Study on the Transmission and Transformation of the Impurities in the Reductive Decomposition Process of Phosphogypsum

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Abstract. To enrich the basic theory of the reductive decomposition process of PG(phosphogypsum), emphasis was laid on the exploration of the impact of the main impurities on the process. Firstly, the simulation computation was done on the systems of pure gypsum mixed with coal with or without impurities under nitrogen atmosphere, and the possible reactions in the process were deduced. Secondly, experiments were conducted in a TG-DTA integrated thermal gravimetric analyzer and a tube furnace. The slag and the flue gas from the experiments were characterized and analyzed to verify the accuracy of theoretical calculation. The results show that silicon dioxide can change the decomposition process of PG and finally transform to Ca_3SiO_5.
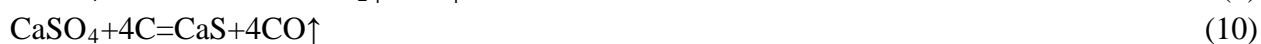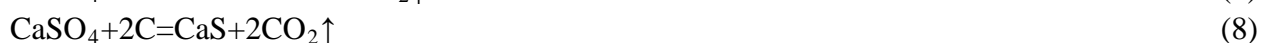
1. Introduction

Phosphogypsum (PG), which is composed primarily of calcium sulfate dehydrate, is a sort of industrial slags from the production of phosphoric acid. As an important source of calcium and sulfur, it can be applied in the production of chemical agents, construction materials and the amendment of soil[1-5].

Much work has been done by our group on the effective decomposition of PG. Different reductants have been used under different atmosphere with or without additives to explore the decomposition process of PG[6-11]. Even so, the basic theory still remains to be consummated.
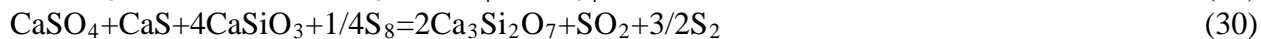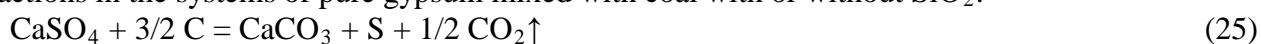
2. Simulation Calculation

There are so many impurities in PG that it's difficult to list out all the reactions. The main reactions are shown below without consideration of the impurities:

$$CaSO_4 = CaO + SO_2\uparrow + 1/2 O_2\uparrow \tag{1}$$

$$C + O_2 = CO_2 \tag{2}$$

$$C + CO_2 = 2CO \tag{3}$$

$$C + 1/2 O_2 = CO \tag{4}$$

$$CaSO_4 + 1/2C = CaO + SO_2 + 1/2CO_2 \tag{5}$$

$$CaSO_4 + C = CaO + CO + SO_2 \tag{6}$$

$$CaSO_4 + 3/2C = CaO + S + 3/2CO_2\uparrow \tag{7}$$

$$CaSO_4 + 2C = CaS + 2CO_2\uparrow \tag{8}$$

$$CaSO_4 + 5/2C = CaS + 3/2CO_2\uparrow + CO\uparrow \tag{9}$$

$$CaSO_4 + 4C = CaS + 4CO\uparrow \tag{10}$$

$$CaSO_4 + CO = CaO + CO_2 + SO_2 \tag{11}$$

$$CaSO_4 + 4CO = CaS + 4CO_2 \tag{12}$$

$$S + O_2 = SO_2 \tag{13}$$

$$CaSO_4+1/2S=CaO+3/2SO_2\uparrow \tag{14}$$
$$CaO+3/2S=CaS+1/2\ SO_2\uparrow \tag{15}$$
$$CaO+3/4S_2=CaS+1/2SO_2 \tag{16}$$
$$CaSO_4+1/3CaS+4/3CO_2=4/3CaCO_3+4/3SO_2 \tag{17}$$
$$CaSO_4+1/3CaS=4/3CaO+4/3SO_2\uparrow \tag{18}$$
$$CaSO_4+3CaS=4CaO+4S \tag{19}$$
$$CaS+3CO_2=CaO+SO_2\uparrow+3CO\uparrow \tag{20}$$
$$CaS+2SO_2=CaSO_4+2S \tag{21}$$
$$CaS+3SO_3(g)=CaO+4SO_2 \tag{22}$$
$$CaS+3/2O_2=CaO+SO_2 \tag{23}$$
$$CaS+2O_2=CaSO_4 \tag{24}$$

FactSage is one of the largest fully integrated database computing systems in chemical thermodynamics in the world. The Reaction Module and Equilib Module are used to deduce the possible reactions in one system in some condition. There are so many impurities like SiO_2, P_2O_5, Al_2O_3 and Fe_2O_3 in PG among which SiO_2 is the most. Thus in the next discussion only the impact of SiO_2 on the reductive decomposition of PG is considered.

