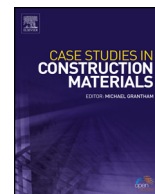




ELSEVIER

Contents lists available at ScienceDirect

Case Studies in Construction Materials

journal homepage: www.elsevier.com/locate/cscm

Case study

Effects of acidic water on hydro-mechanical properties of asphalt concrete

Shan Feng^a, Weibiao Wang^{b,*}, Hang Tan^c, Meng Xue^d, Kaare Höeg^e^a Institute of Water Resources & Hydroelectric Engineering, Xi'an University of Technology, Xi'an, 710048, PR China^b Institute of Water Resources & Hydroelectric Engineering, Xi'an University of Technology, Xi'an, 710048, China^c Southwest Electric Power Design Institute Co., Ltd. Of China Power Engineering Consulting Group, Chengdu, 610066, PR China^d Shaanxi Xixian New Area Fengxi New City Development and Construction (Group) Co., Ltd., Xianyang, 712000, PR China^e Norwegian Geotechnical Institute, NO-0806, Oslo, Norway

ARTICLE INFO

Article history:

Received 6 September 2020

Received in revised form 3 October 2020

Accepted 7 October 2020

Keywords:

Acidic water

Asphalt material

Mass loss

Degradation of properties

Pervious asphalt concrete

Impervious asphalt concrete

Durability

Road pavements

Dams

Storage of tailings

ABSTRACT

Asphalt concrete is widely used in road and airport pavements and more recently also in the construction of impervious facings and central cores in dams and dykes. Asphalt concrete may be subjected to strongly acidic water when used in connection with storage of mine tailings (tailings dams). Acidic water reacts with bitumen and mineral materials and may cause deterioration of the behavior of asphalt concrete with time. The present study investigated effects of acidic water with time on aggregate-bitumen adhesion, bitumen penetration value, softening point and ductility, mass change of asphalt materials, and change in tensile strength for porous and impervious asphalt concrete. The test results show that impervious, hydraulic asphalt concrete is very resistant to acidic water and show insignificant deterioration of properties during the 3-year testing period used in the experiments.

© 2020 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction and scope

Asphalt concrete is commonly used in road and airport pavements, and as described in the literature referred to below, research has been done to study the effects of acid rain on the properties of asphalt concrete used for that purpose. In connection with the storage of mine tailings, asphalt concrete is also being used in impervious upstream facings (linings) or central cores of dams, where the asphalt concrete is exposed to acidic mine drainage (AMD).

The asphalt concrete used for road pavements is usually relatively pervious [1], while the hydraulic asphalt concrete used in dams with air porosity of less than 3 % is relatively impervious with permeability about 10^{-10} m/s [2–5]. Very little research has been done to study the durability of asphalt concrete used for tailings storage facilities [6] and the dam designer has so far attempted to compensate for the potential mass loss and degradation of hydro-mechanical properties with time by adding a more-or-less arbitrary thickness to the dam lining or core. The scope and purpose of the present study is to investigate the effects of acidic water on the strength properties, the resistance to cracking, durability, and watertightness of hydraulic asphalt concrete.

* Corresponding author.

E-mail addresses: fengshan@xaut.edu.cn (S. Feng), weibiaowang@xaut.edu.cn (W. Wang), tanhang@swepdi.com (H. Tan), 2318686513@qq.com (M. Xue), kaare.hoeg@ngi.no (K. Höeg).

2. Overview of previous experimental investigations

Zhang et al. [7–9] performed acidic water corrosion tests on asphalt concrete applied in road pavements using water solutions with pH = 1, 3, and 5.6 by mixing H₂SO₄ and HNO₃ with mole ratio of 3:1 to simulate the acid rain. Marshall asphalt specimens with 4 different mixes were exposed to 4 cycles of 7 days (6-day immersion plus 1-day drying). The test results indicated that after 4 cycles the mass loss and void content of the specimens had increased, while the Marshall stability was reduced with the reduction of pH value.

