Reaction Characteristics of CaSO$_4$/CaSO$_4$$\cdot$1/2H$_2$O Reversible Reaction for Chemical Heat Pump

Hironao OGRA, Masahiro HAGURO, Yasuhiro SHIBATA and Yasufumi OTSUBO
Division of Architecture and Urban Science, Graduate School of Engineering, Chiba University, 1-33, Yayoi-cho, Inage-ku, Chiba-shi, Chiba 263-8522, Japan

Keywords: Chemical Heat Storage, Reactant, Thermogravimetry, Waste Energy Utilization, Energy Saving

We had proposed chemical heat pumps using a reversible calcium sulphate/water reaction system for effective waste energy utilization. However, more reaction kinetics studies are necessary for this reaction system, especially for different atmosphere condition and different materials. As a result, the reaction equilibrium line of CaSO$_4$ in the closed system like CHP system was found to be close to that in the open system. It means that the CHP using CaSO$_4$/CaSO$_4$$\cdot$1/2H$_2$O reversible reaction stores under 373 K level thermal energy, and releases the same level hot heat and 273 K level cold heat. Furthermore, the effects of material size on the reaction rates could be calculated by the proposed equations, which enable the effective CHP reactor design.

Introduction

From the viewpoints of energy savings and environmental impacts, we have been studying on chemical heat pumps (CHPs). We had proposed and developed CHPs using a reversible calcium oxide/water reaction system for effective thermal energy utilization in domestic use (Ogura et al., 1993) and industrial use such as electric power use (Ogura et al., 1998) or drying (Ogura et al., 2000). Furthermore, for lower temperature heat source, we had proposed CHPs using a reversible calcium sulphate/water reaction system for effective waste energy utilization (Ogura et al., 2004). Calcium sulphate has possibility of storing under 373 K level thermal energy and releasing the same level heat and 273 K level cold heat. Also Calcium sulphate is easy to get, inexpensive and safe. However, more reaction kinetics studies are necessary for this reaction system, especially in a closed system like CHP system for different materials. Although the reaction kinetics of CaSO$_4$ has been done by some researchers (Badens et al., 1998; Hudson-Lamb et al., 1996; Strydom et al., 1995), those were done in an open system.

In this study, we examine the reaction equilibrium lines of the hydration of calcium sulphate and the dehydration of calcium sulphate hemihydrate for different kinds of material in an open system, a semi-closed system and in a closed system by considering the heat pump operations. Semi-closed system is assumed to be a closed system with forced convection such as a fan unit for mass transfer enhancement. These different kinds of condition are necessary to consider the CHP conditions. We used an improved thermogravimetry for the vacuumed condition experiments. Furthermore, the effects of material size on the reaction rates of the hydration of calcium sulphate/the dehydration of calcium sulphate hemihydrate are examined in an open system.

1. Operating Principle of CHP

Figure 1 shows a typical gas–solid CHP configuration. The CHP is a closed system of coupled low and high temperature reactors connected to each other. The heat storage and release reactions occur at different pressure levels. The low temperature side reactor has a higher reaction equilibrium pressure line. An evaporation/condensation also can be used for the low temperature side reaction. The CHP, as studied earlier, operates as a batch system with a heat storing step and a heat releasing step.

In the heat storing step, the heat $Q_H$ is stored in the form of thermochemical energy by decomposition of the reactant $A(s)$ in the high temperature side reactor. The released gas $C(g)$ flows into the low temperature side reactor due to a pressure difference between the two reactors. The gas $C(g)$ reacts with the reactant $B(s)$ releasing low temperature heat $Q_L$. As long as the reactant $A(s)$ is separated from the gas $C(g)$,
the reaction heat can be stored for any length of time in the form of chemical energy.

In the heat releasing step, the gas $C(g)$ flows from the low temperature side reactor to the high temperature side reactor by opening a valve due to the pressure difference between the reactors. The exothermic reaction of the reactant $A(s)$ at a high temperature level with the gas $C(g)$ takes place in the high temperature side reactor. The low temperature side reactor stores the low temperature heat $Q_L$ or is cooled down and release cold heat by its decomposition/evaporation heat.

