

Article

Effect of Characteristics of Different Types of Bauxite Clinker on Adhesion

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Abstract: Based on the fact that bauxite clinker has minor thermal conductivity and better skid resistance and wear-resisting property, it can be used in HFST (high friction surface treatment) or the abrasion layer of asphalt mixture to replace or partly replace the existing aggregate. Bauxite clinker is classified into mainly six types according to different chemical composition contents. The selection of bauxite clinker as aggregate is not only for the economic value, but also for improving the adhesion between aggregate and asphalt, which has a certain blindness. This study evaluated the characteristics of different types of bauxite clinker. The adhesion of different types of bauxite clinker with asphalt was evaluated by means of agitating hydrostatic adsorption method and surface free energy theory. The effect of characteristic parameters of bauxite clinker on adhesion was evaluated by grey correlation entropy analysis. The results show that Type B and D bauxite clinker aggregates have the best adhesion to asphalt. The outcome of grey entropy correlation analysis shows that the parameters which characterize the structural indexes of bauxite clinker, such as porosity, water absorption and apparent density, have the greatest effect on the adhesion. The results of study can provide some reference for the selection of bauxite clinker, which is used in different types of highway construction, and a theoretical reference for the applicability research of bauxite clinker in asphalt mixture and the improvement of skid resistance and durability of pavement.

Keywords: bauxite clinker; structural characteristics; phase composition; chemical composition; adhesion; grey relational entropy analysis

1. Introduction

Bauxite clinker is obtained by calcining raw bauxite in a rotary kiln or up-draft kiln at a high temperature to achieve a certain porosity ratio, water absorption ratio and volume density, and then to form relatively stable phase composition and microstructure [1]. Refractory material taking bauxite clinker as aggregate is widely used in steel making, iron smelting and other industries. Based on the fact that bauxite clinker has small thermal conductivity [2] and excellent skid resistance and wear-resisting property [3–5], it can be used in HFST (high friction surface treatment) or the abrasion layer of asphalt mixture to replace or partly replace the existing aggregate [6].

Bauxite clinker is the only aggregate that can provide long-term anti-skid performance [7–9]. It has important practical significance to apply bauxite clinker to replace some or all aggregates in asphalt mixtures to improve the long-term skid-resistance performance of asphalt mixture. The interfacial adhesive property between aggregate and asphalt varies with different aggregate types and the effect of aggregate on water sensitivity is greater than that of asphalt [10]. Therefore, it is necessary to study the adhesion characteristics between bauxite clinker and asphalt.

Several studies have been conducted to evaluate the adhesion of asphalt and aggregate; especially in recent years, with the intersection and integration of multiple disciplines, new evaluation methods emerge, including water-boiling method, static flooding test [11], dynamic oscillation stripping test [12], rotating bottle test [13], SHRP net adsorption method [14], surface energy test [15], ultrasound method [16], pull-out test [17] and peeling test [18].

In addition, the influence of adhesive factors has been studied extensively, especially the influence factors of aggregate properties on adhesion. The aggregate characteristics affecting adhesion majorly include: the shape feature, chemical composition and structural parameters (porosity, density, and pore volume) of aggregates. Zhang Jizhe et al. studied the effect of mineralogical composition of aggregates on adhesion. The results show that the clay, calcite, soda feldspar, quartz and potassium feldspar contained in aggregate have adverse effects on adhesion, while the calcite has positive effects [7]. Yin Yanping analyzed the effects of the mineralogical composition of aggregate (limestone and granite) on the interfacial bond property and pointed out that the bond property of limestone–asphalt interface mainly depends on the chemical composition of aggregate having been transferred to asphalt, while bond property of granite–asphalt interface mainly depends on the physical bonding between aggregate and asphalt [19]. Han, Haifeng et al., Chen, Guoming et al. and others studied the effects on water sensitivity from the angularity of coarse aggregate [20,21]. Gonzalo Valds reported that the geometry of aggregate has an important effect on the adhesion property, especially under the low temperature and aging conditions, and the effect is quite obvious [22]. Dong Wenjiao studied the effect of aggregate morphology on the adhesion property of asphalt–aggregate [23]. Gan Xinli studied the effect of structural characteristic parameters of aggregate, such as the effect of pore structure, porosity, average pore size and others on the adhesion property of asphalt–aggregate [24].

When the aggregate type changes, it will inevitably affect the adhesion, and thus the thermal stability, of asphalt mixture. Bauxite clinker has been classified into six categories, generally based on the content of Al_2O_3 , Fe_2O_3 , TiO_2 , CaO and MgO contained in the bauxite clinker [25]. The higher is the content of Al_2O_3 and the lower are the contents of other components, the higher is the grade of bauxite clinker. The key research questions were: What grade of bauxite clinker exerts the best adhesion with asphalt? What are the negative and positive impacts of different components of bauxite clinker on the adhesion? What grade of bauxite clinker can economically and reasonably improve the road use of asphalt mixture?

To explore the effects of different types of bauxite clinker on the adhesion of asphalt, tests on the chemical composition, phase composition, roughness, microstructure and basic properties of different types of bauxite clinker as the aggregate were conducted. The adhesion of different types of bauxite clinker to asphalt was evaluated by means of agitating hydrostatic adsorption method and surface free energy theory. The effect of clinker characteristic parameters on adhesion was evaluated by grey correlation entropy analysis.

