UTILIZATION OF HIGH TEMPERATURE HEAT USING A CALCIUM OXIDE / LEAD OXIDE / CARBON DIOXIDE CHEMICAL HEAT PUMP

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A new chemical heat pump designed to utilize high-temperature heat above 800°C generated from a high-temperature gas nuclear reactor or other high-temperature industrial process is presented. Based on experimental results, a heat pump that uses a calcium oxide / lead oxide / carbon dioxide reaction system appears to be a suitable system. To demonstrate the validity of the heat pump, the equilibrium relationship and kinetics of calcium oxide / carbon dioxide and lead oxide / carbon dioxide, which comprise the reaction system of the heat pump, are studied experimentally. A study of the equilibrium relationship of lead oxide / carbon dioxide, which consists of a three-step equilibrium, reveals that the highest temperature equilibrium relationship of the three-step equilibrium is associated with optimal heat pump operation. The practical operation conditions of the heat pump are determined based on the equilibrium relationship and kinetic experiments. The proposed heat pump may be able to operate as a heat transformation-type heat pump, and is capable of storing heat above approximately 830°C and transforming the heat to a higher temperature of more than 870°C under sub-atmospheric pressure and thermal driving conditions with no mechanical work. The calculated mean heat output and heat output amount are 670 W/kg-CaCO₃ and 1200 kJ/kg-CaCO₃, respectively, at 870°C, 1 atm for 30 min. Thus, the new heat pump can be applied to a heat storage and heat transformation system for high temperature processes.

Introduction

High-temperature heat above 800°C is normally generated in a high-temperature gas nuclear reactor (HTGR) or other high-temperature processes such as iron smelting and chemical processing. Although, the potential use of high-temperature heat is great due to its high quality, exergy analysis of current systems suggests that wide-spread application of high-temperature heat is not feasible. In order to realize greater use of such heat, improvements in heat storage and transformation technology must be attained. Improvements in heat pump technology ultimately lead to improved utilization of arbitrary temperature heat. Among the different types of heat pumps, the chemical heat pump appears to be the best choice for using heat generated by high temperature processes. Chemical heat pumps are systems that couple exothermic and endothermic chemical reactions to store thermal energy and transform the energy into other types of thermal energy at a desired temperature. These heat pumps enable highly efficient energy use, easy control of the working temperature, and energy storage and transportation in the form of stable chemical substances with little heat loss.

Therefore, the application of chemical heat pump

technology to high-temperature heat processes presents practical possibilities. The characteristics of a heat pump are determined by the employed reaction system. Several systems have been proposed for the utilization of high temperature thermal energy, including a calcium oxide / water chemical heat pump system for temperatures around 600°C (Matsuda *et al.*, 1985) and a magnesium oxide / water system for temperatures around 350°C (Kato *et al.*, 1996b). However, the use of chemical heat pumps for utilization of heat at such high temperature has not yet been studied in sufficient detail.

A calcium oxide/carbon dioxide reaction system (CaO / CO₂) appears to be an appropriate reaction for a high-temperature heat pump at above 700°C (Barker, 1974 and Kyaw Kyaw *et al.*, 1996b). The key consideration in the development of a heat pump that employs this reaction is how to handle and store carbon dioxide produced as the gas phase reactant. Employing a compressor, which would entail mechanical work, and using zeolites or Ca-Mg oxides as the absorbent of carbon dioxide for the gas storage have been proposed (Kyaw Kyaw *et al.*, 1996a and 1996b). A practical solution for carbon dioxide storage that does not entail significant mechanical work has not yet been established.

In our previous study, we examined the feasibility of using an inorganic oxide / carbon dioxide reaction system as carbon dioxide storage materials because of their high reactivity to carbon dioxide and high durability in the high-temperature range as well as economical use of reactants. A lead oxide / carbon dioxide reaction system (PbO

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Fig. 1 Principle of CaO/PbO/CO₂ chemical heat pump - heat transformation type operation-, (a) heat storage mode, (b) heat output mode

/CO₂) was demonstrated to be effective for storage of carbon dioxide. Based on this finding, a heat pump that combines this reaction with the calcium oxide / carbon dioxide reaction system to form a calcium oxide / lead oxide / carbon dioxide (CaO / PbO / CO₂) chemical heat pump was proposed (Kato *et al.*, 1996a). This heat pump is expected to be able to handle heat storage in the range of 700–1000°C. However, the practical application of this heat pump has not been fully investigated. The present study investigates the validity of the heat pump. Furthermore, the practical operation conditions and thermal performance are studied experimentally with respect to the equilibriums and kinetics of the reaction systems.

