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The exploration of making acidproof fracturing proppants using red mud

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ABSTRACT

In this study, the exploration of making acidproof fracturing proppants using red mud was carried out. The main raw materials are red mud and the refractory waste. During the exploration, three methods were explored to enhance the acid resistance of the samples of the fracturing proppants. Eventually, fracturing proppants with good acid resistance were produced using red mud, the refractory waste, barium carbonate and plasticizer. The acid solubility of the samples of the acidproof fracturing proppants was less than 4.5% which reached the demands of The Petroleum and Gas Industrial Standards of China (SY/T5108-2006). The results show that adding barium carbonate to the raw materials can decrease the acid solubility of the samples effectively. The main reason is the monoclinic celsian-$BaAl_2Si_2O_8$ formed in sintering process which can protect the other compositions of the acidproof fracturing proppants to prevent them from erosion by acid. The exploration shows that it is probable to produce fracturing proppants with good acid resistance using red mud.

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1. Introduction

Red mud is the solid waste of aluminum production from bauxite. It is estimated that over 66 million tonnes of this waste is impounded annually in the world [1]. Under normal conditions, when 1 tonne of alumina is produced from bauxite, about 1–1.5 tonnes of red mud is generated as waste [2,3]. In China, aluminum plants generate more than 4 million tonnes red mud annually and most of the red mud is deposited in landfill [4,5]. Red mud includes Fe_2O_3, Al_2O_3, SiO_2, TiO_2, CaO, Na_2O, some less elements and rare metals among which the amount of Fe_2O_3 and alkali is relatively high [6–8]. Due to the large quantity of red mud, huge areas of land have been used around the world for disposing of red mud. These areas are bare of vegetation and susceptible to wind and water erosion, which poses serious threats to the surrounding environment and groundwater [7–10]. With the growth of the production of the alumina, more red mud will be produced and more storage will be necessary, which will become a big economical problem and a big obstacle to aluminum industry [10,11]. The disposal of red mud tailing costs the industry US$ 3 per tonne of alumina production [12].

To solve the disposal problem of red mud and recycle the abundant waste, voluminous research and development work on red mud has been carried out all over the world, but to date effective reuse technologies have mostly not been put into practice because of technical and economic reasons, and no significant quantity of red mud is actually being utilized anywhere in the world [1,7].

Fracturing proppants are solid particles with certain intensity which are used in hydraulic fracturing operations in petroleum or gas industry [13]. Fracturing proppants prop fractures of rock open, which forms channels of higher permeability than the reservoir rock. Gas or oil can flow to the well through the channels [14,15]. Acid resistance is very important to fracturing proppants. It is crucial to the fracture conductivity and bearing time of the fracturing proppants which has great influence on the productivity of the wells [16]. Fracturing proppants with good acid resistance can work effectively in acidic environment, which make gas or oil flow through the channels fluently for long time so that it can increase the productivity of oilfield. However, today, the raw materials of making fracturing proppants with good acid resistance are very limited and the technical process is relatively complex, which cannot satisfy the great demand of petroleum or gas industry. In china, the acid solubility of the fracturing proppants is on the high side generally [13]. The demands on the acid resistance of fracturing proppants of The Petroleum and Gas Indusyrial Standards of China (SY/T5108-2006) put into effect on 1 January 2007 have been dropped to a certain extent, but the acid solubility of fracturing proppants could not reach the standards generally.

In order to solve the disposal problem of red mud and produce cheap fracturing proppants with good acid resistance, the exploration of making fracturing proppants with good acid resistance using red mud was carried out in this study.

There are great advantages in making fracturing proppants using red mud. Such products made using red mud by sintering process as red mud bricks and ceramic tiles are easy to deform, which is a seri-

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Table 1
The main chemical compositions of red mud (wt%)

Fe_2O_3	Al_2O_3	SiO_2	CaO	Na_2O	TiO_2	LOI
42.10	16.11	8.61	14.80	3.53	8.06	8.5

ous obstacle to the production. The technology of making fracturing proppants using red mud need not worry about the deformation for the fracturing proppants are solid particles and most of them with the size less than 1700 μm. It can avoid the threats caused by red mud to the surrounding environment and living organisms for the fracturing proppants work under deep ground. In addition, red mud contains relatively high content of sintering aid such as Fe_2O_3 and some amount of alkali and TiO_2 which can decrease the sintering temperature and sintering time in the production of fracturing proppants. There are hundreds of factories in China and the average annual output of each is more than 10,000 tonnes. If the exploration in this study is workable, it can reuse significant quantity of red mud and decrease the cost of making fracturing proppants.