2. Materials and Methods

2.1. Bitumen

The two kinds of asphalt used in this study have the technical characteristics listed in Tables 1 and 2. One was an asphalt with penetration grade of 60/80 pen, and the other was modified asphalt with penetration grade of 30/60 pen. The test methods in Tables 1 and 2 were conducted in accordance with the procedures given by “the highway engineering asphalt and asphalt mixture test procedures” (JTG E20-2011). Three parallel tests were performed for each test.

Two representative asphalts were selected as materials: one was asphalt with penetration grade of 60/80 pen and the other was asphalt modified with added poly (styrene-butadiene-styrene) (SBS) with penetration grade of 30/60 pen.

Table 1. Physical properties of asphalt with penetration grade of 60/80 pen.

Item	Index	Result	Test Method
Penetration/25 °C, 5 s, 100 g	60–80	66	T0604
Softening point/°C	≥46	47.5	T0606
Ductility at 15 °C/5 cm/min,	≥100	>100	T0605
Ductility /5 cm/min, 10 °C	≥20	30	T0605
Wax content/%	≥2.2	2	T0615
Flash point/°C	≤260	270	T0611
Solubility/%	≤99.5	99.7	T0607
Dynamic viscosity at 60 °C/Pa·s	≤180	210	T0620
Density/g·cm ³	Test data	1.021	T0603
Mass loss/%	±0.8	−0.53	T0610
Penetration ratio at 25 °C	≤61	61	T0604

Table 2. Physical properties of modified asphalt with penetration grade of 30/60 pen.

Item	Index	Result	Test Method
Penetration/25 °C, 5 s, 100 g	30–60	52	T0604
Softening point /°C	≤46	91	T0606
Ductility/ 5 cm/min, 10 °C	≤20	34	T0605
Density/g·cm ³	Test data	1.028	T0603
	RTFOT		
Mass loss/%	≥±1.0	0.01	T0610
Penetration ratio at 25 °C	≤61	87	T0604
Ductility/ 5 cm/min, 5 °C	≤15	39	T0605

2.2. Aggregates

Six different types of bauxite (A–F) were obtained from Yangquan, Shanxi province. They were selected based on their different mineralogical composition. To analyze the influence of aggregate characteristics on adhesiveness, it was necessary to analyze the characteristics of aggregate from a microscopic perspective. XRD, XRF, and other tests were used to objectively analyze the differences in characteristics of bauxite clinker of different types to conduct in-depth research on the influence of the differences in characteristics of bauxite clinker on adhesiveness. All bauxite clinker tests were carried out at room temperature, approximately 20 °C.

The specific test plan is shown in Figure 1.

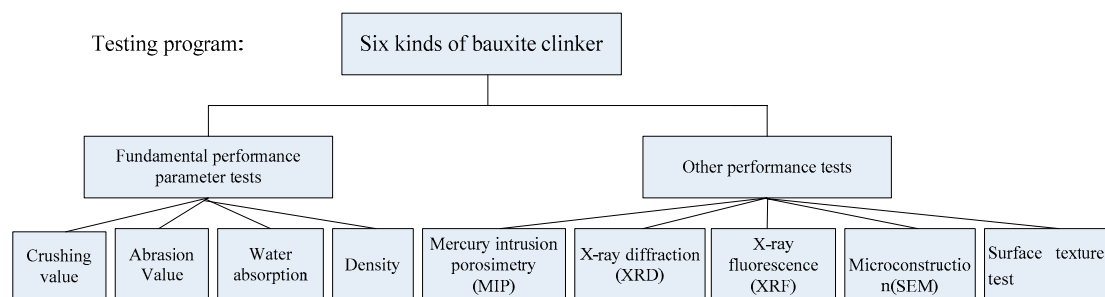
**Figure 1.** Test plan of bauxite clinkers.

Figure 1 shows the testing program, which contains a two-part test. One part was the performance test using bauxite clinker as the aggregate, including the crushing value, abrasion value, water absorption rate, and density. The other part of the test was mainly used to evaluate the micro-performance of the bauxite clinker using XRD, XRF, SEM, and surface texture tests. Through these two aspects, the macro- and micro-performance effects of the aggregate on adhesion were analyzed.

2.2.1. Aggregate Properties

When bauxite clinker is used as aggregate, the characteristics of bauxite clinker must first meet the basic characteristics of an aggregate. Table 3 shows the aggregate abrasion value, crush value, water absorption data and density for the aggregates used in the experiments.

Table 3. Technical properties of different types of bauxite.

Type	Crush Value/%	Abrasion Value/%	Water Absorption/%	Density/g·cm ³
A	14.8	12	1.33	2.970
B	10.8	11	1.01	2.809
C	8.2	9.9	1.15	3.005
D	7.1	9.1	1.21	3.125
E	6.5	7.9	1.35	3.382
F	3.4	6.0	0.95	3.301

Table 3 shows that the crushing value, abrasion value, and density of bauxite clinker increased with increasing Al₂O₃ content in the chemical composition of bauxite clinker. In other words, the higher is the grade of bauxite clinker, the denser is the structure and the greater is the corresponding mechanical strength.

2.2.2. XRD

An X-ray diffraction (XRD, D/MAX2000, Xi'an Jiaotong University, Xi'an, China) test was used to analyze the phase composition of calcined bauxite powders. Six kinds of calcined bauxite aggregate were washed with distilled water and dried in vacuum drier at 105 °C for 8 h. Before tests, aggregates were ground into powder with particle sizes of approximately 40 µm using a grinding machine. The scanning angle spectrum of the test ranged from 10° to 50°.

