INFLUENCE OF CARBON AND ADDITIVES ON THE HIGH-TEMPERATURE DECOMPOSITION BEHAVIOR OF PHOSPHOGYPSUM

VPLIV OGLJIKA IN DODATKOV NA VISOKO-TEMPERATURNI RAZPAD FOSFORNEGA GIPSA

Rui Fang¹, Hongbin Tan^{1,3}, Wenjie Mao², Xiaoling Ma¹, Ying Feng¹, Qian Jiang¹, Feihua Yang⁴

¹State Key Laboratory of Environment-friendly Energy Materials, School of Materials Science and Engineering, Southwest University

²Department of Electrical Engineering &Information Technology, Shandong University of Science and Technology, Jinan Shandong, 250031, China

³Shaanxi Engineering Center of Metallurgical Sediment Resource, Shaanxi University of Technology, Hanzhong Shaanxi 723000, China ⁴State Key Laboratory of Solid Waste Reuse for Building Materials, Beijing Building Materials Academy of Science Research, Beijing 100041, China

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The influence of carbon and iron additives on the high-temperature decomposition behavior of phosphogypsum (PG) is system-The influence of carbon and and generates on the influence decomposition behavior points by paint (10) is system at a triangly investigated using XRD, SEM and EDS. In the absence of carbon, a small amount of anhydrite phase is decomposed after sintering at 1200 °C for 2 h. However, the undesirable oldhamite phase is observed in RG/carbon50, PG/carbon/FeSO₄ mixtures, PG/FeS₂ mixtures embedded in carbon after sintering at 800 °C for 2 h, respectively, which implies a strong reducing atmosphere can promote oldhamite to generate. In the case of a PG/carbon 100 mixture, the diffraction peaks of anhydrite are not observed after sintering at 1100 °C for 2 h. Moreover, the main phases in the mixture are found to be wollastonite-2M, larnite, calico-olivine, gehlenite and lime. Overall, the anhydrite decomposition to lime is mainly influenced by carbon and the sintering temperature

Keywords: phosphogypsum, thermal decomposition, carbon, additives, reducing atmosphere, anhydrite phase

Avtorji v pričujočem članku opisujejo sistematično raziskavo vplivov dodatka ogljika in dodatkov železovih spojin na visoko Temperaturni razpad fosfor-gipsa (PG). To je mavec, ki je nastal kot stranski produkt u ogjnku in dotaktov fosforne kisline. Raziskavo so izvajali z XRD, SEM in EDS. V odsotnosti ogljika je razpadel majhen del anhidritne faze med 2 urnim sintranjem na 1200 °C. Vendar so opazili tudi prisotnost neželene oldhamitne faze (kubični (Ca,Mg)S) v mešanicah RG/carbon50, PG/carbon/FeSO₄ in PG/FeS₂, ki so jih zakopali v ogljik in sintrali 2 h pri 800 °C. To pomeni, da močna reduktivna atmosfera lahko pospešuje tvorbo oldhamita. V primeru mešanice PG/ogljik 100, ki so jo sintrali 2 h na 1100 °C pa avtorji na difraktogramu niso opazili pikov, ki bi odgovarjali anhidritni fazi. Nadalje ugotavljajo, da so v mešanici prisotne glavne faze: volastonite-2M, larnit, kalicijev olivin (Ca₂SiO₄), gehlenit (Ca₂Al[AlSiO₇]) in apno. Od tod sledi, da je razpad anhidrita v apno v glavnem odvisen od ogljika in temperature sintranja.

Ključne besede: fosfor-gips, termični razpad, ogljik, dodatki, reduktivna atmosfera, anhidritna faza

1 INTRODUCTION

*Corresponding author's e-mail: hb-t@163.com (Hongbin Tan)

Phosphogypsum (PG) is a major solid waste that is produced during phosphoric acid (H₃PO₄) manufacturing by a wet acid process, and mainly consists of gypsum (CaSO₄·2H₂O) and a minor amount of poorly crystalline CaSO₄·0.5H₂O and crystalline SiO₂.¹ In general, \approx 4.5–5 kilograms of PG is generated for every kilogram of P₂O₅. Moreover, almost 55 million tons of PG waste is annually generated in China and its annual output is estimated to be ≈ 280 million tons worldwide.^{2,3} Despite the fact that the PG waste is utilized in numerous fields, such as soil-stabilization amendments, agricultural fertilizers, cement retarder, building bricks/blocks and cementitious binder, only a fraction of PG waste (<40 w/%) is reused

