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Energy analysis of CaCO₃ calcination with CO₂ capture

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Abstract

One method for reducing CO₂, the green house gas emissions is to capture CO₂ before it releases into the atmosphere and then sequester it. Active lime (main component, CaO) can be used to capture CO₂ in the exhaust gas or in the reactor from fossil fuels utilization effectively. That is calcium oxide (CaO) absorbs CO₂ to yield calcium carbonate (CaCO₃) (Eq. (1)), then the CaCO₃ is thermally decomposed to CaO again and release nearly pure CO₂ (Eq. (2)) for sequestration.

To obtain a nearly pure CO₂ stream from CaCO₃ decomposition, the heat for decomposing CaCO₃ can be supplied by combusting fossil fuels, such as coal and natural gas, in a calciner with oxygen fuel combustion. The oxygen diluted by CO₂ (CO₂ cycle) or H₂O (steam cycle), in order to obtain near pure CO₂ stream from CaCO₃ decomposition. In our previous studies⁴⁻⁶, it was clarified that calcinations of limestone (main component, CaCO₃) in a fluidized bed calciner can be performed in CO₂ cycle atmosphere when the bed temperature was raised above 1293 K, whereas with 60% steam cycle in atmosphere, limestone can be decomposed at comparatively lower temperature, such as 1173 K. The decomposition conversions of the limestone were about 95% and 98%, in CO₂ cycle and in steam cycle atmospheres, respectively. Reducing the calcinations temperature of limestone was helpful to produce more than 30% active CaO as shown in previous study⁴⁻⁶.

In this study, the energy of CaCO₃ calcination process by H₂O (steam) cycle was analyzed and compared with CaCO₃ calcination process by CO₂ cycle. For process calculations, the mass and energy flows were calculated iteratively, based on the input and output balances, until err [(input – output)/input] was < 0.01. Analysis showed that, although H₂O (steam) cycle calcination had calcination energy more about 3.6% than CO₂ cycle due to water evaporation latent heat loss, however, the calcination energy per active CaO was lowest for H₂O (steam) cycle.

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Keywords: CO₂ sorbent, Limestone calcinations, Reactivity, Energy, Chemical loop

1. Introduction

The reduction of anthropogenic CO₂ emission is becoming increasingly urgent because CO₂ contributes to global warming. One method for reducing CO₂ emission is to capture and sequester CO₂ before it is released into the atmosphere. Calcined lime (main component, CaO) can be used to capture CO₂ in the exhaust gas¹ or in the reactor^{2,3} during the utilization of fossil fuels. That is calcium oxide (CaO) absorbs CO₂ from fuel gas to yield

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calcium carbonate (CaCO₃)(Eq.(1)), and the CaCO₃ is then thermally decomposed to CaO, releasing nearly pure CO₂ for sequestration (Eq. (2)).

In fact, the heat for decomposing CaCO₃ can be supplied by combusting fossil fuels, such as coal and natural gas, in a calciner. To obtain a nearly pure CO₂ stream from CaCO₃ decomposition, CaCO₃ could be calcined by the oxygen fuel combustion with a CO₂/O₂ or with steam/CO₂/O₂ (Fig.1). Steam is added to the calcination atmosphere to reduce CO₂ partial pressure, and the reduction of CO₂ partial pressure can decrease the decomposition temperature of CaCO₃ (Fig.2). The equilibrium constant K_C of CaCO₃ decomposition in Figure 2 was calculated by using a thermodynamic calculation soft HSC 4.0.

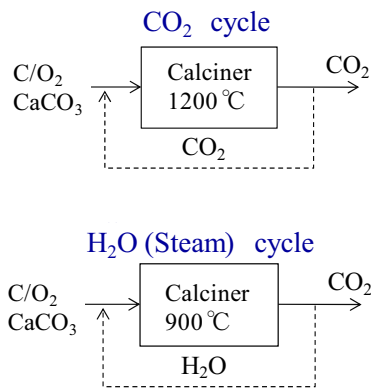
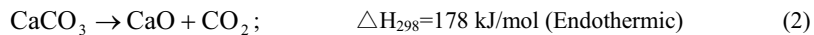
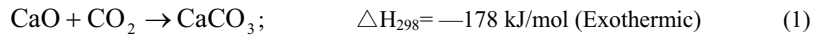


Figure 1 Concepts of CaCO₃ calcination by the H₂O (steam) cycle and CO₂ cycle oxygen fuel combustion.