In the experiments, the samples of fracturing proppants were made using red mud and the refractory waste as main raw materials to which added the additives and plasticizer. During the exploration, three methods were explored to enhance the acid resistance of the samples. Eventually, the samples with good acid resistance were produced successfully using red mud, the refractory waste, barium carbonate and plasticizer as raw materials. The acid solubility of the samples reached the demands of The Petroleum and Gas Industrial Standards of China (SY/T5108-2006). The mechanism of acid resistance of the samples was analyzed.

2. Experimental study

2.1. Materials

2.1.1. Red mud

The red mud was obtained from Pingguo Aluminum Company, China. The main chemical composition of red mud powder sample is shown in Table 1.

2.1.2. The refractory waste

The refractory waste was obtained from Wuhan Iron Company, China. The chemical composition of the refractory waste is shown in Table 2.

2.1.3. Plasticizer

Weiluo Mud is a kind of kaolin with good plasticity which was obtained from Weiluo (an area) of Guangxi Province, China. In the experiments, Weiluo Mud was used as plasticizer to enhance the plasticity of the samples.

2.1.4. Calcium fluoride and barium carbonate

Calcium fluoride and barium carbonate chemicals of AR was produced by Longxi Chemical Plant, China.

2.2. Experimental design

During the exploration, three methods were tried to enhance the acid resistance of the samples of fracturing proppants:

Table 2
The chemical compositions of the refractory waste (wt%)

Al_2O_3	SiO_2	Fe_2O_3	TiO_2	CaO	MgO
80.96	12.28	2.96	2.93	0.61	0.30

Table 3
The mixture ratios and sintering temperature of the samples with different content of Al_2O_3 (wt%)

Samples No.	Red mud	The refractory waste	Plasticizer	Al_2O_3	Sintering temperature (°C)
1	74	16	10	30	1300
2	60	30	10	40	1350
3	45	45	10	50	1350
4	30	60	10	60	1350
5	16	74	10	70	1350

(1) To enhance the content of Al_2O_3 of raw materials. Al_2O_3 can form corundum and react with SiO_2 to form Mullite in sintering process which can make the samples obtain certain acid resistance and high strength.
(2) To increase the ceramic conversion degree of the samples. Increasing the ceramic conversion degree of the samples can make them obtain densification structure with less porosity which can prevent the acid from seeping into the bodies of the samples that can enhance the acid resistance.
(3) To add proper additive to the raw materials. The additive can react with other compositions of the raw materials and form certain content of substances with good acid resistance by sintering process which can protect the other compositions of the samples to prevent them from erosion by acid to enhance the acid resistance of samples.

2.3. Experimental procedure

2.3.1. To enhance the content of Al_2O_3 of raw materials

The content of Al_2O_3 was relatively high in refractory waste. The content of Al_2O_3 was increased by enhancing the content of the refractory waste in raw materials.

First of all, certain amount of red mud and the refractory waste was put into the ball mill equipment and milled for 24 h. Then the material mixtures were prepared by homogenizing red mud, the refractory waste and Weiluo Mud at certain mixture ratio. After homogenization, the mixtures were made into particles by granulating. The particles were dried in an air oven at 100 °C for 2 h, and then sintered for 2 h in box type electrical resistance furnace. The samples of the fracturing proppants prepared in this section are listed in Table 3. The content of Al_2O_3 in raw materials increased from 30 to 70 wt%. Meantime the acid solubility of the samples was tested according to the standards of SY/T5108-2006: add 5 g (m_1) of the samples to 100 ml acid solution of 12–3 HCl–HF acid (specific gravity = 1.08 at 15.6 °C; the mass concentrations of HCl and HF are 12 and 3%, respectively) and heat in a 65 °C water bath for 30 min; then, filter and dry the samples to constant weight (m_2); calculate the acid solubility (s) [$s = 100(m_1 - m_2)/m_1$].

2.3.2. To increase the ceramic conversion degree of the samples

In the experiments, two steps were used to increase the ceramic conversion degree of the samples. Firstly, prolong the ball-milling time to decrease the granules size of the raw materials. Second, adding mineralizer-CaF_2 to the raw materials.

