

## دراسة عن عملية تكوير مساحيق الصخور الفوسفاتية المتوسطة والمنخفضة الحجم

شيه وي مين، هو دونغ شنغ، وو يويوان، شيه تشي هاو، تشي روان، هو جين يانغ  
كلية شينغفا للتعدين، معهد ووهان للتكنولوجيا، ووهان، الصين

### الملخص

في هذا البحث، تم دراسة تأثير العديد من معلمات عملية التكوير على جودة الكريات الناتجة باستخدام جهاز تكوير القرص بواسطة مساحيق صخور الفوسفات المنخفضة والمتوسطة الحجم كمواد خام. وأظهرت النتائج أن مقاومة الضغط المحسنة للكريات الخام والمجففة كانت 12.84 نيوتن و 54.58 نيوتن، على التوالي، عندما كانت درجة دقة المواد 74 ميكرون مع محتوى 86.60%، وكانت كمية البنتونيت المضافة 2.5%، وكانت نسبة الرطوبة 8% وكان محتوى رطوبة الكرية الخام 10%. وصلت مقاومة الانضغاط للمنتج النهائي إلى 930 نيوتن عن طريق التسخين المسبق عند 600 درجة مئوية لمدة 10 دقائق، ودرجة حرارة التكليل 1200 درجة مئوية لمدة 10 دقائق. أظهرت دراسة أجريت على الطور المعدني للكريات الناتجة أن زيادة مقاومة الكريات بعد التكليل نتجت عن تفاعل الحالة الصلبة داخل الكريات أثناء عملية التكليل عالية الحرارة. تسببت هذه العملية في تقلص حجم وانضغاط هيكل الكريات، وتم تلييد جزيئات الكريات في لوح.

# Study on the pelletizing process of medium- and low-grade phosphate rock powders

Xie Weimin, He Dongsheng\*, Wu Yuyuan, Xie Zhihao, Chi Ruan, Hu Yang

College of Xingfa Mining, Wuhan Institute of Technology, Wuhan 430073, China,

\*Corresponding author: csuhy@126.com

## Abstract

The effect of several pelleting process parameters on the quality of the resultant pellets was investigated by using a disk pelletizer with low- and medium-grade phosphate rock powders as the raw materials. The results showed that the optimized compressive strengths of raw and dried pellets were 12.84 N and 54.58 N, respectively, when the material fineness was  $-74\mu\text{m}$  with an 86.60% content. The amount of added bentonite was 2.5%, the wetting moisture was 8% and the raw pellet moisture content was 10%. The compressive strength of the finished product reached 930 N using a preheating temperature of 600 °C for 10 min, and a calcination temperature of 1200 °C for 10 min. A study on the mineral phase of the finished balls showed that the increased pellet strength after calcination was caused by a solid-state reaction within the pellets during the high-temperature calcination process. This process caused volume shrinking and a compacted structure of the pellets, and the pellet particles were sintered into a plate.

**Keywords:** Calcination; compressive strength; low and medium grade phosphate rock powder; pellet; pelletization.

## 1. Introduction

Yellow phosphorus is an important raw chemical that is used to produce many kinds of phosphides and phosphates for a wide range of applications (Zhu, 2008; Yan *et al.*, 2017). After many years of mining, much of the phosphorous-rich lump ore used for the production of yellow phosphorus has been exhausted (He *et al.*, 2017; Sasikumar, 2016), so the future of yellow phosphorus production is unclear. Notably, the mining and processing of phosphate rocks produce many high-grade ore fines. While the average pulverization rate of these materials is approximately 20%, it can be greater than 50% (Luo, 2012). Currently, this part of high-grade ore fines cannot be used to produce yellow phosphorus via electric furnace. If the phosphate ore powder could be prepared as pellets rather than as lump ore, it could be used for phosphorus production. This would allow the waste from ore powder production to be utilized, and it would also add to the supply of high-grade lump ore (Saffar *et al.*, 2018). Using pellet-based methods to produce yellow phosphorus also reduces energy consumption (Wu *et al.*, 1994), saves production costs, and is an economical and environment friendly approach that can effectively allow for the complete use of phosphate rock powders (Cheng, 2015).

