

APPLICABILITY OF CARBONATION/DECARBONATION REACTIONS TO HIGH-TEMPERATURE THERMAL ENERGY STORAGE AND TEMPERATURE UPGRADING

KYAW KYAW, HITOKI MATSUDA AND
MASANOBU HASATANI

*Department of Energy Engineering & Science, Chemical
Engineering, Nagoya University, Chikusa-ku, Nagoya 464-01*

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Storing thermal energy by thermochemical means seems very attractive since large amounts of energy can be stored per unit mass, and such systems can function as a heat pumps. For storing high temperature heat energy such as concentrated solar energy at 773 K, various candidate chemical reactions have been evaluated in terms of energy storage density, turning temperature, toxicity, corrosiveness, and other factors. The dissociation reaction of CaCO_3 is found to be very promising. Three methods for storing the dissociation product CO_2 gas; (i) storing as a compressed gas, (ii) letting the CO_2 gas react with a metal oxide and storing it in the form of another carbonate, and (iii) adsorbing with an appropriate adsorbent and storing as an adsorbed gas; have been proposed and the respective thermal operating efficiencies at various upgraded temperatures are evaluated. The CaO-CO_2 -metal oxide system seems very effective for temperature upgrading around 1273 K and the CaO-CO_2 -compressor system seems suitable for storing and delivering heat energy at the same temperature. Whether the efficiency of the CaO-CO_2 -Adsorbent system is comparable to one of the other two systems or not greatly depends upon the adsorptivity of the adsorbent.

Introduction

In general, energy from fossil fuels and nuclear fuels is extracted as thermal energy in the form of high pressure steam or hot gases, and is converted to electricity in power plants and industrial plants with around 30-40% overall efficiency. Due to uneven demand, power plants which are structured to meet peak demand usually operate at loads lower than the optimum design conditions, which brings about a decrease in the overall operating efficiency. In order to conserve fossil fuel resources and other energy resources, as well as to reduce environmental pollution caused by increases in CO_2 emissions, efficient energy use is required. One possibility is to level the load so that power plants can operate at their design capacity with optimum operating efficiency. The other possibility is to upgrade thermal energy at a certain temperature, for example from solar energy to a more valuable thermal energy of much higher temperature which can be used in industrial processing, or even in power generation.

It is, however, quite difficult to store electrical energy on a large scale. Instead, storing of thermal energy seems much more practical and it is now being investigated for load-leveling, such as night-term heat storage in the form of ice for day-time air-conditioning. Thermal energy storage techniques differ widely according to the objective and temperature range. Relatively low and midium temper-

ature range thermal energy storage has been extensively studied, and some examples are now in practical use. On the other hand, studies on storage of high-temperature heat, for example from solar energy and nuclear power plants are rather scant, because of the difficulty in storing such high temperature heat, of around 773-1273 K (Ervin, 1977, Garg *et al.*, 1985, Wenworth and Chen, 1976). These temperatures are indicative of the required operating efficiency for electric power generation and high temperature industrial process heat applications. Also, extracting thermal energy at around 973-1073 K from a nuclear reactor to use it directly as industrial process heat has recently been proposed. Such a high-temperature level heat storage will bring about a wider variation of the thermal energy utilization.

In general, thermal energy storage can be carried out by: i) sensible heat storage, ii) latent heat storage and iii) thermochemical storage. Among these methods, thermochemical storage seems appropriate for high temperature range heat. It is well known that the higher the temperature, the more difficult the heat storage without proper insulation. In chemical energy storage, almost all the energy absorbed (endothermic reaction) is used for breaking and rearranging the chemical bonds, and is stored as the potential for reverting back into bonds of initial state. This chemical potential energy will be released as heat energy during the reverse exothermic reaction. Thus, chemical energy storage needs a minimum of thermal insulation.

* Received on August 1, 1995. Correspondence concerning this article should be addressed to M. Hasatani.