Wang [10] did a systematic investigation of the effects of acid rain on bitumen and mineral materials. He described the mechanism of acidic water reacting with bitumen and mineral materials and details are presented below in the section on mass change of asphalt materials caused by acidic water corrosion. Feng et al. [11] performed acidic water corrosion tests on bitumen specimens using acidic water solutions with pH = 2 and 4 by mixing H₂SO₄ and HNO₃ with mole ratio of 9:1 to simulate the acid rain. Results from tests in neutral water (pH = 7) were used as comparison. Bitumen specimens were subjected to cycles of 8 days (7-day immersion plus 1 day of drying). The acidity of the water solutions was kept constant during the testing, and the bitumen properties were measured after every cycle. The test results indicated that after 5 cycles the penetration value of the bitumen specimens in the two acidic water solutions increased by only 2%. The viscosity reduced by 6.6% and 4.4%, the softening point increased by 7.9% and 6.5%, and the ductility was reduced by 17.5% and 15.8%, in the pH = 2 and 4 solutions, respectively. The four-component analysis indicated that the saturated hydrocarbon content in the bitumen increased significantly, the aromatic hydrocarbon reduced slightly, the gel content reduced significantly, and the asphaltene content increased slightly. The four components in the bitumen specimens were not significantly changed after the specimens had undergone 5 cycles in the neutral water (pH = 7). The infrared spectrum analysis indicated that before and after the specimens had undergone 5 cycles in the acidic water the locations of absorption peaks were the same and the shapes were similar. However, the strengths of the absorption peaks changed significantly, which indicated that chemical reaction had taken place between the bitumen and acidic water but not produced a new functional group. The saturated hydrocarbon content, aromatic functional group content, sulfoxide compounds, sulfite or sulfate content increased slightly in the acidic water while they reduced slightly in the neutral water (pH = 7).

Zhang et al. [7–9] also investigated the chemical corrosion mechanism and did thermodynamic analysis of acid rain on alkali and acidic aggregates. They concluded that acid substances in acidic water reacted with acidic and alkaline substances in the asphalt mixture and produced water soluble salts. Franzoni and Sassoni [12] investigated the correlation between aggregate microstructural characteristics and material degradation (in terms of mass loss) in acidic water solutions to simulate acid rain with pH = 4, 5, and 5.6 (clean rain). After a 14-day immersion, a good correlation coefficient $r = 0.91–0.93$ (depending on pH of solution) was found between mass loss and the product of carbonate content and specific surface area in the starting materials.

Chandra [13] studied the hydrochloric acid attack on cement mortar specimens with dimensions of 40 mm × 40 mm × 160 mm (cement:sand ratio 1:3). After a period of immersion in the acid water, the specimens were taken out and cut in slices for analyses. A ring of iron was noticed to surround and protect the inside mortar from further deterioration. Liu et al. [14] put marble and red sandstone specimens (φ50 mm × 25 mm and φ50 mm × 100 mm) in a hydrochloric acid water solution (pH = 4) for 30 days. The mass losses of marble and red sandstone specimens (φ50 mm × 25 mm) were 8% and 4%, respectively. The compressive strengths of marble and red sandstone specimens (φ50 mm × 100 mm) reduced by 52% and 41%, respectively. The indirect tensile strength (Brazilian splitting test) of marble and red sandstone specimens (φ50 mm × 25 mm) reduced by 15% and 11%, respectively. Zhong et al. [15] put limestone specimens (φ50 mm × 100 mm) in nitric acid water solutions (pH = 3 and 5) and in neutral water (pH = 7) for 30 days. The void contents increased by 0.18 and 0.03 percentage points for the specimens in pH = 3 and 5 solutions, respectively. Compared with the mechanical behavior of the specimens in neutral water, the compressive strengths reduced by 25% and 10% while the friction angles and cohesion parameters reduced by about 20% and 11%, for the specimens in the pH = 3 and 5 solutions, respectively.

