RECYCLING OF COAL GANGUE TO PREPARE LOW DENSITY CERAMIC PROPPANTS FOR COAL BED METHANE WELLS

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Low density ceramic proppants for coal bed methane wells were successfully prepared using flint clay and solid waste coal gangue as raw materials. The addition of coal gangue greatly reduced the preparation cost. The phase composition and morphology of the proppants were examined by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results showed that the main crystal phases were rod-shaped mullite and granular cristobalite. Furthermore, the suitable amount of coal gangue added was 30 - 40 wt. %. Proppants prepared with 30 wt. % and 40 wt. % coal gangue and sintered at 1300 °C and 1350 °C had bulk densities of 1.252 g·cm⁻³ and 1.291 g·cm⁻³ and breakage ratios of 8.7 % and 6.4 % under 35 MPa closed pressure, respectively, while for those sintered at 1400 °C, the breakage ratio was 8.9 % under 52 MPa closed pressure.

INTRODUCTION

Proppants are the hard solid particles, such as quartz sands or ceramic particles, that prop the fractures in the hydraulic fracturing process that is used in the petroleum and gas wells and coal bed methane wells. The addition of proppants is indispensable in order to keep the fracture open so that the hydrocarbon production from the petroleum and gas wells and coal bed methane wells can be significantly enhanced [1-4]. Therefore, proppants are of extreme importance as they provide the long-term permeability of the fracture [5, 6].

Since the first fracturing operation was done with silica sand proppant in 1947, many materials have been used as proppants, including walnut shells, natural sand, glass, resin coated sand, sintered bauxite and kaolin, and fused zirconia [7]. Even now, sands and ceramic proppants are the two most common proppants in fracturing processes [1, 8]. Quartz sands are traditionally used owing to their low cost. However, quartz sands reduce the permeability of fracture due to their low strength and poor sphericity [8, 9]. By contrast, ceramic proppants have many advantages, such as high sphericity and roundness, high strength and hardness, high melting temperature and good chemical inertness in corrosive environments [10, 11]. Consequently, ceramic proppants are widely used in the deep oil wells. Furthermore, the low density of ceramic proppants allows them to be dragged by the fracture liquid with efficiency and prevents their accumulation in the first part of the fracture [12], whereas high-density proppants can pose severe problems in transport and placement [13]. This indicates that the development of low-density ceramic proppants with better performance is urgently required.

Currently, ceramic proppants available in the market are mainly prepared by bauxite or pure alumina, inevitably increasing the density of the proppants owing to the high alumina content of bauxite [14]. Moreover, these raw materials are expensive due to over-exploitation. Flint clay is a natural ore with rich resource in China and its main composition is Al_2O_3 and SiO_2. The use of calcined flint clay instead of bauxite to prepare ceramic proppants can reduce the density of proppants due to the lower alumina content. Coal gangue is a hazardous by-product of the coal mining industry, and the average production of coal gangue is about 10 - 15 % of raw coal production [15]. The main composition of coal gangue is also SiO_2 and Al_2O_3. The properties of ceramic proppants obtained by flint clay and coal gangue should be in some respects worse than those prepared by bauxite, but nevertheless these proppants should be suitable for coal bed methane wells and shallow oil wells.

In the present work, low-density ceramic proppants were prepared by sintering, using calcined flint clay and solid waste coal gangue as raw materials. The effects of the addition of coal gangue on the properties of ceramic proppants were systematically investigated. The maximum addition of coal gangue and corresponding sintering temperature were also determined.

EXPERIMENTAL

Raw materials

Calcined flint clay and solid waste coal gangue were obtained from the Yangquan area in Shanxi Province, China. The chemical composition of calcined flint clay and coal gangue were measured according to the Chinese Nonferrous Metals Industry Standard (YS/T 575-2007) and National Standard of PRC (GB/T 27974-2011), respectively. The test results are shown in Table 1. For thermogravimetry (TGA) of the raw materials, a TGA/DSC 3+ (Metter Toledo, Switzerland) was used and carried out between 30 °C and 1300 °C in Ar with a rate of heating at 10 °C per minute. The results are displayed in Figure 1a, b.

Table 1. Chemical composition of calcined flint clay and coal gangue (wt. %).