The phosphate rock powder pelletizing process is well-established and includes nodulation in North

America and pellet roasting in Germany. However, there are some limitations when it comes to improving the grade of phosphate rock pellets produced from this process. Most domestic phosphate rock pellets use expensive inorganic binders, resulting in a high overall production cost for yellow phosphorus. Unfortunately, organic binders have low carbonization temperatures, which causes a large number of pellets to be pulverized and which creates a more difficult and costly yellow phosphorus refining process (Luo, 2017). For this study, the pellets were prepared from phosphate rock powder. By optimizing the pelletizing conditions and preheating roasting parameters, finished pellets were obtained that had excellent performance. The mechanism of the roasting process was analyzed. It provided an effective solution for the difficult utilization of phosphate rock powder in yellow phosphorus enterprises.

## 2. Materials and methods

### 2.1 Materials

The phosphate rock for this study was provided by Guizhou Kaiyang Shuangyang Phosphate Mine Co., Ltd. Bentonite was used as the binder. It was received from Wuhan Iron and Steel Company. Deionized water was prepared in our laboratory.

## 2.2 Preparation of pellets

The pelletizing method of phosphate rock is similar to that of iron ore; that is, 89 g of pretreated phosphate rock powder and 3 g of bentonite were evenly mixed. Next, 8 g of distilled water was added to mix artificially, and then directly used to make the pellets. Then a disk pelletizer was used to obtain raw balls. Some of the representative raw balls were taken as samples for the performance tests. The remaining materials were dried. Once the obtain dry balls were obtained, they were calcined using a different roasting system. This resulted in the finished balls. For other tests, a similar process was utilized except the ratios of phosphate rock, bentonite, and distilled water were varied.

## 2.3 Testing and characterization

The main parameters for the disk pelletizer used in the pelletizing test were as follows: disk diameter 800 mm; edge height 210 mm; rotational speed 22 rpm; and inclination angle 40-55°.

Preheating and roasting tests were carried out in a horizontal tube furnace from 25 to 1400 °C, which was made by docking two tube furnaces: an iron-chromium-aluminum wire resistance furnace for preheating and a silicon-carbon tube resistance furnace for roasting. During the testing, the dry balls were installed in the porcelain ark.

The compression strength of the raw and dry pellets was tested using a YHKC-2A particle strength tester (test range 0-500N). The compression strength of the finished pellets was measured by an HX2QT-10C pellet pressure tester (voltage 220V, power 750W, nominal maximum strength 10000N). The compression strengths of the 10 pellets were measured each time and then averaged in units of N/piece. Particle size analysis was carried out with a laser particle size analyzer (Easysizer20).

The X-ray fluorescence (XRF) analysis of phosphate rock and bentonite was obtained using a F-4600 Molecular Fluorescence Spectrometer (Hitachi Ltd.).

Mineral Liberation Analysis (MLA) was used to analyze the phosphate rock, an electron microscope model Quanta 250, an acceleration voltage 200V-30kV. This was supplemented by a EDAX GENESIS Energy Spectrometer and a Scanning Electron Microscopy.

## 3. Results

### 3.1 Related properties of raw materials

The chemical compositions of the phosphate rock and the bentonite are shown in Table 1 and Table 2, respectively. As shown in Table 1, the P<sub>2</sub>O<sub>5</sub> content in the phosphate rock powder is 26.34%, the MgO content is 2.21% and the SiO<sub>2</sub> content is 16.90%. The P<sub>2</sub>O<sub>5</sub> mineral powder has a low grade, which makes it difficult to use directly in the production of wet-process phosphoric acid (Tao, 2008).

