Comparison of Material Composition and Road Performance of Different Natural Asphalts

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Abstract. Because of the differences in material composition and structure, different natural asphalt will lead to different road performances and technical approaches. Based on years of research data, the composition and characteristics of different natural asphalt are reviewed. It is considered that the difference of performance of different natural asphalt is closely related to asphalt content and ash content. Aging property is related to oil content and microstructure of asphaltene. Because the mineral composition of lake asphalt is mostly volcanic ash, it shows different modification effect from natural rock asphalt, and has more advantages in the comprehensive performance of asphalt mixture, especially in low temperature performance and fatigue resistance.

1. Introduction
Natural asphalt is a compound mixed by asphaltene component and mineral substance under a complicated process with very long period. Inside the natural asphalt is the asphaltene organic mixture, which contains a series of macromolecular hydrocarbons and different atomic compounds. Therefore, it is hard to identify the exact chemical constitutes and physical properties of nature asphalt, with a variety of occurrence and micro-structures[1, 2]. In road engineering, only according to the occurrence of natural asphalt, natural asphalt is divided into rock asphalt, lake asphalt and so on. But these classification methods above are primarily based on its occurrence and other macro characteristics. We still have a limited understanding about the structural constitute of natural asphalt so far, which restricts the effective use of it.

Due to the different composition and properties of natural asphalt from different areas, there are significant differences in the application mode and proportion of asphalt pavement. Many practical projects neglect the material design and performance optimization of natural asphalt, and do not fully understand the impact of the type and composition of natural asphalt on the performance of asphalt mixture, resulting in its road performance not fully developed[4].

At the same time, the application standards and specifications of natural asphalt are not perfect. "Technical Specification for Construction of Highway Asphalt Pavement" (JTG F40-2004, Chinese) only stipulates that "quality requirements of natural asphalt should be implemented according to its varieties with reference to relevant standards and successful experience". “Part 5: natural asphalt” (JT/T 860.5) only has some technical requirements for Xinjiang rock asphalt, lake asphalt and others. It emphasizes the minimum increment of softening point of modified asphalt after adding natural asphalt and the conventional performance index of modified asphalt mixture. The imperfection of these specifications is mainly due to the lack of comprehensive evaluation of different natural asphalt.

In view of the above situation, this paper systematically compares and comments on the performance of typical natural asphalt, including Trinidad Lake Asphalt (TLA) and China Qingchuan Rock Asphalt (QRA), Indonesian Buton Rock Asphalt (BRA), Venezuelan Rock Asphalt (VRA) and
Albania Rock Asphalt (ARA). The data in this paper are derived from more than ten years of indoor research results and engineering practice, focusing on the analysis of the road performance and technical characteristics of different types of natural asphalt, hoping to enrich the material research content of natural asphalt and improve the application design and technical guarantee system of natural asphalt.

2. Composition of Natural Asphalt

2.1. Mineral Composition

In general, natural asphalt contains complex mineral components, such as clay minerals, in addition to asphalt composition (asphaltene, resin, aromatics, saturates). The XRD diffraction pattern in Figure 1 shows that the mineral composition of different natural asphalt is different, and the contents of carbonate, silicate and aluminosilicate are obviously different. These mineral compositions constitute the main components of the natural asphalt ash, and provide a certain degree of modification behaviour in the modified asphalt.

![Figure 1. XRD spectrums of natural asphalts.](image)

Table 1 shows that rock asphalt contains two inert minerals, carbonate and quartz. The mineral composition of TLA lake asphalt is mostly volcano ash and has a certain chemical activity composition. The composition determines that there is a certain difference between the effect of Lake Asphalt and rock asphalt.

| Natural asphalt | Mineral compositions                        |
|-----------------|---------------------------------------------|
| VRA             | CaSO₄, SiO₂, CaS, CaCO₃                     |
| ARA             | SiO₂, CaCO₃, CaSO₄, Fe₂O₃, Al₂O₃             |
| TLA             | (Ca₄Al₈Si₈O₃₂)·H₂O₈₆₆₄, SiO₂, Al₂O₃        |
| BRA             | CaCO₃, SiO₂                                  |
| QRA             | CaCO₃, SiO₂, NaAl₅Si₈O₈                   |

2.2. Chemical Composition

The asphalt content of different natural asphalt is significantly different, and the content of 4 components is also very different. The four-component data in Table 2 indicate that the asphalt content of VRA rock asphalt is the highest, and the natural asphaltene content of QRA, ARA, TLA and BRA decreases accordingly. The contents of resin and oil (aromatics and saturates) of different natural asphalt are also significantly different. These four components directly affect the properties and road...
performance of natural asphalt modified asphalt, and there will be differences in high temperature performance, low temperature performance and fatigue performance.