Table 1 ΔH° and T^* of some thermochemical energy storage systems

No.	System	ΔH° [kJ/mol]	T^* [K]
1 Ammonia + Ammonium salts system			
	$2 \text{NH}_3 (\text{g}) \rightleftharpoons \text{N}_2 (\text{g}) + 3 \text{H}_2 (\text{g})$	59	468
	$\text{NH}_4\text{HSO}_4 (\text{l}) \rightleftharpoons \text{H}_2\text{O} (\text{g}) + \text{NH}_3 (\text{g}) + \text{SO}_3 (\text{g})$	335	740
2 Carbonate system			
	$\text{ZnCO}_3 (\text{s}) \rightleftharpoons \text{ZnO} (\text{s}) + \text{CO}_2 (\text{g})$	67	406
	$\text{MgCO}_3 (\text{s}) \rightleftharpoons \text{MgO} (\text{s}) + \text{CO}_2 (\text{g})$	125	670
	$\text{CaCO}_3 (\text{s}) \rightleftharpoons \text{CaO} (\text{s}) + \text{CO}_2 (\text{g})$	176	1110
	$\text{SrCO}_3 (\text{s}) \rightleftharpoons \text{SrO} (\text{s}) + \text{CO}_2 (\text{g})$	234	1381
3 Fluoride system			
	$\text{KBF}_4 (\text{s}) \rightleftharpoons \text{KF} (\text{s}) + \text{BF}_3 (\text{g})$	109	978
	$2\text{NF}_3 (\text{s}) \rightleftharpoons \text{N}_2 (\text{g}) + 3 \text{F}_2 (\text{g})$	130	945
4 Hydride system			
	$\text{LiH} (\text{s}) \rightleftharpoons \text{Li} (\text{s}) + 1/2 \text{H}_2 (\text{g})$	88	1220
	$\text{NaH} (\text{s}) \rightleftharpoons \text{Na} (\text{s}) + 1/2 \text{H}_2 (\text{g})$	88	735
5 Hydroxide system			
	$\text{Mg}(\text{OH})_2 (\text{s}) \rightleftharpoons \text{MgO} (\text{s}) + \text{H}_2\text{O} (\text{g})$	84	531
	$\text{Ca}(\text{OH})_2 (\text{s}) \rightleftharpoons \text{CaO} (\text{s}) + \text{H}_2\text{O} (\text{g})$	109	752
	$\text{Sr}(\text{OH})_2 (\text{s}) \rightleftharpoons \text{SrO} (\text{s}) + \text{H}_2\text{O} (\text{g})$	126	852
	$\text{LiOH} (\text{l}) \rightleftharpoons 1/2 \text{Li}_2\text{O} (\text{s}) + \text{H}_2\text{O} (\text{g})$	59	1004
6 NO₂ system			
	$\text{Ca}(\text{NO}_3)_2 (\text{s}) \rightleftharpoons \text{CaO} (\text{s}) + 2\text{NO}_2 (\text{g}) + 1/2 \text{O}_2$	109	740
	$\text{LiNO}_2 (\text{s}) + \text{LiNO}_3 (\text{s}) \rightleftharpoons 2 \text{LiO} (\text{s}) + 2 \text{NO}_2 (\text{g})$	109	1089
7 Oxide, peroxide systems			
	$\text{BaO}_2 (\text{s}) \rightleftharpoons 2 \text{BaO} (\text{s}) + 1/2 \text{O}_2 (\text{g})$	75	1029
8 Sulfate system			
	$\text{MgSO}_4 (\text{s}) \rightleftharpoons \text{MgO} (\text{s}) + \text{SO}_3 (\text{g})$	280	1470
	$\text{CaSO}_4 (\text{s}) \rightleftharpoons \text{CaO} (\text{s}) + \text{SO}_3 (\text{g})$	402	2145
9 SO₃ system			
	$\text{SO}_3 (\text{g}) \rightleftharpoons \text{SO}_2 (\text{g}) + 1/2 \text{O}_2 (\text{g})$	109	1055
10 Organic systems			
	$\text{C}_2\text{H}_6 (\text{g}) \rightleftharpoons \text{C}_2\text{H}_4 (\text{g}) + \text{H}_2 (\text{g})$	138	1136
	$\text{C}_6\text{H}_{12} (\text{g}) \rightleftharpoons \text{C}_6\text{H}_6 (\text{g}) + 3 \text{H}_2 (\text{g})$	205	568
	$\text{CH}_4 (\text{g}) + \text{H}_2\text{O} (\text{g}) \rightleftharpoons \text{CO} (\text{g}) + 3 \text{H}_2 (\text{g})$	205	961
	$\text{CH}_4 (\text{g}) + \text{CO}_2 (\text{g}) \rightleftharpoons 2 \text{CO} (\text{g}) + 2 \text{H}_2 (\text{g})$	247	959

However, the rate of reaction, together with the degree of conversion, and the stability of the reactant materials under repeated energy absorbing releasing cycles will strongly influence the practical applicability of the reaction for a thermal energy storage system. In this paper, we will evaluate various reaction candidates from a thermodynamic view point.

In this paper, we investigate chemical energy storage in a relatively high temperature range 773-1273 K by considering several candidate reaction systems. Among them, dissociation of CaCO_3 seems very promising because (i) the energy storage density is very high-about $3.26 \text{ GJ}\cdot\text{m}^{-3}$, (ii) CaCO_3 dissociates at 1110 K under 101 kPa of CO_2 pressure, (iii) the reaction products are free from toxicity and corrosiveness, (iv) the $\text{CaO}-\text{CO}_2$ reversible reaction has no side reaction and (v) the CaCO_3 raw material is abundantly available.

