BX08 - Experimental Research on Preparation of Low Density and High Strength Oil Fracturing Proppant with Bauxite Beneficiation Tailings

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Abstract

In this work, the low density and high strength oil fracturing proppant was first prepared using bauxite beneficiation tailings as the main raw material. The effects of raw material pre-calcination, the iron content, sintering temperature, sintering time and additive dosage on proppant performance were studied. The results indicated that the iron content of bauxite beneficiation tailings was reduced to 2.0 % by magnetic separation, then was pre-calcined at 700 °C for 2 hours, the additive dosage of dextrin of 1.2 %, and the raw meal granules were calcined at 1360 °C for 160min, the formed oil fracturing proppant size was between 0.42 and 0.84 mm, its bulk density was 1.54 g/cm^3, apparent density was 2.81 g/cm^3, and breakage rate under 52 MPa closed pressure was 3.53 %.The prepared oil fracturing proppant can meet the SY/T 5108-2014 requirements according to the standard of proppant using for hydraulic fracturing and gravel packed.

Keywords: Bauxite, beneficiation tailings, low density and high strength, oil fracturing proppant, breakage rate.

1. Introduction

In the process of low-grade bauxite beneficiation, a large number of beneficiation tailings will be produced. The tailings output ratio was generally 25~40 %, and the yield of tailings was increased with the reduction of A/S of the raw ore. Beneficiation tailings was usually handled by tailings pond storage or solidified storage, which not only had huge investment in infrastructure in the early stage, but also had high cost of follow-up management and maintenance, which increased the economic burden of enterprises, occupied a large amount of land, and had potential environmental and safety hazards [1-4]. Bauxite beneficiation tailings contain a large number of clay minerals with extremely fine particle size, viscous properties and low alumina content. By reasonably controlling the contents of Fe_2O_3, K_2O and Na_2O in the tailings, it can be used to produce high-quality low-density oil fracturing proppant. At present, the oil fracturing proppant was mainly made from bauxite [5-8].At present, the production capacity of medium density oil fracturing proppant was seriously excessive in China, while the production capacity of high density high strength and low density high strength oil fracturing proppant was seriously insufficient, especially the demand for low density products was strong, and the domestic market production was very limited, which will be an important development direction of oil fracturing proppant in the near future. In view of the low comprehensive utilization rate of bauxite beneficiation tailings and the serious shortage of low density and high strength oil fracturing proppant in China, the experimental research on Preparation of low density and high strength oil fracturing proppant with beneficiation tailings was carried out.

2. Test

2.1 Test Materials

The bauxite beneficiation tailings used in the test came from a bauxite concentrator in Henan Province. The chemical composition analysis of the tailings is shown in Table 1, and the phase analysis results are shown in Table 2.

Table 1. The chemical composition analysis results of bauxite beneficiation tailings.

Element	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	K_2O	Na_2O	CaO	MgO
Content, %	43.78	32.4	5.46	2.75	0.78	0.16	0.35	0.28

Table 2. The phase analysis results of bauxite beneficiation tailings.

Mineral	Diaspore	Kaolinite	Illite	Hematite	Calcite	Rutile	Anatase
Content, %	19.6	58.2	11.1	5.5	0.6	0.9	1.8

It can be seen from table 1 and table 2 that the beneficiation tailings sourced from Henan Province as raw materials, the main aluminum bearing minerals were diaspore, the main silicon bearing minerals were kaolinite and illite, the main ironbearing minerals were hematite, and the main titanium bearing minerals were rutile and anatase. Its chemical composition basically meets the requirements of low-density oil fracturing proppant for main raw materials.

2.2 Experimental Method

The iron minerals were removed from bauxite beneficiation tailings by high gradient magnetic separator; the beneficiation tailings after iron removal was pre-calcined at 650~800 °C, and then mixed with a certain amount of dextrin as additive, and then crushed to a particle size less than 0.0374 mm. The above-mentioned materials were granulated by forced stirring granulator to make 18~35 mesh semi-finished products. The semi-finished granules were dried to moisture content less than 3%, and then sintered in a high-temperature tubular rotary furnace. The sintering temperature was 1280~1360 °C, and the sintering time was 1-3 hours, and the low-density oil fracturing proppant with particle size of 20-40 mesh was prepared.