1. Principle of the Heat Pump

The following CaO / CO₂ and PbO / CO₂ reaction systems are used in the CaO / PbO / CO₂ chemical heat pump.

The principle of the heat pump is shown in **Fig. 1**. This operation-type system is called a heat transformer. Heat that has a higher temperature than that of the original heat source can be obtained by this operation type. The system consists of a CaO reactor and a PbO reactor. The operation settings of the heat pump include a heat storage mode and a heat supply mode. Initially, CaCO₃ and PbO are charged into each reactor. In the storage mode, (a), the CaO reactor bed receives heat (Q_{d1}) from a heat source

Fig. 2 Experimental apparatus for equilibrium and kinetic analysis of CaO / CO₂ and PbO / CO₂ reaction systems

at temperature T_{d1} . Subsequently, CaO and CO₂ are formed as a result of decarbonation of CaCO₃. The CO₂ is reacted with PbO in the PbO reactor at some pressure (P_{c2}) and the exothermic heat of the carbonation is recovered at temperature T_{c2} , yielding PbCO₃. In the heat supply mode, (b), decarbonation of PbCO₃ proceeds in the PbO reactor using heat at temperature T_{d2} , which is higher than T_{c2} . The CO₂ formed at a pressure (P_{d2}) higher than P_{c2} is introduced into the CaO reactor. Carbonation of CaO then proceeds and heat (Q_{c1}) is generated exothermically in the reactor at a temperature (T_{c1}) higher than T_{d1} due to the higher reaction pressure.

This system is exclusively thermally driven without any mechanical work. The lack of mechanical work allows the development of a simple and highly efficient operation.

2. Experimental Procedure

In order to examine the feasibility of the proposed heat pump, the practical reaction condition of each reaction operation was established. The equilibrium and kinetics of the CaO / CO₂ and PbO / CO₂ reaction systems were then studied using the thermobalance system shown in **Fig. 2** under a closed system. Reaction samples were set in a sample cell placed in the balance. During each reaction, the sample weight was monitored continuously and the reacted fraction was calculated based on the change in weight. Temperature was measured directly at the bottom of the cell using a thermocouple. This temperature was considered to be the reaction temperature and was maintained using an electric heater. After residual inert gas in the apparatus was removed using a vacuum pump, the reaction pressure was controlled by means of introducing CO₂ gas, and was measured using a manometer.

The experiments were carried out at a reaction temperature between 300–900°C and under sub-atmospheric reaction pressure. Lead carbonate (PbCO₃) and calcium

Fig. 3 Relationship between reactivity and reaction equilibriums of CaO / CO₂ and PbO / CO₂ reaction systems

carbonate (CaCO₃) (99.9% grade powder form, Kojundo Chemical Laboratory Co., Ltd.) were used as the starting reactants in the amount of 10 mg each.

3. Experimental Discussion

3.1. Equilibrium analysis of the heat pump

In order to establish the reaction conditions for practical operation of the heat pump, the relationship between reactivity and the equilibriums of CaO / CO₂ and PbO / CO₂ were investigated experimentally.

(1) Reactivity of CaO / CO₂ The reactivity associated with the carbonation of CaO was measured under sub-atmospheric conditions and various reaction conditions. The relationship between carbonation reactivity and reaction equilibrium is shown in **Fig. 3**, in which the reaction pressure of CO₂ is the ordinate and the reaction temperature is the abscissa. Carbonation of CaO observed under various conditions is represented by blank rhombuses. The thermal decomposition of CaCO₃ which reflects decarbonation was measured under sub-atmospheric pressure. The result is shown in **Fig. 4**. The initial temperature of decomposition corresponds to the equilibrium of decarbonation. The black rhombuses in **Fig. 3** represent the measured decarbonation conditions. The equilibrium line of CaO / CO₂ calculated based on JANAF data (1971) is represented by the solid line. The reaction conditions of CaO / CO₂ corresponded well with the equilibrium line because of the appearance of carbonation in the carbonation region, which is seen to the right of the equilibrium line, and the appearance of decarbonation in the decarbonation side, which is seen to the left of the line.