**Table 1.** Chemical composition analysis of phosphate rocks (%)

Compound	MgO	Al <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	SO <sub>3</sub>	I
Content	2.21	5.54	26.34	16.90	39.10	1.15	0.16	1.32	0.011
Compound	K <sub>2</sub> O	CO <sub>2</sub>	CuO	BaO	MnO	SrO	TiO <sub>2</sub>	Y <sub>2</sub> O <sub>3</sub>	Total
Content	1.10	5.04	0.025	0.69	0.098	0.065	0.26	0.009	100

**Table 2.** Chemical composition analysis of bentonite (%)

Compound	TFe	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	P	S	Ig
Content	1.45	64.22	13.11	2.7	1.98	1.27	1.87	0.045	0.011	13.00

The ore powder was screened. Figure 1 shows particle size composition. The data indicates that the particle size of the ore powder has an uneven distribution. Approximately 37% of the particles are +5 mm, and approximately 22% are -1 mm. Particles with grain sizes of -5 +4 mm, -4 +3 mm, -3 +2 mm and -2 +1 mm, and all have around 10% content. Due to the coarse particle sizes, it is not possible to make pellets directly, so a crushing step is necessary.

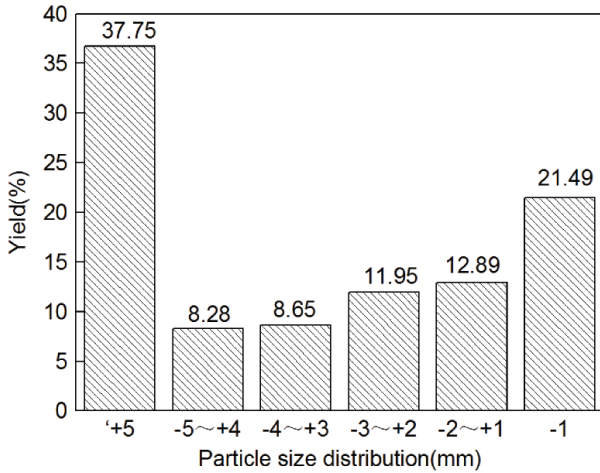


Fig. 1. Mineral particle size composition.

### 3. 2 Pelletizing test

#### 3.2.1 Impact of the material fineness

Within the same material, a finer particle size induces a stronger capillary effect because particles can pack more closely, this results in an increased compressive strength (Sun *et al.*, 2014; Fan *et al.*, 2012). However, during the pelletization process, finer materials have slower water migration, which causes a lower rate of raw ball growth and a more difficult drying process (Xue *et al.*, 2008). Therefore, the fineness of the material used for pelletizing needs to be optimized. An optimized pelletizing time of approximately 18 min (same as below) with 3% bentonite and 8% wetting moisture was selected. The pellets were made directly after wetting. Test results are shown in Figure 2. As the fineness of the material increases, the compressive strength of the raw balls and dry balls increases then decreases. The compressive strength of the raw ball is 11.7 N with approximately 86.60% of material at a fineness of -74 $\mu$ m. The compressive strength of the analogous dry ball is also better, reaching 56.5 N. Considering all these factors, a material fineness of -74 $\mu$ m and a content of 86.60% is optimal.

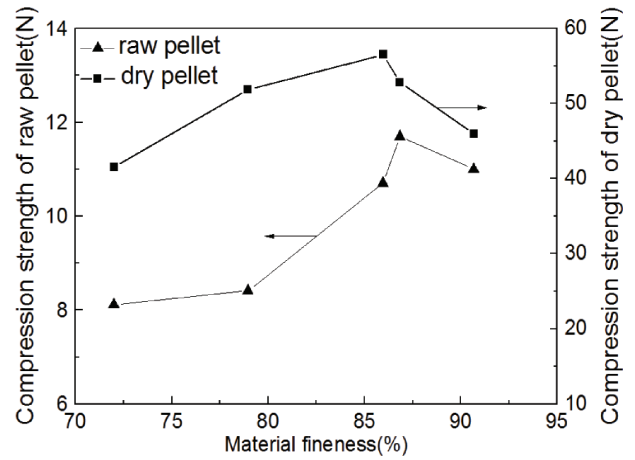


Fig. 2. Impact of material fineness on compressive strength of pellets.

