

Phase diagram of CaSO₄ reductive decomposition by H₂ and CO

Min Zheng^{*,**,*†}, Yanbing Xing^{***}, Simei Zhong^{**}, and Hua Wang^{*,**}

*State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization,
Kunming University of Science and Technology, Kun Ming 650093, China

**Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology,
Kunming 650093, China

***Faculty of Material Science and Engineering, Kunming University of Science and Technology,
Kunming 650093, China

(Received 15 July 2016 • accepted 23 December 2016)

Abstract—The CaSO₄ reductive decomposition is an interesting issue in both the reduction zone of fluidized bed combustors (FBCs) for coal combustion and the fuel reactor of chemical-looping combustion (CLC) system. Under CO or H₂ atmosphere, CaSO₄ is reduced to CaS and CaO, together with the releases of gas sulfides, which causes environmental pollutions. To lessen sulfur release, it is important to figure out the chemical stability of CaSO₄ reductive decomposition. Thus, the chemical stability of CaSO₄/CaS/CaO under CO or H₂ atmosphere was studied in consideration of SO₂, COS and H₂S emissions. The results show that regions I (VI), II (V), and III (IV) are the stability fields of CaSO₄, CaS and CaO, respectively. The range for CaO stability is increasing with reaction temperature and partial pressures of CO₂ and H₂O. Within the reaction temperature range of 800 and 1,000 °C, when the CaSO₄-CO-H₂ reaction system reaches the triple equilibrium point, the main gas sulfur released is SO₂, followed by H₂S, while COS generation is much smaller. In a real reaction system, when the values of real P_{H_2}/P_{H_2O} (P_{CO}/P_{CO_2}), P_{SO_2} , P_{H_2S} (P_{COS}), P_{H_2O} (P_{CO_2}) and T fall into Region I (IV), or II (V), the final product should be CaSO₄ or CaS, and the sulfur release from CaSO₄ reduction can be controlled.

Keywords: CaSO₄ Reductive Decomposition, Phase Diagram, SO₂ Emission, H₂S Emission, COS Emission

INTRODUCTION

CaSO₄ reductive decomposition is an interesting issue in either the reduction zone of fluidized bed combustors (FBCs) for coal combustion or the fuel reactor of chemical-looping combustion (CLC) system. The CaSO₄ reductive decomposition has been intensively investigated in fluidized bed combustors (FBCs). FBCs are well-known for their ability to capture SO₂ in situ via direct reaction with CaO or CaCO₃ sorbent. At typical FBCs temperatures (800-950 °C) and under oxidizing conditions, CaSO₄ constitute is the favored final product of sulfation reaction and is thermodynamically stable [1]. However, localized reducing conditions exist due to volatile plumes or poor fuel distribution, and the dense bed is under reducing condition ($P_{O_2} < 10^{-11}$ bar) for 80-90% of the time [2]. It is found that sulfur is released from CaSO₄ in the dense bed where localized reducing conditions exist, causing the drop in the sulfur capture efficiency [1,2]. The sulfation mechanisms of CaO sorbent at high reaction temperatures are characterized by a two-stage process, with a very fast initial surface reaction and the subsequent product-layer-diffusion-controlled step when a continuous product layer has been formed. The continuous formation of CaSO₄

reduces the access of oxygen to the CaS core. The inner unreacted CaO sorbent is unable to be used, and thus leads to a decline in the utilization of CaO sorbent. The introduction of alkali compounds to CaO sorbent can catalyze the sulfation reactions. Besides, alkali compounds may induce particle fragmentation and large cracks, which increases the number of CaO sites and therefore promotes the overall conversion of CaO sorbent [2,3].

Growing concern has also been cast on the CaSO₄ reductive decomposition in Chemical Looping Combustion system (CLC) with CaSO₄-based oxygen carrier. CLC is very promising technology within the framework of the CO₂ capture options [4]. It typically involves two reactors, a fuel reactor and an air reactor. The oxygen carrier circulates between the fuel reactor and the air reactor and transfers oxygen from air to fuel. In this way, the fuel is isolated from air during the CLC process. The stream from the air reactor is composed of N₂ and residual O₂, and the stream from the fuel reactor mostly consists of CO₂ and H₂O. After the water condensation, virtually pure CO₂ can be obtained without any costly separation process. A successful over-1000-hour long-term operation, with Ni-based particles manufactured by spray-drying of commercial raw materials, has been carried out at Chalmers University of Technology (CHALMERS) [5]. Many works have been done at Korea Institute of Energy Research (KIER) on the development of NiO and NiO-CoO oxygen carriers, and design of the 50 kW_{th} reactors [6-10]. Operations for more than 3,000 hours, with Ni-based and Co-based oxygen-carriers, have been successfully carried out in the second-generation 50 kW_{th} reactors (KIER-2) [10]. The next

[†]To whom correspondence should be addressed.

E-mail: zhengmin1634@163.com

^{*}This paper is reported in the 11th China-Korea Clean Energy Workshop.

Copyright by The Korean Institute of Chemical Engineers.

