

Experimental Research on Preparation of Ultra-Low-Density Ceramsite Proppant with Bauxite Waste Rock

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Abstract

In this work, the ultra-low-density ceramsite proppant was first prepared using bauxite waste rock as the main raw material. The effects of raw material pre-calcination, sintering temperature, sintering time and additive dosage on proppant performance were studied. The results indicated that the Henan bauxite waste rock was pre-calcinated at 750°C for 2 hours, the additive dosage of CMC of 1.5%, and the raw meal granules were calcined at 1320°C for 150min, the formed ceramsite proppant size was between 0.42 and 0.84 mm, its bulk density was 1.41g/cm³, apparent density was 2.53g/cm³, and breakage rate under 52 MPa closed pressure was 5.26%. The prepared ceramsite proppant can meet the SY/T 5108-2014 requirements according to the standard of proppant using for hydraulic fracturing and gravel packed.

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1. Introduction

In the mining process of bauxite, a large number of hard clay ores and low-grade ores stripped from mining roof and floor will be produced. Under the current market economic situation, they are discharged as waste residue, which not only wastes valuable mineral resources and causes economic losses of enterprises, but also occupies a lot of land and funds, which is not conducive to environmental protection^[1,2]. The main contents of bauxite waste rock are SiO₂ and Al₂O₃. By reasonably controlling the contents of Fe₂O₃, K₂O and Na₂O in the waste rock, it can be used to produce low-density ceramsite proppant^[3,4]. At present, the production capacity of medium density ceramsite proppant in China is seriously excessive, while the production capacity of ultra-low-density ceramsite proppant is seriously insufficient, which is an important development direction of ceramsite proppant in the near and future^[5,6]. From the perspective of raw materials, the preparation of high performance ceramsite proppant from industrial solid waste represents the development direction of oil fracturing proppant, and the research of low cost and high performance ceramsite proppant will be highly valued and developed^[7-10]. In view of the low comprehensive utilization rate of bauxite mining waste rock and the serious shortage of ultra-low-density ceramsite proppant productivity in China, the experimental research on the preparation of ultra-low-density ceramsite proppant from mining waste rock was carried out.

2. Test

2.1 Test materials

The bauxite waste rock used in the test came from a bauxite mining plant in Henan Province, , which was hard clay ore. The chemical composition analysis of bauxite waste rock is shown in Table 1, and the phase analysis results are shown in Table 2.

Table 1. The chemical composition analysis results of bauxitewaste rock.

Element	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	TiO ₂	K ₂ O	Na ₂ O	CaO	MgO
Content/%	40.26	42.33	1.30	1.95	0.11	0.01	0.16	0.07

Table 2. The phase analysis results of bauxite waste rock.

Mineral	Diaspore	Kaolinite	Illite	Hematite	Anatase	Rutile
Content/%	5.10	89.90	1.10	1.30	1.55	0.40

It can be seen from Table 1 and Table 2 that the waste rock 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 iron bearing minerals were hematite, and the main titanium bearing minerals were anatase and rutile. Its chemical composition basically meets the requirements of ultra-low-density ceramics proppant for main raw materials.

2.2 Experimental method

The bauxite waste rock was pre-calcined at 650°C to 800°C. It was then mixed with a certain amount of carboxymethyl cellulose (CMC) as additive, and then crushed to a particle size less than 0.0374mm. 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°C to 1360°C, and the sintering time was 1-3 hours, and the ultra-low-density ceramics proppant with particle size of 20-40 mesh was prepared.

2.2.1 Pelletizing process

The highspeed 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 were 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. Then 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”^[11]. In this paper, the x'pert MPD Pro X-ray diffractometer was used to analyze the phase of the samples, and the JSM-6360LV scanning 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 1.65g/cm³, apparent density was less than or equal to 3.00g/cm³, and breakage rate under 52 MPa closed pressure was less than or equal to 9.0%.

3. Results and discussion

3.1 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 waste rock by pre-calcination at different temperatures of 650°C, 700°C, 750°C and 800°C 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	41.15	>0.6	Particle size was not uniform, sphericity was poor
650	49.62	>0.8	Particle size was uniform, sphericity was good
700	55.73	>0.9	Particle size was uniform, sphericity was good
750	62.36	>0.9	Particle size was uniform, sphericity was the best
800	48.35	>0.7	Particle size was not uniform, sphericity was poor, strength was low

It can be seen from Table 3, when the raw material of bauxite waste rock 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 waste rock 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 750°C, the highest yield could reach up to 62.36% 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 was determined as 750°C.

3.2 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 ceramsite proppant. When the sintering time was 150 minutes, the test was carried out to study the sintering temperature of raw meal granules prepared from bauxitewaste rock. The test results are shown in Figure 1.