#### 3.2.2 Impact of the bentonite dosage

Bentonite is a strong water absorber and is therefore an important factor in regulating and controlling the free water content of the pellets. If the free water in the raw pellets reaches the saturation point, the capillary adhesion of the pellets improves, and as a result, the strength of the pellets is enhanced (Feng *et al.*, 2009). Using a material fineness of 86.60% and a wetting moisture of 8%, the effects of various bentonite contents on the properties of the raw dry balls were investigated. The results are shown in Figure 3. The tests show that increased bentonite content causes a gradual increase in the compressive strength of raw and dry balls; however, when the content reached a certain amount, the strength decreased slightly. Maximum strengths were achieved with 2.5% bentonite, where the compressive strength of the raw ball is 12.84 N and the compressive strength of the dry ball is 52.83 N. This indicates that the optimal amount of bentonite is 2.5%.

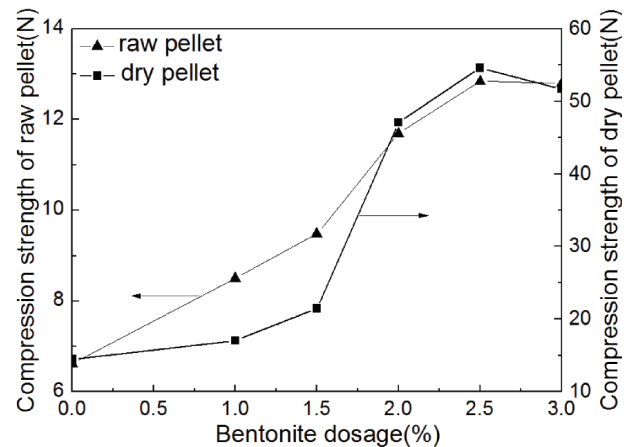
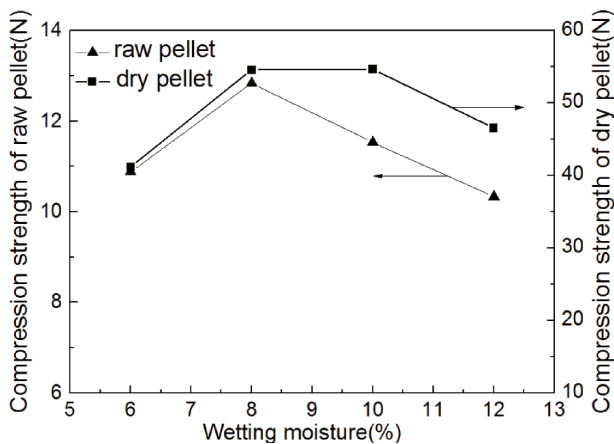


Fig. 3. Effect of bentonite content on compressive strength of pellets.

### 3.2.3 Impact of wetting moisture

The effects of various wetting moistures on the properties of raw and dry balls were investigated using materials with a fineness of 86.60% and 2.5% bentonite content. Experimental results are shown in Figure 4. As the wetting moisture improves, the pellet strength also improves. As the wetting moisture increases, the compressive strength increases then decreases. This is because the capillary moisture between the phosphate rock particles is insufficient in the early stages of pelletizing such that the particles cannot come into close contact. This causes fragile mother balls. Consequently, the raw balls are difficult to grow. During this time, adding a certain amount of water is beneficial to the ball formation process, but if the humidity of the raw material is too large, the mother balls become too wet, bonding and deformation will occur easily. This would then lead to weak ball products with high plasticity. Considering these factors, the optimal wetting water content is 8%.

