Molecular Simulation Study on Modification Mechanism of Red Mud Modified Asphalt

FU Tao, BAO Hui-ming*, Duan xing-xing

College of Civil and Construction Engineering, Guilin University of Technology, Guilin 541004, China

*Corresponding Author

Abstract: This article used red mud, the aluminum industrial wastes, as modified asphalt material, through the study of the routine test of modified asphalt properties, and the micro test of electron microscope scanning, infrared spectrum and differential scanning calorimetry analysis etc to discuss its performance and modification mechanism. The test results show that after mixing red mud, asphalt’s penetration index and 15 ℃ ductility reduced, softening point enhanced, thus the temperature sensitivity and high temperature stability of asphalt improved; Red mud after mixing the matrix asphalt, can form a uniform, stable and matrix asphalt blending system, and improve the asphalt’s thermal stability. Using molecular simulation technology to analyze the asphalt with the temperature change of energy and find in the process of asphalt melting, the largest is the key to influence on bituminous, and van der waals energy is small. It concludes that red mud-modified asphalt material is mainly controlled by bond energy, in order to obtain its favorable property of modification mechanism, red mud of senior activation and molecular bond energy of asphalt is needed to be enhanced. The results of molecular simulation show that the main component of hematite in red mud is the most adsorbed in the asphalt, the asphaltene is the second, the colloid is the worst, but the adsorption capacity of the colloid is the highest.

1. Introduction
Red mud is the industrial waste produced when the alumina is extracted from the aluminum industry. With the vigorous development of aluminum industry, Chinese red mud emissions are increasing, resulting in a serious environmental disaster, how to minimize the harm of red mud and maximize the efficiency of the utilization of red mud has been imminent [1]. At present, domestic and foreign utilization is widely used as organic polymer modified asphalt SBS modified asphalt [2], but in China for high polymer modification technology is not yet mature, and expensive, which greatly limited our countries’ development of asphalt. In recent years, domestic researchers have found that inorganic material modifier [3] can not only improve the interface between asphalt and mineral materials, but also has the characteristics of simple production process, low cost, excellent performance and abundant reserves. In this paper, the basic performance of red mud modified asphalt was studied by microscopic experiment, microscopic test, electron spectroscopy and infrared spectroscopy. The basic mechanism of the modified asphalt was analyzed by molecular simulation technique.

2. Performance test of modified asphalt

2.1 Raw material properties
Asphalt: the experimental substrate asphalt is used by the China Petrochemical Co., Ltd. Maoming
branch produced by the "East China Sea card" 70 # A-class road asphalt, the basic performance indicators shown in Table 1.

| Item                        | Requirement | Test result |
|-----------------------------|-------------|-------------|
| Penetration(25°C)/ (0.1mm)  | 60-80       | 65          |
| Ductility(15°C)/cm          | ≥100        | 104.52      |
| Softening point/°C          | ≥46         | 48.5        |
| Flash point/°C              | ≥260        | 299         |
| Solubility/%                | ≥99.5       | 99.88       |

Red mud: This experiment used industrial waste that Guangxi Pingguo aluminum industry using Bayer industrial alumina produced, the main components of this red mud are Fe2O3, Al2O3, SiO2, CaO, Na2O and so on. The red mud used in this experiment was calcined at 900 °C, and the fineness of red mud was 200 mesh.

2.2 High temperature activation of red mud
1) The red mud was dried in a constant temperature over 100 °C for 24 hours to remove the free water therein.
2) After the drying treatment of red mud, through the grinding treatment and the screening process to select 200 mesh below of the red mud fineness to the next step.
3) Put the red mud that meet the size into the 900 °C roaster furnace for full calcination, and insulation 90min[4].

In the process of grinding, Red mud will has a larger than the previous surface area, which is the result of external force on the red mud powder work. One part of the mechanical energy consumed by the preparation of red mud powder by mechanical force will be stored in the red mud powder as the surface energy. In addition, in the preparation of red mud powder, also will cause the red mud split surface and internal various lattice defects, make the lattice activation. The results show that the surface energy of the powder is much high at the specific surface area in 1-10m2 / g, so that the red mud powder is in an unstable state. Due to the emergence of this unstable state, the structure will be developed to a low energy state, which will cause the red mud be liable to occur the phenomenon of agglomeration in the process of grinding.