2.2.1 Pelletizing Process

The high-speed stirring granulator was used for granulation. Before granulation, the powder and water were added into the container, and then the high-speed mixing was carried out. The powder and water were fully mixed, and then the bulbar nucleus was slowly formed and gradually grew up. When the particle grows to a certain size, the needle rod on the stirring rod will smash the ball particles beyond the size again, and the process of ball growing again. After the particles grew to the target size, a small amount of reserved powder with the same formula was quickly put into use for surface coating and polishing, so that the surface of the particles will be smoother, the interior will be denser and easy to disperse.

2.2.2 Sintering Process

A High temperature tubular rotary furnace was used to sinter the products. The qualified raw meal granules were dried and added into the automatic feeding bin, the heating curve was set, the inclination angle and rotation speed of rotary furnace were adjusted, the proppant sintering test was carried out. The sintered products were screened for 20~40 mesh size, and the properties of roundness, sphericity, bulk density and breakage rate of different closing pressure were measured.

2.3 Measurement Method

The sphericity, bulk density, apparent density and breakage rate of high strength oil fracturing proppant were measured and calculated according to SY/T 5108-2014 "Measurement of properties of proppants used in hydraulic fracturing and gravel-packing operations" [9]. In this paper, the X'pert MPD Pro X-ray diffractometer was used to analyze the phase of the samples, and the JSM-6360LVscanning electron microscope was used to observe the structure of proppant. The 20~40 mesh low density and high strength oil fracturing proppant met the following criteria: roundness and sphericity greater than 0.9, bulk density was less than or equal to 1.65 g/cm^3, apparent density was less than or equal to 3.00 g/cm^3, and breakage rate under 52 MPa closed pressure was less than or equal to 9.0 %.

3. Results and Discussion

3.1 Effect of Iron Removal on Properties of the Finished Pellets

In the test, the iron minerals were removed from bauxite beneficiation tailings by high gradient magnetic separator. When the content of Fe_2O_3 in raw materials after iron removal was 5.0 %, 4.0 %, 3.0 %, 2.0 % and 1.0%, 700 °C was used for pre-calcination, and then granulation and sintering tests were carried out. The test results were shown in Figure 1.

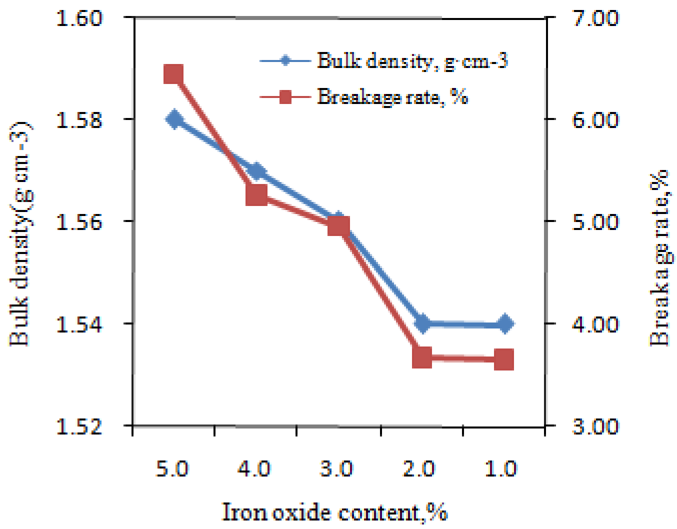

Figure 1. Effect of different Fe_2O_3 content on properties of the finished pellets.

It can be seen from Figure 1 that iron removal from bauxite beneficiation tailings was beneficial to the improvement of product performance. With the decrease of iron content, the bulk density of finished pellets decreased as a whole at the same sintering temperature and sintering time, the breakage rate under 52 MPa closed pressure gradually decreased and tended to be stable. When the Fe_2O_3 content in the raw material was reduced to 2.0 %, the volume density was 1.54g /cm^3, and the breakage rate under 52 MPa was 3.67 %. However, when the Fe_2O_3 content was reduced to 1.0 %, the bulk density and the breakage rate under 52M Pa of the product did not change much. Therefore, considering the production cost, it was appropriate to control the Fe_2O_3 content of the raw ore at about 2.0 %.