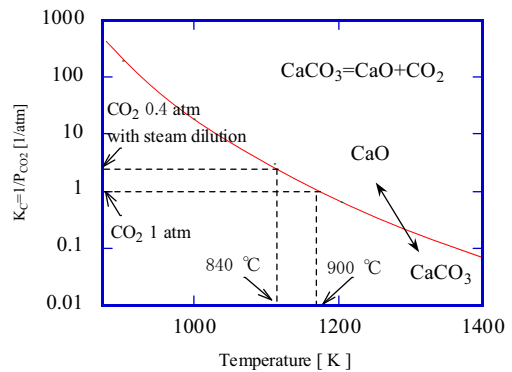


Figure 2 Reaction equilibrium constant for CaCO₃ decomposition.

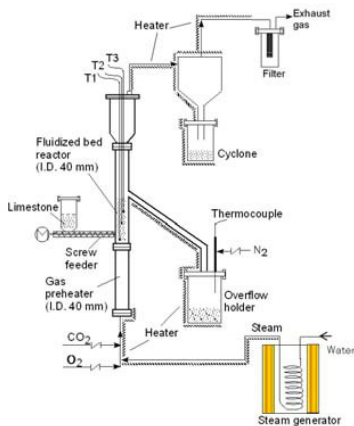


Figure 3 The continuously operating calciner apparatus for limestone calcinations by oxygen fuel combustion with H₂O (steam) and CO₂ cycle⁴⁻⁶.

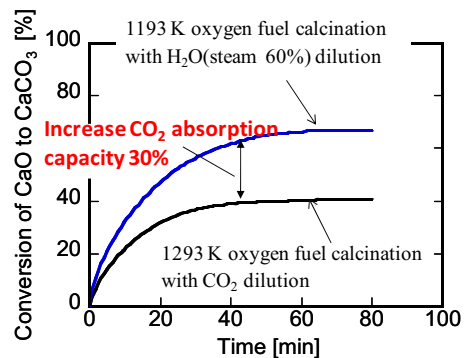


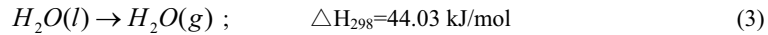
Figure 4 Comparison of CO₂ absorption capacity of CaO obtained by limestone calcination of coal oxygen fuel combustion with H₂O (steam 60%) cycle and CO₂ cycle.

In previous studies^{4,6}, we experimentally studied a limestone (main content is CaCO₃) calcinations with O₂ coal combustion in CO₂/O₂ and steam/O₂ atmospheres by used a fluidized bed calciner (Fig. 3). Table 1 shows limestone decomposition conversion obtained from previous study^{4,6}. Limestone can be near completely decomposed with the H₂O (steam) cycle at comparatively lower temperatures, such as 1173 K.

	1173 K	1193 K	1273 K	1373 K	1473 K
H ₂ O(steam 60%) cycle	98				
CO ₂ cycle		72	89	96	99 (simulated)

After the limestone calcination, we compared the carbonation reactivity of the CaO products with nearly the same decomposition conversions, 98% obtained with 60% H₂O (steam) cycle and 95% obtained with CO₂ cycle by means of TGA (Fig.4). For the carbonation test at 923 K and a CO₂ partial pressure of 0.04 MPa, close to 70% carbonation conversion (CaO→CaCO₃) was obtained with the CaO produced by H₂O (steam) cycle, whereas the conversion was about 40% for the CaO produced by CO₂ cycle, which indicates that the active CaO was greatly improved by limestone calcinations with H₂O (steam) cycle. These results can be explained in terms of the decreased calcination temperature (due to the fact the steam cycle lowered the CO₂ partial pressure) and the shortening of the average residence time of the particles in the fluidized bed, which effectively prevented the sintering of particles. Prevention of sintering enhanced the active CaO produced by increasing the specific surface area and pore volume.

However, there is anxious about that the latent heat loss of water evaporation (Eq.(3)) by H₂O (steam) cycle will increase too much calcinations energy consumption.



Accordingly, in this study, we used thermodynamic calculations to analyze the material and energy balances in the limestone calcinations process by H₂O (steam) cycle and CO₂ cycle in which CO₂ capture is premised. Calcination energies per active CaO which produced by H₂O(steam) cycle calcination was examined and compared with that by CO₂ cycle.

2. Calculation methods

2.1. Thermodynamic calculation

The calculation program and thermodynamic data from HSC Chemistry 4.0 software were used.⁷ In the calculation, the enthalpy of substances is given as

$$H(T) = H_f(298) + \int_{298}^T C_p dT + \sum H_{tr} \quad (4)$$

where $H_f(298)$ is the enthalpy of formation at 298 K, C_p is the heat capacity at constant pressure, T is temperature, and H_{tr} is the enthalpy of phase transformation of the substance. The temperature dependence of the heat capacity in the calculation is used by fitting the experimental heat capacities.

$$C_p = A + 10^{-3} B \cdot T + 10^5 C \cdot T^{-2} + 10^{-6} D \cdot T^2 \quad (5)$$

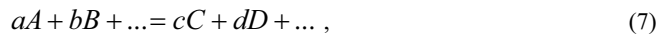
where A, B, C and D are coefficients estimated from experimental data.