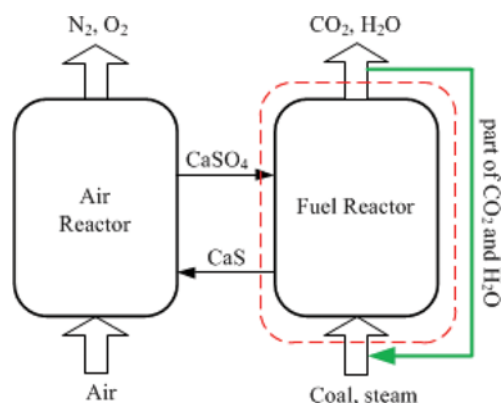


Fig. 1. Schematic illustration of a chemical-looping combustion of coal with a dual fluidized bed.

step in the development of the CLC technology is the scaling-up of the process [11]. The utilization of metal oxides faces major challenge on sulfur poisoning, environment concerns (for example, the emission of vapor Ni to the atmosphere), difficulty in separating metal oxides from coal ash, and loss in metal oxygen carriers caused by the formations of low-melting-point inert ingredients. The CaSO₄ oxygen carrier may be a low-cost oxygen carrier with high oxygen capacity [12,13]. Fig. 1 shows a schematic of a CLC process of coal with CaSO₄ oxygen carrier. During the periodic shifts between CaSO₄ reduction and CaS oxidization, a small amount of gas sulfide is released at high reaction temperatures, leaving CaO byproduct in the solid residual [12,14-16]. The sulfur emission may limit the use of CaSO₄ oxygen carrier in CLC of coal.

It is important to understand the chemical stability of CaSO₄ reductive decomposition for less sulfur release in either FBCs system or CLC with CaSO₄ oxygen carrier. The common reductions of CaSO₄ with CO and H₂ are to form CaS. The side reactions with CaO formation and SO₂ emission also occur under certain conditions. Besides SO₂ emission, H₂S and COS released also are detected. The chemical stability of CaSO₄/CaS/CaO under CO or H₂ atmosphere has been investigated in literature [1,2,13,17]. However, these thermodynamic investigations did not consider COS and H₂S formation. To better understand the chemical mechanism of CaSO₄ reductive decomposition and to suppress sulfur release from CaSO₄, the chemical stability of CaSO₄/CaS/CaO was studied in this work, where the releases of SO₂, COS and H₂S were considered.

CaSO₄ is reduced to CaS and CaO, with the releases of gas sulfides, which may cause environmental pollutions. Thus, it is important to understand the chemical stability of CaSO₄ reductive decomposition for less sulfur release. Our aim was to investigate the chemical stability of CaSO₄/CaS/CaO under H₂ or CO atmosphere, with respect to SO₂, H₂S and COS emissions. The effects of reaction temperature, partial pressure of H₂O, CO₂, SO₂, H₂S and COS, and reductive potential of the gas phase (P_{H_2}/P_{H_2O} , P_{CO}/P_{CO_2}) on the chemical stability were taken into account.

THERMODYNAMIC FUNDAMENTAL

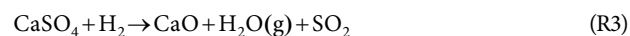
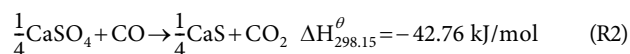
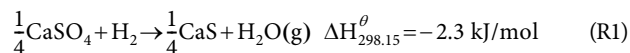
The Gibbs free energy changes of a system, represented as ΔG ,

can be used for predicting the direction of a reaction or process. The Gibbs free energy change of a system is a state function that depends only on the current equilibrium state of the system. It obviously varies with the partial pressures of any gases involved in the reaction system. The standard-state Gibbs free energy change, represented as ΔG^θ , is the Gibbs free energy change under standard state, where standard pressure 101.325 kPa is adopted. The following equation relates the standard-state Gibbs free energy of a reaction to the Gibbs free energy of a reaction at any moment during a reaction (not necessarily under standard-state conditions):

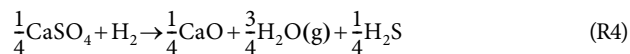
$$\Delta G = \Delta G^\theta + RT \ln Q \quad (1)$$

Q is the reaction quotient, which is the function of the partial pressures and the stoichiometric numbers of gaseous reactants of a reaction during a reaction process. When ΔG equals zero, the reaction system is at equilibrium, and it follows that the equation reaches $\Delta G^\theta = -RT \ln Q = -RT \ln K_p^\theta$.

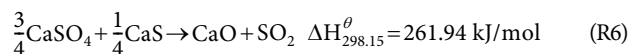
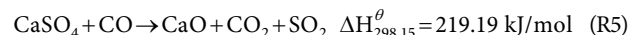
The common reductions of CaSO₄ with H₂ and CO to form CaS are via reactions (R1) and (R2). The side reactions with SO₂ and H₂S emissions also take place under certain conditions.



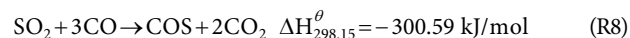
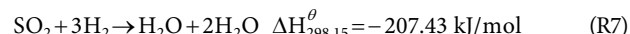
$$\Delta H_{298.15}^\theta = 260.35 \text{ kJ/mol}$$



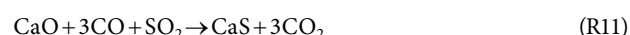
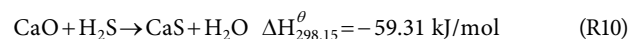
$$\Delta H_{298.15}^\theta = 13.23 \text{ kJ/mol}$$



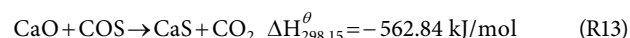
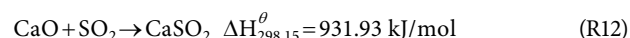
When SO₂ is released from the process of CaSO₄ reduction, SO₂ reacts with CO and is converted to COS [12]. A similar reaction between SO₂ and H₂ may be carried out, with H₂S and H₂O generation as follows.