3.2 Effect of Raw Material Pre-calcination on Pelletizing Property

In order to study the effect of raw material pre-calcination on pelletizing property, four kinds of raw materials were obtained from bauxite beneficiation tailings after iron removal by pre-calcination at different temperatures of 650 ℃, 700 ℃, 750 ℃ and 800 ℃ respectively for 2 hours, and then granulation tests were carried out for the four raw materials respectively. The test results are shown in Table 3.

Table 3. Effect of different pre-calcination temperature on pelletizing property.

Pre-calcination Temperature °C	The properties of 20~40 mesh		Phenomenon
	Yield %	Sphericity	
Untreated	41.35	＞0.6	Particle size was not uniform, sphericity was poor
650	51.46	＞0.8	Particle size was uniform, sphericity was good
700	60.85	＞0.9	Particle size was uniform, sphericity was the best
750	53.47	＞0.8	Particle size was uniform, sphericity was good
800	40.23	＞0.5	Particle size was not uniform, sphericity was poor, strength was low

It can be seen from Table 3, when the raw material of bauxite beneficiation tailings was pelletized, the particle size was not uniform, the sphericity was poor, and the raw meal granules yield of 20~40 mesh was low; compared to when the bauxite beneficiation tailings was pelletized after pre-calcination, the particle size was relatively uniform and the sphericity is good. With the increased of temperature, the raw meal granules yield of 20~40 mesh first increased and then decreased. When the pre-calcination temperature reached 700 °C, the highest yield could reach up to 60.85 % and the sphericity was the best. However, when the pre-calcination temperature reached 800 °C, the powder became dry and loose, the agglomeration between particles was weakened, and the plasticity was poor, which led to the poor pelletizing effect. After comprehensive consideration, the appropriate pre-calcination temperature 700 °C was selected.

3.3 Effect of Sintering Temperature on Properties of the Finished Pellets

The sintering temperature directly affected the grain size, the composition and quantity of liquid phase, as well as the morphology and quantity of pores, which comprehensively affect the properties of the oil fracturing proppant. When the sintering time was 160 minutes, the test was carried out to study the sintering temperature of raw meal granules prepared from bauxite beneficiation tailings after iron removal. The test results are shown in Figure 2.

It can be seen from Figure 2 that the performance of the finished pellets will be affected by too low or too high sintering temperature. When the sintering temperature was 1320 °C, the sintering temperature was too low, so the finished pellets were not completely sintered, which can not form a solid frame, the structure was loose, and the strength was low. When the sintering temperature was 1400 °C, the temperature was too high, the finished pellets will be too sintered, and the particles will bond together, and the strength will also decrease. Therefore, for the bauxite beneficiation tailings after iron removal, combined with product index and production energy consumption, the suitable sintering temperature was 1360~1380 °C.

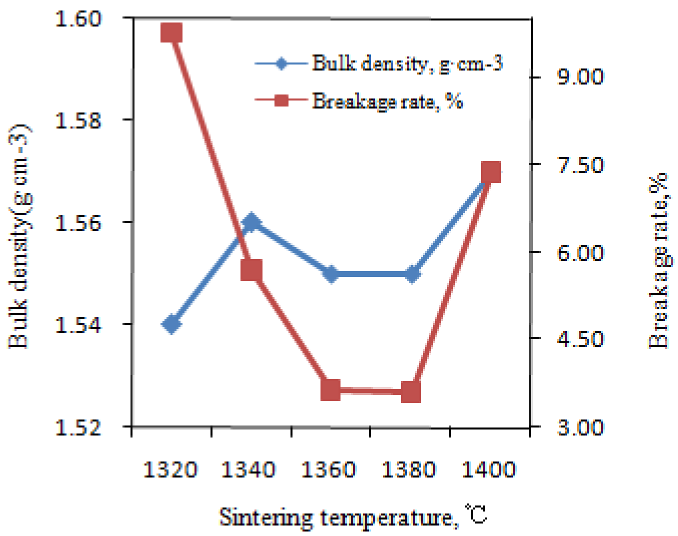

Figure 2. Effect of different sintering temperatures on the properties of the finished pellets.