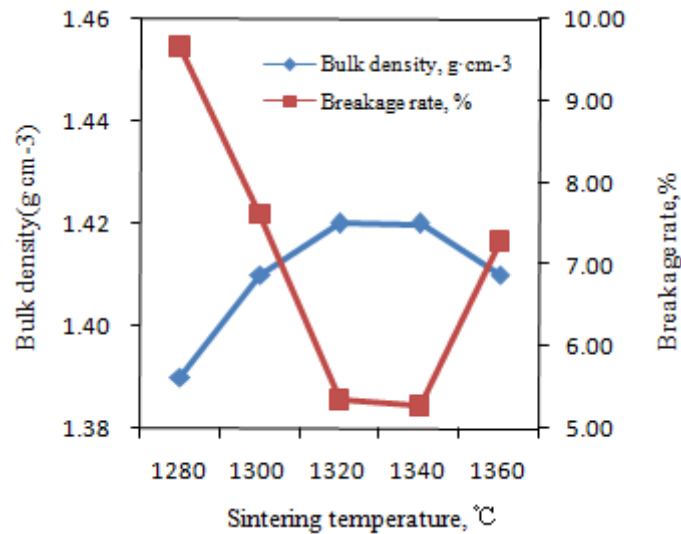


Figure 1. Effect of different sintering temperatures on the properties of the finished pellets.

It can be seen from Figure 1 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 cannot form a solid frame, the structure was loose and the strength was low. When the sintering temperature was 1360°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 bauxitewaste rock, combined with product index and production energy consumption, the suitable sintering temperature was 1320-1340°C.

3.3 Effect of sintering time on properties of the finished pellets

When the sintering temperature was 1320°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 2. It can be seen from Figure 2 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 cannot 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^[12]. Comprehensive comparison shows that the finished pellets can achieve better performance at 1320°C and sintering time of 140-160 minute.

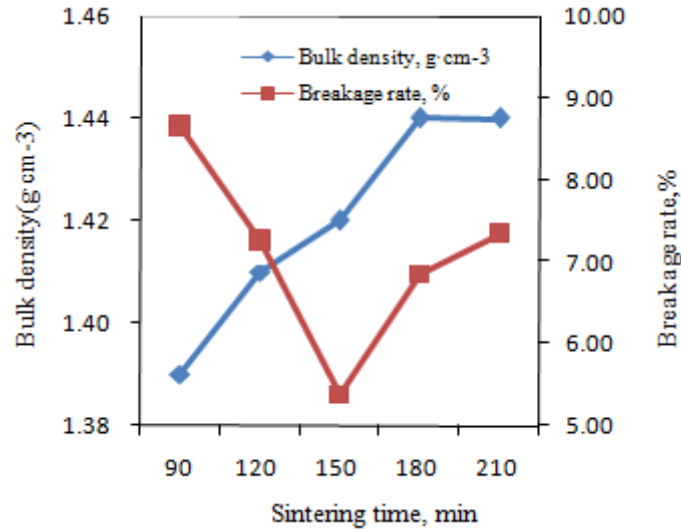


Figure 2. Effect of different sintering time on the properties of the finished pellets.

3.4 Effect of additive dosage on properties of the finished pellets

Carboxymethyl cellulose 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 CMC dosages such as 0%, 0.5%, 1.0%, 1.5%, 2.0% and 2.5% on the bulk density and breakage rate of the finished pellets were carried out. The results are shown in Figure 3.

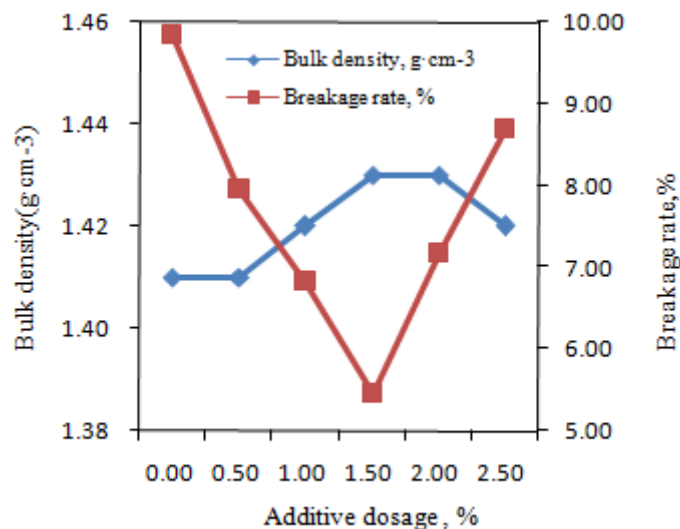


Figure 3. Effect of different additive dosage on the properties of the finished pellets.

It can be seen from Figure 3 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. At a dosage of 1.5% CMC, the lowest breakage rate

of 5.46% was achieved. Considering comprehensively, the additive dosage of bauxite waste rock in granulation was determined to be 1.5%.