(2) Carbonation of PbO The reactivity of PbO carbonation under various reaction conditions was also measured under sub-atmospheric conditions. The open

Fig. 4 Reacted fraction change in thermal decomposition of CaCO₃

Fig. 5 Reacted fraction change in thermal decomposition of PbCO₃

circles in **Fig. 3** represent the carbonation of PbO. The equilibrium line of PbO / CO₂ calculated on the basis of JANAF data (1971) is shown by the solid line. Unlike the case of CaO, the relationship between reactivity and equilibrium does not agree. The reactivity associated with the carbonation is observed in the decarbonation region, which is found to the left of the PbO / CO₂ equilibrium line. Thus, reactivity associated with carbonation occurs at a higher temperature than the equilibrium condition. Lack of agreement between the observed carbonation reactivity and reaction equilibrium must be discussed in order to establish the optimal operation conditions of the heat pump.

(3) Thermal decomposition of PbCO₃ First, the reactivity of PbO / CO₂ is studied by means of a thermal decomposition study of PbCO₃; in other words, decarbonation was examined. **Figure 5** shows the results of thermal decomposition of PbCO₃ at a heating rate of 2°C / min under various reaction pressures. **Figure 5** indicates that decarbonation proceeds through three reaction steps. The reaction steps have already been proposed by Peretti (1957) as follows.

The mole reaction ratios of produced CO_2 and reacted PbO associated with these reaction steps are 1/2, 1/6 and 1/3, respectively. The reaction steps shown in Fig. 5 are in good agreement with those outlined in the above reaction. The temperature at the beginning of each decomposition step corresponds approximately with the equilibrium conditions of the reactions. In Fig. 3, the filled circles and the thicker lined open circles represent the measured decomposition conditions of steps C and B, respectively. These points agree well with proposed equilibrium lines of steps C and B proposed by Peretti, which are shown as a dashed line and skip dashed line, respectively, in Fig. 3. These results suggest that the measured equilibrium of PbO / CO_2 corresponds well with step C equilibrium which is the highest temperature equilibrium relationship.

(4) Reaction mechanism of PbO / CO_2 The repetitive reaction associated with the carbonation and decarbonation of PbO is studied in order to verify the reaction mechanism for the heat pump operation. The thermal decomposition results of PbCO_3 of the second reaction cycle under 0.2 atm is shown to compare with that of first cycle in Fig. 5. A tailing of reacted fraction change is observed at the end of the second cycle. It is likely due to the reaction rate reduction induced by the structural change of PbO materials during cyclic reaction. However, the decomposition temperature and the degree of change in the reacted fraction of the result of the second cycle correspond well with the step C reaction.

Based on these results and the equilibrium relationship in Fig. 3, it is concluded that the decarbonation of PbCO_3 after the second cycle is based on the step C reaction proposed by Peretti. Therefore, when considering heat pump operation, only the step C reaction equilibrium should be considered for the PbO / CO_2 reaction system.

3.2. Kinetic analysis of the heat pump

The kinetics of both reaction systems are studied with respect to their equilibrium relationships in order to evaluate the performance of the heat pump. The carbonation of CaO and PbO were primarily discussed, because high reactivity of decarbonation was observed in both cases in the decomposition experiments. In addition, the carbonation reaction rate has a greater effect on the heat pump operation rate, than does the decarbonation rate.

Carbonations of CaO and PbO To realize heat transformation-type operation of the heat pump, the carbonation temperature of CaO (T_{c1} in Fig. 1) must be higher than the decarbonation temperature (T_{d1}). Increasing the carbonation pressure of CaO allows the reaction temperature to be raised. However, the apparatus employed in this study limits the maximum reaction pressure to 1 atm. Thus, this pressure is used to obtain the upper limit

Fig. 6 Effect of reaction temperature on reactivity of CaO carbonation under 1.0 atm

of the carbonation temperature. **Figure 6** shows the effect of reaction temperature on the reactivity of the carbonation of CaO under a CO_2 reaction pressure of 1.0 atm. A low decarbonation pressure of 0.01 atm was employed to reduce the decarbonation time. The higher the reaction temperature rises, the lower the reaction rate decreases, because the reaction temperature approaches the equilibrium value. The reaction is observed up to a temperature of 870°C . However, the reaction at 890°C can not be observed at this pressure.