2.2.3. XRF

X-ray fluorescence (XRF, Edx4500h, Xi'an Jiaotong University, Xi'an, China) was used to characterize the chemical composition of calcined bauxite powders. The test procedure is the same as above.

2.2.4. Micro-Construction Test

Scanning electron microscope (BEGA3LMU, Northwestern Polytechnical University, Xi'an, China) was used to scan microstructure of different kinds of calcined bauxite. Calcined bauxite has either a smooth oval shape or an irregular block structure. Six kinds of calcined bauxite samples were cut into cuboid samples. Then, the samples were washed with distilled and dried in vacuum drier at 105 °C for 8h. Their surface was sputtered using an ion sputter coater and then measured using a scanning electron microscope.

2.2.5. Surface Texture Test

Scanning microscope (OLYMPUS, Xi'an Jiaotong University, Xi'an, China) was used to investigate the three-dimensional morphology and surface roughness by selecting the particles with aggregate size of 13.2–16 mm for testing, cleaning the selected aggregate particles, and drying them for later use. The flat surface of aggregate particles was used as the test surface. The uneven surface was pressed into plasticine, and then the plasticine was placed on the test stage for testing.

2.2.6. MIP

Mercury intrusion porosimetry (MIP, AutoPore IV 9500V1.09, Lanzhou University, Lanzhou, China) was applied to analyze the pore structure parameters of calcined bauxites by selecting aggregates

with a particle size of 4.75 mm, cleaning and drying. The maximum pressure that mercury intrusion porosimetry used in the test was 228 mpa. The contact angle of mercury and aggregate was 130° and the surface tension value of mercury was 485 dynes/cm.

2.3. Adhesion Test

2.3.1. Agitated Water Adsorption Method

Agitated water adsorption method was used to evaluate the adhesion of asphalt and aggregate. The principle of this method is to characterize the adhesion between asphalt and aggregate by the replacement of asphalt coated on the surface of aggregate by water. The test procedure and calculation method are as follows [26].

Test program: (1) Six kinds of bauxite clinker were prepared with sizes ranging from 4.75 to 9.5 mm. They were first cleaned and dried, and then wrapped with gauze. Each sample should be 50 g. (2) The asphalt–toluene solution was collected. Then, 500 mL of asphalt–toluene solution with the concentration of 4 g/L was put in a conical flask of 1000 mL in reserve. (3) The absorbance of asphalt–toluene solution was determined. First, 2 mL of asphalt–toluene solution with the concentration of 4 g/L was poured from conical flask of 1000 mL into graduated cylinder of 10 mL, into which toluene of 8 mL was poured, thereby diluting it to the concentration of 0.8 g/L. The spectrophotometer was adjusted to get the red light wavelength of 400 nm, and the spectrophotometer was used to determinate the initial absorbance A_0 . (4) The reserved aggregates were put into the solution with the concentration of 4 g/L, respectively, and then the solution was vibrated for 6 h on a vibration table. The 2 mL solution was poured into another conical flask of 1000 mL, into which 8 mL of toluene was added. The spectrophotometer was adjusted to the wavelength of 400 nm, and the spectrophotometer was used to determinate the absorbance A_1 . (5) Then, 8 mL of distilled water was, respectively, added into the solution with aggregate, and the solution was vibrated for 6 h on a vibration table. The 2 mL solution was poured into another conical flask of 1000 mL, into which 8 mL of toluene was added. The spectrophotometer was adjusted to get the wavelength of 400 nm, and the spectrophotometer was used to determinate the absorbance A_2 .

q_1 is the initial adsorption quantity, q_2 is the net adsorption quantity and q_d is the spalling rate of asphalt on aggregate, as shown in Equations (1)–(3).

$$q_1 = \frac{V_C(A_0 - A_1)}{wA_0} \quad (1)$$

$$q_2 = \frac{V_C(A_0 - A_2)}{wA_0} \quad (2)$$

$$q_d = \frac{q_1 - q_2}{q_1} \quad (3)$$

where V is the volume of bitumen–toluene solution, C is the asphalt–toluene solution concentration, and w is the aggregate mass.

2.3.2. Surface Energy Property Test

Contact angle measurements were used to determine the free energy of the asphalt samples (Table 9). The surface energies of three liquids (distilled water, glycerol, and ethylene glycol) and the calculated surface energies of asphalt are listed in Equations (5)–(7). The net absorption method was used to obtain the surface energy of the aggregate (Table 10), using a test procedure described in references [27,28]. Three liquids (distilled water, hexane, and ethylene glycol) with known surface energies and the calculated surface energies of the aggregates are listed in Equations (5)–(7). The work between the bitumen (a) and aggregate (s) is given by Equation (4), peeling work is given by Equation (8), ER1 is given by Equation (9), and ER2 is given by Equation (10).

$$w_{as} = 2 \left(\sqrt{r_a^{LW} r_s^{LW}} + \sqrt{r_a^+ r_s^-} + \sqrt{r_a^- r_s^+} \right) \quad (4)$$

where r_a^+ and r_s^+ are the Lewis acid component; r_a^- and r_s^- are the Lewis base component; and r_a^{LW} and r_s^{LW} are the Lifshitz van der Waals component.