Besides, CaO may react with SO₂, H₂S and COS to form CaS via the following reactions:



$$\Delta H_{298.15}^\theta = -390.22 \text{ kJ/mol}$$



Within the reaction temperature range of 800-1,000 °C, the CaSO₄-

H₂ system containing seven constituents, namely, CaS, CaO, CaSO₄, H₂, H₂O, SO₂, and H₂S, which may be linked together by any three independent reactions chosen among reactions ((R1), (R3), (R4), (R7) and (R9)). The CaSO₄-CO system also has seven constituents, that is CaS, CaO, CaSO₄, CO, CO₂, SO₂, and COS. They may be linked together by any two independent reactions chosen among reactions ((R2), (R5), (R6) and (R11)) and by reaction (R8). The Gibbs phase rule for reaction systems predicts that the system described above has only two degrees of freedom *f*, which is calculated according to Eqs. (2) and (3).

$$f = C - \Phi + 2 \quad (2)$$

$$\text{and } C = N - R - Z \quad (3)$$

where *f* is the number of degrees of freedom, *C* refers to the number of components (chemically independent constituents), Φ is the number of phases in thermodynamic equilibrium with each other, *N* the number of components, *R* is the number of independent equilibrated chemical reactions involving these species, and *Z* is the number of additional independent stoichiometric restraints interrelating their concentrations or activities beyond the requirement that the mole fractions in each phase must sum to 1. Thus, at a given temperature and pressure the chemical stabilities of CaSO₄-CO or CaSO₄-H₂ system are completely determined.

RESULTS AND DISCUSSION

Phase diagrams are built with the reaction equilibrium relationships. Related thermodynamic data can be retrieved from Aspen Plus Data. The phase boundaries for CaS, CaO and CaSO₄ stabilities are based on any of the three reactions (R1), (R3) and (R9) for CaSO₄-H₂ system or reactions (R2), (R5) and (R11) for CaSO₄-CO system. Each phase is stable within the stability area, bordered by solid lines that represent the coexistence within another

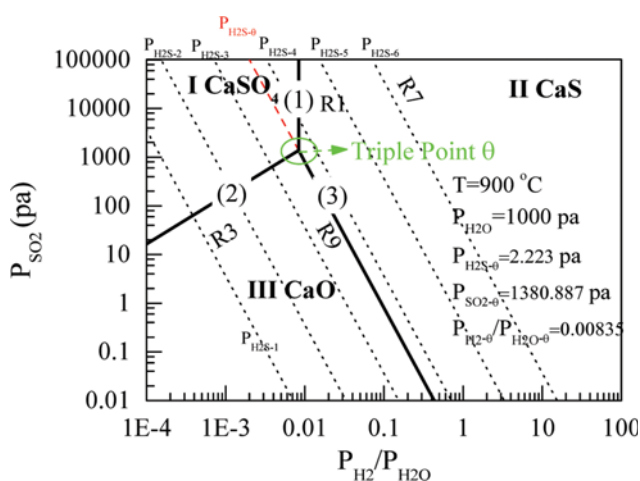


Fig. 2. Phase diagram of CaSO₄/CaS/CaO as a function of SO₂ partial pressure, H₂S partial pressure and reductive potential P_{H_2}/P_{H_2O} at 900 °C under the H₂O partial pressure of 1,000 pa ($P_{H_2S-1}=1 \times 10^{-5}$ pa, $P_{H_2S-2}=1 \times 10^{-3}$ pa, $P_{H_2S-3}=1 \times 10^{-1}$ pa, $P_{H_2S-4}=10$ pa, $P_{H_2S-5}=1,000$ pa, $P_{H_2S-6}=101,325$ pa).

phase. The slope of each curve is determined by the stoichiometry of the corresponding reaction. The intersection point of three solid lines (the triple point) represents the coexistence within the three phase CaS/CaO/CaSO₄. The CaSO₄ reduction is dependent on the factors reaction temperature, the partial pressures of SO₂, COS, H₂S, H₂O and CO₂, and reductive potential of the gas phase, as represented by the ratio of partial pressures (e.g., P_{CO}/P_{CO_2} , P_{H_2}/P_{H_2O}) [1,12,17].

1. Diagram of CaSO₄-H₂ System

Fig. 2 shows the phase diagram for CaSO₄-H₂ system as a function of SO₂ partial pressure and the reductive potential of the gas phase P_{H_2}/P_{H_2O} at 900 °C and with H₂O partial pressure of 1,000 pa. As illustrated in Fig. 2, lines (1), (2) and (3) are, respectively, the equilibrium line for reactions (R1), (R3) and (R9). The boundary lines between any two stability fields (CaSO₄/CaS, CaSO₄/CaO, CaS/CaO) denote the coexistence of two phases. For example, Line (1) in Fig. 2 denotes the coexistence of CaSO₄ and CaS. In a real reaction system, when the values of real P_{H_2}/P_{H_2O} , P_{SO_2} , P_{H_2S} , P_{H_2O} and *T* just fall upon Line (1), CaSO₄ and CaS exist simultaneously.