The CO_2 gas produced from the dissociation of CaCO_3 has to be stored (i) as compressed gas, (ii) in the form of a chemical substance as other metal carbonates or (iii) as adsorbed CO_2 in appropriate adsorbents. In this work, we propose three thermal energy storage systems

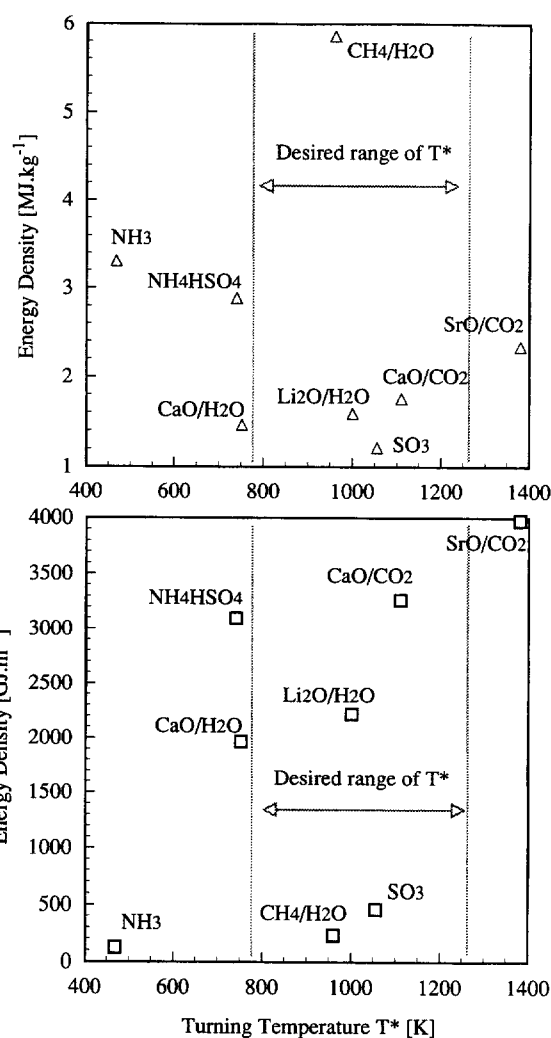


Fig. 1 Energy Density and related turning temperature of various thermochemical energy storage systems

based on the CaO/CO_2 reaction for heat upgrading with different CO_2 storage methods. The corresponding COP (Coefficient Of Performance) and the upgraded temperatures are also evaluated.

1. Evaluation of Reaction Candidates for Storing Thermal Energy at High Temperature Range Around 773-1273 K

Table 1 lists some of the typical reaction candidates which can be considered for storing thermal energy in the high temperature range above $\sim 773 \text{ K}$ and their respective heat of reaction and turning temperatures T^* (For a reversible reaction of the type $aA \rightleftharpoons bB + cC$ the turning temperature T^* is defined as the temperature at which the reaction rate constant K is equal to 1, and is approximated as $T^* = \Delta H^\circ / \Delta S^\circ$. As $K < 1$ when $T > T^*$ and $K > 1$ for $T < T^*$, turning temperature T^* can serve as a guide for judging whether a reaction will react in favor of forming products at a certain temperature) (Garg *et al.*, 1985, Wenworth and Chen, 1976, Williams and Carden, 1979). The details of the reactions and their related works are cited

for more information.

By plotting the energy storage density and the turning temperature T^* (Garg *et al.*, 1985, Wenworth and Chen, 1976, Williams and Carden, 1979) of these reaction systems as in Fig. 1, we can see that the storage capacity $\Delta H^0/V$ of the CaO/CO₂ system is high (3.26 GJ.m⁻³) with the T^* falling conveniently in the middle of the desired range 773-1273 K (Ervin 1977, Garg *et al.*, 1985, Wenworth and Chen, 1976). However, with the exception of hydroxide and ammonium hydrogen sulfate systems, the other systems generate gases such as N₂, O₂, and H₂, which cannot be condensed at room temperature. Consequently, the molar volume of the products is large and the storage capacity $\Delta H^0/V$ of the related system is small.

For the decomposition of ammonium hydrogen sulfate system (Garg *et al.*, 1985, Prengle *et al.* 1976, Prengle *et al.* 1980, Wenworth and Chen, 1976), the turning temperature T^* of 740 K is only slightly below the desired range 773-1273 K and the storage capacity $\Delta H^0/V$ of 3.09 GJ.m⁻³ is also high since all the products (H₂O, SO₃ and NH₃) can be stored as liquid. However, efficient separation as well as great care is needed to separate and store the gaseous products SO₃ and NH₃, which are very toxic and corrosive.

A hydroxide system (Beruto *et al.*, 1980, Braton and Brindley, 1981, Criado *et al.* 1992, Ervin, 1977, Fujii *et al.*, 1985, Garg *et al.*, 1985, Halstead and Moore, 1957, Kanazawa and Arai, 1981, Kato *et al.*, 1993, Matsuda *et al.*, 1985, Murthy *et al.*, 1986, Ogura *et al.*, 1991, Ogura *et al.*, 1992, Ogura *et al.*, 1993, Razouk *et al.*, 1981a, Razouk *et al.*, 1981b, Samms and Evans, 1969, Wenworth and Chen, 1976), such as decomposition of Ca(OH)₂, Sr(OH)₂, Ba(OH)₂ or LiOH, produces steam which is not toxic and not corrosive. The energy storage capacity $\Delta H^0/V$ is reasonably good for these compounds, being in the order of 2.09-2.51 GJ.m⁻³. Based only on the criterion for T^* , the hydroxide system seems suitable for high temperature thermal energy storage. However, it is subjected to high temperatures above 873 K where the steam pressures is excessively high.