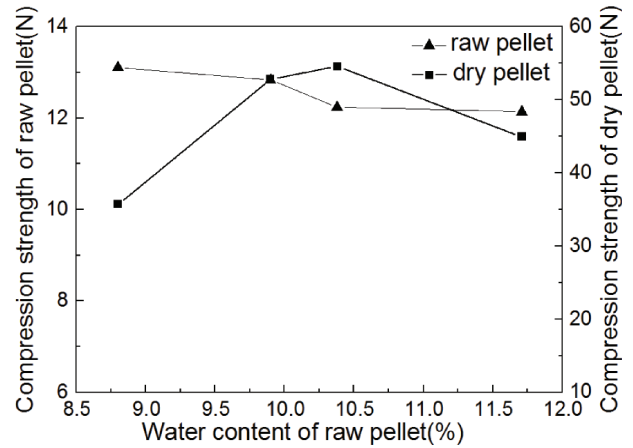


**Fig. 4.** Effect of wetting moisture on compressive strength of pellets.

### 3.2.4 Impact of water content of raw pellets

Using a material fineness of 86.60%, 2.5% bentonite and a wetting moisture of 8%, the influence of pellet water content on the properties of the pellets was examined. The test results are shown in Figure 5. As increasing amounts of water are added during the pelletizing process, the compressive strength of the raw pellets decreases gradually, while the compressive strength of the dry pellets first increases and then decreases. The measured strengths varied significantly, indicating that the wetting water within the raw material was optimal. In the process

of ball formation, only a small amount of water was added to form the mother balls. The optimal water content is approximately 10% and gives a compression strength of 12.84 N for the raw balls and a compression strength of 54.58 N for the dry balls.



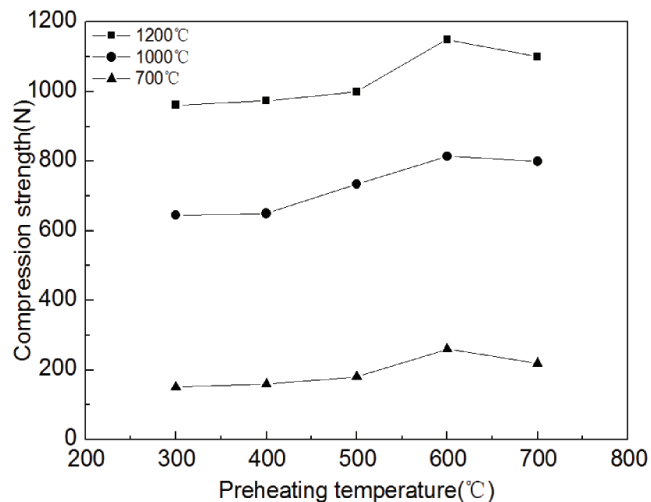
**Fig. 5.** Effect of raw pellet water content on compressive strength of pellets.

## 3.3 Preheating and roasting tests

### 3.3.1 Impact of temperature

The raw pellets were dried, preheated and roasted to obtain the finished balls. The preheating and roasting times were both 30 min. The roasting temperatures were 700 °C, 1000 °C, and 1200 °C. The effect of the preheating temperature on the strength of the finished ball was investigated. Figure 6 shows the test results. The compressive strength of the finished balls increases with increasing preheating temperature. When the preheating temperature is 600 °C, the compressive strength reaches a peak value of 1150 N. As the preheating temperature continues to rise, the compressive strength decreases slightly, so the optimal preheating temperature is 600 °C. The three calcination temperature curves indicate that higher calcination temperatures give the finished balls higher compression strengths; however, increasing the calcination temperature also increases the energy consumption. As such, the optimal calcination temperature is 1200 °C, which gives compressive strengths that best meet the requirements of yellow phosphorus production.

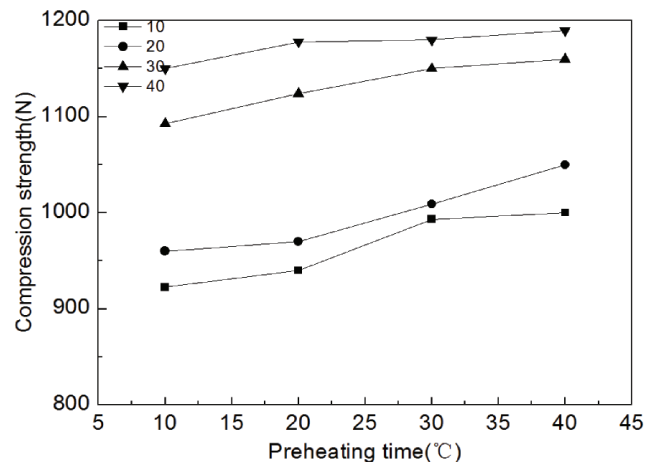




**Fig. 6.** Impact of preheating temperature on compressive strength of finished balls at different calcination temperatures.