Certain amount of red mud and the refractory waste was put into the ball mill equipment and grinded to the powders with the average particle size about 0.8 μm. Then the material mixtures were prepared by homogenizing red mud, the refractory waste and Weiluo Mud with CaF_2 additions up to 10 wt% at 2.5 wt% increments. After homogenization, the mixtures were made into particles by granulating. The particles were dried in an air oven at 100 °C for 2 h, and then sintered at 1350 °C for 2 h in box type electrical resistance furnace. The samples prepared in this section are listed in Table 4. Then the acid solubility of the samples was tested according to the standards of SY/T5108-2006.

Table 4
The samples prepared in Section 2.3.2

Samples No.	Red mud	The refractory waste	Plasticizer	Mineralizer	Sintering temperature (°C)
1	16	74	10	0	1350
2	16	74	10	2.5	1350
3	16	74	10	5	1350
4	16	74	10	7.5	1350
5	16	74	10	10	1350

2.3.3. To add proper additive to the raw materials

Fist of all, certain amount of red mud and the refractory waste was put into the ball mill equipment and milled for 24 h. Then the material mixtures were prepared by homogenizing red mud, the refractory waste, barium carbonate and Weiluo Mud at certain mixture ratio. After homogenization, the raw mixtures were made into particles by granulating. The particles were dried in an air oven at 100 °C for 2 h, and then sintered for 2 h in box type electrical resistance furnace. The samples prepared in this section are listed in Table 5. Then the acid solubility of the samples was tested according to the standards of SY/T5108-2006.

In this section, the bulk density and the crush resistance of the samples were also tested.

2.3.4. X-ray diffraction (XRD) and the scanning electron microscopy (SEM)

In order to analyse the mechanism of the acid resistance, the scanning electron microscopy and X-ray diffraction techniques were employed. The X-ray diffraction patterns were carried out on the X'Pert PRO made by PANaiyticai B.V. with Cu Kα radiation operated at 40 kV and 40 mA. The SEM is a JSM-6380LV scanning electron microscopy.

2.3.5. To test the bulk density and crush resistance

In the experiments, the bulk density and crush resistance of some samples with the acid solubility reached the standards of SY/T5108-2006 were tested. The procedure of the test of the bulk density: Fill a 100-ml volumetric flask with the samples of fracturing proppants to 100 ml mark; calculate the bulk density (ρ, g/cm^3) [$\rho = (W_{f,p} - W_f)/100$]. $W_{f,p}$ is the weight of the flask and the samples and W_f is the weight of the flask. The procedure of the test of the crush resistance is to test the breaking rate (f) of the samples under a load of 69 MPa (140 kN). Breaking rate $f = 100w_f/w_p$, where w_f is the weight of fines generated under a load of 69 MPa and w_p is the weight of proppants.

3. Results and discussion

3.1. The influence of the content of Al_2O_3 on the acid solubility of the samples

The influence of the content of Al_2O_3 on the acid solubility of the samples is listed in Table 6. The diameter range of samples is 0.85–1.15 mm (16–29 mesh).

Table 5
The mixture ratios and sintering temperature of the samples in Section 2.3.3

Samples No.	Red mud	The refractory waste	Plasticizer	$BaCO_3$ (additive)	Sintering temperature (°C)
1	35	55	10	0	1370
2	35	55	10	5	1370
3	35	55	10	10	1370
4	35	55	10	15	1370
5	40	50	10	17	1370
6	50	40	10	20	1350
7	60	30	10	25	1300

Table 6
The influence of the content of Al_2O_3 on the acid solubility of the samples (wt%)

Samples No.	Red mud	The refractory waste	Plasticizer	Acid solubility	Al_2O_3
1	74	16	10	15.5	30
2	60	30	10	14.7	40
3	45	45	10	14	50
4	30	60	10	13.5	60
5	16	74	10	13	70

Table 7
The demands on acid solubility of fracturing proppants in SY/T5108-2006

The proppants size (μm)	Acid solubility (%)
1700–850	≤5.0
1180–850	≤5.0
850–425	≤5.0
600–300	≤5.0
425–250	≤7.0

The demands on acid solubility of fracturing proppants in SY/T5108-2006 are shown in Table 7.