The dissociation of the CaCO₃ system (Barker, 1973, Barker 1974, Beruto *et al.*, 1980, Criado *et al.* 1992, Ervin, 1977, Dedman and Owen, 1962, Ervin, 1977, Flament *et al.*, 1986, Garg *et al.*, 1985, Haul and Markus, 1952, Salman and Khraishi, 1986, Wenworth and Chen, 1976) has, in addition to having high energy storage density;

- T^* of 1110 K and;
- the product gas CO₂, which is free from toxicity and corrosiveness, other attractive features such as;
- the CaO-CO₂ reversible reaction which is free from side reactions and -the raw material CaCO₃, which is abundantly available.

Since CO₂ is rather difficult to liquefy, two alternate methods for storing the product CO₂ are considered, namely;

- (1) by reacting the product CO₂ gas with other metal oxides and storing in the form of metal carbonates, or
- (2) by adsorbing the product CO₂ gas with an appropriate

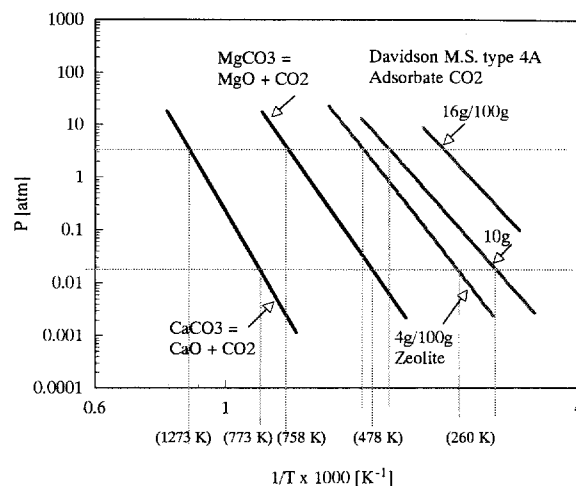


Fig. 2 Equilibrium dissociation pressures and temperatures of CaCO₃, MgCO₃, and of adsorption isosteres of zeolite-CO₂

adsorbent and storing as an adsorbed CO₂.

2. Principle of Chemical Energy Storage by CaO/CO₂ Reaction System

Energy is absorbed during the dissociation of the CaCO₃ and is released again when the dissociation products CaO and CO₂ are mixed and let to react and formed back into CaCO₃. If the pressure of CO₂ during the carbonation process is higher than the pressure of CO₂ during the decomposition process, then the carbonation reaction will occur at temperatures higher than the temperature where dissociation had occurred. In this temperature upgrading mode (Raldow and Wenworth, 1979), the low level temperature heat can be transformed to heat with a temperature higher than 1273 K by adjusting the CO₂ pressure around 1100 kPa [see Fig. 2]. On the contrary, if CaCO₃ is exposed to the condition where CO₂ pressure is lower than that at the equilibrium state, the CaO is regenerated by this energy storing mode.

Since the mode of the CaO-CO₂ thermal energy storage system is governed by the CO₂ pressure of the carbonation process in relation to that of the CO₂ pressure of the decomposition process, the means of storing the produced CO₂ gas and of pressurizing the stored CO₂ gas for the subsequent carbonation reaction are necessary. Storage of the produced CO₂ gas can be generally carried out as:-

- (1) by compressing the CO₂ gas and storing it as a compressed CO₂ gas: a CaO-CO₂-compressor system;
- (2) by letting the CO₂ gas react with other metal oxides and storing it in the form of a metal carbonate: a CaO-CO₂-metal oxide system or
- (3) by absorbing the CO₂ gas with an appropriate adsorbent and storing it in the form of adsorbed CO₂: a CaO-CO₂-adsorbent system.

For comparing the above three storage methods, we will investigate the COP and the upgraded temperatures of each CaO-CO₂ energy storage system.