	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	CaO	L.O.I
Calcined flint clay	45.58	37.82	1.13	2.61	0.47	12.39
Coal gangue	36.29	45.75	3.29	1.02	0.32	13.33

Preparation of proppants

The proppants were prepared by pelleting, drying, screening and sintering. The raw material mixture ratios for the different samples are shown in Table 2. First, a certain proportion of calcined flint clay and coal gangue was stirred for 2 min in a strong mixing machine (R02, Eirich Co. Ltd, Germany) and subsequently spherical green bodies were formed with water. Second, the green bodies were dried at 90 °C for 2 h in a drying box (DH-101-2BS, Tianjin Central Experiment Furnace Co. Ltd, China), and then the dried bodies were passed through a set of 20/40 mesh sieves (aperture size 0.85 - 0.43 mm). Third, the 20/40 mesh green particles were sintered in a high temperature box-type sintering furnace (KBF1700, Nanjing Bo Yun Tong Instrument Technology Co. Ltd, China) at certain temperature for 2 h in air with a heating rate of 5 °C·min⁻¹. Finally, the cooled proppants were passed through the 20/40 mesh sieves.

Table 2. Raw material mixture ratios of the samples prepared (wt. %).

Samples	C1	C2	C3	C4	C5
Calcined flint clay	90	80	70	60	50
Coal gangue	10	20	30	40	50

Characterization

Thermogravimetry (TG) and differential scanning calorimetry (DSC) was carried out between 30 °C to 1300 °C in Ar with a heating rate of 10 °C per minute, using a TGA/DSC 3+ (Metter Toledo, Switzerland). According to the Chinese Petroleum and Gas Industry

Standard (SY/T5108-2014), bulk density and apparent density were measured by a calibrated density bottle (pyconometer), and the breakage ratio was calculated by the formula: $\eta = \omega_c/w_0 \times 100~\%$, where ω_c and w_0 were the weights of crushed specimens after and before testing, respectively. The phase composition of the proppants was identified by X-ray diffracion / XRD (X'Pert PRO; Philips Co. Ltd, Holland), utilizing Ni-filtered Cu Kα radiation (40 kV voltage). The microstructure was examined by field emission scanning electron microscopy / SEM (FESEM, S-4800; Hitachi, Japan) operated at 10 kV voltage.

RESULTS AND DISCUSSION

The TG and DSC curves for the raw materials are displayed in Figure 1. The DSC curve of calcined flint clay (Figure 1a) shows an endothermic peak at 515 °C and an exothermic peak at 990 °C. The endothermic peak is caused by the dehydroxylation of donbassite and kaolinite contained in the flint clay. Correspondingly, in the TG curve in the temperature range 400 - 700 °C there
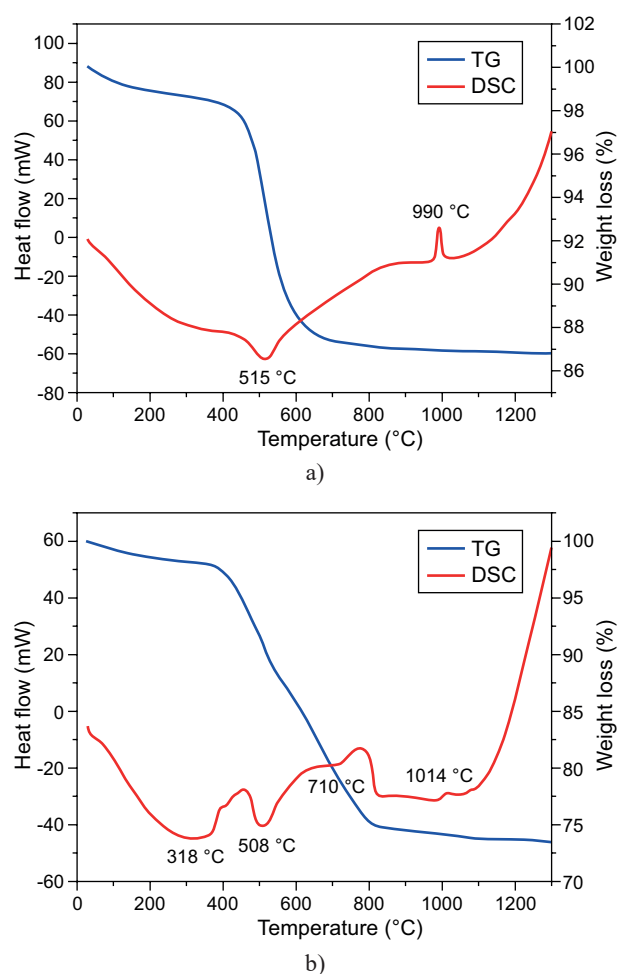
a)

b)