In Fig. 2, regions I, II, and III are the stability fields of CaSO₄, CaS and CaO, respectively. CaS is stable at high partial pressures of SO₂ and H₂S. However, CaO is stable under lower partial pressures of SO₂ and H₂S. There is critical partial pressure of SO₂ and H₂S ($P_{SO_2-\theta}$, $P_{H_2S-\theta}$) for CaSO₄ conversion to CaS or CaO. To be exact, the critical partial pressure of SO₂ and H₂S is the equilibrium partial pressure of SO₂ and H₂S when the three-solid phases of CaSO₄, CaS and CaO are in balanced coexistence. For example, the critical partial pressure of SO₂ and H₂S at 900 °C under the H₂O partial pressure of 1,000 pa is, respectively, 1,380.887 and 2.223 pa. CaS becomes stable when either partial pressure of SO₂ and H₂S in the gas phase exceeds the critical partial pressure.

The critical partial pressure of SO₂ is the SO₂ pressure at the intersection of lines (1) (2) and (3), and it is determined by the three reactions (R1), (R3) and (R9). Line (1), which is the equilibrium line for reaction (R1), is perpendicular to the x axis. At a certain reaction temperature, the equilibrium reductive potential of the gas phase P_{H_2}/P_{H_2O} is definitive. Lines (2) and (3), which are the equilibrium lines for reactions (R3) and (R9), are slanted. The slopes of lines (2) and (3) just vary with the reaction temperature. Thus, the critical partial pressure of SO₂ depends on reaction temperature. While the critical partial pressure of H₂S is determined by reactions (R1), (R3), (R9), and reaction (R7) as well, the equilibrium of Reaction (R7) varies with the reaction temperature, P_{H_2O} , P_{H_2}/P_{H_2O} and P_{SO_2} . Thus, the critical partial pressure of SO₂ only depends on the reaction temperature, while that of H₂S is a function of reaction temperature, P_{H_2O} , P_{H_2}/P_{H_2O} , and P_{SO_2} .

The effects of reaction temperature and H₂O partial pressure on the phase diagrams were investigated, and the results are shown in Figs. 2-3. The range for CaO stability is increasing with temperature and H₂O partial pressure, while those for CaS and CaSO₄ stabilities are decreasing. Also in Fig. 2 and Fig. 3 an increase in temperature will shift the equilibrium point of CaSO₄/CaS/CaO upwards and thereby reduce the stabilities of CaSO₄ and CaS, and increase that of CaO correspondingly.

The partial pressures of SO₂ and H₂S at the triple point (the equilibrium point of CaSO₄/CaS/CaO) are increasing with reaction

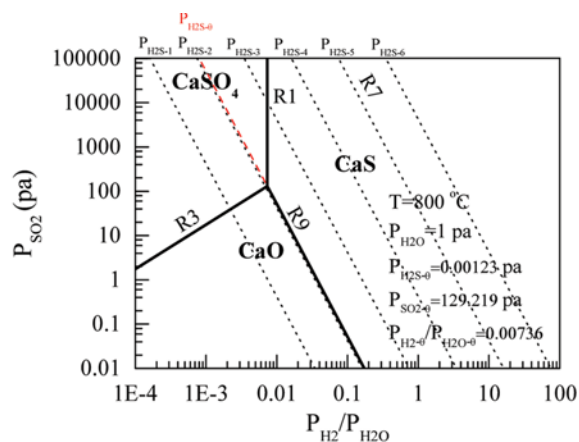
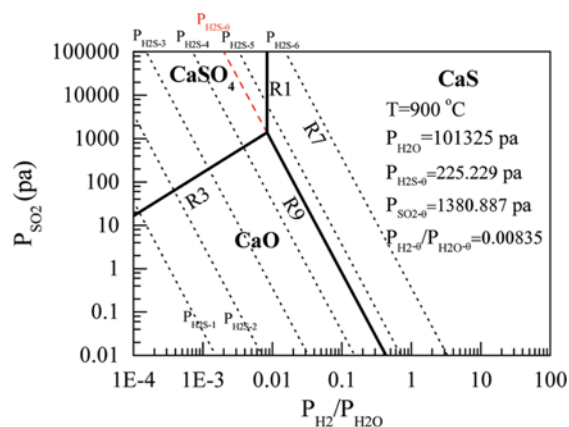
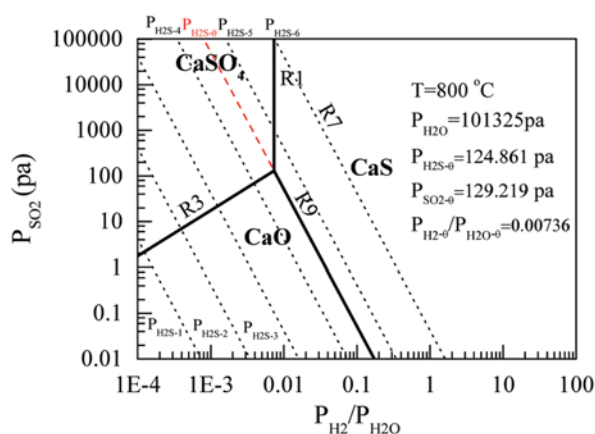
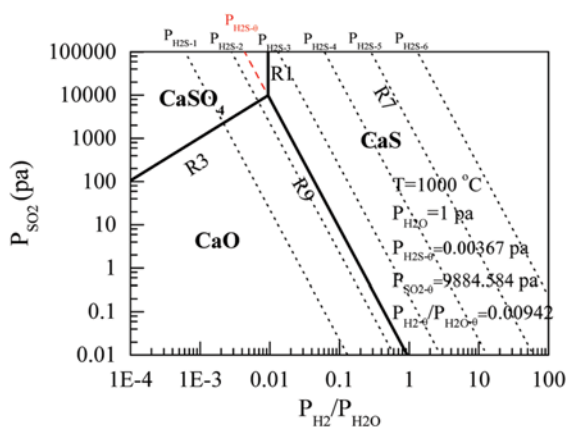
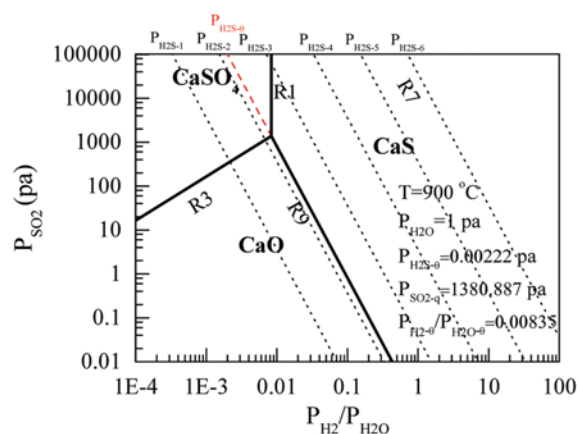
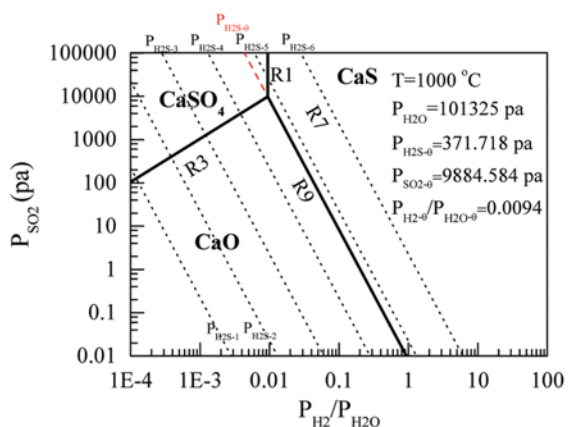
(a) 800 °C under H₂O partial pressure of 1 pa(d) 900 °C under H₂O partial pressure of 101325 pa(b) 800 °C under H₂O partial pressure of 101325 pa(e) 1000 °C under H₂O partial pressure of 1 pa(c) 900 °C under H₂O partial pressure of 1 pa(f) 1000 °C under H₂O partial pressure of 101325 pa