Entropy values can be calculated from the heat capacity by using eq. (9) and numerical integration.

$$S = S^0(298) + \int_{298}^T (C_p / T) dT + \sum H_{tr} / T_{tr} \quad (6)$$

where $S^0(298)$ is the standard entropy of the substance, which can be calculated by integrating the C_p/T function from 0 to 298 K, and T_{tr} is the temperature of phase transformation.

The Gibbs energy G is defined by as $G \equiv H - T \cdot S$. The Gibbs energy change, ΔGr , for a chemical reaction,



is calculated as the difference in the Gibbs energy between the products and the reactants:

$$\Delta G_r \equiv \sum v_i G_i(\text{products}) - \sum v_i G_i(\text{Reactants}) \tag{8}$$

$$= (c \cdot G_C + d \cdot G_D + \dots) - (a \cdot G_A + b \cdot G_B + \dots)$$

where a is the stoichiometric coefficient of a species G_A in reaction and so on; and v is the stoichiometric coefficient of a species in the reaction. The equilibrium products for the reactants can be obtained by minimizing the Gibbs energy of the system under a desired set of conditions (temperature and pressure).

2.2. Mass and energy flow calculation

Given the input mass flow and the operating conditions (temperature and pressure), for a reactor, the output mass flow is obtained by calculating the equilibrium composition. Then the heat contained in the output mass flow is calculated. For process calculations, the mass and energy flows were calculated iteratively, based on the input and output balances, until $\text{err} = (\text{input} - \text{output})/\text{input}$ was < 0.001 .

2.3. CaCO₃ Calcination process components

The main components of the limestone calcinations process are one calciner and two heat exchangers for exhaust gas (heat exchanger (a)) and exhaust solid (heat exchanger (b)). Calciner is a reactor for coal combustion and for CaCO₃ decomposition, which produce CO₂ gas and lime (CaO) solid. Heat exchangers (a) and (b) are used for sensible heat recovery of exhaust gases and solid from calciner.

The operating temperature of calciner is 1173 K for H₂O (steam) cycle and 1173 K to 1473 K for CO₂ cycle, as determined from experimental results.⁴⁻⁶

3. Results and discussion

Figure 5 shows the results of energy and material balances for CaCO₃ calcination with H₂O (steam 60%, O₂ 40%) cycle. Calcination temperature was set at 1173 K, with limestone decomposition conversion be about 98% from the fluidized bed calciner shown in previous study⁴⁻⁶. The sensible heat recovery efficiency for heat exchangers (a) and (b) were suggested as 80%. It can be seen that, the reaction heat of CaCO₃ decomposition is 178kJ/mol-CaCO₃, and the exhaust heat (423K) after heat exchanger is 43.6kJ/mol-CaCO₃ which contained sensible heat 26% with latent heat of water evaporation 74%. The exhaust sensible heat (423K) after heat exchange (a) and (b) were 19.07 and 8.8 kJ/mol-CaCO₃. The latent heat of water evaporation was 32.3 kJ/mol-CaCO₃. The exhaust heat (423 K) is used about 9.67 kJ/mol-CaCO₃ to preheat water. Accordingly, total energy consumption of calcination is 228.51 kJ/mol-CaCO₃, reflected the total heat loss is 50.51 kJ/mol-CaCO₃. Accordingly, the energy excess for the H₂O (steam) cycle calcination is as

$$\text{Energy excess} = \frac{\text{Total energy consumption of calcination}}{\text{Energy of CaCO}_3 \text{ decomposition}} = \frac{228.51}{178} = 1.28$$

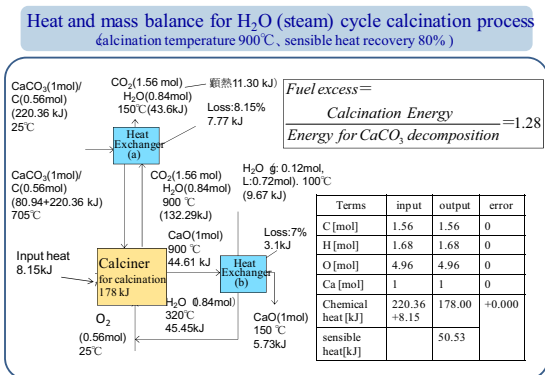


Figure 5 Calculation result of mass and heat balance for H₂O (steam) cycle calcination.