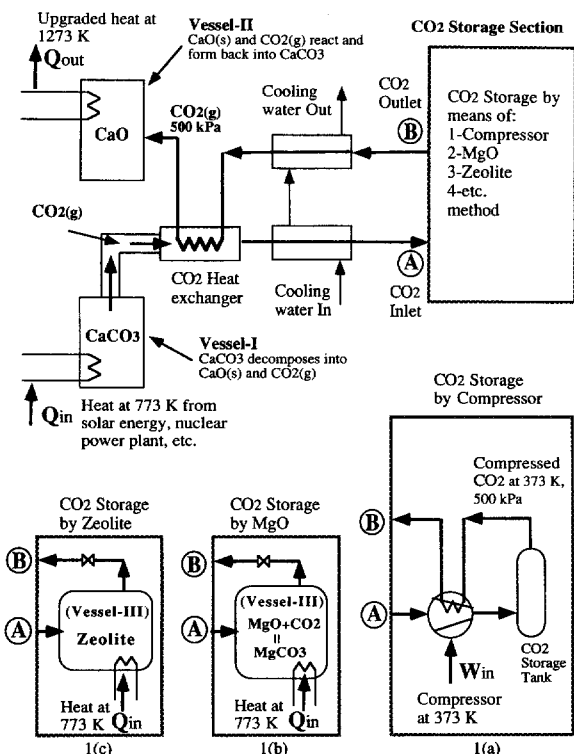


Fig. 3(a) Conceptual flow diagrams of CaO-CO₂ energy storage system in a heat upgrading mode. Some CO₂ storage methods are shown in boxes

2.1 Case study of CaO-CO₂ Energy Storage systems in heat upgrading mode

2.1.1 CaO-CO₂-Compressor system

Figure 3 (a) shows a conceptual flow diagram of a CaO-CO₂-compressor energy storage system for upgrading thermal energy at 773 K. CaCO₃ in Vessel-I absorbs heat energy at 773 K and decomposes into CaO and CO₂ gas. After passing through the heat exchanger and water cooler, the product CO₂ gas at 0.01 kPa pressure and 373 K is isothermally compressed to a pressure P_H, and is stored in a CO₂ storage tank. The stored CO₂ gas is heated by passing through the CO₂ heat exchanger and sent to carbonate the CaO present in Vessel-II. Due to formation of CaCO₃, thermal energy will be released, which will in turn elevate the temperature of Vessel-II to temperature T_H. In the next cycle, Vessel-II containing CaCO₃ can be used as a heat absorber and Vessel-I containing CaO can be used as a heat generator. Figure 3 (b) shows the corresponding schematic operation diagram of the CaO-CO₂-compressor energy storage system in a heat upgrading mode. From this figure, it is obvious that the CaO-CO₂ reaction in Vessel-II will occur at temperature 1213 K if the pressure P_H of CO₂ from storage is 500 kPa.

For an energy storage system in the heat upgrading mode, the COP or the thermal efficiency is defined as (Garg *et al.*, 1985, Raldow and Wenworth, 1979):

$$COP = \frac{\text{Heat available at upgraded temperature}}{\text{Heat supplied for regeneration}} \quad (1)$$

where,

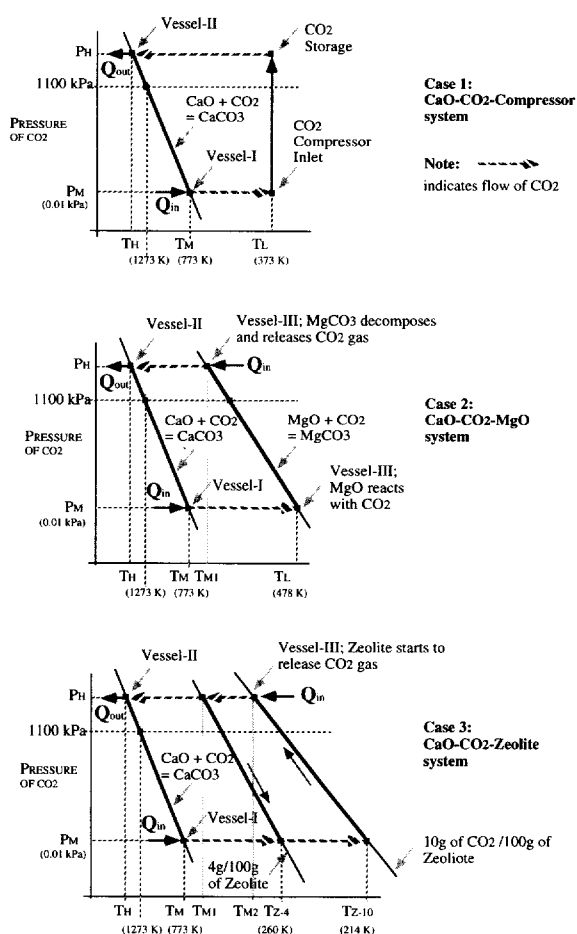


Fig. 3(b) Schematic diagrams of CaO-CO₂ energy storage systems with three different CO₂ gas storage methods

- (a) Heat available at upgraded temperature is equal to
 - heat of formation of CaCO₃ at the upgraded temperature T_H
 - minus heat for heating the reactants CaO and CO₂ from 773 K to the reaction temperature T_H
- (b) Heat supplied to the system for regeneration is
 - heat for decomposing the CaCO₃ at 773 K and
 - heat for heating the CO₂ gas from storage to temperature 773 K.