Using the Young–Dupre equation to form three continuous formulas (Equations (5)–(7)), the surface energy parameters of the materials to be measured were obtained.

$$r_{L_1}(1 + \cos \theta_{a_1}) = 2 \left(\sqrt{r_a^{LW} r_{L_1}^{LW}} + \sqrt{r_a^+ r_{L_1}^-} + \sqrt{r_a^- r_{L_1}^+} \right) \quad (5)$$

$$r_{L_2}(1 + \cos \theta_{a_2}) = 2 \left(\sqrt{r_a^{LW} r_{L_2}^{LW}} + \sqrt{r_a^+ r_{L_2}^-} + \sqrt{r_a^- r_{L_2}^+} \right) \quad (6)$$

$$r_{L_3}(1 + \cos \theta_{a_3}) = 2 \left(\sqrt{r_a^{LW} r_{L_3}^{LW}} + \sqrt{r_a^+ r_{L_3}^-} + \sqrt{r_a^- r_{L_3}^+} \right) \quad (7)$$

where r_L^+ , r_L^- , and r_L^{LW} are the surface energies parameters of three liquids (distilled water, glycerol, and ethylene glycol, respectively). The surface energies of the aggregates were obtained by Equations (5)–(7), and the contact angles were obtained by the capillary rise method.

The work of debonding (Equation (8)) is the reduction in bond strength of a bitumen–aggregate system in the presence of moisture.

$$\begin{aligned} w_{asw}^{wet} = & \left[2 \sqrt{r_s^{LW} r_w^{LW}} + 2 \sqrt{r_s^+ r_w^-} + 2 \sqrt{r_s^- r_w^+} + 2 \sqrt{r_a^{LW} r_w^{LW}} \right] \\ & + 2 \sqrt{r_a^+ r_w^-} + 2 \sqrt{r_a^- r_w^+} - 2 r_w^{LW} - 4 \sqrt{r_w^- r_w^+} - 2 \sqrt{r_s^{LW} r_a^{LW}} \\ & - 2 \sqrt{r_s^+ r_a^-} - 2 \sqrt{r_s^- r_a^+} \end{aligned} \quad (8)$$

Equations (9) and (10) were used to calculate the moisture compatibility ratios [16,29,30]. Higher ratio values suggest a higher resistance to moisture damage.

$$ER_1 = \left| \frac{w_{as}}{w_{asw}^{wet}} \right| \quad (9)$$

$$ER_2 = \left| \frac{w_{as} - w_{aa}}{w_{asw}^{wet}} \right| \quad (10)$$

The use of ER as an index to evaluate the water stability of asphalt mixtures is based on the fact that the water sensitivity of a mixture is directly proportional to the strength of adhesion between asphalt and aggregate in the anhydrous state and is inversely proportional to the exfoliation power in the aqueous state. However, ER1 does not consider the wettability of asphalt with respect to the aggregate. Cheng et al. further proposed the index ER2 by noting that the water damage resistance of an asphalt mixture is directly proportional to the wettability of asphalt with respect to the aggregate and inversely proportional to the exfoliation power [31].

3. Results and Discussion

3.1. Aggregate Characteristics

3.1.1. XRD Test

Figure 2 shows that the main composition of the calcined bauxite samples were corundum and mullite. The amount of corundum increased as the amount of Al_2O_3 increased, while mullite showed the opposite trend. Aluminum titanate appeared when the amount of Al_2O_3 in bauxite exceeded 75% [25].

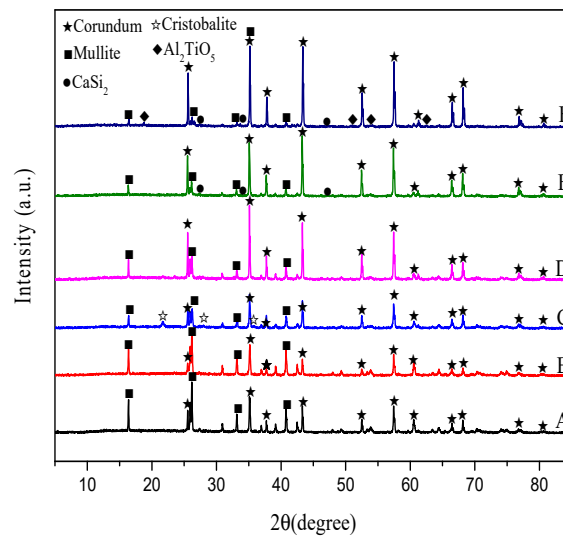


Figure 2. Phase composition of different types of bauxite.

Different types of bauxite clinker have obviously different compositions, which is convenient for subsequent analysis of the influence of chemical composition changes on adhesion.

3.1.2. XRF Test

The XRF results are shown in Table 4. Al_2O_3 , SiO_2 , Fe_2O_3 , and TiO_2 were the main compounds in calcined bauxite. Al_2O_3 , SiO_2 , and TiO_2 were in the ranges 67.61–76%, 7.85–24.02%, and 5.77–8.13%, respectively. The amount of TiO_2 showed an increasing trend as Al_2O_3 increased. Fe_2O_3 made up 5.46–9.69% of the calcined bauxite, while other impurity substances made up less than 1%