In the sintering process, there are two main forms of the theory: for the larger particles, the sintering process is based on the dense accumulation of particles; and for smaller particles, the atomic diffusion of particles is dominant in the sintering process. The sintering process of red mud powder is mainly by atomic diffusion. Under this condition, the larger the red mud is, the greater the distance between the particles, and lead to the more resistance it needs to overcome and the higher the activation energy be required. Therefore, the smaller the particles of red mud powder, the smaller the gap between the particles, the more difficult the particles to dense accumulation, so in the sintering process of red mud powder, the finer particles, the easier it is to be sintered, and thus the degree of densification can be further accelerated, such that the sintered red mud powder will has a certain sintering activation energy.

2.3 modified asphalt basic performance
The red mud material is added to the asphalt matrix for modification. In order to make the effect of the red mud particles fully, it must be uniformly dispersed in the asphalt to avoid the occurrence of agglomeration [5]. The disposed red mud(3%, 5%, 7%, 9%, 11%, 13%, 15%) was added to the matrix asphalt by using Exosmosis method in a high speed shearing machine at a temperature of 170 °C and the speed of 8000r / m, the shear time was 30min, the red mud modified asphalt was obtained and its indexes were tested, compared with the matrix asphalt. The experimental results are shown in Table 2.
Table 2 Test results of basic performance index of red mud modified asphalt [11]

| Quantity/% | Penetration(15℃)/(0.1mm) | Penetration(25℃)/(0.1mm) | Penetration(30℃)/(0.1mm) | Softening point/℃ | Ductility(15℃)/mm |
|------------|--------------------------|---------------------------|---------------------------|-------------------|------------------|
| 0          | 23.3                     | 65.6                      | 111.7                     | 49                | 1231             |
| 3          | 21.6                     | 64.9                      | 109.4                     | 54.5              | 511.5            |
| 5          | 22.2                     | 59.8                      | 107                       | 57.3              | 499              |
| 7          | 21.5                     | 58.2                      | 103.2                     | 58.5              | 416.5            |
| 9          | 20.2                     | 55.7                      | 99.6                      | 59.5              | 435              |
| 11         | 20.9                     | 60                       | 99.9                      | 57.8              | 411              |
| 13         | 22.7                     | 52.9                      | 86.1                      | 61.5              | 525              |
| 15         | 23.3                     | 54.9                      | 90.3                      | 65.2              | 530              |

As can be seen from Table 2 (25 ℃ as an example for analysis): (1) the same temperature, under different dosage of red mud modified asphalt penetration is lower than the matrix asphalt, and both in the red mud content 13% minimum penetration time. It shows that the incorporation of red mud improves the consistency of matrix asphalt and the ability of asphalt to resist deformation. (2) After the incorporation of red mud, the softening point of the asphalt has also been significantly improved and reached a maximum at a concentration of 15%, and its value is 65.2 °C. (3) The incorporation of red mud makes the asphalt ductility greatly reduced. It can be concluded that the asphalt with red mud modification is hardened and the resistance to deformation is enhanced, and the temperature sensitivity is significantly reduced and the high temperature performance is obviously improved [5].

3. Analysis of Mechanism of Red Mud Modified Asphalt

3.1 Scanning electron microscopy analysis

The phase structure of modified asphalt can be analyzed by scanning electron microscopy. The phase structure of the modified asphalt is the distribution of the polymer in the asphalt, which mainly includes the shape, size and uniformity of the polymer particles and the continuous condition of the asphalt and the polymer. The phase structure of the modified asphalt in a large extent decides the modified asphalt heat storage stability and other properties [8]. From Fig. 1-2, it is found that the red mud can be more uniformly attached to the asphalt surface, because the red mud has a large specific surface area, and the specific surface area is larger than the surface area. It means that the red mud and asphalt bonding area, make the red mud absorb the oil in the asphalt, so that the force between the two molecular increases, it will increase the thickness of the structure of asphalt, improve the total adhesion force between asphalt and mineral, so this adsorption not only make the red mud modified material more stable compatible with the asphalt, which will improve the technical performance of asphalt. On the other hand, due to the chemical effect of the mechanical force, the composition and particle morphology of the red mud minerals are changed, it results in irregular block vitreous rupture and roughening the surface; from the point of view of the bond energy Explanation: The mechanical force acts to reduce the bond between Si-O and Al-O bonds and expose the active components of the core, while the Si (Al) tetrahedron has increased the degree of distortion and the surface activity of the red mud particles enhanced; And the red mud powder has a high grain boundary volume fraction. The grain boundary stores a large amount of excess enthalpy, which provides the thermodynamic conditions for the chemical effect of mechanical force [7]. It is seen from Fig. 3 that there is a reunion phenomenon in the red mud, and a more obvious micro-block, which is due to the intergranular π-π effect, asphaltene between the layers of layered phenomenon format, red mud molecules into asphaltene and oil saturation, resulting in the obvious accumulation and the formation of lumps. Through the quantitative analysis of the SEM images of activated red mud and red mud modified asphalt, the comparison shows that the red mud particle size on the surface of the asphalt is between 0.27um and 1.20um, and the particle size of the activated red mud is mainly concentrated among 0.49-2.75um, which may be due to the red mud is dispersed adsorption by the tiny size of the asphalt molecules, and the formation of red mud - asphalt molecules between the organic and inorganic interpenetration, so that after adding red mud between asphalt and red mud phase the interface becomes more blurred, which leading to the formation of a network between the two
cross-linked structure, and increasing the integrity of modified asphalt, thereby improving the stability of the asphalt, is shown in Fig. 4 and 5.