Xia et al. [16] put 7 kinds of carbonate rock specimens (φ 38 mm × 8 mm) with different formation ages in AMD (pH = 2.3) from an abandoned mine. Three specimens of each of the 7 kinds were immersed in 3000 mL AMD for 5, 10, 15, 25, 30, and 60 days, respectively. Mass loss (erosion) was measured at the predetermined times. Scanning electron microscope and an energy dispersive spectrometer were used after the specimens had been immersed in the AMD for 30 days. The erosion rate was in the range 22–31 × 10⁻⁴ g/cm²/day at the 5th day and 4–8 × 10⁻⁴ g/cm²/day at the 60th day for the 7 kinds of specimens. The erosion rate was reduced in the first 30 days from an average rate of about 25 × 10⁻⁴ g/cm²/day at the 5th day to an average rate of about 10 × 10⁻⁴ g/cm²/day at the 30th day. In addition to the increase of pH value in the 3000 mL AMD due to the chemical reactions, the crystallization rate of calcium sulfate on the rock surfaces was one of the key factors reducing the erosion rate of carbonatite in the carbonate rocks. The dissolution of magnesium carbonate (Mg²⁺) was an important factor to reduce the crystallization rate of calcium sulfate.

Mellado et al. [17] evaluated the resistance to acid attack of ordinary Portland cement (OPC) and alkali-activated pastes. The test results showed that OPC paste suffered the most degradation, while the alkali activated pastes with the lowest calcium content had the best performance.

3. Materials and methodologies

For the present study, the widely-used Chinese bitumen type B90 from the Kelamayi refinery (denoted by K) and from the refinery of China National Offshore Oil Corporation (denoted by Z) were selected. Common limestone filler (less than 0.075 mm), crushed limestone sand (0.075 mm–2.36 mm) and aggregates (2.36 mm–19 mm) were used. Test methods and procedures followed the Chinese standard and test code for bitumen and asphalt concrete for highway engineering and impervious facings and cores [18,19] with some modifications to suit the specific study.

3.1. Materials

The properties of the bitumen from the two refineries are shown in Table 1. Chemical components of limestone in filler, sand and aggregates are shown in Table 2. The asphalt concrete mix used for an impervious core in an embankment dam built in China was used in this study and is shown in Table 3. Fig. 1 shows the aggregate gradation curve.

The acidity of water solutions with pH = 2, 4, and 6 was adjusted by using H₂SO₄. And neutral water (pH = 7) was used as reference.

3.2. Methodologies

(1) Test to determine bitumen - aggregate adhesion

The aggregate-bitumen adhesion (bonding) is known to have a very important effect on the hydro-mechanical properties of asphalt concrete, for instance the tension and cracking resistance. Water is known to have a potentially detrimental effect on the adhesion, and the susceptibility to moisture is therefore considered to be a good indicator of the bonding strength.

One of the most used control methods is the Texas Boiling Test (ASTM D3625–2000), but the tests conducted in this paper followed the above-mentioned Chinese specifications. Using the Chinese code, one classifies the quality of aggregate adhesion into five grades. Five clean aggregate particles, size 13.2 mm–19 mm, are heated and covered with bitumen. The particles are cooled and then boiled in water for 3 min. The quality of aggregate adhesion is classified by the observations of the conditions of the bitumen film (membrane) left on the particles after boiling, as shown in Table 4.

In order to investigate the effect of acidic water on aggregate-bitumen adhesion the test procedure was slightly modified. Limestone aggregate particles, size 13.2 mm–19 mm, and bitumen type B90 from the Kelamayi refinery (denoted by K) were used in the test. The initial grade of the aggregate-bitumen adhesion was Grade 5. Four glass bottles with volume of 750 mL were separately filled with 450 mL acidic water with different pH values. In each bottle there were put 6 bitumen-covered aggregate particles submerged in the water. The bottles were sealed and kept at 20 °C, and the conditions of the bitumen-covered aggregate particles were observed with time. Each week one bitumen-covered particle from each of the four bottles was taken out and the Boiling Test was performed. The acidity of the water in the four bottles was measured by pH meter.

(2) Test of effects of acidic water on bitumen properties

The penetration value, softening point and ductility are the important properties of bitumen and the test methods followed the above-mentioned Chinese specifications.