Fig. 3. Phase diagram of CaSO₄/CaS/CaO as a function of SO₂ partial pressure, H₂S partial pressure and reductive potential P_{H_2}/P_{H_2O} at 800, 900, 1,000 °C under the H₂O partial pressure of 1 and 101,325 pa ($P_{H_2S-1}=1 \times 10^{-5}$ pa, $P_{H_2S-2}=1 \times 10^{-3}$ pa, $P_{H_2S-3}=1 \times 10^{-1}$ pa, $P_{H_2S-4}=10$ pa, $P_{H_2S-5}=1,000$ pa, $P_{H_2S-6}=101,325$ pa).

temperature. The increase of SO₂ partial pressure with reaction temperature is more remarkable than that of H₂S. Besides, high partial pressure of H₂O favors H₂S generation. Within the reaction temperature range of 800 and 1,000 °C and the H₂O partial pressure range of 1 and 101,325 pa, SO₂ partial pressure exceeds that of H₂S

at the three equilibrium point, where the H₂S partial pressure is nearly 6.8×10^{-7} to 0.96 of SO₂ partial pressure. It denotes that when the CaSO₄ reduction under H₂ atmosphere reaches the tripe equilibrium point, SO₂ is the main gas sulfur released from CaSO₄. H₂S generation is rather considerable at 800 °C with 101,325 pa

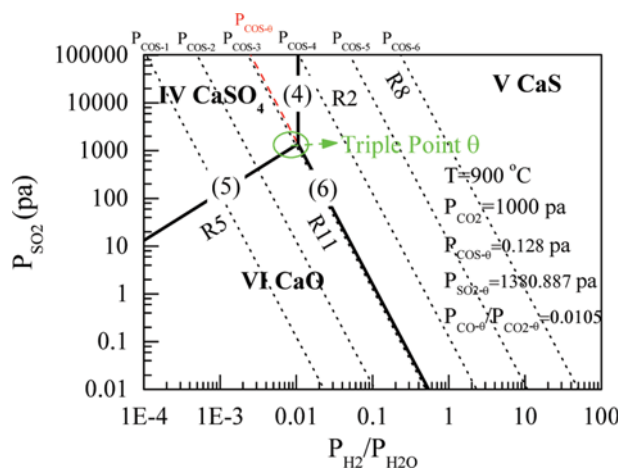


Fig. 4. Phase diagram of $\text{CaSO}_4/\text{CaS}/\text{CaO}$ as a function of SO_2 partial pressure, COS partial pressure and reductive potential $P_{\text{CO}}/P_{\text{CO}_2}$ at 900°C under the CO_2 partial pressure of 1,000 pa ($P_{\text{COS-1}}=1\times 10^{-5}$ pa, $P_{\text{COS-2}}=1\times 10^{-3}$ pa, $P_{\text{COS-3}}=1\times 10^{-1}$ pa, $P_{\text{COS-4}}=10$ pa, $P_{\text{COS-5}}=1,000$ pa, $P_{\text{COS-6}}=101,325$ pa).

partial pressure of H_2O . As soon as the temperature exceeds 900°C , the H_2S partial pressure is just below 17% of SO_2 partial pressure, and H_2S generation is much smaller than that of SO_2 .