3.4 Effect of Sintering Time on Properties of the Finished Pellets

When the sintering temperature was 1360 °C, the determination on the influence of sintering time on the bulk density and breakage rate of the finished pellets was carried out. The results are shown in Figure 3. It can be seen from Figure 3 that with the extension of sintering time, the breakage rate under 52 MPa closed pressure of the finished pellets decreased first and then increased. Because of the short sintering time the raw material surface can not fully melt and form a closed structure. With the increased of the opening rate, the strength of proppant decreased, resulting in the increase of its breakage rate. With the increase of sintering time, new solid phase precipitated, and new grain boundaries were produced. The original grains grew up gradually, which will deteriorate the homogeneity of microstructure and increase the breakage rate [10]. Comprehensive comparison shows that the finished pellets can achieve better performance at 1360 °C and sintering time of 150~170 minutes.

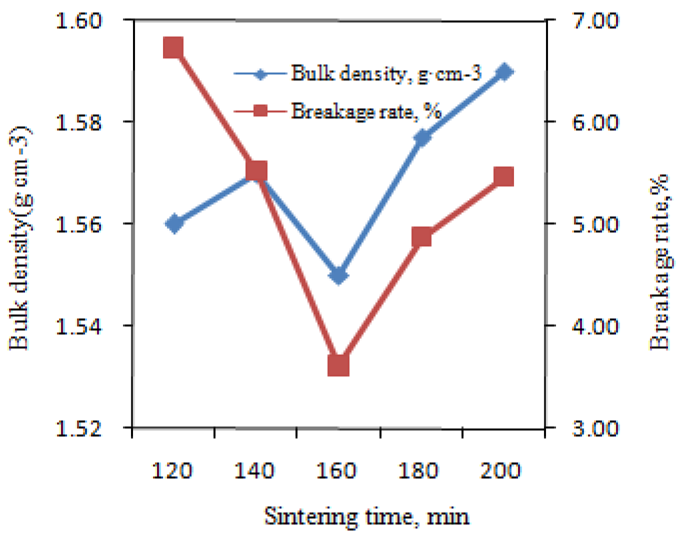

Figure 3. Effect of different sintering time on the properties of the finished pellets.

3.5 Effect of Additive Dosage on Properties of the Finished Pellets

Dextrin can be used as an additive in the granulation process because it has a certain bond effect, when it is directly mixed with the powder and added with a certain amount of water. The use of additives in granulation was not only to increase the performance of the finished pellets, but also to increase the viscosity of the powder, reduce the difficulty of granulation and prevent the failure of granulation due to the weak viscosity of the powder. However, when the additive was excessive, it led to the agglomeration of the pellets and made the granulation effect worse. In order to investigate the effect of additive dosage on properties of the finished pellets, the effects of different dextrin dosages such as 0%, 0.8 %, 1.0 %, 1.2 %, 1.4 % and 1.6 % on the bulk density and breakage rate of the finished pellets were carried out. The results are shown in Figure 4.

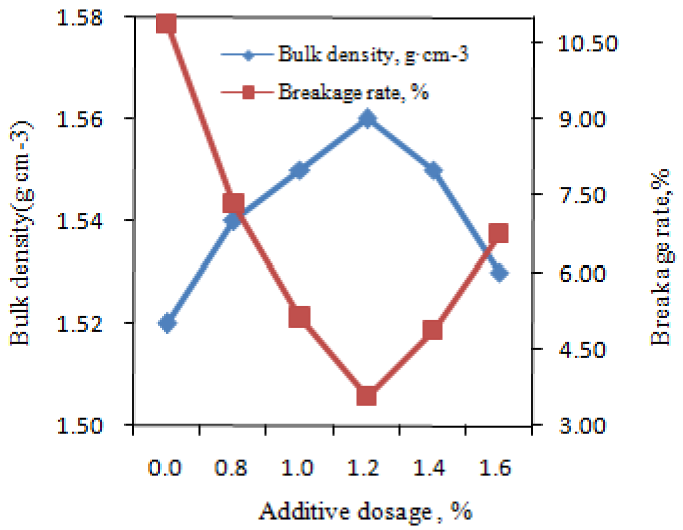

Figure 4. Effect of different additive dosage on the properties of the finished pellets.