Figure 1. DSC and TG curves of: a) calcined flint clay and b) coal gangue.

is indication of a mass loss of 10.54 %. The exothermic peak at 990 °C corresponds to the transformation of amorphous SiO_2 into cristobalite. In Figure 1b, three endothermic peaks and an exothermic peak are observed on the coal gangue DSC curve. The first endothermic peak at 200 - 400 °C was due to the removal of crystal water, which is accompanied by a mass loss of 2.5 % at 200 - 400 °C in the TG curve. The second endothermic peak at 450 - 600 °C and the third small endothermic peak at 650 - 780 °C are caused by the dehydroxylation of kaolinite and muscovite contained in the coal gangue. The mass loss in these two intervals was 11.8 % and 7 %, respectively, in the TG curve. The small exothermic peak at 1014 °C corresponds again to a crystallization phenomenon, that is, the crystllization of cristobalite from the amorphous phase.

The bulk density and apparent density of the proppants sintered at different temperatures are shown in Figure 2a and 2b. As seen in Figure 2a, the bulk density increased in most cases as the sintering temperature increased, only that of samples C1 and C2 exhibited a slight decrease for sintering temperatures above 1400 °C. The bulk densities of C1 and C2 sintered at

different temperatures were lower than 1.3 g·cm⁻³ and reached maxima of 1.284 g·cm⁻³ and 1.275 g·cm⁻³, respectively, for a sintering temperature of 1400 °C. The bulk density of C2 was clearly lower than that of C1, which indicated that adding a small amount of gangue could reduce the density of the proppants. However, when more coal gangue is added (C3 and C4), the bulk density for low sintering temperature increased, mainly for sintering temperatures above 1350 °C. On the other hand, when the amount of coal gangue added was as high as 50 wt. %, the bulk density (C5) was significantly reduced. Bulk densities observed for C3, C4 and C5 sintered at 1400 °C were 1.389 g·cm⁻³, 1.427 g·cm⁻³ and 1.357 g·cm⁻³, respectively.

In Figure 2b, the apparent density first gradually increased and then decreased with increasing sintering temperature. This could be attributed to the generation of liquid phase with increasing temperature, which promoted the densification. The apparent density of C1 was obviously higher, while the apparent density of C5 was lower than that of other samples. The apparent density of C1 and C2 reached a maximum 2.807 g·cm⁻³ and 2.791 g·cm⁻³, respectively, for a sintering temperature of 1400 °C, while the apparent densities of the other three samples (2.758 g·cm⁻³, 2.729 g·cm⁻³ and 2.679 g·cm⁻³, for C3, C4 and C5, respectively) reached the maximum for a sintering temperature of 1350 °C. The apparent density of C3 and C4 remained more or less constant as the proppants were sintered between 1300 and 1400 °C. The apparent density of C5 was much lower than that of the other samples, obviously because of the high addition of coal gangue.