2. Diagram of $\text{CaSO}_4\text{-CO}$ System

The phase diagram for $\text{CaSO}_4\text{-CO}$ system as a function of SO_2 partial pressure and the reductive potential of the gas phase $P_{\text{CO}}/P_{\text{CO}_2}$ is shown in Figs. 4 and 5. It is similar to that of $\text{CaSO}_4\text{-H}_2$ system. As illustrated in Fig. 4, Lines (4), (5) and (6), respectively, are the equilibrium lines for reactions (R2), (R5) and (R11). The effects of reaction temperature and CO_2 partial pressure on phase diagram are studied. CaS is stable at high partial pressures of SO_2 and COS as shown in Figs. 4 and 5. CaO is the stable species at the lower partial pressures of SO_2 and COS. The range for CaO stability is increasing with temperature and CO_2 partial pressures. It can also be seen from Fig. 5 that an increase in temperature will shift the equilibrium point of $\text{CaSO}_4/\text{CaS}/\text{CaO}$ upwards.

At the triple point (the equilibrium point of $\text{CaSO}_4/\text{CaS}/\text{CaO}$), both the partial pressures of SO_2 and COS are increasing with reaction temperature. The increase of SO_2 partial pressure with reaction temperature is more remarkable than that of COS. Additionally, high partial pressure of CO_2 is favorable for COS generation. Within the reaction temperature range of 800 and $1,000^\circ\text{C}$ and the CO_2 partial pressure range of 1 and 101,325 pa, SO_2 equilibrium partial pressure is much higher than that of COS at the equilibrium point of $\text{CaSO}_4/\text{CaS}/\text{CaO}$, where the partial pressure ratio of COS to SO_2 is nearly 4.62×10^{-8} to 4.16×10^{-2} . It denotes that when the CaSO_4 reduction under CO atmosphere reaches the equilibrium point of $\text{CaSO}_4/\text{CaS}/\text{CaO}$, SO_2 is the main gas sulfur released, and COS generation is rather small. With the rising reaction temperature, the partial pressures of COS and SO_2 at the triple point are increasing, and a more obvious growth in the partial pressure of SO_2 has been observed. It indicates that increasing reaction temperature is more favorable for SO_2 generation than COS generation. For the $\text{CaSO}_4\text{-CO-H}_2$ reaction system, rising reaction temperature mainly favors SO_2 formation, and the increases in H_2O

and CO_2 partial pressures facilitate H_2S and COS releases. Within the temperature range of $800\text{-}1,000^\circ\text{C}$ and the H_2O and CO_2 partial pressure range of 1 and 101,325 pa, when the $\text{CaSO}_4\text{-CO-H}_2$ reaction system reaches the three equilibrium point, SO_2 and H_2S are the main gas sulfides released at 800°C under 101,325 pa H_2O partial pressure. When the reaction temperature exceeds 900°C , the main gas sulfur released is SO_2 , followed by H_2S , while COS generation is much smaller.

In a real reaction system, when the values of real $P_{\text{H}_2}/P_{\text{H}_2\text{O}}$ ($P_{\text{CO}}/P_{\text{CO}_2}$), P_{SO_2} , $P_{\text{H}_2\text{S}}$ (P_{COS}), $P_{\text{H}_2\text{O}}$ (P_{CO_2}) and T fall into Region I (IV), or II (V), the final product should be CaSO_4 or CaS , without gas sulfides released. In other words, in the reduction zone of fluidized bed combustors (FBCs) for coal combustion, CaSO_4 is the stable desulfurization product. Reducing decomposition of CaSO_4 may cause a decline in sulfur removal efficiency from coal. The CaS produced in a reducing atmosphere is further converted to CaSO_4 or SO_2 in an oxidizing atmosphere. It is better to control the reaction conditions ($P_{\text{H}_2}/P_{\text{H}_2\text{O}}$ ($P_{\text{CO}}/P_{\text{CO}_2}$), P_{SO_2} , $P_{\text{H}_2\text{S}}$ (P_{COS}), $P_{\text{H}_2\text{O}}$ (P_{CO_2}) and T) in Regions I and IV (CaSO_4 stability field) for sulfur removal from coal.

For the fuel reactor in CLC system with CaSO_4 oxygen carrier, when the values of real $P_{\text{H}_2}/P_{\text{H}_2\text{O}}$ ($P_{\text{CO}}/P_{\text{CO}_2}$), P_{SO_2} , $P_{\text{H}_2\text{S}}$ (P_{COS}), $P_{\text{H}_2\text{O}}$ (P_{CO_2}) and T fall into regions II and V, the final product should be CaS . Although full conversion could not be obtained in the redox equilibrium system CaSO_4 to CaS for both H_2 and CO fuels, just few unreacted H_2 and CO (0.8-1.3% for H_2 , and 0.6-1.5% for CO) remain in the gas products within the reaction temperature range of $800\text{-}1,000^\circ\text{C}$. They are calculated on the basis of lines (1) and (4) in Figs. 2-5 of phase diagrams for $\text{CaSO}_4\text{-H}_2$ and $\text{CaSO}_4\text{-CO}$ systems.