With the help of the Equilib Module, reaction (18), (25) ~ (32) were deduced as the possible reactions in the systems of pure gypsum mixed with coal with or without SiO_2:
$$CaSO_4 + 3/2\ C = CaCO_3 + S + 1/2\ CO_2\uparrow \tag{25}$$
$$CaCO_3 + 1/8S_8 = 3/4\ CaS + 1/4\ CaSO_4 + CO_2 \tag{26}$$
$$CaSO_4 + 1/3\ CaS = 4/3\ CaO + 4/3\ SO_2\uparrow \tag{18}$$
$$CaS + CO_2 = CaO + CO + 1/2\ S_2 \tag{27}$$
$$CaCO_3+SiO_2+S=CaSiO_3+CO_2\uparrow+1/8S_8\uparrow \tag{28}$$
$$2CaCO_3+2SiO_2+S=2CaSiO_3+2CO_2\uparrow+1/8S_8\uparrow \tag{29}$$
$$CaSO_4+CaS+4CaSiO_3+1/4S_8=2Ca_3Si_2O_7+SO_2+3/2S_2 \tag{30}$$
$$3CaSO_4+CaS+4Ca_3Si_2O_7=8Ca_2SiO_4+4SO_2\uparrow \tag{31}$$
$$Ca_2SiO_4+CaO=Ca_3SiO_5 \tag{32}$$

The Reaction Module is used to figure out some key parameters of the reactions involved in the decomposition process of phosphogypsum:

Table 1 The thermodynamic parameters of the reactions involved in the decomposition process of PG

Reaction	Reaction Temperature/℃	Enthalpy Change	Reaction	Reaction Temperature/℃	Enthalpy Change
(1)	×	-	(17)	×	-
(2)	√	< 0	(18)	> 1160	> 0
(3)	> 710	> 0	(19)	×	-
(4)	√	< 0	(20)	×	-
(5)	> 830	> 0	(21)	< 760	< 0
(6)	> 800	> 0	(22)	√	< 0
(7)	> 470	> 0	(23)	√	< 0
(8)	> 200	> 0	(24)	√	< 0
(9)	> 300	> 0	(25)	√	> 0
(10)	> 450	> 0	(26)	> 390	> 0
(11)	> 890	> 0	(27)	×	-
(12)	√	< 0	(28)	> 310	> 0
(13)	√	< 0	(29)	> 300	> 0
(14)	> 1030	> 0	(30)	> 770	> 0
(15)	√	> 0(< 440℃) < 0(> 440℃)	(31)	> 970	> 0
(16)	√	< 0	(32)	> 1300	> 0

Remarks: The signal "×" represents the reaction can't proceed spontaneously from 0 to 1400 ℃; the signal "√" represents the reaction can proceed spontaneously from 0 to 1400 ℃; the signal "-" means the value is no sense.

3. Experiments

The ultimate analysis of the coal used in the experiments is shown in Table 2. The particle size of coal is selected as 120 ~ 140 mesh according to Zheng Shaocong[10].

Table 2 The ultimate analysis of coal

Compositions	$FC_d/\%$	$S_{t,ad}/\%$	$M_{ad}/\%$	$A_d/\%$	$V_{daf}/\%$
Contents (wt.%)	77.36	0.22	6.79	12.68	11.40

To avoid the unnecessary interference from other impurities, pure gypsum is chosen as the raw material instead of PG. The proportion of gypsum and coal is 10:1, and the one of gypsum, coal and SiO_2 is 10:1:1. Experiments were done in a TG-DTA integrated thermal gravimetric analyzer with a flow of nitrogen at 25 mg/min from room temperature to 1400 ℃ at 10 ℃/min. The tube furnace experiments were carried out with a flow of nitrogen at 100 mg/min from room temperature to 1400 ℃ at 10 ℃/min. The slag and the flue gas from the experiments were characterized and analyzed.

4. Results and Discussion

4.1 The Reductive Decomposition of Pure Gypsum.

As can be seen from Fig. 1 and Fig. 2, the mass loss and endothermic effect from 70 ℃ to 145 ℃ are due to the removal of the crystallization water of pure gypsum and the outer moisture of coal.

