Optimization Method of a Low Cost, High Performance Ceramic Proppant by Orthogonal Experimental Design

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Abstract. This study focused on optimization method of a ceramic proppant material with both low cost and high performance that met the requirements of Chinese Petroleum and Gas Industry Standard (SY/T 5108-2006). The orthogonal experimental design of L₉(3⁴) was employed to study the significance sequence of three factors, including weight ratio of white clay to bauxite, dolomite content and sintering temperature. For the crush resistance, both the range analysis and variance analysis reflected the optimally experimental condition was weight ratio of white clay to bauxite=3/7, dolomite content=3 wt.%, temperature=1350 ℃. For the bulk density, the most important factor was the sintering temperature, followed by the dolomite content, and then the ratio of white clay to bauxite.

1. Introduction
Proppant material is a key factor widely employed in the hydraulic fracturing process which is an effective method for exploitation of unconventional oil and gas resources.[1] Choosing the suitable proppant during the mining operation can improve service years of the gas well, increase its production rate and reduce the mining cost.[2,3] In the early mining process, the quartz sands was selected as the proppant. Although the quartz sand is of low cost and easy to obtain, it is usually limited by the unfavorable factors, such as low breakage resistance, low level of sphericity, poor diversion ability, etc. Ceramic proppant material, by contrast, possesses high breakage resistance, good diversion ability, high level of sphericity, and so on.[4] At present, manufacturing ceramic proppant with high performances mainly depends on the high grade bauxite as raw material. Consequently, the following two questions would be caused. First, reserves of the high grade bauxite resource would be drastically reduced. Second, adoptively high grade bauxite with high cost would enhance the cost of mining the unconventional oil and gas.[5,6] Selecting raw materials with low cost to replace the high grade bauxite is deemed as future trends for both the proppant industry and the unconventional oil and gas industry. At present, the methods of additives, such as adding iron ore, manganese ore, etc. are generally adopted to improve the performance of the ceramic proppants.[7,8] However, limited research on the low cost and low grade bauxite with dolomite ore as additive is available.
For the present study, the low-cost 3rd grade bauxite and white clay were chosen as the starting materials and dolomite as the additive to prepare the ceramic proppants. The mechanical properties of the proppants were thoroughly investigated using the orthogonal experiment design.
2. Experimental

2.1. Materials preparation
The low-cost raw materials of 3rd-grade bauxite and white clay, both of which are widely produced from Yangquan in Shanxi Province, were ground to an average size of 0.05 mm (300 mesh) and then calcined at 300℃ to remove the adsorbed water and other volatile impurities. The chemical compositions of the raw materials were listed in Table 1. The mixture of bauxite and white clay was moved to a powerful ball machine (R02, Eirich Co. Ltd., Germany) to form spherical green bodies. Then they were sieved to remain the spheres with 0.5-0.9 mm in size. These spheres were placed single layer in a rectangular corundum crucible and then sintered in a box-type electrical furnace (KF1700, Nanjing Boyuntong Instrument Technology Co. Ltd., China) in air atmosphere at a temperature range of 1250℃ and 1350℃ for 2 h with the heating rate of 5℃ /min and a furnace cooling. The as-sintered proppants were passed through a set of 20/40-mesh sieves (aperture size of 0.85-0.425 mm) to finally obtain the particular ceramic proppants.

2.2. Measurements
The bulk density and crush ratio under a constant pressure of 52 MPa were measured according to the Chinese Petroleum and Gas Industry Standard (SY/T 5108-2006). The bulk density is calculated from the formula

\[ \rho_b = \frac{M}{V_s}. \]  

(1)

where \( M \) is the weight of the ceramic proppant [g] and \( V_s \) is the naturally stacked volume [cm³]. The crush ratio of the proppant is calculated by the formula

\[ \eta = \frac{w_c}{w_0} \times 100\%. \]  

(2)

where \( w_c \) is the weight of crushed specimens [g] after testing and \( w_0 \) is the weight of initial specimens [g]. The crush resistance of the proppant sample is expressed by

\[ R_c = 1 - \eta = (1 - \frac{w_c}{w_0}) \times 100\%. \]  