Since the system employs a mechanical compressor for compressing the CO₂ gas in the regeneration process, 'energy' instead of 'heat' supplied for regeneration is considered in evaluating the COP of this system. Thus,

$$COP = \frac{\text{Heat available at upgraded temperature}}{\text{Energy supplied for regeneration}} \quad (2)$$

Equation 2 is used for calculating the COP of the CaO-CO₂-compressor system for upgrading heat energy at 773 K to various temperatures. It is assumed that there is no heat exchange between the produced CO₂ gas and the stored CO₂ gas. The heat of formation and heat capacity data are taken from Perry (Perry and Green, 1984). It can be seen from Fig. 4 that the thermal efficiency of the system is highest when it is used only for storing and delivering thermal energy at the same temperature and the efficiency of

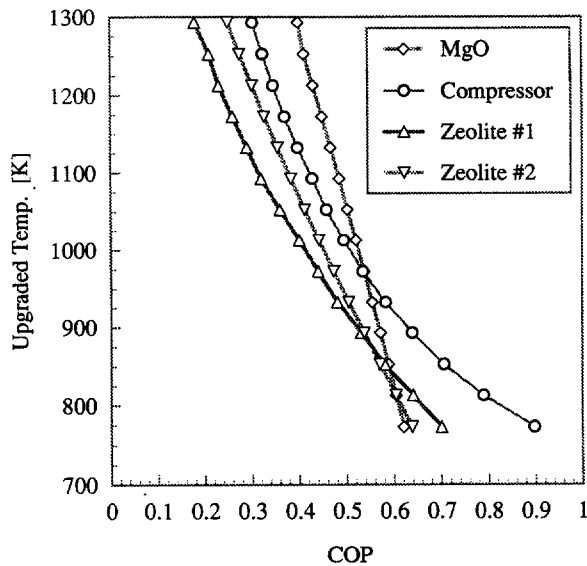
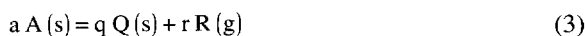


Fig. 4 COP vs. upgraded temperature of CaO-CO₂ energy storage systems with various CO₂ storage systems. Note: In Zeolite #1 system, it is assumed that adsorption of CO₂ by zeolite occurs within (4g/100g) to (10g of CO₂/100g of zeolite) whereas in Zeolite #2 it is within (4g/100g) to (16g of CO₂/100g of zeolite)

the system falls gradually with the increase in upgraded temperature (COP is 0.9 for storing and delivering the thermal energy at 773 K and is 0.30 if the thermal energy at 773 K is upgraded to 1273 K).

2.1.2 CaO-CO₂-MgO system

The flow concept of a CaO-CO₂-metal oxide system is almost the same as the CaO-CO₂-compressor system which is shown in Fig. 3 (a). The only difference is that there is a metal oxide vessel (Vessel-III) in the CO₂ storage section instead of a compressor and gas storage tank. The CO₂ gas at P_M , which is produced from the dissociation of CaCO₃, is sent from Vessel-I through the heat exchanger and water cooler to Vessel-III. There, it is mixed and reacted with a metal oxide at T_L and formed into a metal carbonate. Vessel-III is sealed off and heated to T_{M1} where the formed metal carbonate decomposes. The CO₂ gas released at P_H from Vessel-III is then heated to T_M by exchanging heat with the product CO₂ gas before it is sent to Vessel-II to react with CaO. In this system, the metal carbonate should have an equilibrium dissociation temperature lower than that of CaCO₃ when the two carbonates are heated under the same CO₂ pressure. The dissociation of carbonates is of the form



where A is a metal carbonate MCO₃, Q is the metal oxide MO and R is the CO₂ gas. With CO₂ being the only gaseous product, the equilibrium constant K_p becomes

$$K_p = P_{CO_2} \quad (4)$$

For a reaction, the Helmholtz free energy change ΔG_T can be written as

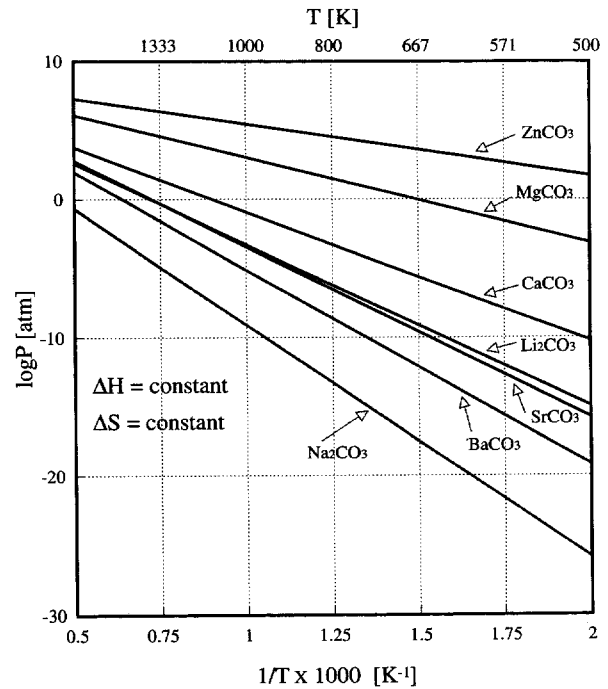


Fig. 5 Equilibrium dissociation pressures and temperatures of some carbonate materials

$$\Delta G_T = \Delta G_T^{\circ} + RT \ln K_p \quad (5)$$

where ΔG_T is the free energy change at reaction temperature T , and ΔG_T° is the free energy change for the reaction when all the reactants are at the standard state.