From 450 to 660 ℃, there was a mass loss and a exothermic process. The concentrations of CO and CO_2 both increased as the temperature increased, while there was few SO_2 produced. Thus it's likely that CO is generated via the pyrolysis of coal, and CO_2 is yielded by reaction (7) ~ (9), (25) and (26).

There was no obvious mass loss at the interval of 660 to 1000 ℃. In the flue gas, the concentration of CO decreased sharply while the one of CO_2 stay at a high level. There was still few SO_2 produced. As the mass loss of reaction (25) is tiny, it's possible that this reaction happens at this condition. The concentration decrease of CO is due to the cease of the pyrolysis of coal.

When the temperature was up to 1000 ℃, the concentration of SO_2 rise until to the peak at 1080. After that, it began to drop until to 0 at 1200 ℃. For it needs at least 27 minutes to evacuate the gases in the tube furnace, we can find that there wasn't SO_2 generated above 1080 ℃. What's more, there wasn't obvious mass loss or sharp decrease of the CO_2 concentration. So reaction (16) and (25) are the most likely reactions that may happen at this stage.

When the temperature was heated to 1170 ℃ or higher, big mass loss and endotherm could be seen. The endotherm effect at 1217 ℃ is caused by the polymorphism transformation of calcium sulfate which indicates that calcium sulfate doesn't all decomposed before 1217 ℃. In the flue gas, CO and CO_2 were increasing while SO_2 was also increasing but at a low level which stoped at 1280 ℃. The XRD pattern of the slag in Fig. 3 shows that the most decomposition product is CaO while CaS is also exist. It can be deduced from the phenomenon above that CaO is generated mainly by reaction (7), while CaS is by reaction (8) ~ (10).
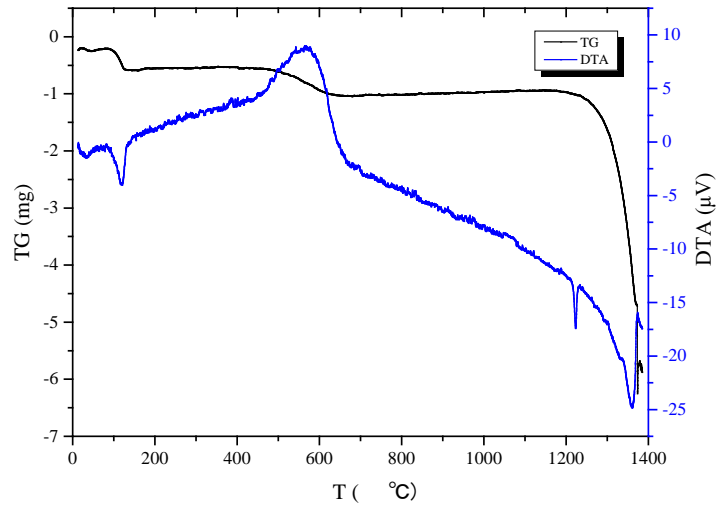
Fig. 1 The TG-DTA curves of gypsum mixed with coal under nitrogen atmosphere
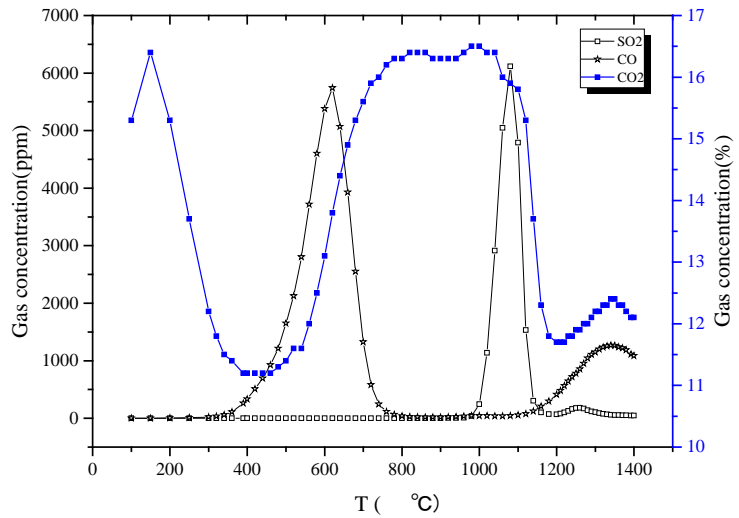

