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Research Article

Low-Density and High-Strength Fracking Proppant Made by High-Alumina Fly Ash

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Coal Combustion and Gasification Products

High-alumina fly ash is defined to have alumina (Al_2O_3) content of no less than 40%, according to the Chinese power industry standard DL/T 2297. Specification for resource utilization categorization of fly ash from coal-fired power plant (Standard No. DL/T 2297-2021), and is considered a valuable raw material to replace bauxite for making aluminum, refractory materials, and fracking proppants, etc. A low-density and high-strength proppant, conventionally made with bauxite, has been successfully made by high-alumina fly ash and commercially used in the market. This new high-alumina fly-ash–derived proppant has some advantages compared with the bauxite-derived proppant: (1) lower raw material cost, (2) fewer processing steps and less energy consumption, (3) equal or better performance.

1. INTRODUCTION[1]

Because of a quickly growing economy and increasing energy demands, China has become the largest coal-producing and -consumption country in the world and generates more than 50% of global fly ash in volume. Among the estimated 112 billion tons of Chinese coal reserves, China has a proven reserve of high-alumina coal of about 32 billion tons (~28% of the total coal reserve), mostly located in northern Shanxi province and midwest Inner Mongolia regions. Currently, the annual production of high-alumina fly ash in China is about 25 million (<5% of the total fly ash) with a utilization rate of less than 20%.

China also has a proven bauxite reserve volume of 830 million tons, ranks in the ninth place worldwide, and has produced more than 44 million tons from its bauxite mine since 2010. The consumption of bauxite in China has reached 100 million tons, with more than 48% imported since 2013 (Zhang 2012). The application utilization of bauxite in China is about 80% aluminum industry, 15% refractory materials, and 5% ceramics and others (Yan 2013). The use of high-alumina fly ash for bauxite-based applications not only reduces solid waste, but also preserves natural resources.

The Chinese power industry standard DL/T 2297-2021 (2021), specification for resource utilization categorization of fly ash from coal-fired power plant, specifies fly ash with alumina (Al_2O_3) content no less than 40% as high-alumina fly ash. It is a highly valuable raw material to replace bauxite in many bauxite-based applications. One of the applications is to extract aluminum from high-alumina fly ash by either an acidic or a basic method. However, the extraction process produces about 3–8 times more by-products in volume, which necessitates additional technologies to convert these by-products into useful commodities. Even though the entire process and overall economy is challenging, aluminum extraction from high-alumina fly ash is considered a strategic national resource for China.

Another application of high-alumina fly ash is as a replacement for bauxite for making fracking proppants. A low-density and high-strength fracking proppant using high-alumina fly ash in the conventional bauxite-based commercial process has been developed (Ding 2017), and is commercially made and sold on the market.

2. FRACKING PROPPANTS FOR OIL AND NATURAL GAS WELLS

Fracking proppants are the solid particles used to support the channel formation of fractured rock using the hydraulic fracturing technique to let the subterranean oil and gas flow through the cracked channel in the process of producing oil, natural gas, or shale gas. The desired properties of fracking proppants are high crush strength, low apparent den-

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Table 1. Various material types of proppant in different density and crush-strength ranges.

	Bulk density	<1.35	1.35–1.65	1.65–1.8	>1.8
	Apparent density	<2.35	2.35–3.0	3–3.35	>3.35
Crush strength	Types	Ultra low	Low	Medium	High
28 MPa	Low	Nut shell	Quartz sand		
52 MPa	Mid		New trend	Ceramics	
69 MPa	Mid-high			Ceramics	Ceramics
86 MPa	High				Coated ceramics
103 MPa	Ultra high				Coated ceramics

sity, good acid erosion resistance, high sphericity, and high flow conductivity to increase the gas output and exploitation rate. Depending on the size and capacity of the well, each well can consume up to 1,000 tons of proppants. The global market value for proppant is about 7.4 billion USD in 2013 (Visiongain 2013). The fracking proppants are classified according to material types (natural and man-made), density, crush strength, and size. Different types of materials are used to meet the different bulk/apparent density and crush strength as listed in Table 1. Bauxite is the typical raw material to make ceramics-type, high-strength proppants.