(3)

Table 1. The chemical compositions of raw materials. [wt.%]

| components  | \( \text{Al}_2\text{O}_3 \) | \( \text{SiO}_2 \) | \( \text{Fe}_2\text{O}_3 \) | \( \text{CaO} \) | \( \text{MgO} \) | LOI  |
|-------------|-----------------|-----------------|-----------------|-----------------|-----------------|------|
| Bauxite     | 59.7            | 13.9            | 6.5             | 0.15            | 0.24            | 19.51 |
| White clay  | 29.6            | 40.6            | 5.7             | --              | --              | 24.1  |
| Dolomite    | 0.23            | 0.46            | 0.2             | 34.7            | 19.24           | 45.17 |

3. Orthogonal experimental design
This paper aims to study the effect of the following three factors: (A) white clay/bauxite ratio (W/B), (B) dolomite content, (C) sintering temperature on the crush resistance and bulk density of the ceramic proppants. Since the full factorial design requires 27 groups of experiments, using the orthogonal experimental method can effectively reduce the experiment number to 9 groups. Each factor has three levels (Table 2). A standard orthogonal experimental design table of \( L_9(3^4) \) was adopted. Since there are only three factors studied, a blank column was set as the error column (Table 3).

Table 2. The experiment variables design.

| Levels | W/B (A) | Dolomite content (%) (B) | Temperature (℃) (C) |
|--------|---------|--------------------------|---------------------|
| 1      | 1/9     | 1                        | 1250                |
| 2      | 2/8     | 2                        | 1300                |
| 3      | 3/7     | 3                        | 1350                |
Table 3 The orthogonal experimental design table.

| Exp. No. | A  | B  | C  | Blank(error) | Crush resistance (%) | Bulk density (g/cm³) |
|----------|----|----|----|-------------|----------------------|---------------------|
| 1        | 1/9| 1  | 1250| 1           | 86.3                 | 1.29                |
| 2        | 1/9| 2  | 1300| 2           | 89.9                 | 1.32                |
| 3        | 1/9| 3  | 1350| 3           | 90.6                 | 1.47                |
| 4        | 2/8| 1  | 1300| 3           | 88.7                 | 1.35                |
| 5        | 2/8| 2  | 1350| 1           | 89.8                 | 1.44                |
| 6        | 2/8| 3  | 1250| 2           | 88.2                 | 1.33                |
| 7        | 3/7| 1  | 1350| 2           | 90.7                 | 1.38                |
| 8        | 3/7| 2  | 1250| 3           | 91.2                 | 1.41                |
| 9        | 3/7| 3  | 1300| 1           | 92.7                 | 1.36                |

4. Results and discussion

4.1. Range analysis of the crush resistance

Since the optimal ceramic proppant sample or the best experimental condition could not be obtained directly from the experimental data in Table 3, a further orthogonal analysis was required. In the range analysis of orthogonal experiment (Table 4), I_j, II_j, III_j, are defined as the sum of the values of three levels in the specific factor j (j=A, B, C, D). R_j represents the range between the maximum and minimum value of I_j, II_j, III_j in a specific factor j. The dominant degree of each factor can be evaluated by comparing R_j. As seen from Table 4, the influence of the three factors on the crush resistance follows the sequence: A>B>C. This result indicates the most important factor for the crush resistance is the white clay/bauxite ratio (W/B), followed by the dolomite content, and then the sintering temperature. The optimal sample was obtained as A_3 B_3 C_3, which means the best experimental condition is: W/B=3/7, dolomite content=3 wt.%, temperature=1350°C.