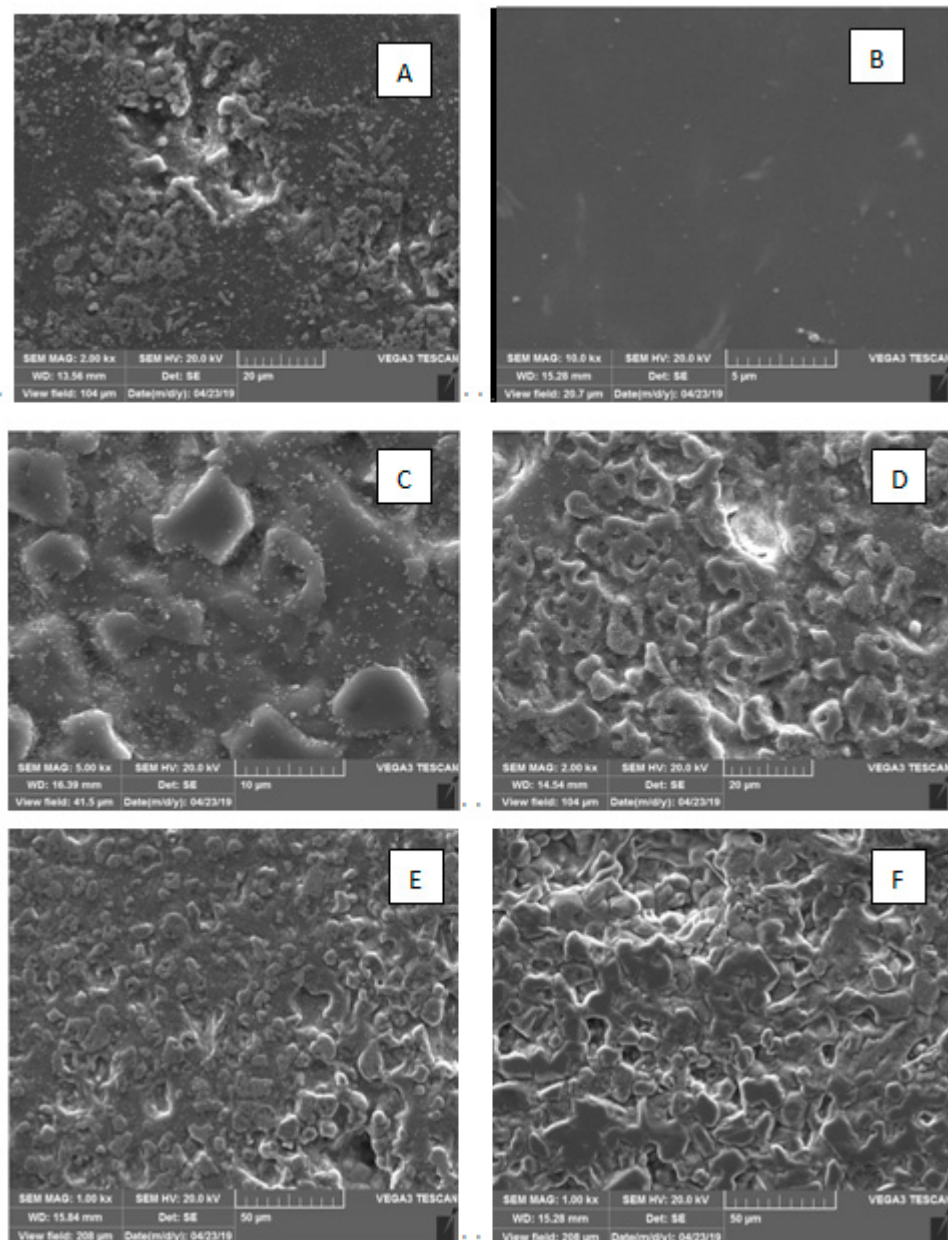
Table 4. Technical properties of different types of bauxite.

Types	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5	Other Ingredients
A	24.02	5.93	57.61	8.01	0.15	2.32	0.31	0.59	0.39	0.67
B	23.98	5.77	59.79	6.65	0.12	1.91	0.29	0.44	0.32	0.73
C	20.96	6.89	61.55	7.79	0.15	1.13	0.24	0.32	0.30	0.68
D	16.27	6.09	64.45	9.69	0.13	1.49	0.30	0.43	0.41	0.75
E	12.34	7.19	69.56	7.65	0.11	1.44	0.26	0.26	0.40	0.78
F	7.85	8.13	76.00	5.46	0.10	0.91	0.17	0.21	0.45	0.72

* The six types of calcined bauxite are labeled A–F, with increasing Al_2O_3 content.

3.1.3. Microstructural Test

The structures of Figure 3C–F are similar. Crystallographically, mullite is a needle and columnar shaped crystal, while corundum is a crystal with rod like shape. Corundum and mullite are connected with each other and closely distributed, forming a network. The microstructures of Figure 3A,B show the presence of few columnar crystals (the principal crystalline phase) and mullite, and a scattered particle distribution. This occurred because Al_2O_3 decomposed and SiO_2 dissociated during calcining. During the process of bauxite incineration, the inadequate decomposed Al_2O_3 from the decomposing stage and the free SiO_2 caused the deficient secondary hydrodesulfurization and recrystallization. Thus, the production of the secondary mullite was very slow, as was the growth of the crystals of corundum and mullite.



* The six types of calcined bauxite are labeled A–F, with increasing Al_2O_3 content.

Figure 3. Microstructure of different kinds of calcined bauxite. The surface of type (A) and type (B) relatively smooth, while the surface of type (C–F) is relatively rough.