Table 2. Chemical compositions of natural asphalts.

| Natural asphalt | Insoluble content (%) | asphaltene (%) | Resin (%) | Aromatics (%) | Saturates (%) |
|-----------------|-----------------------|----------------|-----------|---------------|---------------|
| VRA             | 3.1                   | 59.3           | 21.3      | 12.5          | 3.8           |
| QRA             | 42.2                  | 47.9           | 6.7       | 2.6           | 0.6           |
| ARA             | 28.2                  | 27             | 18.5      | 15.4          | 11            |
| TLA             | 36                    | 20             | 21        | 16.1          | 6.9           |
| BRA             | 75                    | 11.1           | 5.5       | 5.5           | 2.9           |

In theory, the microstructure of natural asphalt will change with the change of geological conditions, and the asphalt will change from amorphous structure to microcrystalline structure, and finally to quasi crystalline structure[2, 4].

Table 3 is the structural parameters of asphaltenes in natural asphalt calculated by XRD diffraction data, which shows that the structural parameters of asphaltenes in natural asphalt are quite different from those of petroleum asphaltenes, mainly reflected in the smaller aromatic carbon ratio ($F_a$), the lower average accumulation height of aromatic layer ($L_c$), and the smaller effective aromatic layers ($M_e$) than petroleum asphaltenes, which are distributed in about 2-4 layers. This difference in microstructure shows that the molecular structure of natural asphalt is closely stacked, which can more effectively limit the infiltration of oxygen production and bring about better oxidation-aging resistance of natural asphalt, which is one of the reasons for the good aging resistance of natural asphalt modified asphalt.

Table 3. Structural parameters of natural asphalt and petroleum asphaltene

| Structural parameter                          | QRA    | BRA    | VRA    | petroleum asphaltene[4] |
|----------------------------------------------|--------|--------|--------|-------------------------|
| Aromaticity carbon rate $F_a$                 | 0.1    | 0.11   | 0.03   | 0.4                     |
| Aromatic layer spacing $D_{at}$ (Å)           | 3.58   | 3.73   | 3.51   | 3.55-3.7                |
| Saturated part spacing $D_r$ (Å)              | 5.8    | 7.29   | 5.79   | 5.5-6.0                 |
| Average diameter of aromatic layer $L_a$ (Å)  | 16     | 9.9    | 30.5   | 8.5-15                  |
| Average height of aromatic layer $L_c$ (Å)    | 7.65   | 4.86   | 14.9   | 16-20                   |
| Effective aromatic layers $M_e$               | 2.14   | 1.3    | 4.24   | 5                       |

3. Modified Asphalt by Natural Asphalt

Natural asphalt can improve the consistency and high temperature performance of modified asphalt, and has a negative effect on extensibility and low temperature performance. The high temperature performance of modified asphalt is closely related to asphaltene and resin content, while the low temperature performance is related to saturated content and aromatic content[5]. Different rock asphalt will bring different properties of modified asphalt due to the difference of four components and mineral content.

3.1. Penetration and Softening Point

A large number of tests have shown that the penetration and softening point of modified asphalt varies linearly with natural asphalt content. By using the relation curve of natural asphalt content and asphalt index, the modification effect of natural asphalt is examined with the change slope. In this paper, the relation slope between penetration and the content of natural asphalt is called the Pen-decrease rate, and the relation slope between softening point and the content is called the SP-increase rate.

Figure 2 shows that the sensitivity of modified asphalt to different natural asphalt content is different. In terms of the SP-increase rate and the Pen-decrease rate, the modification effect is in accordance with QRA, VRA, ARA, TLA and BRA, that is to say, QRA rock asphalt and VRA rock asphalt are most sensitive to the improvement of high-temperature performance; TLA Lake Asphalt
and BRA rock asphalt are relatively weak to the improvement of high-temperature performance due to the large content of mineral substances and the small content of asphaltene.

Figure 3 shows the relationship between asphaltene and softening point in different natural asphalt modified asphalt. It shows that the increase of asphaltene content can improve the softening point of asphalt, and is directly related to the contribution of asphalt consistency and high temperature performance.