The breakage ratios of the proppants under 35 MPa closed pressure is shown in Figure 3, while the inset shows the breakage ratio under 52 MPa closed pressure. As shown in Figure 3, the breakage ratio of the proppants gradually decreases with increasing sintering temperature, obviously due to the denser structure formed by sintering at higher temperature. However, for
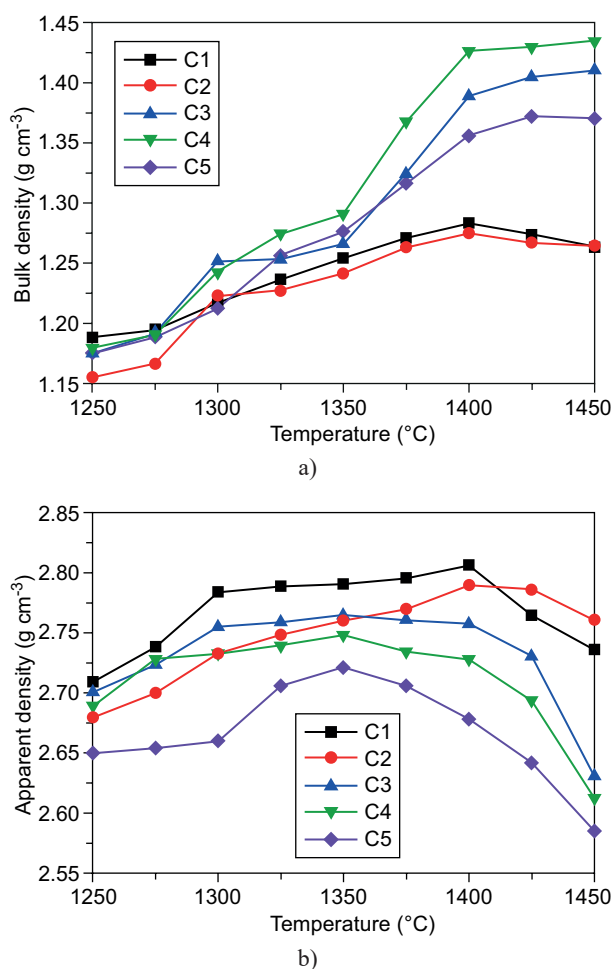

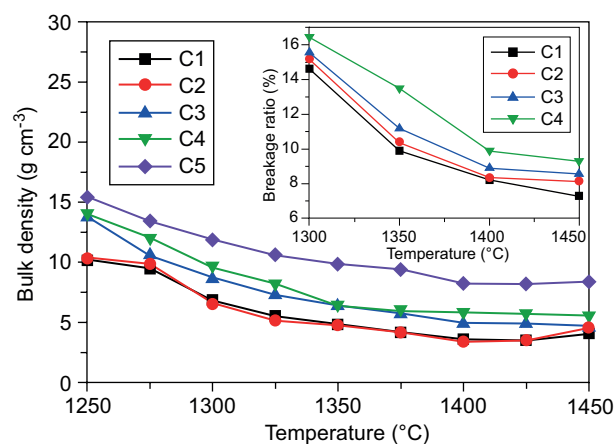Figure 2. Bulk density (a) and apparent density (b) of the proppants.

Figure 3. Breakage ratio of the proppants under 35 MPa closed pressure (or 52 MPa in the inset) as a function of the sintering temperature.

sintering temperatures higher than 1400 °C the breakage ratio does not change any more. The breakage ratios of C1 and C2 are very close (lower than 7 % under 35 MPa closed pressure for sintering temperatures above 1300 °C). When adding more coal gangue, the breakage ratio gradually increases. The breakage ratios (for 35 MPa) of C3 and C4 were 8.73% and 9.50 %, respectively, after sintering at 1300 °C, but 6.42 % and 6.36 %, respectively, after sintering at 1350 °C. The breakage ratio (for 35 MPa) of C5 was 9.82 % after sintering at 1350 °C and 8.19 % after sintering at 1400 °C. The inset in Figure 3, shows the breakage ratios under 52 MPa closed pressure. The breakage ratios observed for C1, C2, C3 and C4 under 52 MPa were 8.22 %, 8.36 %, 8.89 % and 9.87 %, respectively. The breakage ratio of C4 exceeded the standard requirement. Although adding coal gangue can further reduce the preparation cost, adding too much gangue will increase the sintering temperature and the breakage ratio will be too high. Therefore, the suitable amount of coal gangue is 30 - 40 wt. %.