In order to investigate the effects of acidic water on the properties of the bitumen with time, twenty-two (22) bitumen specimens (B90, K specimen) 300 mm in diameter and about 3 mm thick were prepared. The 3 mm thickness of bitumen specimens was designed by referring to the thin film oven test (TFOT). In order to increase the test accuracy, the

Table 1
Properties of the bitumen B90 [4,20,21].

Test properties	Standard	K	Z
Penetration (25 °C, 100 g, 5 s)/(0.1 mm)	80–100	87	86
Ductility (15 °C, 5 cm/min)/(cm)	≥150	>150	>150
Softening point (TR&B)/(°C)	45–52	46	46
Density (25 °C)/(g/cm ³)	–	0.982	1.006
TFOT	–0.8% - +0.8 %	0.01	0.10
Loss by mass (%)	≥70	86	72
Residual penetration (%)	≥100	>150	>150
Residual ductility (cm)	–	27.9	21.2
Four components (%)	–	31.7	32.6
Saturated hydrocarbon	–	38.7	40.4
Aromatic hydrocarbon	–	1.7	5.8
Gel	–	–	–
Asphaltene	–	–	–

Table 2

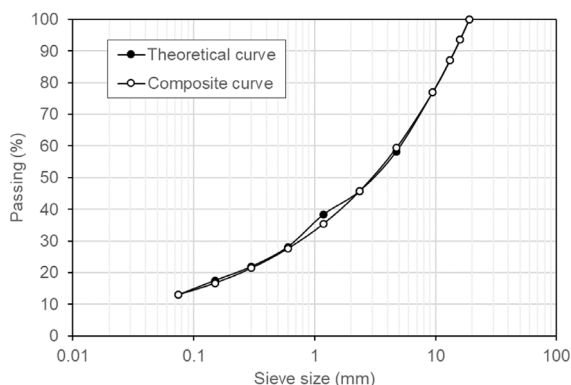
Chemical components of limestone in filler, sand and aggregates.

Component	CaO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	MgO	TiO ₂
Content (%)	27.08	8.82	0.14	1.54	19.28	0.07
Component	MnO	FeO	K ₂ O	P ₂ O ₅	Na ₂ O	Loss on ignition
Content (%)	0.02	0.54	0.76	0.02	0.04	41.69

Table 3

Asphalt mix design used in this study (% of mineral weight).

Sieve size (mm)						Bitumen content
13.2–19	9.5–13.2	4.75–9.5	2.36–4.75	0.075–2.36	0–0.075 (Filler)	
13	10	19	12	33	13	6.9

**Fig. 1.** Aggregate gradation curve used in this study.

diameter of the bitumen specimens in this study was larger than that in TFOT (300 mm vs.140 mm). One group of 11 bitumen specimens was put in acidic water with pH = 2 and another group of 11 bitumen specimens was put in neutral water with pH = 7. The acidity of the water was kept constant and the temperature was 20 °C. One specimen of each group was taken out for testing.

(3) Test of mass change of asphalt materials by acidic water corrosion

The test method was designed in this study to measure the mass change of different combinations of asphalt materials by acidic water corrosion. Bitumen type B90 from the two refineries were used. Three kinds of asphalt material specimens were prepared, i.e., pure bitumen, asphalt mastic, and sandy asphalt mastic. Asphalt mastic consisted of bitumen and limestone filler (less than 0.075 mm), while sandy asphalt mastic consisted of bitumen, filler, and crushed limestone sand (0.075 mm–2.36 mm). Ten kinds of asphalt material specimens were tested as shown in Table 5.