![Figure 2](image_url1)

**Figure 2.** Modified effects contrast by natural asphalt.

![Figure 3](image_url2)

**Figure 3.** Modified effects and asphaltene in natural asphalt.

### 3.2. Ductility and Thermal Aging Property

Figure 4 shows the relationship between penetration and ductility of natural asphalt modified asphalt. When the penetration of natural asphalt modified asphalt is less than 40 DMM, the ductility index decreases seriously. As a result, the low temperature performance and ductility of natural asphalt modified asphalt are poor. In order to meet the needs of modified asphalt technology, the content of natural asphalt has an upper limit.

Due to long time geological effects, natural asphalt has undergone a long change in nature and tends to be stable. In addition, the structure of asphaltene is more compact, and its thermal aging resistance and oxidation resistance are greatly improved, which can improve the anti-aging properties of asphalt. Fig. 5 is the penetration ratio of short-term aging residues of different natural asphalt modified asphalt. The matrix asphalt is TIPCO, Shell and Caltex matrix asphalt. It can be seen that the penetration ratio of different natural asphalt modified asphalt has been improved, indicating that natural asphalt has good anti-aging effect.
Figure 4. Relation between ductility and penetration of natural asphalt modified asphalt.

Figure 5. Residual penetration ratio contrast for modified asphalt with different natural asphalt.

4. Pavement Performance Contrast

Natural asphalt can generally improve the high temperature stability and water stability of asphalt mixture, but different natural asphalt has different improvement effects.

Fig. 6 shows that QRA rock asphalt and VRA rock asphalt perform best in improving the asphalt mixture's high temperature performance, and the lower amount of usage can significantly improve the dynamic stability of the mixture. However, at low temperature and water stability, with the increase of asphalt content, the low temperature performance of asphalt mixture will decrease as Figure 7 described, and there is an inflection point on the relationship curve between water stability and dosage in Figure 8. It shows that there is an optimum proportion of any natural asphalt. In specific applications, the design and performance verification of different types of natural rock asphalt should be carried out.

Different from natural rock asphalt, TLA lake asphalt can not only improve the high-temperature stability and water stability of asphalt mixture, but also improve the low-temperature performance. Its comprehensive performance is better than that of rock asphalt natural asphalt, which is related to the high content of volcanic ash minerals in lake asphalt, as well as the high oil composition content (saturation and aromatics).
Figure 6. Dynamic stability ratio changes with different natural asphalt contents.

Figure 7. Water stability ratio changes with different natural asphalt contents.
Figure 8. Low temperature performance ratio changes with different natural asphalt contents.

Note: in order to horizontally compare the road performance indexes of different natural asphalt modified asphalt mixtures, the ratio of performance indexes is adopted to avoid the influence of different matrix asphalt. Among them, the ratio of dynamic stability: the ratio of dynamic stability of modified asphalt mixture to that of unmodified asphalt mixture; the ratio of freeze-thaw splitting strength and the ratio of maximum bending tensile strain are explained in the same way.

In the aspect of fatigue performance, rock asphalt and lake asphalt also show different characteristics. Taking QRA rock asphalt as an example, Figure 9 shows that there is an inflection point of dissipation energy in the process of fatigue test when the content of QRA rock asphalt is 7.5%, and the corresponding fatigue times and dissipation energy are the largest. In Figure 10, the fatigue performance of TLA lake asphalt is much better than that of 70 and 90 matrix asphalt mixtures at 40% content. It shows that the high proportion of lake asphalt can still obtain better fatigue resistance, which is closely related to the composition of lake asphalt.

Figure 9. Fatigue performance of modified asphalt by QRA.
Figure 10. Fatigue performance of modified asphalt by TLA.

5. Conclusions
Natural asphalt has low price, good solubility in asphalt, simple modification process, low cost, improved asphalt mixture performance and significant environmental benefits. This has become the original intention of many engineering applications. However, different natural asphalt has different material composition and structure, which will lead to different road performance and technical approaches.

The performance difference of different natural asphalt is closely related to asphalt content, four component content and ash content. Because the mineral composition of lake asphalt is mostly volcanic ash, it shows different modification effect from natural rock asphalt, and has more advantages in the comprehensive performance of asphalt mixture, especially in low temperature performance and fatigue resistance.

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7. References
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