In short, in order to meet the requirements of the Chinese Petroleum and Gas Industry Standard SY/T 5108-2006 (breakage ratio < 9 %, when the proppants are applied to 35 MPa closed pressure), considering the sintering temperature and raw material cost, 30 wt. % of coal gangue could be added to prepare the proppants at 1300 °C, while 40 wt. % of coal gangue could be added if the sintering temperature is increased to 1350 °C. The greater the amount of coal gangue added, the higher the sintering temperature. In proppants suitable for 52 MPa closed pressure, maximally 30 wt. % of coal gangue could be added to prepare the proppants at 1400 °C.
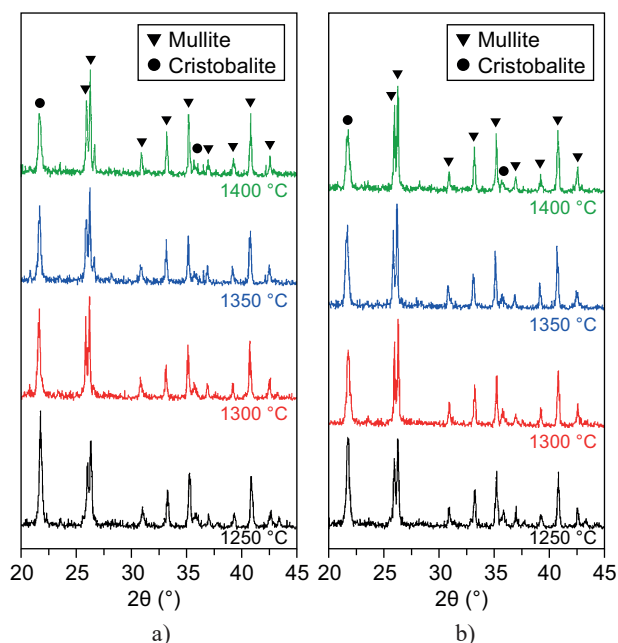
Figure 4a and 4b present XRD patterns of C3 and C4 sintered at different temperatures. The pattern are very similar, and their main diffraction peaks could be attributed to mullite ($Al_6Si_2O_{13}$, JCPDS: 15-0776) and cristobalite (SiO_2, JCPDS: 27-0605). Mullite resulted from the decomposition of the clay minerals (mainly kaolinite present in the flint clay), and cristobalite was formed from the transformation of quartz or via recrystallization from the (originally amorphous) silica released from the clay minerals. From Figure 4, when the samples (C3 and C4) were sintered at 1250 °C, the diffraction peaks of mullite phase were distinct and sharp, as expected for these temperatures, which are much higher than the temperatures of the decomposition of clay minerals and the subsequent transformation reactions. The diffraction peak intensity of cristobalite was lowest for the samples sintered at 1400 °C. At the same time, the diffraction peak intensity of mullite reached the highest value for the samples sintered at 1400 °C. Thus, with increasing sintering temperature, the diffraction peak intensity of cristobalite gradually decreases, while that of mullite phase gradually increases, indicating the formation of secondary mullite (by reprecipitation from the glass melt) or the dissolution of cristobalite in the glass melt.