In Table 6, the acid solubility decreases from 15.5 to 13% with the increase from 30 to 70% of the content of Al_2O_3. It shows that the increase of the content of Al_2O_3 in raw materials can decrease the acid solubility of the samples of fracturing proppants. But when the content of Al_2O_3 reaches 70% and the amount of the refractory waste is 74%, the acid solubility is 13% which still cannot reach the demands on acid solubility in SY/T5108-2006. If more refractory waste is continued to add to the raw materials, the efficiency of using red mud will decrease.

Al_2O_3 can form corundum and react with SiO_2 to form Mullite in high temperature. Corundum and Mullite has high strength and certain acid resistance. So the acid solubility of the samples decreases with the content of Al_2O_3 in raw materials being increased. However, the corundum and Mullite cannot resist the erosion by HF. So, the acid solubility of the samples cannot reach the standard of SY/T5108-2006 by only enhancing the content of Al_2O_3.

3.2. The influence of the ceramic conversion degree on the acid solubility of the samples

The influence of the ceramic conversion degree on the acid solubility of the samples prepared in Section 2.3.2 is listed in Table 8. The diameter range of samples is 0.85–1.15 mm (16–29 mesh).

In Table 8, from the samples of No. 1 to No. 3, the acid solubility decreases from 13 to 12%. From the samples No. 3 to No. 5, however, the solubility increases. The solubility cannot reach the standards of SY/T5108-2006.

It shows that decreasing the granules sizes of the raw materials and adding certain amount of mineralizer can decrease the acid solubility of the samples to certain extent. Decreasing the granules sizes of the raw materials and adding certain amount of mineralizer to the raw materials can accelerate the sintering process

Table 8
The influence of the ceramic conversion degree on the acid solubility of the samples (wt%)

Samples No.	Red mud	The refractory waste	Plasticizer	Mineralizer	Acid solubility
1	16	74	10	0	13
2	16	74	10	2.5	12.5
3	16	74	10	5	12
4	16	74	10	7.5	12.9
5	16	74	10	10	15.3

Table 9
The influence of $BaCO_3$ on acid solubility of the samples (wt%)

Samples No.	Red mud	The refractory waste	Plasticizer	$BaCO_3$ (additive)	Acid solubility
1	35	55	10	0	14.4
2	35	55	10	5	11
3	35	55	10	10	6
4	35	55	10	15	3.3
5	40	50	10	17	3.1
6	50	40	10	20	4.2
7	60	30	10	25	4.5

and increase the ceramic conversion degree of the samples which makes the samples obtain densification structure with less porosity. The densification structure can prevent the acid from seeping into the bodies of the samples. But it is very limited to decrease the acid solubility by this method. When the content of the mineralizer is excessive, the acid solubility increased for the mineralizer can bring some basic compositions to the samples.

So the method of increasing the ceramic conversion degree of the samples cannot decrease the acid solubility effectively.

3.3. The influence of the barium carbonate additive on the acid solubility of the samples

The influence of barium carbonate on the acid solubility of the samples is listed in Table 9. The diameter ranges of samples is 0.85–1.15 mm (16–29 mesh).

From Table 9, we can find out that the acid solubility of the number 1–4 decreases distinctly with the increase of the amount of $BaCO_3$, and the acid solubility of the number 4 reaches the standards of SY/T5108-2006. From the No. 4 to No. 7, it exhibits that with the amount of $BaCO_3$ increasing, the amount of red mud in the materials can reach 60%, and the acid solubility still can reach the standards of SY/T5108-2006.

The bulk density and crush resistance of the No. 4 and No. 6 is listed in Table 10.

The maximum breaking rate of SY/T5108-2006 is 20% under 69 MPa. It shows the crush resistance of the samples reaches the standard of SY/T5108-2006.

3.4. The analysis of acidproof mechanism of the fracturing proppants

In Table 9, the raw materials of the samples of No. 1 and No. 4 have the same composition except that the No. 1 has no $BaCO_3$ and the No. 4 has $BaCO_3$ with the amount of 15%. However, the acid solubility of the No. 1 is 14.4% and that of the No. 4 is 3.3%. The content of red mud in the raw materials of the No. 6 is 50% and the content of $BaCO_3$ is 20%, the acid solubility is only 4.2%.