3.5 Product analysis

Under the above optimal conditions, the 20-40 mesh ceramsite proppant products were prepared by pre-calcination, granulation and sintering of the bauxite waste rock in Henan Province. The XRD phase analysis and SEM morphology analysis of the products were shown in Figure 4 and Figure 5 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 ceramsite proppant was measured and calculated. The results are shown in Table 4.

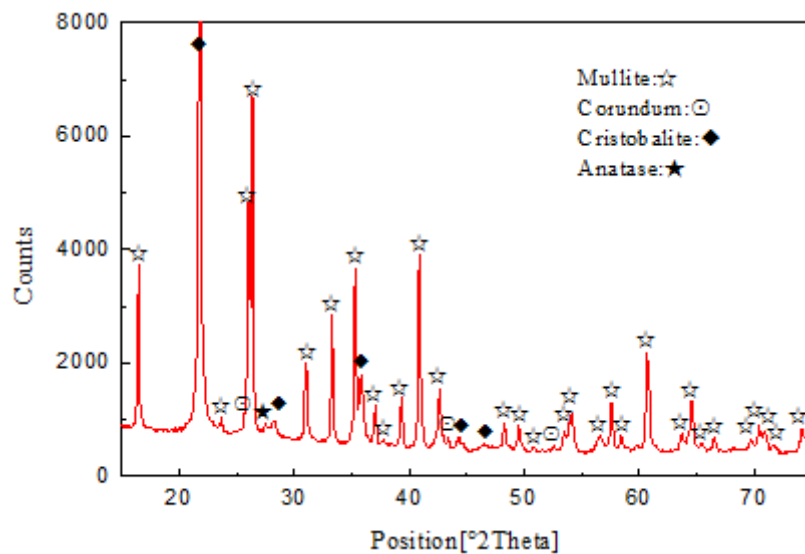


Figure 4. XRD analysis of the ceramsite proppant samples.

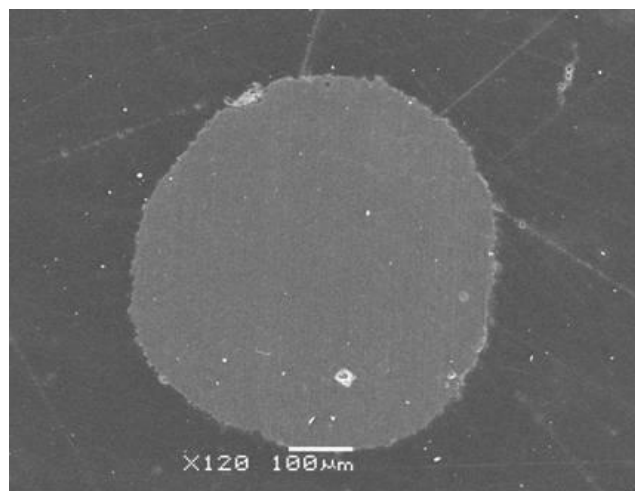


Figure 5. SEM microstructure of the ceramsite proppant samples.

Table 4. The test results of the ceramsite proppant from bauxite waste rock.

Test items	Detection result	Standard requirements	Result judgment
Bulk density, g/cm ³	1.41	≤1.65	Qualified
Apparent density, g/cm ³	2.53	≤3.00	Qualified
Breakage rate under 52 MPa closed pressure, %	5.26	≤9.0	Qualified
Roundness	0.9	≥0.80	Qualified
Sphericity	0.9	≥0.80	Qualified
Turbidity, FTU	55	≤100	Qualified
Acid solubility, %	3.2	≤5.0	Qualified

It can be seen from Figure 4 and Figure 5 that under the optimal conditions, the main phase composition of ceramsite proppant prepared from bauxite waste rock was mullite, corundum and cristobalite. Ceramsite proppant has dense internal structure and complete crystal development, mainly mullite phase, which improved the compressive strength of the product. According to the test results in Table 4, the product indexes prepared by bauxite waste rock met the requirements of low density and high strength ceramsite proppant standard.

4. Conclusions

The bauxite waste rock used as raw materials was sourced from Henan Province, which was pre-calcined at 750°C for 2 hours, the additive dosage of CMC of 1.5%, the ultra-low-density ceramsite proppant was prepared after granulation and sintering. The raw meal granules were calcined at 1320°C for 150min, the formed ceramsite proppant size was between 0.42 and 0.84 mm, its bulk density was 1.41g/cm³, apparent density was 2.53g/cm³, and breakage rate under 52 MPa closed pressure was 5.26%. The prepared ceramsite 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, corundum and cristobalite. The internal structure was dense and the crystal was fully developed, which improved the compressive strength of the product.

The ultra-low-density ceramsite proppant prepared by using bauxite waste rock, compared with using conventional raw materials to produce the low density ceramsite proppant, can realize the efficient utilization of bauxite waste rock.

This will effectively reduce the environmental and safety risks in the process of waste rock stacking, with low production cost and has significant economic and social benefits.

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