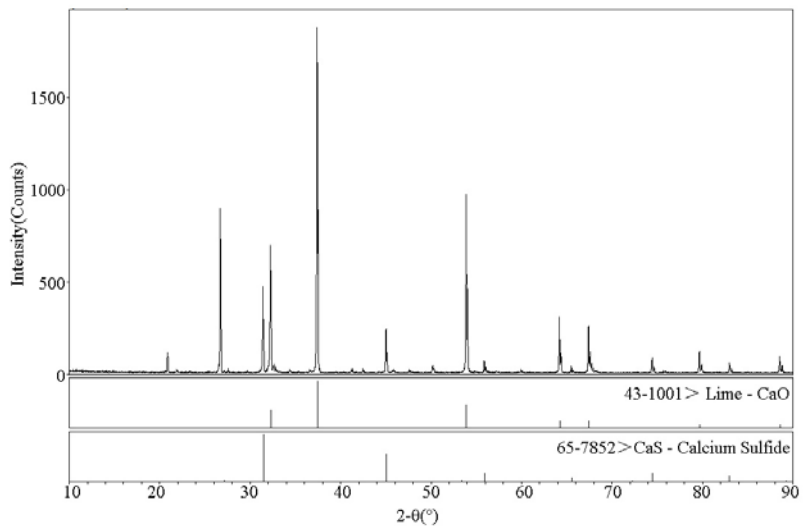Fig. 2 The flue gas components of gypsum mixed with coal under nitrogen atmosphere

Fig. 3 The XRD pattern of the residue from the decomposition process of gypsum and coal under nitrogen atmosphere

4.2 The Impacts of SiO_2 on the Decomposition of Pure Gypsum.

As can be seen from Fig. 4 and Fig. 5, the changes of the system were very similar to that without SiO_2 from 380 to 640 ℃. When the temperature was higher than 640 ℃ the concentration of CO decreased down to 0 at 720℃, while the one of CO_2 kept increasing and to a high value at 760 ~ 820 ℃. Thus it's likely reaction (25) is happening at the above interval.

Big mass loss could be observed from 1150 ℃, and it got alleviated above 1373 ℃. The endothermic peak at 1220 ℃ is still caused by the polymorphism transformation of calcium sulfate. Three more endothermic peaks appeared at 1319, 1347 and 1373 ℃. There wasn't any thermal effect except the above four. SO_2 was generated above 1140 ℃, which was different from the situation without the addition of SiO_2 in 4.1, and it kept increasing until to the peak value at 1333 ℃. At 1375 ℃, or 27 minutes later, there was few SO_2 exist in the tube furnace. The concentration of CO and CO_2 kept increasing from 1100 to 1375 ℃.

The XRD pattern of the slag in Fig. 6 shows that the main products are Ca_3SiO_5 and Ca_2SiO_4. There was also a little $CaSO_4$ stay unreacted. Ca_2SiO_4 can be produced via reaction (31), while Ca_3SiO_5 can be generated by reaction (32). As there have mass loss and generation of SO_2, reaction (31) can only happen from 1140 to 1333 ℃ according to the concentration change of SO_2. When it's above 1373 ℃ where there are a little mass loss and no generation of SO_2 and CO, it's reaction (32) that cause the endothermic effect. The existence of reaction (31) and (32) should be based on the existence of reaction (28) or (29) and thus of $CaCO_3$ and CaS. Therefore, reaction (25), (28) and (29) are likely to happen before reaction (31).

Among the reactions that can generate SO_2, CO or CO_2 from 1150 to 1319 ℃, only reaction (16) is a exothermic one of which the only solid reactant is CaO and the only gas product is SO_2. There exists CO_2 in the gas products in reaction (28) and (29), so there should be endothermic reactions with solid product CaO or gas product CO except reaction (16), (28) and (29). In view of this, reaction (7) and (10) are the most likely reactions from 1150 to 1319 ℃.
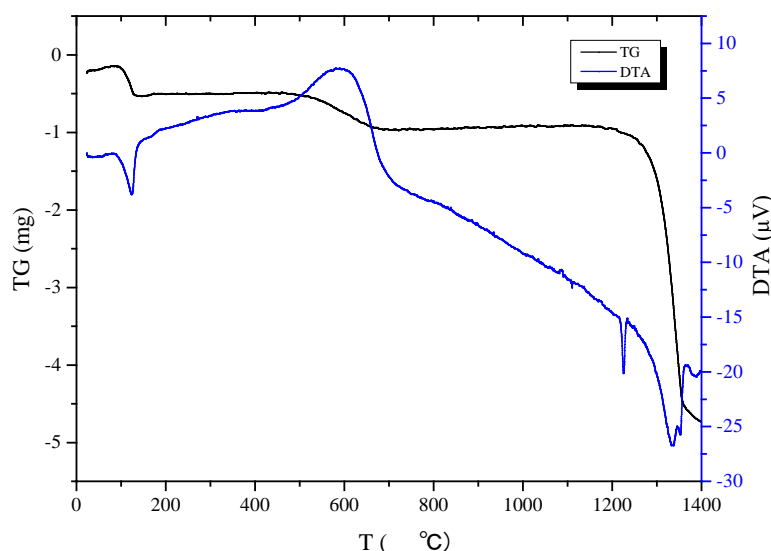