The sustainable and effective recycling of PG can be realized by using it as a substitute for lime and sulfuric acid during the production process.⁶ It has been reported that the reductive decomposition of CaSO₄ in the presence of CH₄, H₂, C and CO generates SO₂ and lime, which can be utilized for the production of sulfuric acid and for acid-liquid neutralization, respectively.7-10 Thermal decomposition is usually recommended for the efficient recycling of PG; however, it has not been studied in detail.7

Coal (carbon) is an industrial fuel, which can be utilized, as a heat source, to decompose PG and produce a reducing atmosphere, which further facilitates the PG decomposition. Herein, we present the influence of carbon

and a large proportion is treated by outdoor stacking, which induces additional costs and raises environmental concerns.3-5

R. FANG et al.: INFLUENCE OF CARBON AND ADDITIVES ON THE HIGH-TEMPERATURE DECOMPOSITION ...

on the thermal decomposition of PG, showing a deeper understanding of the given process.

The addition of iron additives to $CaSO_4$ resulted in a marked reduction in the decomposition temperature of CaSO₄, and the amount of unfavorable product CaS can decrease with an increase in the amount of additives; however, the interactive influence of iron additives and carbon on the CaSO₄ decomposition has not been unveiled yet.

2 EXPERIMENTAL PART

Activated carbon and ferrous sulfate (analytical grade) were provided by Tianjin Dengke Chemical Reagent Co. Ltd., China. Pyrite (analytical grade) was provided by Strem Chemicals Inc., USA. PG (industrial grade) was provided by Sichuan Lomon Co. Ltd., China.

The chemical composition and X-ray diffraction (XRD) pattern of PG are presented in **Table 1** and **Figure 1**, respectively. The PG contained 50.75 w/% SO₃, 37.88 w/% CaO, 7.20 w/% SiO₂, 0.88 w/% P₂O₅, etc. The PG phases were mainly of CaSO₄·2H₂O, a minor amount of CaSO₄·0.5H₂O, and SiO₂.

Then, 1.0 g of PG was mixed with 0.5/1.0 g carbon powder, 0.5 g carbon and 0.15 g ferrous sulfate powder, and 0.5g pyrite (PG/carbon 50/100, PG/carbon/FeSO₄, PG/FeS₂), respectively. And then, the mixture was transferred into a 10-mL covered ceramic crucible. To PG/carbon 50, PG/carbon/FeSO₄, PG/FeS₂ mixture samples and according to references,¹¹ the 10-mL ceramic crucible was placed in a 100-mL covered ceramic crucible, and filled with carbon. These crucibles were placed in a muffle furnace and heated at different temperatures, ranging from 800 °C to 1200 °C, at a heating rate of 10 °C/min.



Figure 1: XRD pattern of PG

 Table 1: Chemical composition of PG (w/%)

CaO	SO_3	SiO_2	Al_2O_3	P_2O_5	Fe ₂ O ₃	SrO	K ₂ O	MgO
37.88	50.75	7.20	1.54	0.88	0.77	0.22	0.20	0.06



Figure 2: XRD patterns of PG calcined at different temperatures for 2 h

X-ray diffraction (XRD) analysis was carried out by using an X'pert PRO X-ray diffractometer (PANalytical, Netherlands), equipped with $\text{Cu}-K_{\alpha}$ radiation ($\lambda = 0,154178$ nm). The surface morphology was observed by using a scanning electron microscopye (SEM, TM-4000, Hitachi, Japan), equipped with an energy-dispersive spectrometer (EDS, 550i, IXRF, America) for compositional analysis.

3 RESULTS AND DISCUSSION

XRD patterns of PG, calcined at different temperatures for 2 h, are presented in **Figure 2**. The results reveal that the sample mainly consists of anhydrite phase (CaSO₄, PDF: 72-0619) after sintering in the temperature range 800 °C to 1200 °C. However, the intensity of the diffraction peaks decreases with n aincreasing sintering temperature, indicating the decomposition of anhydrite phase.