Acid-resistant borosilicate dishes of inside diameter 100 mm were used to hold the specimens. Each dish was weighed and labeled. The hot bitumen and asphalt mastic were separately poured into the dishes. The thickness of the thin bitumen and asphalt mastic specimens was designed to be as thin as 2 mm. The thickness of the sandy asphalt mastic specimens was 5 mm because the maximum size of the crushed sand particles was 2.36 mm. After the asphalt materials cooled down, each dish with the specimen was weighed, and the original weight of each specimen was obtained by deducting the weight of the dish. All the dishes with specimens were put in a polyethylene (PE) plastic container that was filled with acidic water with pH = 2 and kept at 20 °C. Only the top face of the bitumen and asphalt mastic specimens was in contact with the acidic water, while both the top and bottom faces of the sandy asphalt mastic specimens contacted the acidic water by using a special support under the bottom face of the specimens. The corrosion process lasted 16 months while the acidity of the water with pH = 2 was kept constant. At the predetermined times the dishes with the specimens, but without the water, were weighed. After weighing, the dishes with specimens were put back in the container. The mass change of each specimen was calculated in percent by comparing with the original weight.

Table 4
Grade of aggregate adhesion to bitumen according to Chinese code [19,22].

Condition of bitumen film left on the particles after 3-min boiling	Grade
Complete aggregate surface area still covered by bitumen, and no film is removed	5
Less than 10 % of the bitumen-covered area is removed, and the film is not significantly deformed	4
Less than 30 % of the bitumen-covered area is removed. Part of the film is significantly deformed but still stays on the aggregate surfaces	3
More than 30 % of the bitumen-covered area is removed. A significant part of the film is deformed but stays on the aggregate surfaces	2
The aggregates are substantially bare, and the rest of the bitumen film is totally deformed or floats in water	1

Table 5
Ten kinds of asphalt material specimens.

Name	Sample	Mass ratio (bitumen: filler: sand)	Thickness (mm)
Bitumen	K1, K2 Z1, Z2	1:0:0	2
Asphalt mastic	KF1-1, KF1-2	1:1:0	2
	ZF1-1, ZF1-2		
	KF2-1, KF2-2	1:2:0	2
	ZF2-1, ZF2-2		
Sandy asphalt mastic	KF3-1, KF3-2	1:3:0	2
	ZF3-1, ZF3-2		
	KFS ZFS	1:2:2	5

Note: K and Z mean the bitumen from Kelamayi refinery and from the refinery of China National Offshore Oil Corporation, respectively. F and S mean filler and sand, respectively. KF1-1 means sample No.1 of asphalt mastic mix No.1 using K bitumen.

(4) Test of effect of acidic water on tensile strength of asphalt concrete

The indirect tensile test (Brazilian splitting test) was used to give a quantitative measure of the cracking resistance and tensile strength. The size of the cylindrical specimens was 100 mm in diameter and 63.5 mm high (Marshall specimen size). The test method followed the above-mentioned Chinese specifications. Indirect tensile tests were carried out at a displacement rate of 1 mm/min at 20 °C to get the tensile strength and the corresponding tensile strain before a crack opened.

In order to investigate the effect of acidic water on the behavior of asphalt concrete, two kinds of asphalt concrete specimens were tested, i.e., porous (pervious) and impervious asphalt concretes. The porous asphalt concrete allows water to penetrate into the asphalt pores while the impervious asphalt concrete prevents significant penetration. Water solutions with pH = 2 and 7 were used to compare the effects on the behavior of the porous asphalt concrete, and water solutions with pH = 2, 4, 6, and 7 were used for the impervious asphalt concrete. The asphalt concrete mix is shown in Table 3. The porous asphalt specimens were obtained by compacting with 15 blows on each face to yield specimens with void content (air porosity) in the range 3 %–7 %, that is typical for the asphalt used in road and airfield pavements. The average value of the porosity of all the porous asphalt specimens was 5%. The impervious asphalt specimens were obtained by compacting with 35 blows on each face to yield specimens with porosity in the range 1 %–2 %. The average value of the porosity of all the impervious asphalt specimens was 1.5 %. This is typical for the porosity of the asphalt used in the core of embankment dams. The test program for the porous asphalt concrete is shown in Table 6. Table 7 shows the test program for the impervious asphalt concrete.

Forty-five (45) porous asphalt specimens and ninety-nine (99) impervious asphalt specimens were separately put in polyethylene (PE) plastic containers filled with acidic water with different pH values. The acidity of the water was kept constant at 20 °C.

At the predetermined times (every 3 months in the first 15–24 months) the asphalt specimens were taken out. Each specimen was only subjected to the indirect tensile test once.