The market trend for the hydraulic fracking technology is to use fewer chemicals and lower-density, higher-crush-strength proppants, for example, an apparent density less than 3.00 g/cm^3 (bulk density less than 1.65 g/cm^3) and strength no less than 52 MPa. The global market volume for low-density and high-strength proppant is about 2 million tons, and is expected to grow to 4 million tons in 2025.

Performance requirements of low-density and high-strength proppants are specified in various standards, including International Standard (ISO) 13503-02 and Chinese Standard SY/T 5108-2014 (2014) based on ISO 13503-02 (2006). The fracking proppants are also classified by size, ranging from 8 to 140 meshes (2.36 mm–106 μm). The size classifications include 12/20 mesh (840–1,680 μm), 16/20 mesh (840–1,180 μm), 16/30 mesh (600–1,180 μm), 20/40 mesh (420–840 μm), 30/50 mesh (300–600 μm), 40/60 mesh, 40/70 mesh (212–420 μm), 70/140 mesh (106–212 μm), etc. The most common and most frequently referred to size is 20/40 mesh. Table 2 lists the performance requirements of 20/40 low-density and high-strength proppants according to Chinese Standard SY/T 5108-2014 (2014).

The main industrial process used to make proppant is the sintering process (Fitzgibbon 1989), because it leads to higher yield, consumes less energy, and results in less pollution as compared with the electrical melting process (Zhou 1989). The process includes crushing, calcination, mixing and grinding, pelletization , drying, sintering, screening for suitable size, and packaging for sale.

Most ceramic proppants are fabricated using bauxite, kaolin, or clay as the raw materials (Qu 1993; Guan 2001; Xu 2002; Ding 2010, 2012). Some research on fly-ash–derived proppant has been reported. There are no commercial fly-ash–derived proppants currently on the market. Wu et al. (2017) prepared ceramic proppants with low density and high strength, using fly ash as the main raw material. Wu's

Table 2. Chinese Standard SY/T 5108-2014 (2014) for 20/40 low-density high-strength proppants.

Properties/samples		Chinese Standard SY/T 5108-2014 (2014) requirements
Sieve analysis (wt%)		
U.S. mesh	Micrometers	
16	1,180	≤0.1
20	850	≤7
25	710	≥90
30	600	
35	500	
40	425	
50	300	≤1
Pan		
Crush rate at 52 MPa (7,500 psi)		≤9.00%
Bulk density (g/cm^3)		≤1.65
Apparent density (g/cm^3)		≤3.00
Roundness		≥0.70
Sphericity		≥0.70
Acid solubility (by weight)		≤7.0%
Turbidity (NTU)		≤100

research showed that the original chemical components in the fly ash played important roles in the process of preparing ceramic proppants. Low-density and high-strength proppants were fabricated using fly ash as one of the main raw materials among eight different compositions (He 2021). The as-fabricated proppants sintered at 1,160°C for 60 min had the lowest crushing rate of only 18.2% at 52 MPa and a corresponding bulk density of 1.165 g/cm^3.

Famous ceramic proppant manufacturers in the world include Carbo Ceramics in the United States, Saint-gobain Proppant in France, Diamond Ceramics in China, and Curimbaba Group in Brazil. Carbo Ceramics and Saint-gobain are the oldest ceramic proppant suppliers and have produced ceramic proppants since the 1980s. In recent years more than 50% of global ceramic proppants have been produced in China. Top Chinese proppant suppliers include Shandong Jingang New Materials Co. Ltd., Xinmi Wanli In-

Table 3. Property comparison between 20/40 competitive and high-Al_2O_3 fly-ash–derived proppants.