Figure 3: XRD patterns of RG/carbon 50 mixtures embedded in carbon and calcined at different temperatures for 2 h

Materiali in tehnologije / Materials and technology 54 (2020) 6, 861-865

It has been reported that the CaSO₄ slowly decomposes till the sintering temperature of 1200 °C; however, the decomposition rapidly proceeds at T > 1250 °C. However, the initial decomposition temperature of CaSO₄ is reduced by 20–50 °C and decomposition is completed before 1300 °C after the addition of Fe₂O₃.¹² Despite the presence of Fe₂O₃ in the PG, the decomposition temperature remained lower than 1200 °C, resulting in the minor decomposition of the CaSO₄ phase. One should note that the high decomposition temperature consumes more energy and increases the operating costs. Therefore, carbon was added to reduce the decomposition temperature, which changed the reaction atmosphere and lowered the decomposition temperature.

XRD patterns of PG/carbon 50 mixtures embedded in carbon, calcined at different temperatures for 2 h, are shown in Figure 3. The undesirable oldhamite product (CaS, PDF: 77-2011) is observed after calcination in the temperature range 800 °C to 1200 °C. Only the diffraction peaks of oldhamite are observed by sintering in the temperature range 900 °C to 1200 °C. According to the Reaction Module of FactSage software, the oldhamite is easily generated at low temperature (>200 °C).7 Moreover, the catalytic role of Fe₂O₃ accelerates the reduction of CaSO₄, resulting in the formation of CaS. Furthermore, the formation of a new intermediate phase, i.e., CaFeSO, also inhibited the side reactions of sulfur release due to its excellent thermal stability.¹³ Briefly, both CaS and CaO were generated due to CaSO₄ decomposition, as described below:13

$$2C + O_2 \Rightarrow CO \tag{1}$$

$$CaSO_4 + 2CO \Rightarrow CaS + 2CO_2$$
(2)

$$CaSO_4 + 2CO \Rightarrow CaO + SO_2 + 2CO_2$$
(3)

It has been reported that the CaS/CaO ratio depends on the reaction temperature and the CO concentration. Only oldhamite phase was observed after embedding the mixture in carbon and sintering in the temperature range



Figure 4: XRD patterns of PG/carbon/FeSO₄ mixtures embedded in carbon and calcined at different temperature for 2 h

Materiali in tehnologije / Materials and technology 54 (2020) 6, 861-865

900 °C to 1200 °C. One should note that these samples experienced a strong reducing atmosphere due to the high concentration of CO.

Furthermore, the XRD patterns of the PG/carbon/ FeSO₄ mixtures embedded in carbon, calcined at different temperatures for 2 h, are shown in **Figure 4**. Only the weak diffraction peaks of oldhamite are observed after sintering at 800 °C. As seen from **Figure 4**, compared with **Figure 3**, the FeSO₄ hinders the oldhamite generation, possibly because FeSO₄ is easier to reduce than CaSO₄. As a result, the reduction of CaSO₄ is delayed.

XRD patterns of PG/FeS₂ mixtures embedded in carbon, calcined at different temperatures for 2 h, are shown in **Figure 5**. The main phases are anhydrite and old-hamite after sintering at 800 °C. As seen from **Figure 5**, compared with **Figure 3**, the diffraction peaks of old-hamite become weak after sintering at 1100 °C, possibly because the oldhamite decomposed to CaO. Further research is needed to continue to define these dependencies.

XRD patterns of PG/carbon 100 mixtures, calcined at different temperatures for 2 h, are shown in Figure 6. At the calcination temperature of 900 °C, the main phases are found to be anhydrite (CaSO₄, PDF: 72-0916), wollastonite-2M (CaSiO₃, PDF: 76-0186) and calico-olivine (Ca2SiO4, PDF: 70-2450), a minor amount of quartz (SiO₂, PDF: 85-0457), larnite (Ca₂(SiO₄), PDF: 83-0460) and lime (CaO, PDF: 82-1690). At the calcination temperature of 1000 °C, the main phases are wollastonite-2M, larnite, calico-olivine and gehlenite (Ca₂Al(AlSi)O₇, PDF: 89-5917), and a minor amount of lime. Moreover, the diffraction peaks of anhydrite are not observed. These results confirm that the presence of carbon and the high temperature improved the decomposition of anhydrite and the formation of other phases. At the calcination temperature of 1100 °C, the main phases in the mixture are the same as the sample calcined at



Figure 5: XRD patterns of PG/FeS₂ mixtures embedded in carbon and calcined at different temperature for 2 h

R. FANG et al.: INFLUENCE OF CARBON AND ADDITIVES ON THE HIGH-TEMPERATURE DECOMPOSITION ...

1000 °C, but the content of gehlenite increases and the content of wollastonite-2M decreases.