### 3.3.2 Impact of time

Using a preheating temperature of 600 °C and a calcination temperature of 1200 °C, the effects of various preheating times on the strength of the finished balls were examined. The test results are shown in Figure 7. These four curves represent the relationship between compressive strength and preheating time using roasting times of 10, 20, 30 and 40 min. Figure 7 indicates that, as preheating time is prolonged, the compressive strength of the finished pellets increases slightly. However, this change is not significant, indicating that the preheating time has little effect on the roasting process. Therefore, the optimal preheating time is set at 10 min. The compressive strengths of the finished balls trend similarly under different calcination times. Longer calcination times give greater compressive strengths, which indicates that the roasting time has a stronger effect on the performance of the finished pellets than preheating time. Prolonging the roasting time increases the pellet density. Combined with the increased compressive strength, this suggests a more perfect recrystallization. Since the calcination time is only 10 min, this process meets the requirements for yellow phosphorus production. The roasting time is set at 10 min to reduce the energy consumption and meet production requirements.

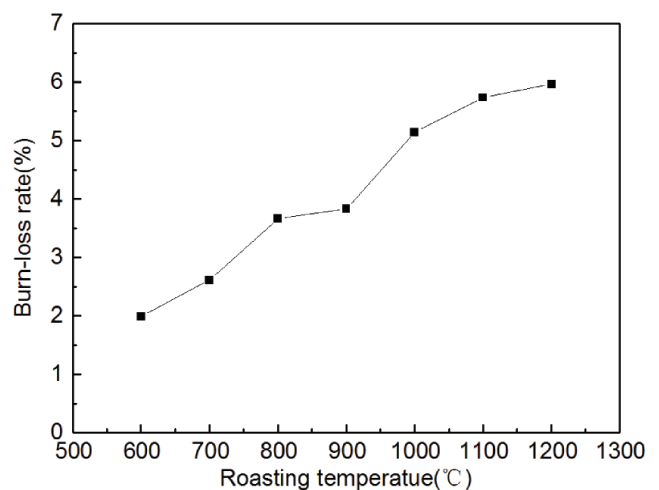


**Fig. 7.** Effect of preheating time on compressive strength of finished balls at different roasting times.

## 3.4 Mechanism analysis of roasting process

### 3.4.1 Burn-loss rate of the roasting process

The burn-loss rates of the finished balls at different calcination rates were examined. Figure 8 shows the results. The burn-loss rate increases gradually as the calcination temperature increases, and the maximum rate is reached when the calcination temperature is 1200 °C. This suggests decomposition of hydrates, carbonates and some oxides occurs during the calcination process, which results in the decreased quality (Cai *et al.*, 2014). After testing, the grade of  $P_2O_5$  increased from 26.34% to 28.14% when the preheating temperature was 600 °C.



**Fig. 8.** Effect of calcination temperature on burn-loss rate of finished balls (Preheating temperature was 600 °C, time was 10 min, and calcination time was 10 min.).

