction and operating (reaction) time. It clearly revealed that the temperature on the inner wall is remarkable rise, and this tendency is prove from the simulation results in figure 4. However, regarding the comparison of calculated value with experimental one on the center point of temperature, the temperature of the experiment rose earlier than that of the simulation on the operating time, and the reaction end time was shorter than that of experiment. It is seemed that this is because the above thermodynamics properties and parameters are constant in the operating time in this simulation and effective thermal conductivity λ , thermal diffusivity α and overall heat transfer coefficient U vary with the composition (e.g. the packed density) in the reaction process.

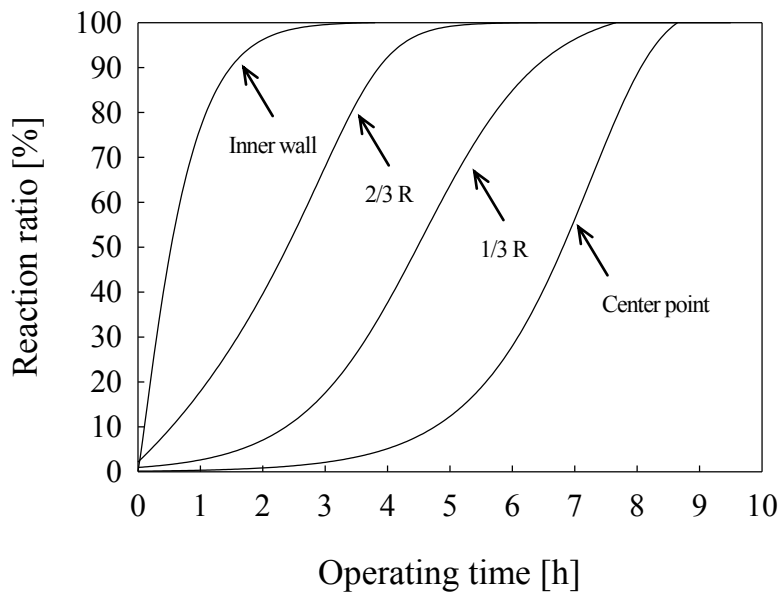


Figure 4. Relation between reaction ratio on the radius direction and operating time.

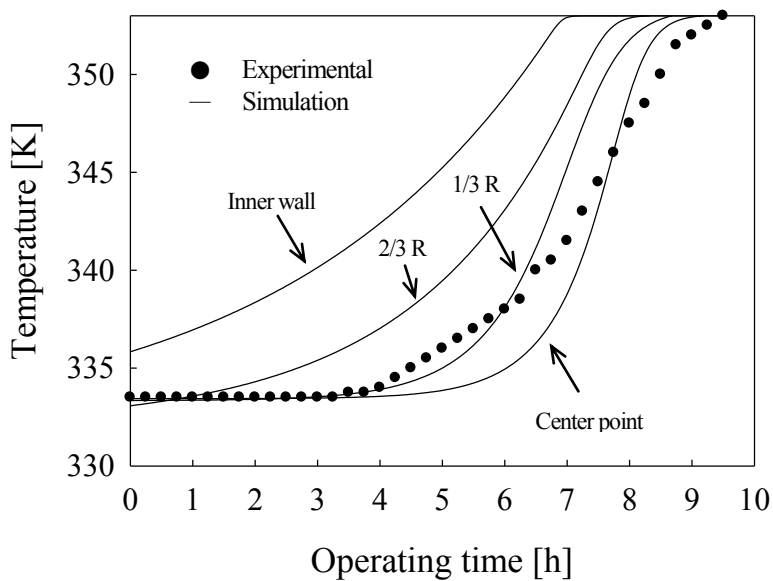


Figure 5. Relation between temperature change on the radius direction and operating time.

5. CONCLUSIONS

In this study, in order to develop the thermal energy storage system using $\text{CaCl}_2 \cdot n\text{NH}_3$ system, the numerical simulation model for the reaction system (Deammoniation reaction) was proposed, and the simulation results were compared with the experimental results. As a result, the following conclusions were obtained.

The end time of the reaction of this simulation model was shorter than that of the experiment, and it was found that the comparison of calculated value with experimental one on the end time of reaction indicated the error of approximately 15 %.

According to the simulation results, the end time of reaction on the inner wall was shortest among those of other points, and the end time of reaction on the inner wall was approximately 30 % shorter than that on the central point. The temperature of the experiment rose earlier than that of the simulation on the operating time, and the reaction end time was shorter than that of experiment. Regarding the differences in the above results of the simulation and the experimental, it is seemed that the heat loss of the experimental apparatus and the thermodynamics properties and parameters are influenced. Consequently, these results on this simulation are useful for the optimum design of this thermal storage unit.

ACKNOWLEDGEMENTS

The author is grateful to Professor Hideki Yamamoto of Kansai University for the support to this study.

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