Fig. 4 The TG-DTA curves of gypsum and coal under nitrogen atmosphere with the addition of SiO_2
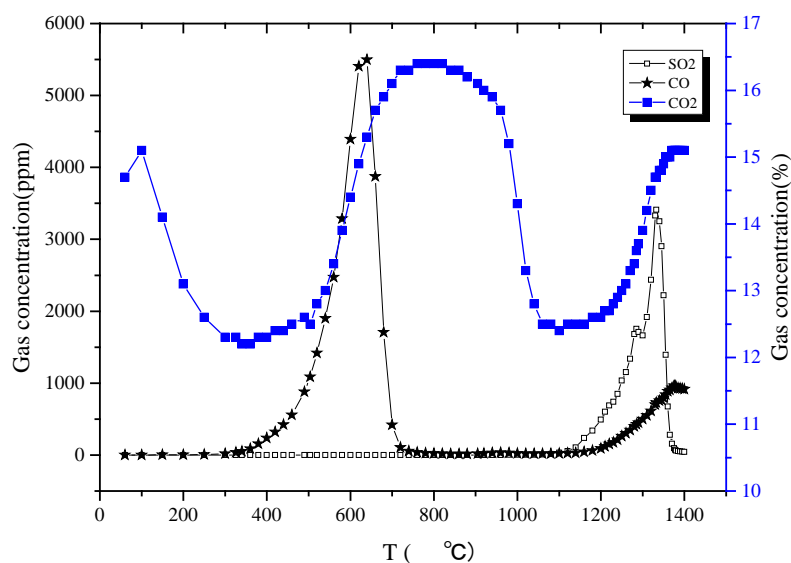
Fig. 5 The flue gas components of gypsum mixed with coal under nitrogen atmosphere with the addition of SiO_2
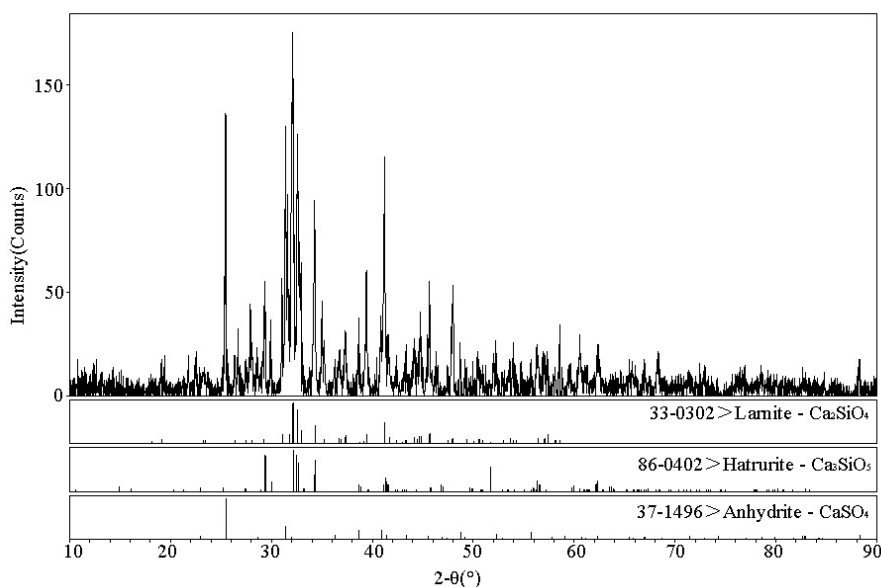

Fig. 6 The XRD pattern of the residue from the decomposition process of gypsum and coal under nitrogen atmosphere with the addition of SiO_2

5. Conclusion

a) Most of SO_2 in the gas products is generated via reaction (16). With the addition of SiO_2, it will scramble for elemental sulfur via reaction (28) or (29) against reaction (16) which will lead to the lag of the large production of SO_2.

b) SiO_2 will change the decomposition route of $CaSO_4$ and be transformed to Ca_2SiO_4 or Ca_3SiO_5, which is in good consistence with the theoretical results.

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