Table 1 shows that the PG contains small amounts of Al_2O_3 and SiO_2 , whereas the XRD pattern shows strong diffraction peaks, corresponding to the wollastonite-2M and gehlenite phase. Moreover, the diffraction peaks of the lime phase were also observed. As mentioned earlier, the anhydrite decomposition depends on the reaction temperature and the CO concentration.^{14,15}

One should note that the impurity phases in PG, including SiO_2 and Al_2O_3 , accelerate the $CaSO_4$ decomposition.¹⁶ Briefly, $CaSO_4$ reacts with the impurity phases and yields composite oxides, as described below:^{6,16,17}

$$CaSO_4 + SiO_2 + CO \Rightarrow CaSiO_3 + SO_2 + CO_2 \quad (4)$$

$$CaSO_4 + SiO_2 + CO \rightarrow Ca_2SiO_4 + SO_2 + CO_2$$
 (5)

$$CaSO_4 + Al_2O_3 + SiO_2 + CO \Rightarrow Ca_2Al(AlSiO_7) + + 2SO_2 + 2CO_2$$
(6)

On the other hand, Fe₂O₃ can improve the CaSO₄ decomposition because a little of the Fe₂O₃ is present in PG. Moreover, Fe₂O₃ first reacted with CaO to form $Ca_2Fe_2O_5$ and, then, the $Ca_2Fe_2O_5$ phase reacted with Fe_2O_3 to produce CaFe₂O₄. Ca₂Fe₂O₅ (40.66 %), and CaFe₂O₄ (47.76 %) phases are observed after sintering at 750 °C for 9 h, whereas CaFe₂O₄ became the major phase after sintering at 850 °C.18 The dense CaSiO3 ceramic with a densification temperature range of 930-970 °C are successfully fabricated via a traditional solid-state preparation process.¹⁹ The belite cements (Ca₂SiO₄) were synthesized at low temperature (1000 °C) by using silica fume and natural zeolite as the raw materials.²⁰ In this work, the PG has CaSO₄ and SiO₂ with a thin diameter, and a low-melting-point impurity, such as P₂O₅, K₂O, CaF₂, etc., which can reduce the reaction temperature of the CaSO₄ and SiO₂.

The SEM image and EDS spectrum of the PG/carbon 100, calcined at 1100 °C for 2 h, are presented in **Figure 7**. Some nonuniform and irregular particles are ob-



Figure 6: XRD patterns of PG/carbon 100 mixtures calcined at different temperature for 2 h





Figure 7: SEM image and EDS spectrum of PG/carbon 100 calcined at 1100 $^{\circ}\mathrm{C}$ for 2 h

served. The EDS analysis reveals that the particle (spot-A), with a smooth and molten morphology might be a larnite or calico-olivine (**Figure 7a**).²¹ On the other hand, the small flaky particle (spot-B) corresponds to the gehlenite (**Figure 7b**). Moreover, the coralloid particle (spot-C) represents the presence of CaO (**Figure 7c**). The whisker particle (spot D) corresponds to CaO with a Si and Fe background (**Figure 7d**).

4 CONCLUSIONS

In the absence of carbon, only a small amount of anhydrite decomposed after sintering at 1200 °C for 2 h. Moreover, undesirable oldhamite products were observed after sintering in the temperature range 800 °C to 1200 °C in a PG/carbon50 mixture, PG/carbon/FeSO₄ mixtures, and PG/FeS₂ mixtures embedded in carbon, respectively.

After calcination at 1100 °C for 2 h, the diffraction peaks of the anhydrite phase were not observed in the

Materiali in tehnologije / Materials and technology 54 (2020) 6, 861-865

PG/carbon100 mixtures. The main phases were wollastonite-2M, larnite, calico-olivine and gehlenite, and a minor amount of lime. Interestingly, it can be concluded that the reducing atmosphere, provided by the carbon, renders a more prominent influence of anhydrite decomposition to lime than the $FeSO_4$ and FeS_2 .

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