It can be seen from Figure 4 that with the increased of additive dosage, the bulk density of the finished pellets increased first and then decreased, and the breakage rate under 52 MPa closed pressure decreased first and then increased. When the dosage of dextrin was 1.2 %, the lowest breakage rate can reach 3.57 %. Considering comprehensively, the additive dosage of bauxite beneficiation tailings in granulation was determined to be 1.2 %.

3.6 Product Analysis

Under the above optimal conditions, the 20~40 mesh oil fracturing proppant products were prepared by magnetic separation, pre-calcination, granulation and sintering of the bauxite beneficiation tailings in Henan Province. The XRD phase analysis and SEM morphology analysis of the products are shown in Figure 5 and Figure 6 respectively. According to SY/T 5108-2014 "Measurement of properties of proppants used in hydraulic fracturing and gravel-packing operations", the performance index of the best oil fracturing proppant was measured and calculated. The results are shown in Table 4.

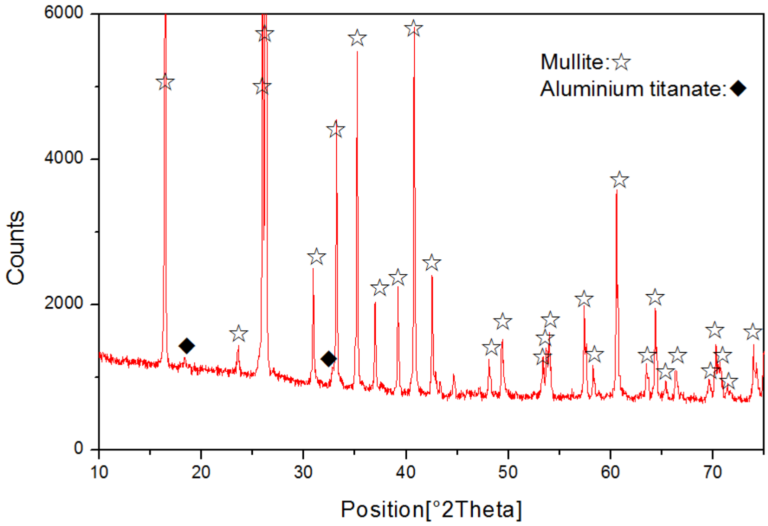

Figure 5. XRD analysis of the oil fracturing proppant samples.

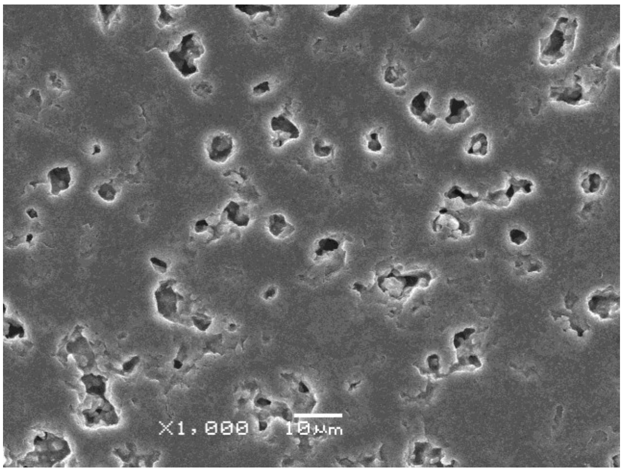

Figure 6. SEM microstructure of the oil fracturing proppant samples.

Table 4. The test results of the oil fracturing proppant from bauxite beneficiation tailings.