3.1.4. Surface Texture Test

The arithmetical mean deviation of the profile was divided into 14 categories (Table 5) by the surface roughness parameters and their values (GB 1031-1995). According to the result of the roughness of calcined bauxite (Table 6), the roughness of calcined bauxite ranged from Grade 1 to Grade 4. The roughnesses of limestone and basalt are 1.243 and 0.930 [24], which are classified as types 7 and 8, respectively. The surface texture test result indicates that the roughness of calcined bauxite was larger than those of limestone and basalt. This means, compared with limestone and basalt, calcined bauxite has better adhesion with asphalt under similar conditions. Since the particle size and shape should be taken into consideration during testing, this test result only represents the specific particle size of the aggregate used in this study.

Table 5. Roughness classification.

Ra(μm)	Roughness Grade 14	0.012	Roughness Grade 7	1.6
	Roughness Grade 13	0.025	Roughness Grade 6	3.2
	Roughness Grade 12	0.05	Roughness Grade 5	6.3
	Roughness Grade 11	0.1	Roughness Grade 4	12.5
	Roughness Grade 10	0.2	Roughness Grade 3	25
	Roughness Grade 9	0.4	Roughness Grade 2	50
	Roughness Grade 8	0.8	Roughness Grade 1	100

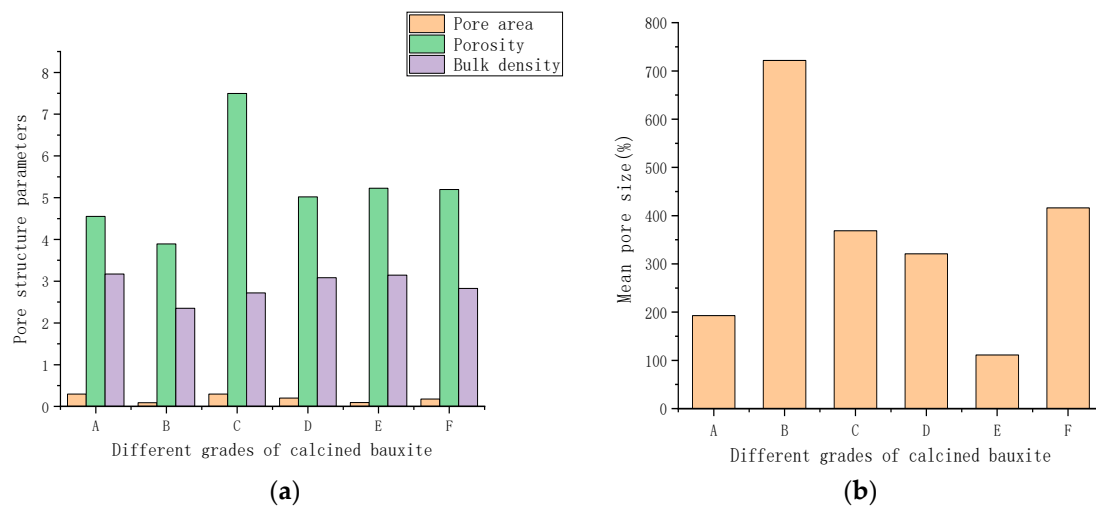
Table 6. Average surface texture parameters of aggregates.

Grade	Ra/μm	Rp/μm	Rq/μm	Rz/μm	Rv/μm
A	28.291	59.649	34.180	156.119	96.470
B	73.511	157.422	86.216	301.284	143.862
C	68.732	144.962	78.222	300.233	155.271
D	70.001	147.072	78.750	299.074	152.001
E	14.855	34.231	19.527	73.736	39.505
F	20.229	48.472	24.518	101.257	52.785

* The six types of calcined bauxite are labeled A–F, with increasing Al_2O_3 content.

3.1.5. Analysis of Pore Structure Parameters

Figure 4 (a) shows that the porosity of bauxite clinker of Type C is the largest, followed by Types E, F, D, A and B, sequentially. Pore area of Type C is the largest, followed by Types A, F, D, B and E, sequentially. The bulk densities of Types D and E are the biggest, followed by Types A, F, E and B, sequentially. Figure 4 (b) shows that the mean pore size of bauxite clinker of Type B is the largest, followed by Types F, C, D, A and E, sequentially.



* The six types of calcined bauxite are labeled A–F, with increasing Al_2O_3 content.

Figure 4. Pore structure parameters of different types of calcined bauxite.

3.2. Aggregate-Bitumen Adhesion

3.2.1. Agitated Water Adsorption Method

Table 7 shows the asphalt stripping ratios of types of calcined bauxite. Zhang [27] established the relationship between stripping rate and adhesion. The adhesion grade of asphalt was determined based on the stripping rate in Table 8.

Table 7. Asphalt stripping rate.

Parameter	Type of Asphalt	F	E	D	C	B	A
Adsorption (mg/g)	60/80 pen asphalt	0.0077	0.0054	0.0077	0.0073	0.0065	0.0072
Net adsorption (mg/g)	60/80 pen asphalt	0.0062	0.0040	0.0068	0.0050	0.0056	0.0056
Stripping ratio (%)	60/80 pen asphalt	20.18	25.93	12.29	31.13	14.41	21.78

* The six types of calcined bauxite are labeled A–F, with increasing Al_2O_3 content.

Table 8. Asphalt adhesion grading index.

Stripping Ratio (%)	Adhesion Grade	Description of Stripping
≤ 5	5	Asphalt membrane is in good condition and extremely little stripping exists at the edge.
5–20	4	Asphalt membrane is in good condition, and little stripping exists at the mineral aggregate surface.
20–35	3	Asphalt membrane is partially stripped, and up to 20% to 35% of the area in the mineral aggregate is exposed.
35–60	2	Large area of stripping in the asphalt membrane, and the exposed area is 35% to 60% in the mineral aggregate.
> 60	1	Most asphalt membrane is stripped, and the exposed area is more than 60% in the mineral aggregate.