CONCLUSION

With the consideration of SO_2 , COS and H_2S generation, we investigated the chemical stability of $\text{CaSO}_4/\text{CaS}/\text{CaO}$ under H_2 or CO atmosphere. The effects of reaction temperature, the partial pressures of SO_2 , COS, H_2S , H_2O and CO_2 , and reductive potential of the gas phase, as represented by the ratio of partial pressures (e.g., $P_{\text{CO}}/P_{\text{CO}_2}$, $P_{\text{H}_2}/P_{\text{H}_2\text{O}}$) on the chemical stability of $\text{CaSO}_4/\text{CaS}/\text{CaO}$ were carried out. Results obtained were as follows:

(1) For CaSO_4 reduction under H_2 or CO atmosphere, CaS is stable at high partial pressures of SO_2 , H_2S and COS. However, CaO is stable at lower partial pressures of SO_2 , COS and H_2S . The range for CaO stability is increasing with reaction temperature, and the partial pressures of H_2O and CO_2 .

(2) An increase in temperature shifts the equilibrium point of $\text{CaSO}_4/\text{CaS}/\text{CaO}$ upwards and thereby reduces the stability fields of CaSO_4 and CaS , but increases that of CaO correspondingly. At the triple point (the equilibrium point of $\text{CaSO}_4/\text{CaS}/\text{CaO}$), the partial pressures of SO_2 , H_2S and COS are increasing with rising reaction temperature, and the growth of SO_2 partial pressure is more remarkable. Additionally, high partial pressures of H_2O and CO_2 favor H_2S and COS generations. Within the reaction temperature range of 800 and $1,000^\circ\text{C}$, when the $\text{CaSO}_4\text{-CO-H}_2$ reaction system reaches the triple equilibrium point, the main gas sulfur released is SO_2 , followed by H_2S , while COS generation is much

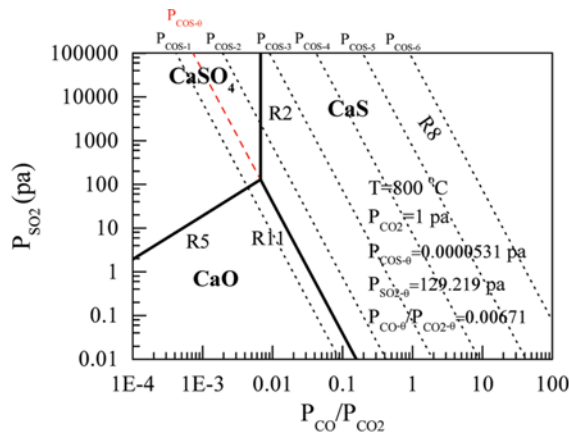
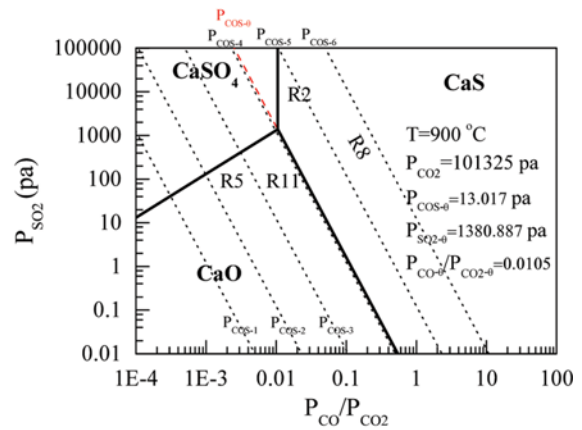
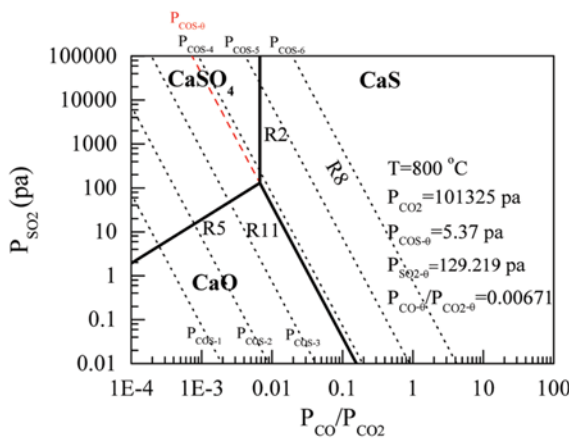
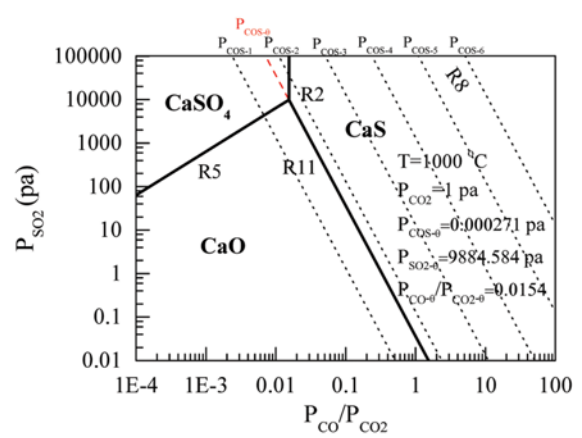
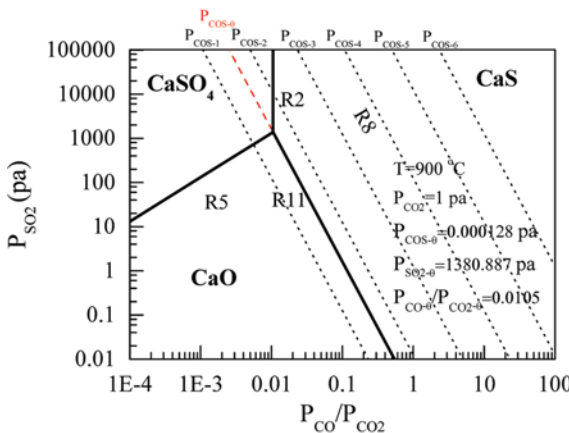
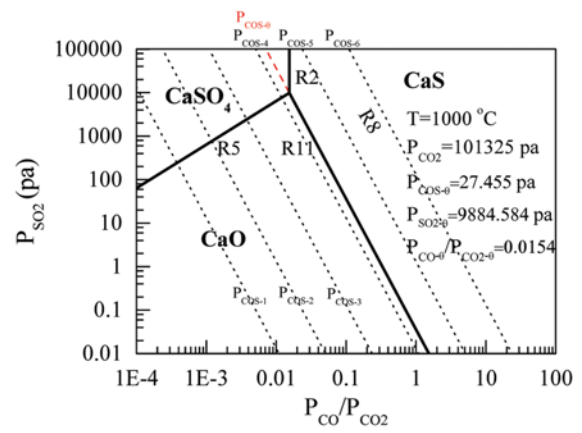
(a) 800 °C under CO₂ partial pressure of 1 pa(d) 900 °C under CO₂ partial pressure of 101325 pa(b) 800 °C under CO₂ partial pressure of 101325 pa(e) 1000 °C under CO₂ partial pressure of 1 pa(c) 900 °C under CO₂ partial pressure of 1 pa(f) 1000 °C under CO₂ partial pressure of 101325 pa