3.2 Infrared spectroscopy analysis

The equipment used for the test is the Nicofe7t40FTIR Fourier transform infrared spectrometer produced in the United States. The resolution is 4cm-1 and the scanning frequency is 32 times. The test range is 400-4000cm-1. From Fig. 6, it can be seen that the FTIR spectrum analysis of matrix asphalt shows that the strong absorption peak of the asphalt at 3000 ~ 2800cm-1 has a strong absorption peak as the symmetric stretching vibration peak of CH bond, which is saturated and unsaturated Hydrocarbon dividing line. The absorption peak at 1610 cm -1 is, on the one hand, caused by the symmetric stretching vibration peak of the conjugated double bond C = C and the other caused by C = O; the absorption peak at 1600 ~ 1450 cm -1 is the C = C (benzene ring skeleton vibration) double bond symmetrical stretching vibration peak. The peak at 1376 cm-1 is the bending vibration peak of C-H, and the fingerprint of the outer ring is 900-6 cm. Through the analysis of the infrared spectrum of asphalt, the asphalt is mainly composed of alkanes, naphthenes, aromatic and heteroatom derivatives of the mixture. Comparing with analysis of matrix asphalt and red mud modified asphalt can be obtained that the infrared spectrum is not
a new endothermic peak and the characteristic endothermic peak position did not appear obvious displacement, it means that no new functional groups, and the added red mud did not occur chemical change with the substrate asphalt, but a physical blending process.

3.3 Differential scanning calorimetry analysis based on molecular simulation techniques
Asphalt, as the same with the polymer material, with the temperature rising, the phase of asphalt changes on the performance of the peak in the DSC curve, but what the difference with the polymer material is because the asphalt is composed of many components of the mixture, and the phase transition temperature of the different components is different, so the asphalt on the DSC curve shows a multi-component phase transition peak of an overlapping peak [9].

The equipment used for the test was ZetzsehDSC204 produced in Germany at a rate of 10 °C / min, a nitrogen flow rate of 30 ml / min, a measurement starting temperature of 10 °C and an end temperature of 200 °C. The case of matrix asphalt and 13% by volume of red mud modified asphalt, is shown in Fig. 7 and 8, it can be concluded that: (1) the endothermic peak of asphalt is reduced after modification with red mud. From the surface chemistry point of view, the added red mud make its modification process not just a simple blend, but also change the asphalt naturally. (2) Asphalt and red mud modified asphalt which from the glass to viscous state, viscous state to viscous flow of the heat absorption, peak temperature and peak width, can be seen that after the red mud modified, asphalt suction and the thermal stability of the asphalt is improved, and the rheological properties of the asphalt are changed, and the temperature of the asphalt is improved.

![Fig.7 DSC of matrix asphalt](image1)
![Fig.8 DSC of modified asphalt](image2)

In the process of heating the asphalt, the thermal motion of the particles in the asphalt increases continuously. As the temperature increases, the particles will gradually deviate from the equilibrium position. When the temperature reaches the dissolution temperature of the solid, the regularity of the solid is destroyed, which from the orderly state to disorderly liquid. This process of melting is related to the entropy increasing process of the system, and the energy of the system increases with increasing temperature [10].

4. Simulation of red mud adsorption asphalt based on Monte Carlo method

4.1 The construction of the model
Based on the previous research on the composition of red mud, select the most content of the material hematite to study [13,14].