Based on Tables 7 and 8, the adhesion grade of Types B and D is 4, whereas other samples were Grade 3.

3.2.2. Surface Free Energy Theory

The work of adhesion represents the energy required for an object to generate a new surface per unit area, and is evaluated by surface energy parameters [32]. In terms of asphalt and aggregate adhesion, two aspects of energy need to be considered: one is to overcome the adhesion of asphalt to itself, and the other is to overcome the adhesion between asphalt and aggregate interface. The adhesion between aggregate and asphalt was evaluated by the magnitude of work done in these two aspects.

Table 9 shows the surface energy parameters of 60/80 pen asphalt and 30/60 pen asphalt.

Table 9. Surface energy parameters of asphalt.

Type of Asphalt	r_a	r_a^{LW}	r_a^{AB}	r_a^+	r_a^-
60/80 pen asphalt	15.72	12.23	3.49	1.22	2.50
30/60 pen asphalt	22.11	17.78	4.33	0.83	5.64

Table 10 shows the surface energy parameters of calcined bauxites.

Table 10. Surface energy parameters of aggregates.

type	r_s	r_s^{LW}	r_s^{AB}	r_s^+	r_s^-
F	25.73	14.66	11.07	0.685	44.76
E	31.98	18.20	13.78	1.048	45.30
D	16.42	12.36	4.058	0.035	117.6
C	23.83	14.61	9.224	0.734	28.98
B	24.28	14.72	9.562	0.349	65.50
A	25.48	14.92	10.56	0.707	39.41

* The six types of calcined bauxite are labeled A–F, with increasing Al_2O_3 content.

Higher values of ER_1 and ER_2 indicate that a sample has a better water stability. Table 11 shows that, for 60/80 pen asphalt, the order of ER_1 and ER_2 was: $D > B > E > F > A > C$. For 30/60 pen asphalt, the order was: $B > E > F > C > A > D$. The work of adhesion for 60/80 pen asphalt was: $D > E > B > F >$

A > C. For 30/60 pen asphalt, it was: E > D > B > F > A > C. The stripping work for 60/80 pen asphalt followed the order: C > A > F > E > D > B. For 30/60 pen asphalt, it was D > C > A > F > E > B.

Table 11. Calculated value of adhesion evaluation index between asphalt and aggregates.

Type of Asphalt	Index	A	B	C	D	E	F
60/80 pen asphalt	ER1	2.035	5.251	1.453	5.295	3.071	2.413
	ER2	0.565	1.706	0.357	1.906	1.056	0.695
	Stripping work/mJ/m ²	21.40	8.870	28.44	9.280	15.61	18.31
	Adhesion work/mJ/m ²	43.54	46.58	41.33	49.14	47.94	44.18
30/60 pen asphalt	ER ₁	3.670	8.605	2.256	2.407	6.645	4.955
	ER ₂	0.291	9.827	0.091	0.291	1.113	0.429
	Stripping work/mJ/m ²	13.08	0.580	20.44	20.90	7.990	9.768
	Adhesion work/mJ/m ²	48.01	49.91	46.11	50.30	53.10	48.41

* The six types of calcined bauxite are labeled A–F, with increasing Al₂O₃ content.

According to the obtained surface energy values, the adhesive properties had no obvious correlation with the different types of bauxite clinker, and the chemical composition had no obvious influence on the adhesive properties of bauxite clinker.

The above results show that the adhesion of aggregate–bitumen samples of Types B and D were the best.

4. Effects of Aggregate on Adhesion

4.1. Effects of Chemical Components on Adhesion of Asphalt

From the chemical composition analysis of these six types of calcined bauxite (Table 4), the content range of SiO₂ was 6.74–29.12%. The acid aggregate stone had an SiO₂ content greater than 65%, neutral aggregate stone had a content between 52% and 65%, and alkaline aggregate stone had a content less than 52% [33]. Therefore, calcined bauxite is an alkaline aggregate. Calcined bauxite's dominant mineral components are Fe₂O₃, Al₂O₃, and SiO₂, and the main difference between the chemical compositions of different types of calcined bauxite was the Al₂O₃ content.

He [34] applied an improved SHAP net adsorption method and carried out adhesion and de-bonding tests on Fe₂O₃, Al₂O₃, SiO₂, and CaO with three different asphalts. The results are summarized in Figures 5 and 6. With respect to the adsorption and hydrolysis resistance and de-bonding performance, the adhesive abilities of these four oxides were: Al₂O₃ > Fe₂O₃ > CaO > SiO₂.

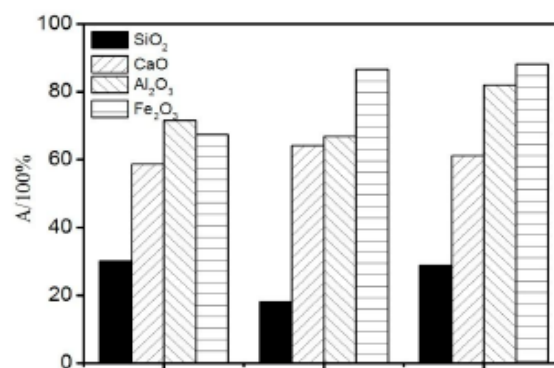


Figure 5. Adhesion among four different oxides and three different asphalts [34].

