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Preparation and characterization of ceramic proppants with low density and high strength using fly ash

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ABSTRACT

Low-density high-strength and mullite-based ceramic proppants were prepared from fly ash in this study. All of the original chemical components in the fly ash played important roles in the process of preparing ceramic proppants. The phase composition and microstructure of the proppants at different sintering temperatures were investigated by X-ray diffraction and scanning electron microscope. At the best sintering temperature of 1370 °C, the performances were 5.7% of acid solubility and 5.0% of breakage ratio under 52 MPa. Moreover the apparent density was 2.61 g/cm^3. Consequently, using fly ash to prepare ceramic proppants could be an another applicable way to utilize fly ash efficiently.

1. Introduction

Since coal firing has been the main technology for power generation, the product fly ash has been one of the most current industrial waste residue which has reached 30 million tons a year in China at present stage. Together with the development of the power industry, the amount of fly ash will increase year by year. The problem of the fly ash disposal is only expected to get worse as the demand for energy grows. More and more land would be occupied to store fly ash. At the same time, the underground water could be polluted by the toxic metal. When exposed in the atmosphere, fly ash would be a threat to human health and respiratory tract, causing diseases. Definitely the comprehensive utilization of the hazardous material fly ash is urgent and is of importance to the long-term and sustainable development of industry and environment.

Fly ash is generated during the combustion of coal at the temperature between 1200 and 1700 °C which depends on the various inorganic and organic constituents of the coal [1]. Thus as the product of minerals combustion including experiencing high temperature and sudden cooling, fly ash is composed of mullite, glass and other compounds of trace elements such as magnetite. Mangialardi [2] researched four different kinds of fly ash and investigated their thermal behaviors. Wang et al. [3] investigated the relevant variations of the apparent density, compressive strength, moisture absorption, and heavy metals leachability of the sintered products as a result of the changing of the sintering temperature and time. Fly ash is generally grey in color, abrasive, mostly alkaline, and refractory in nature [4].

To solve the disposal problem and recycle the abundant waste, on the basis of the properties of various fly ash, a variety of researches on the utilization of fly ash were carried out. Kockal [5] evaluated the influence of varying proportions of different types of fly ash (used in place of feldspar) and different sintering temperatures on the sintered properties of ceramic tile bodies. After thermal treatment fly ash was proved to be suitable for use as aggregates in Portland cement or asphaltic concretes for roadways, as well as for walking or garden tiles and high temperatures mineral wool insulation [6]. The characteristics of lightweight fly ash aggregates with various binders produced by different heat treatments were investigated [7]. Besides, there were studies on ceramic membranes prepared by fly ash. A series of porous ceramic membrane supports made of waste fly ash (high-aluminum) and calcium carbonate mixtures were fabricated by in-situ reaction sintering method [8]. Ceramic microfiltration membranes with uni-axial dry compaction method and fly ash, quartz and calcium carbonate as

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inorganic precursors were fabricated [9]. Morever, fly ash can be applied to prepare porous ceramic bodies [10]. Ji et al. [11] proposed a novel method to fabricate the ceramic tile by using fly ash as the main raw material. And the rupture modulus of the samples containing 60 wt% FA and 4 wt% quartz can reach 51.28 MPa at 1200 °C.

But due to the different areas the coal derived from, the components of fly ash varies. In this study, the fly ash used is from China's Inner Mongolia whose most distinctive property is high content of alumina which can be equal for the middle-grade bauxite. In previous works, many types of low-density ceramic proppants were prepared from high-alumina bauxite used as the main raw material [12–14]. But to the best of our knowledge, no study has been reported on the low-density and high-strength ceramic proppants using fly ash. Hydraulic fracturing technology is a stimulation treatments used in many low-permeability reservoirs [15–18]. The process involves injecting fluid at a sufficient rate and pressuring to rupture the rock formation, thereby creating a crack or fracture, and thereafter placing proppants in the formation to keep the fracture walls open by resisting the forces that tend to close the fracture [19,20]. The proppants is of extreme importance as it provides the long term conductivity of the fracture. Proppants, millimeter-sized solid spherical particles with low density and high strength, form the channels to make the oil and gas flow through fluently so that the well production can be enhanced significantly [21]. The main function of the proppants is to provide and maintain conductive fractures during well production where proppants should meet closure stress requirement and show resistance to diagenesis under downhole conditions [22]. Meanwhile the fluid to carry the proppants is always organic solvents which is bad for the environment, thus the density of the proppants should be as lower as possible to reduce the harm and cost. Hence, the density crush resistance and acid resistance are vital properties for the quality of the proppants.