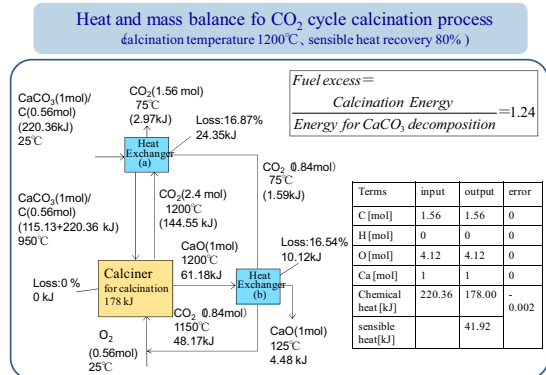


Figure 6 Calculation result of mass and heat balance for CO₂ cycle calcination.

Figure 6 shows the results of energy and material balances for CaCO₃ calcination with CO₂ cycle (CO₂ 60%, O₂ 40%) cycle. Calcination temperature was set at 1473 K, with limestone decomposition conversion be about 99% from the fluidized bed calciner shown in previous study⁴⁻⁶. The sensible heat recovery efficiency for heat exchangers (a) and (b) were suggested as 80%. It can be seen that, with the heat for CaCO₃ decomposition 178kJ/mol-CaCO₃, the exhaust sensible heat (348K) after heat exchanger (b) is 2.97 kJ/mol-CaCO₃ while the exchange loss is 24.35 kJ/mol-CaCO₃. The exhaust sensible heat after heat exchange (a) and (b) were 2.97 and 4.48 kJ/mol-CaCO₃. Accordingly, total energy consumption of calcination is 220.36 kJ/mol-CaCO₃, reflected the total heat loss is 42.36 kJ/mol-CaCO₃. Accordingly, the energy excess for the CO₂ cycle calcination is as

$$Energy\ excess = \frac{Calcination\ energy}{Energy\ of\ CaCO_3\ decomposition} = \frac{220.36}{178} = 1.24.$$

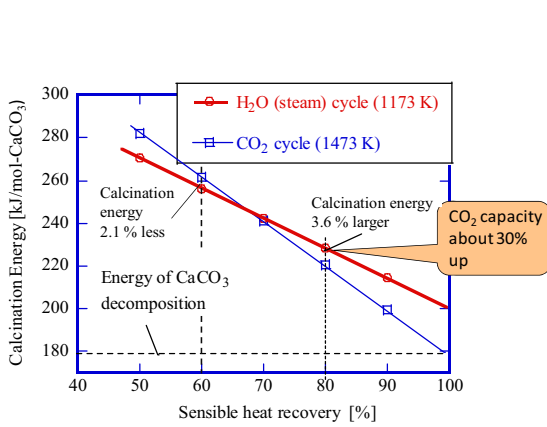


Figure 7 Comparison of energy consumption of H₂O (steam) cycle with CO₂ cycle under various sensible hear recovery

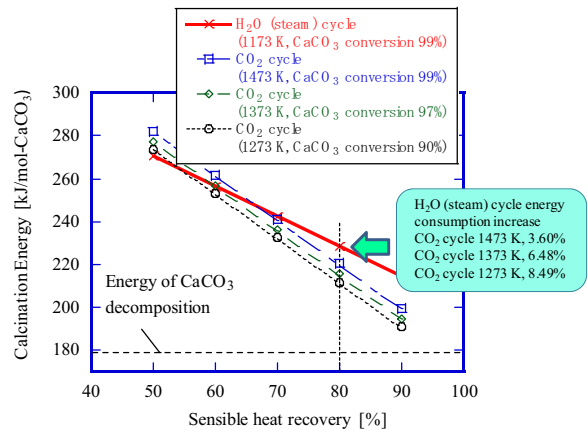


Figure 8 Comparison of calcinations energy consumption of H₂O (steam) cycle with CO₂ cycle with calcinations temperature changed from 1273 K to 1473 K.

The sensible heat in exhaust gas and solid after calcianer for CO₂ cycle is larger than that for H₂O (steam) cycle, since the calcination temperature is higher for CO₂ cycle (1473 K) than that for H₂O (steam) cycle (1173K). Figure 7 shows effect of the sensible heat recovery on the calcination energy for both of H₂O (steam) cycle and CO₂ cycle. It is seen that, the sensible heat recovery strongly affects calcination energy for CO₂ cycle than for H₂O (steam) cycle, such as when the sensible heat be recovered over 70%, the calcination energy for H₂O (steam) cycle is larger than CO₂ cycle, whereas calcination energy of H₂O(steam) cycle will be smaller than CO₂ cycle. It is seen that at the sensible heat recovery 80%, calcination energy of H₂O(steam) cycle is 3.6% more than CO₂ cycle, and at the sensible heat recovery efficiency 60% , calcinations energy of H₂O (steam) cycle is 2.1 % less than CO₂ cycle.