Properties/samples		Chinese Standard SY/T 5108-2014 (2014)	High-Al_2O_3 fly-ash–derived proppants	Competitive A	Competitive B
Sieve analysis (wt%)					
U.S. mesh	Micrometers				
16	1,180	≤0.1	0.0	0.0	0.0
20	850	≤7	1.1	0.0	2.5
25	710	≥90	20.1	33.6	24.7
30	600		54.1	60.5	48.0
35	500		24.2	5.8	21.6
40	425		0.4	0.1	3.0
50	300	≤1	0.0	0.0	0.1
Pan			0.0	0.0	0.0
Crush rate (% fines) at 52 MPa (7,500 psi)		<9.00%	2.70%	2.4%	2.3%
Crush rate (% fines) at 68 MPa (10,000 psi)		–	6.80%	5.7%	6.1%
Bulk density (g/cm^3)		≤1.65	1.58	1.59	1.56
Apparent density (g/cm^3)		≤3.00	2.70	2.87	2.84
Roundness		≥0.70	0.8	0.7	0.8
Sphericity		≥0.70	0.8	0.8	0.8
Acid solubility		≤7.0%	3.4%	6.1%	6.2%
Turbidity (NTU)		≤100	52	26	120

dustry Development Co., Ltd., Henan Tianxiang New Materials Co. Ltd., Yu Count Oil Fracturing Proppant Co., Ltd., Yangquan Changqing Oil Fracturing Proppant Co., Ltd., Guizhou Xinyineng Ceramic Proppant Co., Ltd., Panzhihua Bingyang Technology Co. Ltd., and others.

3. HIGH-ALUMINA FLY-ASH–DERIVED PROPPANTS

In this work, a unique proppant using the high-alumina fly ash with more than 80% in the total composition has been developed. The high-alumina fly-ash–derived proppant (a NICE-made product) and two competitive bauxite-based proppants (commercial products) were tested by Stim Lab (Duncan, Oklahoma). The results listed in Table 3 show NICE-made proppants have slightly lower density at the similar crush rate and have much lower acid solubility. The high-alumina fly-ash–derived proppant has been made in the industrial bauxite-based proppant-making process. The use of high-alumina fly ash has two processing advantages: (1) it is not necessary to crush bauxite, and (2) the process can be done at a lower sintering temperature. Differences between using bauxite versus high-Al_2O_3 fly ash to make proppant in the sintering process are shown in Figure 1.

The first industrial production of 2,000 tons was conducted and the high-alumina fly ash proppant was commercially sold in 2019. The properties of the produced 20/40 proppants are listed in Table 4. The product properties completely meet ISO 13503-2 (2006) and Chinese Standard SY/T5108-2014 (2014). The production cost of this high-alumina fly-ash–derived proppant was about 150 USD (950 RMB)/ton lower than the production cost of 276 USD (1,750 RMB)/ton for conventional bauxite-derived proppants. Lower production cost of high-alumina fly-ash–derived proppants is mainly attributed to the lower raw material cost (fly ash versus bauxite), fewer processing steps (no bauxite crush), and lower sintering temperature (1,350°C versus 1,500°C).

4. CONCLUSIONS

High-alumina fly ash has an alumina (Al_2O_3) content of not less than 40%, according to the Chinese power industry standard DL/T 2297 (2021). The low-density and high-strength proppant has been successfully made by using more than 80% high-alumina fly ash. The advantages of high-alumina fly-ash–derived proppants are lower material cost, less processing energy consumption, and equivalent or better properties as compared with bauxite-based proppants.

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Table 4. Properties of 2,000 tons of high-Al_2O_3 fly-ash–derived 20/40 proppants produced in an industrial production line.

Properties/samples		High-Al_2O_3 fly-ash–derived proppants in industrial production
Sieve analysis (wt%)		
U.S. mesh	Micrometers	
16	1,180	0
20	850	0
25	710	0.4
30	600	0.45
35	500	36.17
40	425	46.34
50	300	16.57
Pan		0
Crush rate at 52 MPa (7,500 psi)		4.60%
Crush rate at 69 MPa (10,000 psi)		8.20%
Bulk density (g/cm^3)		1.41
Apparent density (g/cm^3)		2.65
Roundness		≥90
Sphericity		≥90
Acid solubility (by weight)		≤5.5%
Turbidity (NTU)		≤80