The aim of this study was to make full use of the special waste and hazardous material. For this purpose, ceramic proppants were prepared from fly ash which was used as the main raw material after taking all the advantages indicated as follows into account.

About the phase composition, as mentioned above, fly ash is comprised of mullite crystal nucleus which would play an important role in the formation of the complete mullite crystals and other compounds of metals that contributes to lowering the sintering temperature. Besides, as for physicochemical characteristics, fly ash has good water holding capacity and much big surface area which make it a suitable kind of raw material for plastic molding when accompanied with certain amount of plastic clay.

To reach the expectation of making waste profitable, ceramic proppants for oil fracturing were prepared from fly ash and tests were carried out to characterize proppants.

2. Experimental

2.1. Raw materials

The fly ash used was from China's Inner Mongolia. The most distinctive property of this kind of fly ash was its high content of alumina. The chemical compositions of the fly ash powder were shown in Table 1. In addition, other three kinds of raw materials except fly ash were used to produce the proppants.

Bauxite was added to enhance the molar ratio (Al_2O_3/SiO_2) of the whole formula. The bauxite derived from Henan Province of China was composed mainly of 64 wt% Al_2O_3 and 13 wt% SiO_2.

Clay was used as the plasticizer to improve the plasticity of the mixtures which was vital for the process of forming the spherical proppants. The chemical compositions of the clay were shown in Table 1.

The composite mineralizers were consisted of fluxes (substances to molten powders at low temperatures to provide bonding together) aiming to reduce the sintering temperature and ingredients which aimed to decrease the acid solubility of the proppants. The mineralizers were added to promote the sintering process and the formation of ceramic structure in a positive way in firing [10].

2.2. Experimental procedure

All the powders were mixed and homogenized by ball milling for 2 h according to the certain ratio of the mixture and water. Then nearly all the wet mixture was passed through a 300 mesh sieve. After drying, the dried lumps were crushed and passed through a sieve with an aperture size of 120 mesh. Afterwards, parts of the fine powders were put into the sugar-film coating machine to grow into the cores of the proppants for about 2 h. Then the nucleuses were coated densely by the fine powders and finally grew into spherical green bodies with certain size after rolling 3 h in the machine. At last, the samples were heated at a rate of 8 $°C \cdot min^{-1}$ to 1000 °C and afterwards at the rate of 2 $°C \cdot min^{-1}$ to certain sintering temperature ranged from 1300 to 1400 °C in the box type electrical resistance furnace. After cooling, the proppants were passed through meshes and tested.

2.3. Tests

2.3.1. Apparent density tests

Apparent density was measured by Archimedes' method and calculated with the following formula, $\rho = M/V$ where M was the weight of proppants (g) and V was the true volume (cm^3).

2.3.2. Breakage ratio and acid solubility tests

The breakage ratio was measured by the 50.8 mm cylinder whose size was strictly following the SY/T5108-2014 standards [23]. After crushing, the breakage ratio of the proppants was calculated by the following formula: $f = 100W_c/W_0$, where W_c was the weight of crushed specimens (g) while W_0 was the weight of the specimens (g) before tests.

According to the Chinese Industry Standards SY/T5108-2014 [23], the acid solubility was tested in a 12-3 hydrochloric-hydrofluoric acid solution (i.e., 12 wt% HCl and 3 wt% HF) at the specific temperature. At first 5g (W_s) proppants were added to the 100 ml acid solution and then all of them were heated in the water bath at 65 °C for 30 min. Next the sample after acid treatment were washed with deionized water and dried in an oven at 105 °C for 1 h. After getting the weight (W_a) of the sample which was treated with the acid solution, then the acid solubility (S) was got by calculating with the following Eq. (A.1).

$$S = \frac{Ws - Wa}{Ws} \times 100\% \quad (A.1)$$

Table 1
Chemical compositions of fly ash and clay (wt%).

Chemical Composition (wt%)	Al_2O_3	SiO_2	Fe_2O_3	CaO	TiO_2	K_2O	BaO	Na_2O	L.O.I
Fly Ash	49.81	43.41	2.44	2.51	1.53	0.26	0.04	–	–
Clay	39.13	44.10	0.21	0.83	1.09	0.54	–	0.26	13.84