Figure 8 shows the energy consumption of CO₂

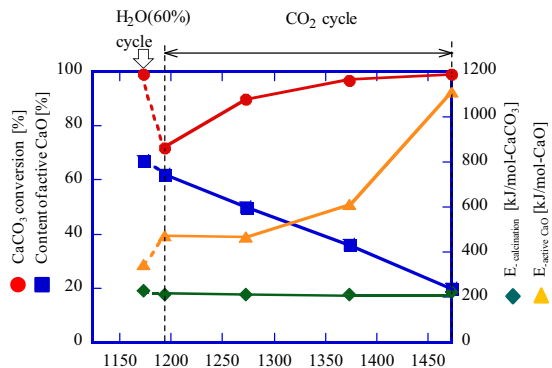


Figure 9 Comparison of CaCO₃ conversion, active CaO content, energy of calcinations consumption and energy consumption per active CaO of H₂O (steam) cycle with CO₂ cycle with calcination temperature changed from 1273 K to 1473 K.

cycle under various operating temperature. It is seen that calcinations energy for CO₂ cycle falls with the decrease of operating temperature of CO₂ cycle calcination. However, as reported in previous experimental, low operating temperature may causes reducing calcination rate of CaCO₃ particle, consequently reduces CaCO₃ decomposition conversion (Table 1).

Since the property of the limestone calcinations is that to produce active lime (CaO) for CO₂ capture, here, an estimation of “calcination energy per active CaO” must be given. Figure 9 shows the CaCO₃ decomposition conversion, the active CaO content, the calcinations energy and the calcinations energy per active CaO, with H₂O (steam) cycle under 1173 K and with CO₂ cycle under a temperature range of 1193 K to 1473 K. It is seen that the CaCO₃ decomposition conversion and active CaO for H₂O (steam) cycle were highest since the CO₂ partial pressure and calcination temperature were low. Calcination for CO₂ cycle also have been performed at low temperature, but the CaCO₃ decomposition conversion was much lower than that for H₂O (steam) cycle. The CaCO₃ decomposition conversion of CO₂ cycle shown an increase with calcination temperature, however, active CaO content was decrease quickly with increase of calcination temperature. Consequently, as a result shown in the Figure 9, the calcination energy per active CaO is lowest for H₂O (steam) cycle.

Conclusion

The mass and energy balances of a limestone (CaCO₃) calcination process with CO₂ capture for producing active lime (CaO) were analyzed by means of thermodynamic calculations. This process involves a calciner with oxygen fuel combustion by CO₂ cycle or H₂O (steam) cycle, and two heat exchanges for exhaust gas and solid sensible heat recovery. Analysis showed that, although H₂O (steam) cycle calcination had a higher calcination energy than CO₂ cycle due to water evaporation latent heat loss, however, the calcination energy per active CaO is lowest for H₂O (steam) cycle.

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References

1. Gupta, H.; Fan, L.S. *Ind. Eng. Chem. Res.* 2002, 41, 4035-4042
2. Lin, S. Y.; Suzuki, Y.; Hatano, H.; Harada M. *Proceedings of 10th Int. Conf. on Coal Sciences* 1999, Taiyuan, China, B-24.
3. Lin, S. Y.; Harada M.; Suzuki, Y.; Hatano, H. *Fuel* 2002, 81, 2079-2085.
4. Wang Y., Lin SY., Suzuki Y., “Limestone Calcination with CO₂ Capture(I), Decomposition behavior in a CO₂ atmosphere, *Energy Fuels*, 2007, 21, 3317-3321.”, *Energy Fuel*, 2007, 2008, 2009
5. Wang Y., Lin SY., Suzuki Y., “Limestone Calcination with CO₂ Capture(II), Decomposition behavior in CO₂/steam and CO₂/N₂ atmospheres”, *Energy Fuels*, 2008, 22, 2326-2331
6. Wang Y., Lin SY., Suzuki Y., “Limestone Calcination with CO₂ Capture(III) Characteristics of Coal Combustion during Limestone Decomposition”, *Energy Fuels*, 2009, 23, 2804-2809
7. *HSC Chemistry* version 4.0; Outokumpu, Place of Publication, 1999