The key to successful molecular modeling is the effective establishment of molecular models. Asphalt modeling methods are mainly the following two: one is the average molecular method; one is the assembly method. Asphalt contains about 105-106 kinds of chemical composition, according to the existing technical means, it is difficult to structure its complete structure out. In this paper, asphalt is divided into asphaltene, oil and glial three components to study, to build three components of the most representative of the molecular model.
The asphaltene molecular model is selected from the average molecular structure obtained by Arto
k [15] after nuclear magnetic resonance analysis; the colloidal molecular model is selected from the gr
oup consisting of 1,7-dimethylnaphthalene molecules with similar molecular structures as early format
ion of asphaltenes [16]; The molecular model of oil is selected from C_{22}H_{46} [17,18], which is consiste
nt with the softening point and boiling point of most asphalt oil, as shown in Fig 9.
MS software in the Sorption module is a Monte Carlo method to build the amorphous model of the too
l can be used to build composite model, small molecule solution model, the channel filling model and
a variety of components in different mix of polymer blending Model and so on. The hematite structure
is directly imported from the Import file. Before the surface adsorption simulation, the optimized hem
atite structure is cut along the (0 0 1) plane by using the commands under the build menu in the MS so
ftware. The model is placed in a box with a periodic structure to create a vacuum layer. Using the thre
e-component structure of the asphalt, the sorption module under the adsorption calculation, task select
Fixed loading, the temperature is set to 298K, the calculation method to select Metropolis, force field s
lection of the force field, electrostatic interaction selection Ewald & Group for processing, van der W
aals interaction Select Atom Based, and calculate 100000 Monte Carlo steps to balance and analyze. A
fter the simulation is completed according to the above calculation, the equilibrium structure and relate
d adsorption information of the asphalt adsorbed on the two crystal faces can be obtained.

**Figure 9** Asphalt three-component structure (followed by asphaltene, resin and saturate)

4.2 MS Simulation Results and Discussion

**Figure 10** hematite adsorption asphalt model and adsorption energy map(followed by asphaltene, resin
and saturate)

The adsorption of different components on the red mud as shown in the figure 10, asphaltene has a
small amount of molecules gathered in the red mud between the vacuum layer, almost no adhesive mainly rely on the adhesion of the surface attached to the red mud, and oil in the vacuum layer The maximum; from the figure can be seen red mud structure and not because of the addition of bitumen and destruction, which also shows that red mud modified asphalt is a physical modification. The adsorption of bitumen, glial and oil in red mud is shown in Fig. . The glial is only adsorbed in a specific position, but the adsorption energy of the colloid is the largest, this result may be due to the red mud and bituminous components of the polarity of the molecule, similar to the similar chemical compatibility principle. The simulation results also confirm the conclusion that the red mud can absorb the oil in the asphalt, thus enhancing the adhesion between the two, thereby improving the performance of asphalt.

5. Conclusion
In this study, through the laboratory asphalt penetration test, softening point test, ductility test, scanning electron microscope, using the penetration, penetration index, equivalent softening point, equivalent brittle point and the degree of delay as the basic technical indicators, and using infrared spectrum, electron microscope scanning, molecular simulation technology and differential scanning calorimetry analysis to analyze the mechanism and modification of behavior of red mud asphalt from the microscopic point of view, and the following conclusions were drawn:

1) The incorporation of red mud improves the consistency of matrix asphalt, improves the ability of asphalt to resist deformation, and improves the high temperature performance of matrix asphalt. When the content of red mud is less than 10%, the change rule of modified asphalt is not very obvious, and the reason for further study is needed.

2) From the analysis of the results of scanning electron microscopy, red mud, as a modifier, is a separate form of uniform fraction in the asphalt, and because of its large surface area and small particle size, thus red mud absorbs part of the oil in the asphalt enhance the adhesion between the two, thereby enhancing the performance of asphalt.

3) The infrared spectrum analysis showed that the asphalt was mainly composed of alkanes, naphthenes, aromatic and other derivatives. Compared with the asphalt, the absorption peaks of the modified asphalt were not strengthened, indicating that the red mud and the asphalt Between the intermolecular forces, the incorporation of red mud and no chemical reaction with the asphalt, but a simple physical blending.

4) After differential scanning calorimetry, the endothermic peak of the asphalt decreased and the heat absorption decreased, which indicated that the thermal stability of the modified asphalt was improved and the temperature was decreased.