Test items	Detection result	Standard requirements	Result judgment
Bulk density, g/cm^3	1.54	≤1.65	Qualified
Apparent density, g/cm^3	2.81	≤3.00	Qualified
Breakage rate under 52 MPa closed pressure, %	3.53	≤9.0	Qualified
Roundness	0.9	≥0.80	Qualified
Sphericity	0.9	≥0.80	Qualified
Turbidity, FTU	58.3	≤100	Qualified
Acid solubility, %	3.6	≤5.0	Qualified

It can be seen from Figure 5 and Figure 6 that under the optimal conditions, the main phase composition of oil fracturing proppant prepared from bauxite beneficiation tailings was mullite and aluminum titanate. The internal structure of oil fracturing proppant was dense, the crystal was fully developed, mainly mullite phase, pore distribution was uniform, there was a certain amount of mullite grain in the pore, which improved the compressive strength of the product. According to the test results in Table 4, the product indexes prepared by bauxite beneficiation tailings met the requirements of low density and high strength oil fracturing proppant standard.

4. Conclusions

The bauxite beneficiation tailings used as raw materials was sourced from Henan Province, the iron content was reduced to 2.0 % by magnetic separation, then was pre-calcined at 700 °C for 2 hours, the additive dosage of dextrin of 1.2 %, the low density and high strength oil fracturing proppant was prepared after granulation and sintering. The raw meal granules were calcined at 1360 °C for 160 min, the formed oil fracturing proppant size was between 0.42 and 0.84 mm, its bulk density was 1.54 g/cm^3, apparent density was 2.81 g/cm^3, and breakage rate under 52 MPa closed pressure was 3.53 %. The prepared oil fracturing proppant met the SY/T 5108-2014 requirements according to the standard of proppant using for hydraulic fracturing and gravel packed.

Through the analysis of the micro morphology and phase of the sample, the main crystalline phase was mullite, the internal structure was dense, the crystal was fully developed, pore distribution was uniform, there was a certain amount of mullite grain in the pore, which improved the compressive strength of the product.

The low density and high strength oil fracturing proppant prepared by using bauxite beneficiation tailings, compared with using conventional raw materials to produce the low density and high strength oil fracturing proppant, can realize the efficient utilization of bauxite tailings, effectively reduce the environmental and safety risks in the process of ore dressing tailings stockpiling, with low production cost and has significant economic and social benefits.

5. References

1. Wang Erxing, Study on the paste stocking technology of bauxite flotation tailings, *Light Metals* 2013, (7): 4-7.
2. DuanWeiping, Guo Jinfeng, Wang Bin, Stacking process of metal mine tailings in china and its development trend, *Metal Mine*, 2013, (12):118-122.
3. Chen Dianzhu, Analysis and research of stacking process and comprehensive utilization of solid mine-tailings, *Hunan Nonferrous Metals*, 2016, (4): 5-8.
4. Chen Zhongxian, Risk analysis and countermeasure for safe operation of dry stacking tailings reservoir, *World Nonferrous Metals*, 2019, (15): 89-90.
5. ChenYe, Lu Jiaxuan, The development of a new oil fracturing proppant, *Journal of Guizhou University of Technology (Natural Science Edition)*, 2003, (4): 24-26.
6. Lv Baoqiang, Liu Shun, Bi Weiyu, Study on preparation process for low density ceramisite proppant, *Foundry Technology*, 2012, (7): 771-773.
7. Xu Na, Li Yonggang, XuYafei, Investigation of preparing oil fracturing proppant using low grade bauxite, *Mining & Metallurgy,* 2016, (5): 55-58.
8. Xu Yafei, Xu Na, Li Yonggang, Study on pelletizing process of oil fracturing proppant preparation by monohydrallite with high iron content, *Mining& Metallurgy*, 2016, (6): 55-59.
9. SY/T 5108-2014, The PRC oil and gas industry standards. Measurement of properties of proppants used in hydraulic fracturing and gravel-packing operations, *Petroleum Industry Press*, 2015, 5-22.
10. Lv Baoqiang, Liu Shun, Bi Weiyu, Study on preparation process for low density ceramisite proppant, *Foundry Technology*, 2012, 33 (7): 771-773.