In order to decrease the decarbonation temperature of CaCO_3 (T_{d1} in Fig. 1), which enables a decrease in the temperature of the heat source generated by a high temperature process, for the heat transformation operation, the decarbonation pressure must be lowered. In order to reduce the decarbonation pressure, the carbonation pressure of PbO (P_{c2}) must be lowered because the pressure corresponds to the decarbonation pressure of CaCO_3 . Whether the operation of the heat pump can be driven thermally depends on the low pressure reactivity of PbO . On the other hand, along with the temperature rise of PbO carbonation, the reaction rate rises, however, the apparent rate decreases gradually because the reaction temperature approaches the equilibrium value. Then the carbonation reactivity of PbO has a maximum versus the reaction temperature (Kato *et al.*, 1996a). The carbonation reactivity has a maximum at around 300°C in the low pressure range. **Figure 7** shows the effect of reaction pressure on the carbonation reactivity of PbO at 300°C . A low decarbonation pressure of 0.01 atm is employed also for reduction in the decarbonation time. This reaction can be observed above a pressure of 0.4 atm, but can not be detected at a pressure less than 0.3 atm at 300°C .

3.3. Practical heat pump cycle

Examples of the practical operation conditions of the heat pump based on the above equilibrium and kinetic analyses are shown in **Fig. 8**. The filled circles represent the measured carbonation conditions. On the other hand, open circles represent calculated decarbonation

Fig. 7 Effect of reaction pressure on reactivity of PbO carbonation at 300°C

Fig. 8 Sample conditions for practical operation of CaO / PbO / CO₂ chemical heat pump

equilibrium conditions. Because the decarbonation has a higher reactivity in the neighborhood of the equilibrium condition in both cases (Figs. 4 and 5), than does the carbonation, the equilibrium values of the decarbonation reaction are employed as measures of the condition. This figure shows that the heat storage mode of the heat pump of Fig. 1 (a) proceeds under the following conditions: pressure (P_{d1}) of 0.4 atm, decarbonation temperature of CaCO₃ (T_{d1}) of 824°C and carbonation temperature of PbO (T_{c2}) of 300°C. A higher decarbonation temperature is required to increase the reaction rate for practical application. Since decarbonation of CaCO₃ at 855°C under 0.42 atm (a black rhombus in Fig. 8) was confirmed in the experiment, this temperature can be employed as a candidate for the practical temperature of decarbonation. The heat output mode proceeds at a carbonation temperature of CaO (T_{c1}) of 870°C under 1.0 atm by the decarbonation of PbCO₃ at temperature (T_{d2}) of 438°C. This figure suggests that heat transformation-type operation of the

Fig. 9 Relationship between carbonation temperature of CaO and mean heat output (W_m) and heat output amount (Q)

heat pump is possible under a thermal driving condition with no mechanical work. These temperatures represent only a sampling of possible temperature ranges. If the reaction pressure of the reactor is not restricted, higher temperature output by CaO carbonation (T_{c1}) can be realized by raising the CaO carbonation pressure (P_{d2}), which is achieved by raising the temperature of PbCO₃ decarbonation (T_{d2}).

4. Numerical Discussion

To estimate the feasibility of the heat pump, heat output performance and the reactant amount ratio of the CaO and PbO reactors are calculated using the experimental results.

4.1. Heat output performance

High-temperature output (T_{c1}) can be obtained from the carbonation of CaO in the heat pump operation. The heat output amount (Q [kJ/kg-CaCO₃]) and the mean heat output (W_m [W/kg-CaCO₃]) were calculated from results of the carbonation of CaO. Q and W_m are defined as follows:

$$Q = \frac{x_1 \Delta H_1^\circ}{M_{\text{CaCO}_3}} \quad (3)$$

$$W_m = Q / t_{c1} \quad (4)$$

where x_1 represents a reacted fraction at a carbonation time of CaO (t_{c1}). These values are based on the initial charged CaCO₃ of 1 kg. Figure 9 shows the calculated results under the assumption of a carbonation pressure of 1.0 atm, decarbonation of PbCO₃ occurring at 300°C and 0.4 atm, and decarbonation of CaCO₃ occurring at above 824°C and 0.4 atm. At 870°C, the W_m and Q at 30 min were 670 W/kg-CaCO₃ and 1200 kJ/kg-CaCO₃, respectively.