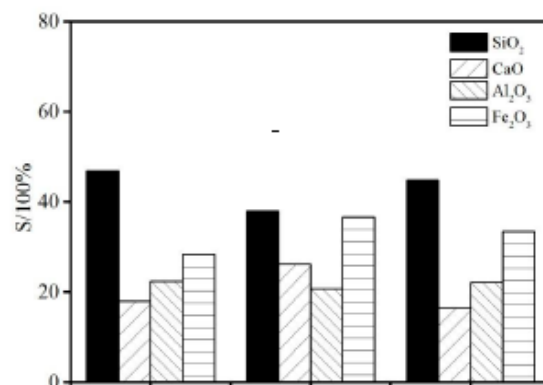


Figure 6. Stripping rate among four different oxides and three different asphalts [34].

In the six calcined bauxite samples in this study, Fe_2O_3 accounted for 1–3% of content, whereas Al_2O_3 made up 50–90%. This means Al_2O_3 plays a main role in affecting the adhesion. When compared with calcined bauxite with lower amounts of Al_2O_3 , calcined bauxite containing high amounts of Al_2O_3 showed a stronger adhesion with the asphalt when exposed to a dry environment. The hydrolysis resistance was in the order: $\text{CaO} > \text{Fe}_2\text{O}_3 > \text{Al}_2\text{O}_3 > \text{SiO}_2$. CaO showed the best adhesion with asphalt when water was present, whereas SiO_2 was worse, and Al_2O_3 showed the lowest hydrolysis resistance.

4.2. Grey Relation Entropy Analysis of the Effects of Aggregate on Adhesion

Grey relation analysis is based on the similarity or difference of the trends of each factor, and then the correlation of each factor is evaluated. The correlation between the target value (reference sequence) and influencing factors (comparative sequence) is calculated first, and then the main factors that affect the target value are determined by sorting them [35,36]. By analyzing the weight of each factor affecting adhesion, the adhesion of asphalt was expressed by the stripping ratio. The comparative sequence in this study was considered: surface roughness, porosity, pore volume, pore surface area, mean pore diameter, water absorption, and density.

Different dimensionless analyses lead to different outcomes in a grey relation analysis [37,38]. Grey relation entropy analysis can overcome this, thus it was used to analyze the effects of different factors on adhesion.

The basic procedure of a grey relation entropy analysis is: (a) calculate the correlation coefficient of the sequence; (b) calculate the density value of the grey relation the entropy distribution; (c) calculate the sequence grey relation entropy; (d) calculate the correlation of the sequence grey relation entropy; and (e) determine the main factor from the calculated correlation of sequence grey relation entropy. More details for the calculation can be found in Reference [38]. Based on the above principles, the calculated results are listed in Table 12.

Table 12. Calculation results of grey entropy correlation degree.

Item	Pore Area (m ² /g)	Porosity/%	Mean Pore Diameter/nm	Bulk Density (g/mL)	Roughness	Water Absorption (%)	Density (g/mL)
Grey correlation	0.9826	0.9946	0.9802	0.9879	0.9692	0.9920	0.9903
Correlation sequence	5	1	6	4	7	2	3

The anti-stripping property of the aggregates and results of grey relation entropy analysis are: porosity > water absorption > apparent density > bulk density > pore surface area > mean pore diameter > roughness. As a result, the main factors affecting the anti-stripping property of an aggregate are related to pore structure parameters such as porosity, water absorption, and apparent density. This shows that pore structure can accurately reflect the adsorption capacity of an aggregate to asphalt,

and it has an important influence on the adhesion between asphalt and an aggregate. The most influential pore characteristic on adhesion was the large pore size in the aggregate [24].

5. Conclusions

(1) The main phase compositions of the six different types of calcined bauxite were corundum and mullite, which accounted for 91.3–96.9% of the aggregate. The amount of corundum increased with an increasing Al_2O_3 content, while mullite showed a different trend. During the incineration of bauxite of low grades, the inadequately decomposed Al_2O_3 from the decomposing stage and the free SiO_2 caused the deficient secondary hydrodesulfurization, sintering, and recrystallization. Thus, the structure was not well developed, resulting in bad mechanical properties and affecting the performance of the asphalt mixture.

(2) The roughness of calcined bauxite ranged from Grade 1 to Grade 4, while the roughness of limestone and basalt are 1.243 and 0.930, which are classified as Grades 7 and 8. The adhesion of Types B and D to asphalt were both Grade 4, and the remaining the calcined bauxite samples were Grade 3. The Al_2O_3 content in the aggregate showed a positive relationship with adhesion to asphalt under dry conditions, whereas the hydrolysis resistance of the aggregate became worse when water was present.

(3) Grey relation entropy analysis of factors influencing the anti-stripping performance of aggregate showed that the order of the anti-stripping ability was: porosity > water absorption > apparent density > bulk density > pore surface area > mean pore diameter > roughness. Therefore, the main factors affecting the anti-stripping property of an aggregate were related to its pore structure parameters such as porosity, water absorption, and apparent density.

Many tests were performed to evaluate the performance of bauxite clinker, including its physical and mechanical properties, especially its abrasion resistance and compression resistance against sliding. The test results show that bauxite clinker has a great advantage over ordinary aggregates with respect to anti-sliding wear resistance and also a high thermal stability. To comprehensively understand the durability characteristics of bauxite clinker, a study on its acid and alkaline resistance should be conducted in the future.

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