The SEM photomicrographs of the exterior surfaces of the sample of No. 1 and No. 4 in Table 9 are shown in Figs. 1 and 2. We can find out the surface of No. 1 is smooth and compact. The surface of No. 4 is rough and porous. However, the acid solubility of the No. 1 is far more than that of the No. 4. The results show the smooth exterior surfaces of the samples play a minor role to decrease the acid solubility. Though the smooth exterior surface of the samples can reduce the surface areas susceptible to attack by acid, they can-

Table 10
The bulk density and crush resistance of the samples

Samples No.	Bulk density (g/cm^3)	Crush resistance (breaking rate%/69 MPa)
No. 4	1.74	3.01
No. 6	1.73	6.60

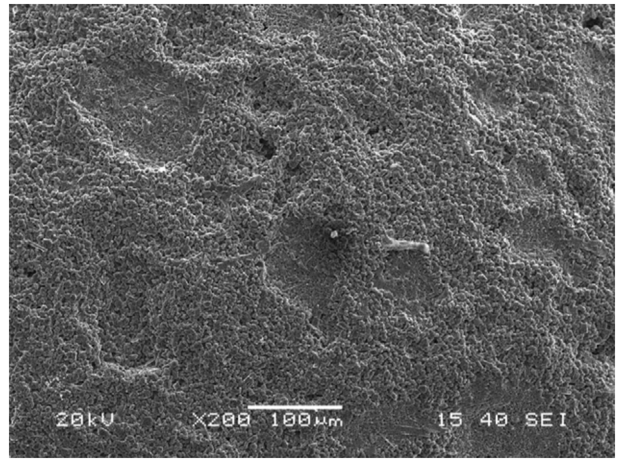

Fig. 1. SEM photomicrographs of the exterior surface of No. 1 in Table 9.

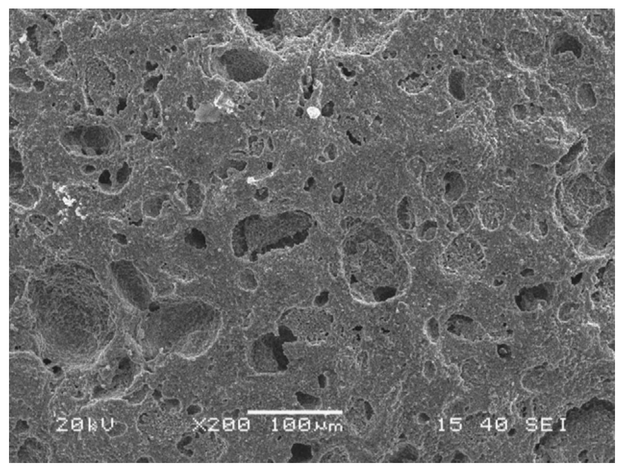

Fig. 2. SEM photomicrographs of the exterior surface of No. 4 in Table 9.

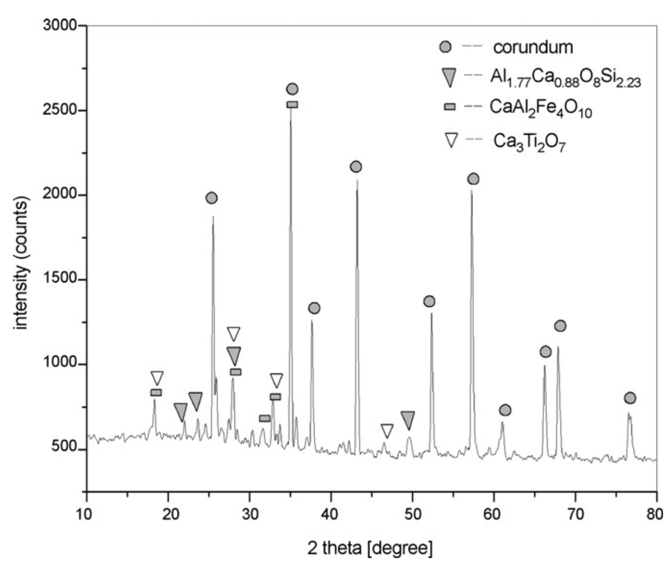

Fig. 3. The XRD of the sample of No. 1 in Table 9.