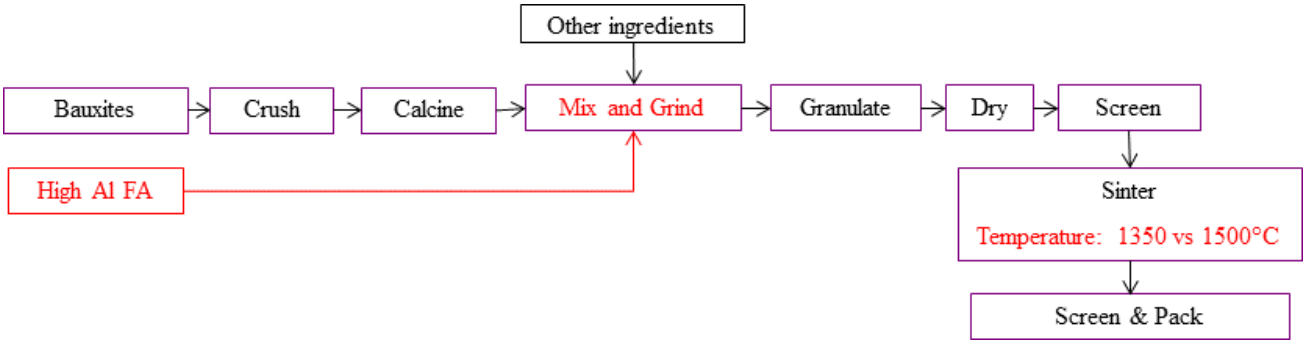

Figure 1. Comparison between high-alumina fly ash and bauxite in the sintering process.

REFERENCES

Chinese Standard. 2014. Specification for resource utilization categorization of fly ash from coal-fired power plant (Standard No. DL/T 2297-2021).

———. 2021. Specification for resource utilization categorization of fly ash from coal-fired power plant (Standard No. DL/T 2297-2021).

Ding, S.Q. 2010. Fracturing proppant with high density and high strength and its manufacture method. Chinese Patent No. CN102061159A, issued 2010.

———. 2012. Light and porous fracturing proppant and its manufacture method. Chinese Patent No. CN101696114A, issued 2012.

———. 2017. Composition for preparing fracking proppant, fracking proppant and preparation method of fracking proppant. Chinese Patent No. CN107474820B, issued 2017.

Fitzgibbon, J.J. 1989. Sintered spherical pellets containing clay as a major component useful for gas and oil well proppants. U.S. Patent No. US4879181, issued 1989.

Guan, C.L. 2001. Manufacture method of high-strength proppant. ETC Chinese Patent No. CN1179907C, issued 2001.

He, C., et al. 2021. "Preparation and Characterization of Fly Ash Ceramsite Petroleum Fracturing Proppant." *Journal of Ceramics* 42 (1): 116–21.

International Organization for Standardization. 2006. Petroleum and natural gas industries—Completion fluids and materials—Part 2: Measurement of properties of proppants used in hydraulic fracturing and gravel-packing operations (ISO Standard No. 13503-02).

Qu, Z.P. 1993. Manufacture method of high-strength proppant from bauxite. ETC Chinese Patent No. CN1085288A, issued 1993.

Visiongain. 2013. "The Proppants Market 2013–2023." London.

Wu, Xiulan, Zhezhe Huo, Qiang Ren, Huanhuan Li, Fei Lin, and Tengyue Wei. 2017. "Preparation and Characterization of Ceramic Proppants with Low Density and High Strength Using Fly Ash." *Journal of Alloys and Compounds* 702 (April): 442–48. https://doi.org/10.1016/j.jallcom.2017.01.262.

Xu, H.C. 2002. Solid proppant and its manufacture method. ETC Chinese Patent No. CN1367306A, issued 2002.

Yan, G.G. 2013. "Reasonable Utilization of Chinese Bauxite Resource." *China Quality Supervision* 6: 62–63.

Zhang, L.H. 2012. "Reasonable Development and Utilization of Bauxite Resource." *Light Metals* 2: 3–11.

Zhou, S.W. 1989. Solid proppant and its manufacture method. ETC Chinese Patent No. CN1046776A, issued 1989.