## 2. Experiments

### 2.1 Experimental unit

**Figure 2** shows an example of the experimental unit. This figure shows the open system unit. A thermogravimetry (TGA-50H, Shimadzu Corp.) is connected with an evaporator/condenser controlled by a temperature control bath. For the open system experiments, the evaporated water vapor is introduced to the thermogravimetry by $N_2$ gas flow (100 ml/min). For the semi-closed system experiments, the water is evaporated and introduced to the thermogravimetry by vacuuming from the thermogravimetry side. For the closed system experiments, the reactor and the evaporator/condenser are vacuumed to the appropriate pressures. The reactor is heated up with 5–10 K/min and kept at constant temperature for 10 min. The joint valve connecting the reactor and the evaporator/condenser is opened, and $CaSO_4\cdot1/2H_2O$ is dehydrated in this heating-up stage as a heat-storing step. After that, the hydration reaction of $CaSO_4$ occurs as a heat-releasing step with the reactor temperature cooling down with 5–10 K/min. The hydration and the dehydration operations were repeated. The reaction conversion changes and the reaction heat were calculated from the weight changes of the reactants. This reaction occurs between $\beta$-$CaSO_4\cdot1/2H_2O$ and $\gamma$-$CaSO_4$ in our experimental temperature range (Badens et al., 1998).

### 2.2 Working materials

For the experiments, the calcium sulphate hemihydrate: $CaSO_4$·1/2$H_2O$ (Calcium Sulfate, Calcined, Wako Corp.) and the chemical gypsum: $CaSO_4\cdot2H_2O$ (Calcium Sulfate Dihydrate, Wako Corp.) were used as chemical materials. Also, the natural gypsoms $CaSO_4\cdot2H_2O$ (Produced in Australia, mean diameter: 40 $\mu$m under, 100–500 $\mu$m and 500–1000 $\mu$m) were used as start materials.

### 2.3 Experimental procedure

For the thermogravimetry experiments, 10 mg of the $CaSO_4\cdot1/2H_2O$ and natural gypsum are installed in the cell of the thermogravimetry. For the open system experiments, the evaporated water vapor is introduced to the thermogravimetry by $N_2$ gas flow (100 ml/min). For the semi-closed system experiments, the water is evaporated and introduced to the thermogravimetry by vacuuming from the thermogravimetry side. For the closed system experiments, the reactor and the evaporator/condenser are vacummed to the appropriate pressures. The reactor is heated up with 5–10 K/min and kept at constant temperature for 10 min. The joint valve connecting the reactor and the evaporator/condenser is opened, and $CaSO_4\cdot1/2H_2O$ is dehydrated in this heating-up stage as a heat-storing step. After that, the hydration reaction of $CaSO_4$ occurs as a heat-releasing step with the reactor temperature cooling down with 5–10 K/min. The hydration and the dehydration operations were repeated. The reaction conversion changes and the reaction heat were calculated from the weight changes of the reactants. This reaction occurs between $\beta$-$CaSO_4\cdot1/2H_2O$ and $\gamma$-$CaSO_4$ in our experimental temperature range (Badens et al., 1998).

## 3. Results and Discussion

### 3.1 Reaction equilibrium

**Figure 3** shows the reaction equilibrium line of $CaSO_4/ CaSO_4\cdot1/2H_2O$ reversible reaction obtained by the reference (Lee et al., 1986) and the reaction
equilibrium plots by our experimental data in different systems. All of the data reproduce well the reference equilibrium line. However, for the same reaction pressure, the open system data needs slightly higher temperature than the others. It is probably because that the water vapor reacts with CaSO₄ effectively in the semi-closed and closed system. From these results, it can be seen that the chemical and the natural material less than 1000 µm mean diameter can use the reference reaction equilibrium line although the reaction rates need to be considered in different ways.

3.2 Reaction rate

At this stage, it is not easy to get many data on reaction rate in the closed system. So, we examined reaction rates in the open system especially focused on the effects of the reactant diameter. In the similar reaction system using CaO/H₂O reaction, it was found that the reaction rate in the open system is not so different from that of the semi-closed system (Shokrat et al., 2005). We believe that even the open system data can be important data for CHP reactor design.

Equations (1) and (2) are reference equations (Lee et al., 1986).

\[
1 - (1 - X_h)^{1/3} = k_h \Delta P_h t, \quad \Delta P_h = (P - P_e)/(P_s - (P - P_e)) \tag{1}
\]

\[
1 - (1 - X_d)^{1/3} = k_d \Delta P_d t, \quad \Delta P_d = (P_e - P)/(P_s - (P_e - P)) \tag{2}
\]

In order to use Eqs. (1) and (2) for reaction rate calculation, we need to prove that our experimental data follow the grain model concept. Figures 5 and 6 show that the \(F_{1h} = 1 - (1 - X_h)^{1/3}\) changes and the \(F_{1d} = 1 - (1 - X_d)^{1/3}\) changes for natural gypsiums. These figure show that all materials have almost linear relationships between \(F_{1h}/F_{1d}\) and time. So, all natural materials can be thought to follow the grain model concept.
However, the influence of material diameter is not considered in Eqs. (1) and (2). We propose Eqs. (3) and (4) that include the influence of mean diameter of material. $\eta_r$ is a term of the diameter effect.