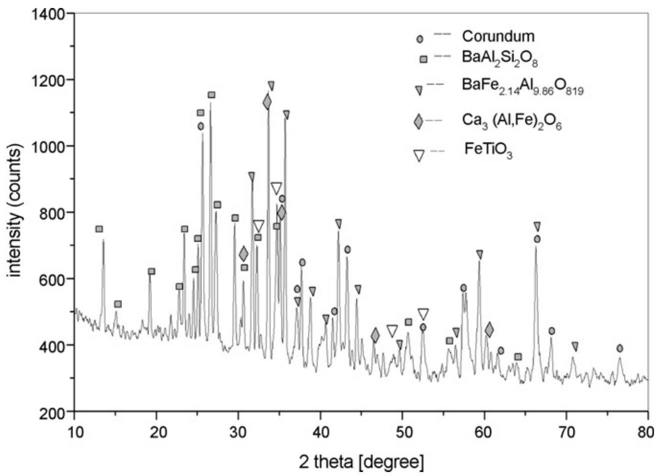

Fig. 4. The XRD of the sample of No. 4 in Table 9.

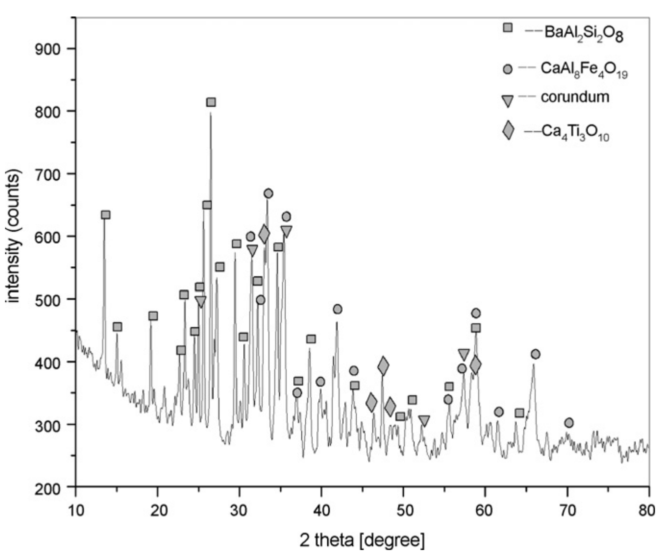

Fig. 5. The XRD of the sample of No. 6 in Table 9.

not make the samples resist the erosion by the solution of HCl-HF acid.

The X-ray powder diffraction analysis of the samples of No. 1, No. 4 and No. 6 in Table 9 are shown in Figs. 3–5, respectively.

From Figs. 4 and 5, it could be found that certain content of the monoclinic celsian-$BaAl_2Si_2O_8$ formed in the samples of the No. 4 and the No. 6. From Fig. 3, it could be found out that no monoclinic celsian-$BaAl_2Si_2O_8$ formed in the samples of the No. 1.

In addition, we found out certain content of the monoclinic celsian-$BaAl_2Si_2O_8$ also formed in the samples of No. 2, No. 3, No. 5 and No. 7 in Table 9.

We tried to synthesized the celsian-$BaAl_2Si_2O_8$ using Al_2O_3, $BaCO_3$, SiO_2 and $Na_2B_4O_7{\cdot}10H_2O$. The hexagonal celsian-$BaAl_2Si_2O_8$ and the celsian-$BaAl_2Si_2O_8$ with mixed crystal structure of the monoclinic and the hexagonal system was synthesized finally. Then the acid solubility of the celsian-$BaAl_2Si_2O_8$ was tested according to the standards of SY/T5108-2006. The acid solubility is only 1.01–1.70%, which shows that monoclinic celsian-$BaAl_2Si_2O_8$ and hexagonal celsian-$BaAl_2Si_2O_8$ has good acid resistance to the solution of 12–3 HCl–HF acid.

The results show that the monoclinic celsian-$BaAl_2Si_2O_8$ plays an important role in increasing the acid resistance of the acid-proof fracturing proppants. $BaCO_3$ reacted with Al_2O_3 and SiO_2 in sintering process and formed certain amount of monoclinic celsian-$BaAl_2Si_2O_8$ with good acid resistance which can protect the other compositions of the acidproof fracturing proppants to prevent them from erosion by acid.

4. Conclusions

(1) The acid resistance of the samples of fracturing proppants cannot be enhanced effectively by increasing the content of Al_2O_3 of raw materials or increasing the ceramic conversion degree of the samples.
(2) Adding barium carbonate to the raw materials can enhance the acid resistance of the samples of fracturing proppants effectively and make the acid solubility reach the standards of SY/T5108-2006.
(3) It is probable to produce fracturing proppants with good acid resistance using red mud.

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