At an equilibrium state, $\Delta G_T \sim 0$. Then Eq. (5) becomes

$$\Delta G_T^{\circ} = -RT \ln P_{CO_2}^* \quad (6)$$

According to the Gibbs-Helmholtz relation

$$\left[\frac{\partial}{\partial T} \left(\frac{\Delta G_T^{\circ}}{T} \right) \right]_p = - \frac{\Delta H^{\circ}}{T^2} \quad (7)$$

Substituting Eq. (6) into Eq. (7),

$$\frac{d \ln P_{CO_2}^*}{dT} = - \frac{\Delta H^{\circ}}{RT^2} \quad (8)$$

$$\frac{d \ln P_{CO_2}^*}{d\left(\frac{1}{T}\right)} = - \frac{\Delta H^{\circ}}{R} \quad (9)$$

If ΔH° is constant for all the temperature values, then the equilibrium constant K_p or the equilibrium dissociation pressure $P_{CO_2}^*$ will form a direct relationship with the temperature as

$$\ln P_{CO_2}^* = - \frac{\Delta H^{\circ}}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^{\circ}}{R} \quad (10)$$

Accordingly, equilibrium dissociation pressure and temperature of the carbonates can be approximated as in Fig. 5. By using this figure, one can discern the carbonate materials with decomposition temperatures lower than that of CaCO₃ if the carbonates are heated to decompose under the same CO₂ pressure. Respective metal oxides of these

carbonate materials can be used in conjunction with the CaCO_3 in the CaO-CO_2 energy storage system. It is worth mentioning here that when solar collectors can concentrate the solar energy at temperatures above 1273 K, the energy storage system with carbonates will consist of the following carbonate pairs: $\text{BaCO}_3\text{-CaCO}_3$, $\text{SrCO}_3\text{-CaCO}_3$ or $\text{Li}_2\text{CO}_3\text{-CaCO}_3$. The carbonates which have very high dissociation temperatures, such as BaCO_3 , SrCO_3 and Li_2CO_3 , are used for heat absorption and CaCO_3 will be used in the CO_2 storing operation. However, to store thermal energy at temperatures around 773 K, CaCO_3 is used for heat absorption and the carbonates which have low dissociation temperatures, such as MgCO_3 and ZnCO_3 , will be used in the CO_2 storing operation. As MgCO_3 is abundantly available and is not poisonous, MgO is selected for CO_2 storage in the CaO-CO_2 energy storage system.

A schematic operation diagram of a CaO-CO_2 energy storage system combined with MgO for upgrading thermal energy at 773 K is shown in Fig. 3 (b). Dissociation of CaCO_3 occurs at 773 K and the product CO_2 gas at 0.01 kPa pressure is cooled and sent to react with MgO at 478 K to form MgCO_3 . As the heat releasing step, MgCO_3 is heated to T_{M1} so that it releases CO_2 during decomposition. The released CO_2 gas at pressure P_H is then heated to 773 K and sent back to react with CaO . Due to the heat of reaction, the temperature is elevated to T_H , which is in the equilibrium state for the loaded pressure P_H . Accordingly, when calculating COP with Eq. 1, the term heat needed for regeneration will involve:

- (1) heat for heating MgCO_3 from 478 K to T_{M1} and
- (2) heat of decomposition of MgCO_3 at T_{M1} , as well as
- (3) heat of decomposition of CaCO_3 at 773 K and
- (4) heat for heating of CO_2 gas from T_{M1} to 773 K before it is sent from storage to the reactor.

The thermal efficiency values are calculated and plotted in Fig. 4 for various upgraded temperatures. It can be seen that this $\text{CaO-CO}_2\text{-MgO}$ system performs well at higher upgraded temperatures; for instance, the COP is 0.4 compared to a COP of 0.30 for the $\text{CaO-CO}_2\text{-compressor}$ system if both systems are used to upgrade the heat energy at 773 K to the same temperature of 1273 K.