Fig. 5. Phase diagram of CaSO₄/CaS/CaO as a function of SO₂ partial pressure, COS partial pressure and reductive potential P_{CO}/P_{CO_2} at 800, 900, 1,000 °C under the CO₂ partial pressure of 1, 101,323 pa ($P_{COS-1}=1 \times 10^{-5}$ pa, $P_{COS-2}=1 \times 10^{-3}$ pa, $P_{COS-3}=1 \times 10^{-1}$ pa, $P_{COS-4}=10$ pa, $P_{COS-5}=1,000$ pa, $P_{COS-6}=101,325$ pa).

smaller.

(3) In a real reaction system, when the values of real P_{H_2}/P_{H_2O} (P_{CO}/P_{CO_2}), P_{SO_2} , P_{H_2S} (P_{COS}), P_{H_2O} (P_{CO_2}) and T fall into region I (IV), or II (V), the final product should be CaSO₄ or CaS, and the sulfur release from CaSO₄ reduction can be controlled.

ACKNOWLEDGEMENT

This work was supported by the National Natural Science Foundation of China (No. 51306084), Scientific and Technological Leading Talent Projects in Yunnan Province (No. 2015HA019),

and Natural Science Foundation of Kunming Science and Technology (KKZ3201352030).

REFERENCES

1. E. J. Anthony and D. L. Granatstein, *Prog. Energy Combust.*, **27**, 215 (2001).
2. J. Cheng, J. Zhou, J. Liu, Z. Zhou, Z. Huang, X. Cao, X. Zhao and K. Cen, *Prog. Energy Combust.*, **29**, 381 (2003).
3. A. Al-Shawabkeh, H. Matsuda and M. Hasatani, *J. Chem. Eng. Jpn.*, **28**, 53 (1995).
4. J. Adanez, A. Abad, F. Garcia-Labiano, P. Gayan and L. F. de Diego, *Prog. Energy Combust.*, **38**, 215 (2012).
5. C. Linderholm, T. Mattisson and A. Lyngfelt, *Fuel*, **88**, 2083 (2009).
6. H. J. Ryu, D. H. Bae and G. T. Jin, *Korean J. Chem. Eng.*, **20**, 960 (2003).
7. H. J. Ryu, N. Y. Lim, D. H. Bae and G. T. Jin, *Korean J. Chem. Eng.*, **20**, 157 (2003).
8. H. J. Ryu, G. T. Jin, D. H. Bae and C. K. Yi, Proc 5th China-Korea Joint Workshop on Clean Energy Technology, Qingdao, China (2004).
9. H. J. Ryu, Y. Seo and G. T. Jin, Proc. of the Regional Symp on Chem Eng, Hanoi, Vietnam (2005).
10. H. J. Ryu, S. H. Jo, Y. Park, D. H. Bae and S. Kim, Proc. 1st Int Conf on Chemical Looping, Lyon, France (2010).
11. A. Lyngfelt, T. Mattisson, C. Linderholm and M. Ryden, Proc. 4th International Conference on Chemical Looping, Nanjing, China (2016).
12. L. Shen, M. Zheng, J. Xiao and R. Xiao, *Combust. Flame*, **154**, 489 (2008).
13. Q. Song, R. Xiao, Z. Deng, L. Shen and M. Zhang, *Korean J. Chem. Eng.*, **23**, 592 (2009).
14. Q. Song, R. Xiao, Z. Deng, W. Zheng, L. Shen and J. Xiao, *Energy Fuels*, **22**, 3661 (2008).
15. H. Tian, Q. Guo and J. Chang, *Energy Fuels*, **22**, 3915 (2008).
16. M. Zheng, L. Shen and J. Xiao, *Int. J. Greenh. Gas Con.*, **4**, 716 (2010).
17. P. F. B. Hansen, K. Dam-Johansen and K. Østergaard, *Chem. Eng. Sci.*, **48**, 1325 (1993).