Table 4 The range analysis on crush resistance.

|     | A  | B  | C  | error |
|-----|----|----|----|-------|
| I_j | 266.8 | 265.7 | 265.7 | 268.8 |
| II_j| 266.7 | 270.9 | 271.1 | 268.8 |
| III_j| 274.6 | 271.5 | 271.3 | 270.5 |
| R_j | 7.9  | 5.8  | 5.6  | 1.7   |

4.2. Variance analysis of the crush resistance

The variance analysis was introduced to investigate whether the effect of factors on the crush resistance was significant or could be ignored. The sum of squares (SS), degree of freedom (DF), F value (F) for all factors were shown in Table 5. The most important parameter is F value, which is obtained from the following equation:

\[ F_j = \frac{SS_j / DF_j}{SS_e / DF_e} \]  \hspace{1cm} (4)

where SS_j and SS_e are the sums of squares in the j column and the error column, DF_j and DF_e are the degree of freedom in the j column and the error column. The F value is used to indicate the magnitudes of the effects of factors and the prominence of data can be verified by F–test. To a specific F_a, obtained from the distribution table of F value, if F_j>F_a, the effect of factor j is prominent. On the other hand, if F_j≤F_a, the effect of factor j for the results is not prominent. The critical values of F_a...
($\alpha=0.01, 0.05, 0.1, 0.25$) obtained from the distribution table of $F$ value were also listed in Table 5. For example, as the $F$ value of factor A (21) is greater than $F_{0.05}$ (19), the effect of weight ratio of white clay to bauxite on the crush resistance is prominent in $\alpha=0.05$. Obviously effect of the three factors follows the sequence: $A > B > C$, as is consistent with the result of range analysis. It indicates that the most important factor of the crush resistance is the weight ratio of white clay to bauxite, followed by the dolomite content, and then the sintering temperature.

Table 5 The variance analysis on crush resistance.

|     | A    | B    | C    | error |
|-----|------|------|------|-------|
| SS  | 13.68| 6.76 | 6.7  | 0.65  |
| DF  | 2    | 2    | 2    | 2     |
| V   | 6.84 | 3.38 | 3.35 | 0.325 |
| $F_j$ | 21  | 10.4 | 10.3 |       |
| $F_{0.01}$ | 99 | 99 | 99 |       |
| $F_{0.05}$ | 19 | 19 | 19 |       |
| $F_{0.1}$ | 9  | 9  | 9  |       |
| $F_{0.25}$ | 3  | 3  | 3  |       |

4.3. Range analysis of the bulk density
Listed in the last column of Table 3 is the bulk density of the ceramic proppants. The range analysis on the bulk density is shown in Table 6. The influence of the three factors on the bulk density follows the sequence: $C > B > A$, according to the value of $R_j$. It means the most important factor for the bulk density is the sintering temperature, followed by the dolomite content, and then the ratio of white clay to 3rd bauxite (W/B). This may be resulted from the facts that enhancing the sintering temperature and increasing the content of dolomite could be easier to promote the generation of liquid phase, thus increasing the bulk density of the ceramic proppants.[9,10] Further studies on effect of several factors on the structure and mechanism of liquid phase generation have been in progress.

Table 6 The range analysis on bulk density.

|     | A    | B    | C    | error |
|-----|------|------|------|-------|
| I   | 4.08 | 4.02 | 4.03 | 4.09  |
| II  | 4.12 | 4.17 | 4.03 | 4.03  |
| III | 4.15 | 4.16 | 4.29 | 4.23  |
| $R_j$ | 0.07 | 0.15 | 0.26 | 0.2   |

5. Conclusion
(1) Low-cost, high performance ceramic proppants made from locally produced 3rd-grade bauxite, white clay and the addition of dolomite were successfully prepared.
(2) The experimental condition of ceramic proppants with the best crush resistance was determined to be ratio of white clay to bauxite=3/7, dolomite content=3 wt.%, temperature=1350°C, by the orthogonal analyses.
(3) According to the range analysis of bulk density, the most important factor for the bulk density lies in the sintering temperature, followed by the dolomite content (%), and then the ratio of white clay to the 3rd bauxite.
(4) In order to satisfy the ceramic proppant industry standard, the optimally experimental condition is $A_3B_3C_3$ according to the orthogonal analyses.

6. References
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