Figure 5 shows SEM images of fracture section of C3 and C4 sintered at different temperatures. It is clear from Figure 5a that the proppants (C4) prepared by adding 40 wt. % coal gangue at 1350 °C had a denser microstructure. The large amount of interlaced rod-shaped mullite grains, with interdispersed cristobalite grains, are expected to improve the strength of the proppants. Moreover, less pores are present, which improves the performance of the samples, as shown in Figure 4. Figure 5b and 5c are SEM images of C3 and C4 sintered at 1400 °C. In comparison, the proppants (C4) sintered at 1400 °C possess a more compact structure than those sintered at 1350 °C, owing to the
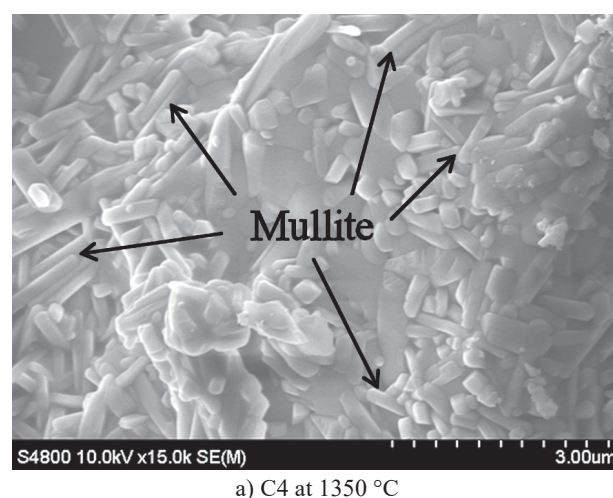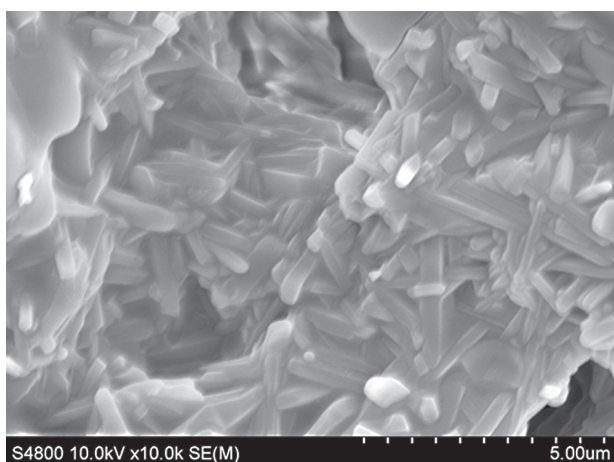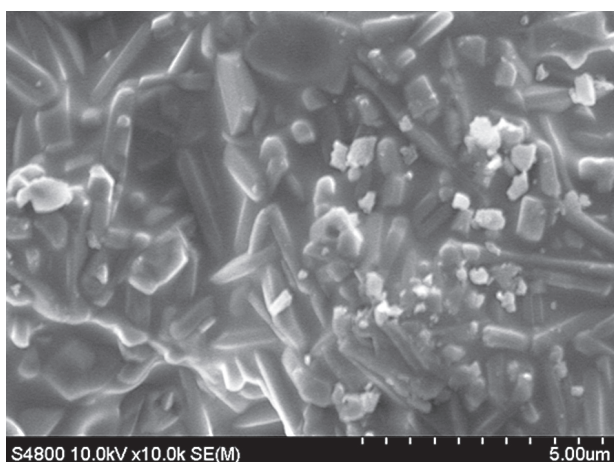

Figure 4. XRD patterns of: a) C3 and b) C4 sintered at different temperatures.

a) C4 at 1350 °C

Figure 5. SEM images of fracture sections of: a) C4 at 1350 °C. *(Continue on next page)*

b) C3 at 1400 °C

c) C4 at 1400 °C

Figure 5. SEM images of fracture sections of: b) C3 and c) C4 at 1400 °C

obvious vitreous phase. In Figure 5b and 5c, mullite grains can be seen to have grown, and the boundaries between mullite grains became diffuse, probably due to vitreous phase generated at high temperature. The content of vitreous phase in C4 (Figure 5c) was higher than in C3 (Figure 5b), mainly due to the higher amount of coal gangue. Furthermore, the content of rod-shaped mullite was obviously higher in C3 than in C4, which is why better performance is expected for C3 than for C4. This observation is consistent with the performance results shown in Figure 3, because mullite is responsible for toughening in the structure. Sample C3 exhibited a small amount of closed pores, see Figure 5b, while no pores were observed in sample C4, which is also related to the higher content of coal gangue.

CONCLUSIONS

Low-density ceramic proppants for coal bed methane wells were successfully fabricated from flint clay and solid waste coal gangue. The density of the proppants was significantly reduced by flint clay instead of bauxite,

and the preparation cost was greatly decreased by the addition of coal gangue. XRD patterns and SEM images suggested that the proppants were mainly composed of rod-shaped mullite and granular cristobalite. Proppants for application at 35 MPa closed pressure could be sintered at 1300 °C by adding 30 wt. % coal gangue, and sintered at 1350 °C by adding 40 wt. % coal gangue. Bulk densities were 1.252 $g \cdot cm^{-3}$ and 1.291 $g \cdot cm^{-3}$, and breakage ratios 8.7 % and 6.4 %, respectively. Proppants, suitable for 52 MPa closed pressure could be sintered at 1400 °C by adding 30 wt. % coal gangue, resulting in a bulk density of 1.389 $g \cdot cm^{-3}$ and a breakage ratio of 8.9 %. These low-density ceramic proppants met the requirements of ideal fracturing materials. Thus it has been confirmed that it is feasible to prepare proppants using flint clay and coal gangue, and these proppants could become ideal candidates for fracturing proppants in future applications of coal bed methane wells.

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