### 3.4.2 Primary mineral composition before and after calcination of the phosphate rock powder

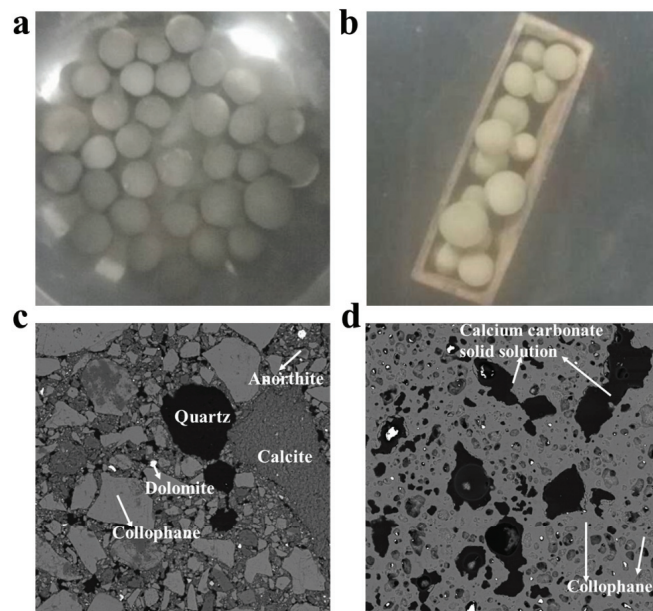
Table 3 shows that before roasting, the content of calcite and dolomite in the pellets was 10.12% and 3.35%, respectively, for a combined total of 13.47%. In the process of pellet roasting, dolomite and calcite are pyrolyzed to produce CO<sub>2</sub> gas and solid CaO and MgO. The main reaction is shown in formulas (1-3) (Zheng *et al.*, 1998). After calcination, the primary minerals in the phosphate rock pellets are collophane and a colloidal calcium silicate solid solution with a content of 17%. This means that the calcium and magnesium carbonate minerals are fully decomposed during the roasting process. At the same time, the solid phase reaction occurs during the roasting process, resulting in the volume shrinkage and compacted structure of the pellets. These both increase the mechanical strength of the finished pellets.

### 3.4.3 Comparison of pellets before and after roasting

Figure 9 shows images of the pellets before and after roasting. Comparing Figure 9(a) and (b), it can be clearly seen that pellet color has changed after roasting, indicating that chemical reactions have taken place throughout the pellets during roasting. In combination with the changes of the chemical composition of the pellets before and after combustion (shown in Table. 3), it can be determined that a chemical reaction has occurred between the components of the pellets. In order to better understand the pellet structure changes before and after roasting, an MLA analysis was performed. Figure 9(c) shows that, after adding bentonite, the particles agglomerate; however, the individual particles are still clearly visible. After roasting at 1200 °C (Figure 9(d)), the pellets have been completely sintered into a plate, which indicates the occurrence of a solid-state reaction that causes the pellets to shrink in volume and compact in structure. This changed during the process improves the mechanical strength of the finished pellets.

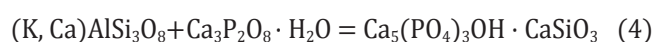
**Table 3.** Main mineral composition before and after calcination of pellets (%)

Mineral name	Pre-roasting mass ratio	Mass ratio after roasting
Calcite	10.12	0
Dolomite	3.35	0
Collophane	71.91	81.67
Quartz	6.27	0.38
Anorthite	4.47	0.44
Orthoclase	0.77	0.06
Calcium silicate solid solution in phosphate rock	0	17.42



**Fig. 9.** Images of pellets (a) before roasting, (b) after roasting. SEM images of pellets (c) before roasting, (d) after roasting.

Based on the morphology of the pellets before and after roasting in Figure 9, combined with the composition comparison in Table 3, the possible chemical reactions of the pellets during the calcination process can be inferred, as shown in Formula 1-4.



#### 4. Conclusions

- (1) The optimized pelletizing conditions are: material fineness:  $-74\mu\text{m}$  at 86.60%; bentonite dosage: 2.5%; wetting moisture: 8%; water content of the raw pellet: 10%. The compressive strengths of the resultant raw pellets and dry pellets are 12.84 N and 54.58 N, respectively. Calcination temperature has the greatest influence on the compressive strength of the finished balls. The optimal preheating and roasting conditions are: preheating temperature, 600 °C; preheating time, 10 min; roasting temperature, 1200 °C; roasting time, 10 min. The compressive strength of the finished balls can reach 930 N, which meets the requirements of yellow phosphorus production.
- (2) During the pellet roasting process, the dolomite and calcite are thermally decomposed. After calcination at 1200 °C for 10 min, the burn-loss rate is approximately 6%, and the grade of the  $\text{P}_2\text{O}_5$  increases by 1.74%. This reduces the energy consumption during the yellow phosphorus production process.
- (3) The primary minerals in the phosphate rock pellets are colloidal phosphate and a colloidal calcium silicate solid solution with a content up to 17%. After calcination at 1200 °C, the pellets were sintered into a plate, which accounts for their significant improvement in strength.

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