4.2. Reaction amount ratio

When the values of Figs. 6 and 7 are compared, the reaction rate and reaction amount of PbO are clearly lower

Fig. 10 Relationship between reaction amount ratio (r) and carbonation time of PbO (t_{c2}), (a) Effect of reaction operation time of CaO carbonation (t_{c1}), (b) Effect of reaction pressure of PbO carbonation (P_{c2})

than those of CaO. Thus, the low reactivity of the PbO carbonation process is believed to be the rate limiting step of the operation. Next, the effect of the difference in reaction on the heat pump operation was studied. The reaction amount ratio r [-] ($=[\text{mol\%/mol\%}]$) was defined as the ratio of the carbonation mole amount of PbO (x_2 [mol%]) to that of CaO (x_1 [mol%]) as calculated by the following equation:

$$r = X_1 / x_2 \quad (5)$$

where r represents the required amount of PbO to complete the reaction of CaO / CO₂. **Figure 10 (a)** shows the effect of CaO carbonation time on r under CaO carbonation conditions of 870°C and 1.0 atm, and PbO carbonation conditions of 300°C and 0.4 atm. The abscissa shows the carbonation time of PbO, t_{c2} . When the carbonation time of CaO was 30 min, r at $t_{c2}=30$ min was 7.2. This suggests that 7.2 times more PbO than CaO was needed in order to complete the PbO carbonation operation in the same time. Thus, even if the carbonation of PbO was allowed to continue for 120 min, 4.0 times the amount of PbO would be required. Figure 10 (b) shows

the effect of the carbonation pressure of PbO on r . As the PbO carbonation pressure increases, the r value becomes smaller. Such a change would allow the reaction amount of PbO to approach that of CaO, and thus facilitate a more compact heat pump system. However, increasing the PbO carbonation pressure (P_{c2} in Fig. 1) entails an increase in the CaCO₃ decarbonation pressure and temperature (Fig. 8), and thus would require a higher temperature heat source (at T_{d1}). Ultimately, the temperature difference between T_{d1} and T_{c1} in Fig. 1 decreases, reducing its applicability as a heat transformer-type heat pump. Therefore, the balance between reaction amount and reaction pressure of PbO must be considered in the design of a practical heat pump.

Due to the limitations which originate in the pressure limit of the thermobalance, higher temperature operation of the heat pump was not investigated in the present study. However, higher temperature output of the heat pump may be possible by raising the pressure of PbCO₃ decarbonation and CaO carbonation. From extrapolation of the equilibrium relationship in Fig. 8 with a consideration of melting points of these reaction materials, heat outputs above 1000°C would be expected. Such a system would allow a wider high-temperature heat region of high-temperature processes to be utilized.

Conclusion

The feasibility of a CaO / PbO / CO₂ chemical heat pump was discussed experimentally. The following results were obtained:

1. A thermally-driven and heat-transformation-type heat pump was proposed and the practical use of the heat pump was demonstrated experimentally.
2. The PbO / CO₂ reaction equilibrium for the heat pump operation corresponded to the highest equilibrium step proposed by Peretti.
3. Using the heat pump, a heat source at a temperature above 824°C can be stored by the decarbonation of CaCO₃. Furthermore, heat output of approximately 870°C was obtained by the carbonation of CaO under a reaction pressure of up to 1 atm. Simultaneously, heat output of 300°C by the carbonation of PbO was obtained. The mean heat output and heat output amount by the carbonation of CaO were 670 W/kg-CaCO₃ and 1200 kJ/kg-CaCO₃, respectively, at 870°C, 1 atm for 30 min.
4. The difference in the reactivity between carbonation of CaO and that of PbO should be considered in the design of a practical heat pump.

Nomenclature

M_{CaCO_3}	= molecular weight of CaCO ₃	[kg/mol]
P	= reaction pressure	[atm]
Q	= heat output amount	[J/kg-CaCO ₃]
r	= reaction amount ratio	[-] ($=[\text{mol\%/mol\%}]$)
T	= temperature	[°C]
t	= carbonation time	[min]
W_m	= mean heat output	[W/kg-CaCO ₃]

X	= fixed reacted fraction	[mol%]
x	= reacted fraction	[mol%]
ΔH°	= standard reaction enthalpy	[J/mol]

< Subscript >

1	= CaO / CO ₂ reaction system
2	= PbO / CO ₂ reaction system
CO ₂	= carbon dioxide
c1	= carbonation of CaO
c2	= carbonation of PbO
d1	= decarbonation of CaCO ₃
d2	= decarbonation of PbCO ₃

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