(hydration reaction)

$$X_h = 1 - (1 - k_h \eta_r (\Delta P_h) t)^3,$$

$$k_h = 5.76 \times 10^6 \exp(-5.36 \times 10^4/RT)$$  (3)

(dehydration reaction)

$$X_d = 1 - (1 - k_d \eta_r (\Delta P_d) t)^3,$$

$$k_d = 6.96 \times 10^4 \exp(-3.01 \times 10^4/RT)$$  (4)

$k_h$ and $k_d$ are reaction rate constants of reference (Lee et al., 1986). We revised $k_d$ to reproduce the reference calculated line to the reference experimental data.

Figures 7 and 8 show the $k_h \times \eta_r$, $k_d \times \eta_r$ data calculated by $F_{1h}$, $F_{1d}$ in Figures 5 and 6 in comparison with reference line. These figure show that the larger mean diameter of material are the smaller $k_h \times \eta_r$, $k_d \times \eta_r$. This result is expected to be caused by the heat and mass transfer existence (Shokrat et al., 2005). We assume that the $k_h \times \eta_r$, $k_d \times \eta_r$ are affected mainly by the mean diameter of material.

From Figures 7 and 8, we calculated the diameter effect $\alpha$ by Eq. (5)

$$\alpha = \ln(k, \eta_{10}) - \ln(k, \eta_r)$$  (5)

By Eq. (5), we got $\eta_r$ for $\eta_{10} = 1$.

$$\eta_r = 1.012 \times e^{-0.0013r}$$  (6)

Figures 9 and 10 are example of conversion changes for natural gypsums in hydration and dehydration reactions. It can be seen from these figures that all of the calculated lines by Eq. (3)–(6) reproduce the experimental data well. The difference between calculated data and experimental data in the mean diameter 500–1000 $\mu$m might be caused by using average of hydration $\eta_r$ and dehydration $\eta_r$ when we calculate $\eta_r$.

From these results, we can simulate the reaction rates considering the material size by the proposed Eqs. (3) and (4) in CHP operations, and estimate the CHP power using CaSO$_4$/CaSO$_4$.1/2H$_2$O reversible reaction.

Conclusions

The reactivity of the hydration of calcium sulphate and the dehydration of calcium sulphate hemihydrate were studied by an improved thermogravimetry.

As a result, the reaction equilibrium line of CaSO$_4$ in the closed system like CHP system was close to that in the open system. It means the CaSO$_4$/CaSO$_4$.1/2H$_2$O reversible reaction is considered as one of the best candidates for low-temperature CHP reactant, that stores under 373 K level thermal energy and releases hot/cold heat. Furthermore, the effects of material size on the reaction rates are calculated by our proposed equations. So, the chemical heat pump power using different size CaSO$_4$/CaSO$_4$.1/2H$_2$O can be estimated by the proposed equations, and it enables the effective CHP design.
Nomenclature

\[ F_{1i} = 1 - (1 - X)^{1/3} \]

\[ k_i = \text{reaction rate constant} \quad \text{[1/min]} \]

\[ P = \text{dimensionless partial pressure of water vapor} \quad \text{[—]} \]

\[ P_e = \text{reaction equilibrium pressure} \quad \text{[—]} \]

\[ P_w = \text{saturated vapor pressure} \quad \text{[—]} \]

\[ T = \text{temperature} \quad \text{[K]} \]

\[ T_w = \text{condenser and evaporator temperature} \quad \text{[K]} \]

\[ \tau = \text{reaction time} \quad \text{[min]} \]

\[ X = \text{conversion} \quad \text{[—]} \]

\[ \Delta P = \text{driving pressure term} \quad \text{[—]} \]

\[ \eta_i = \text{term of mean diameter influence} \quad \text{[—]} \]

\(<\text{Subscript}> \]

\[ d = \text{dehydration} \]

\[ g = \text{gas} \]

\[ h = \text{hydration} \]

\[ l = \text{liquid} \]

\[ r = \text{mean diameter (10, 25, 300, 750)} \]

\[ s = \text{solid} \]

Discussion

Fig. 9 Conversion changes for natural gypsiums in hydration reaction

Fig. 10 Conversion changes for natural gypsiums in dehydration reaction

Literature Cited