2.1.3 $\text{CaO-CO}_2\text{-Zeolite}$ system

CO_2 gas produced from the dissociation of CaCO_3 can be stored by means of adsorbing the CO_2 gas with an appropriate adsorbent and storing as adsorbed CO_2 . The flow concept is the same as the $\text{CaO-CO}_2\text{-metal oxide}$ energy storage system (see Fig. 3 (a)). The only difference is that Vessel-III is packed with adsorbents in a $\text{CaO-CO}_2\text{-adsorbent}$ system instead of a metal oxide. The product CO_2 at pressure P_M (0.01 kPa) from the decomposition of CaCO_3 at T_M (773 K) is cooled down and sent to Vessel-III where it is adsorbed by the adsorbent. Vessel-III is isolated and heated to desorb the CO_2 from zeolite. The desorbed CO_2 at P_H is heated to 773 K by heat exchanging with the product CO_2 before it is sent to Vessel-II to react with the CaO . A schematic operation diagram of a $\text{CaO-CO}_2\text{-zeolite}\#1$ system for upgrading heat energy at

773 K is shown in Fig. 3 (b). In this pressure/temperature diagram, the equilibrium dissociation line of CaCO_3 and some extrapolated adsorption isosteres of $\text{CO}_2/\text{Davison zeolite 4A}$ (Fuji Davison, 1995) are plotted. It is assumed that the adsorption of CO_2 by zeolite occurs within two adsorption isostere lines of (4g/100g) to (10g of $\text{CO}_2/100\text{g}$ of zeolite). Thus, CO_2 gas at 0.01 kPa produced from the dissociation of CaCO_3 at T_M (773 K) is cooled down and adsorbed by zeolite at T_{Z-4} (260 K). Adsorption will finish at T_{Z-10} (214 K), where 100g of zeolite has adsorbed 10g of CO_2 . Desorption of CO_2 will start when the temperature of the zeolite reaches T_{M2} and will finish at T_{M1} . The desorbed CO_2 at P_H is then heated and sent back to react with CaO at T_M (773 K).

Accordingly, 'heat needed for regeneration' in Eq. 1 for calculating COP is assumed to contain

- (1) heat for heating the zeolite from 214 K to T_{M2} ,
- (2) heat of desorption of CO_2 from zeolite at T_{M2} ,
- (3) heat for heating the desorbed CO_2 gas from T_{M2} to 773 K and
- (4) heat of decomposition of CaCO_3 at 773 K.

Heat capacity and heat of adsorption data for zeolite are taken from Shimizu (1993). It can be seen from the graph of COP values vs. upgraded temperatures, Fig. 4, that the thermal upgrading efficiency of the $\text{CaO-CO}_2\text{-zeolite}\#1$ system, in which the adsorption of CO_2 by the zeolite is carried out between the two isosteres of (4g/100g) and (10g $\text{CO}_2/100\text{g}$ zeolite), is a bit lower than the other two systems. However, if adsorption of CO_2 by the Davison zeolite 4A in a $\text{CaO-CO}_2\text{-zeolite}\#2$ system occurs between two isosteres of (4g/100g) and (16g $\text{CO}_2/100\text{g}$ zeolite), the thermal operating efficiency of this $\text{CaO-CO}_2\text{-zeolite}\#2$ system is much higher than the $\text{CaO-CO}_2\text{-zeolite}\#1$ system. It can be seen in Fig. 4, that the efficiency of the zeolite system ($\text{CaO-CO}_2\text{-zeolite}\#2$) becomes comparable to that of the $\text{CaO-CO}_2\text{-compressor}$ system when the upgraded temperature is higher than 1000 K. From the practical point of view, an adsorbent with higher adsorptivity is favored in order to obtain higher thermal efficiency from an energy storage system.

Conclusion

Reversible chemical reactions are investigated for storing high-temperature thermal energy and it has been found that the dissociation of CaCO_3 reaction seems very promising because

- it has a high energy storage density,
- it has a turning temperature of 1110 K,
- it has reactants that are free from toxicity and corrosiveness,
- it has the CaO-CO_2 reaction that involves no side reactions and
- it uses CaCO_3 as a raw material, which is abundantly available.

CaO-CO_2 energy storage systems with three different methods for storing the produced CO_2 gas are

investigated and the corresponding operating efficiency and upgraded temperature are evaluated. It has been found that the CaO-CO₂-MgO system is the best in transforming heat energy at 773 K to temperatures around 1273 K. On the other hand, the CaO-CO₂-compressor system is the most suitable for storing and delivering thermal energy at the same temperature. The efficiency of CaO-CO₂-zeolite systems is strongly governed by the adsorptivity of the zeolite. It can be seen that the efficiency of the zeolite system increases with the increase in adsorptivity and it is comparable to that of a CaO-CO₂-compressor system at some high adsorption values of zeolite.

However, the main attractive feature of the CaO-CO₂-metal oxide and CaO-CO₂-adsorbent systems is that no mechanical energy is needed for their operation. Related works concerning these two systems: such as the behavior of CaO-CO₂, MgO-CO₂ reactions and zeolite-CO₂ adsorption when undergoing repeated energy storing/releasing steps; reaction kinetics as well as adsorption isotherms at elevated temperatures and pressures are being studied.

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