5) The molecular simulation shows that the bond can have the greatest influence on asphaltenes during the process of asphalt melting, and van der Waals have little effect. It is shown that the modification of the red mud asphalt is mainly controlled by the bond. To achieve good modification performance, it is necessary to carry out advanced activation of the red mud and enhance its molecular bond energy with the asphalt.

Acknowledgment
Fund Project: National Natural Science Foundation of China (51368015)

Reference
[1] Miroslav M, Ian T B, Matthias R, et al. Red mud a byproduct of aluminum production contains soluble vanadium that causes genotoxic and cytotoxic effects in higher plants [J]. Science of the Total Environment, 2014, 493: 883-890.
[2] WANG Xilin, CHENG Songbo, YU Jianying, GAO Tao, CHEN Liang. Properties of Grafted SBS Modified Bitumen with Different Monomers [J]. Petroleum Asphalt, 2008, 04:26-29.
[3] WANG Jinggang, Inorganic Powder Modified Asphalt Preparation and its Modified Mechanism Research[D]. Wuhan University of Technology, 2009.
[4] LI Shaochun, ZHANG Guoli, ZHAO Tiejun, WANG Haitao, JIN Zuquan. Effect of Activation Method
for Bayer Red Mud on Properties of Cement Based Materials[J]. Concrete, 2013, 06: 29-32+39.

[5] SUN Lu, XIN Xiantao, WANG Hongyao, GU Wenjun. Microscopic Mechanism of Modified Asphalt by Multi-Dimensional and Multi-Scale Nanomaterial[J]. Journal of The Chinese Ceramic Society, 2013, 06: 29-32+39.

[6] ZENG Menglan, ZHAO Yu, PAN Hanzhi, MENG Jijun. An Experiment Study On Performance Of European Rock Asphalt Modified Asphalt Binder[J]. Journal of Hunan University (Natural Sciences), 2016, 05: 125-130.

[7] XIE Meidong, LI Xiangqiong. Experimental Study on Properties and Modification Mechanism of Natural Rock Asphalt Modified[J]. Hunan Communication On Science And Technology, 2007, 03: 1-3+62.

[8] SUN Henghu, FENG Xi,XING LIU Xiaoming, BAI Xue, NIU Xuelian. The Influence of Mechnochemistry on the Structure Speciality and Cementitious Performance of Red Mud[J]. Rare Metal Materials and Engineering, 2007, S2: 568-570.

[9] BAO Yanni. Study on Diatomite Modified Asphalt[D]. Changan University, 2005.

[10] HUA Min, ZHANG Chao, LI Zuzhong. Effect of Natural Asphalt on Temperature Sensitivity of Matrix Asphalt[J]. Petroleum Asphalt, 2011, 03: 37-41.

[11] XIANG Baowei, YU Xuefen, LUO Zhaowen. Research Progress of Simulated Annealing Algorithm in Optimization[J]. Journal of Taizhou University, 2005, 06: 6-9.

[12] DUAN Xingxing. Study on Conventional Performance and Mechanism of Modified Asphalt[D]. Guilin University of Technology, 2016.

[13] Soldan M, Kobeticova H, Gerulova K. Photocatalytic degradation of methylene blue using glass fibers catalytic layer covered with red mud[J]. Journal of Materials and Applications, 2017, 6(1): 23.

[14] Agblevor F A, Elliott D C, Santos A D M, et al. Red Mud Catalytic Pyrolysis of Pinyon Juniper and Single-Stage Hydrotreatment of Oils[J]. Energy & Fuels, 2016, 30(10): 7947-7958.

[15] Artok L, Su Y, Hirose Y, et al. Structure and reactivity of petroleum-derived asphaltene[J]. Energy & Fuels, 1999, 13(2): 287-296.

[16] Kowalewski I, Vandenbroucke M, Huc A Y, et al. Preliminary results on molecular modeling of asphaltenes using structure elucidation programs in conjunction with molecular simulation programs[J]. Energy & Fuels, 1996, 10(1): 97-107.

[17] Chemistry of asphaltenes[M]. American Chemical Society, 1982.

[18] Storm D A, Edwards J C, DeCanio S J, et al. Molecular representations of Ratawi and Alaska north slope asphaltenes based on liquid-and solid-state NMR[J]. Energy & fuels, 1994, 8(3): 561-566.

[19] Greenfield M L, Zhang L. Developing model asphalt systems using molecular simulation[J]. 2009.