4. Test results and analyses

4.1. Effect of acidic water on aggregate-bitumen adhesion

The test results are shown in Fig. 2. The results with neutral water (pH = 7) were taken as reference values. After the 6 bitumen-covered aggregate particles were put in the acidic water with pH = 2, chemical reactions with small bubbles occurred at the edges and corners of the particles. The bubbles first grew, but then their size and number decreased and they disappeared with time. Some of the aggregate edges and corners became bare, and the surface color became dark brown due

Table 6

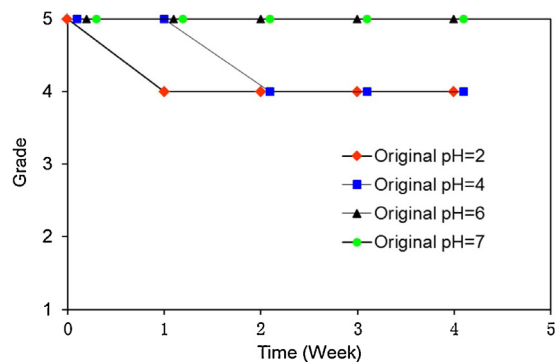
Test program and number of porous (pervious) asphalt specimens in this study.

pH	Time (Month)						
	0	3	6	9	12	15	25
2	3	3	3	3	3	3	6
7	–	3	3	3	3	3	6

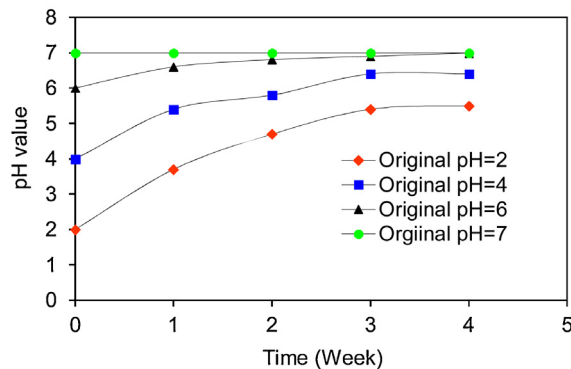
Table 7

Test program and number of impervious asphalt specimens in this study.

pH	Time (Month)								
	0	3	6	9	12	15	21	24	38
2	3	3	3	3	3	3	3	3	3
4	–	3	3	3	3	3	3	3	3
6	–	3	3	3	3	3	3	3	3
7	–	3	3	3	3	3	3	3	3



(a) Grade of aggregate-bitumen adhesion.



(b) Water acidity.

Fig. 2. Grade of aggregate-bitumen adhesion and acidity in the 450 mL acidic water versus time.

to the acidic corrosion. Fig. 2a shows that the Grade of the aggregate-bitumen adhesion in the acidic water with the original pH = 2 was reduced from 5 to 4 in one week, and Grade 4 was kept in the following 3 weeks. Similarly, chemical reactions and small bubbles occurred at edges and corners of the particles in the acidic water with the original pH = 4. However, the size and number of bubbles were smaller than in the water with pH = 2. Fig. 2a shows that the Grade of the adhesion in the acidic water with the original pH = 4 was reduced from 5 to 4 in 2 weeks, and Grade 4 was kept in the following 2 weeks. There were no bubbles developed in the acidic water with the original pH = 6 and neutral water with pH = 7, and the bitumen film on the aggregates was not changed. Grade 5 was kept in the 4 weeks of testing.

When aggregate particles were covered with bitumen, the bitumen film at some edges and corners of the particles were thin. Acidic water would contact the particles through interconnected voids in the thin bitumen film. Reaction of H_2SO_4 in the water solution with CaO and MgO in the limestone aggregate particles occurred and produced bubbles. Fig. 2b shows the increase in the acidity of the 450-mL water solutions with time. The increasing acidity of the water documents that the acidic water reacted with the aggregates by penetrating (diffusing) through the bitumen films.

Experimental results have documented that bitumen modified with anti-stripping agent increases the bitumen-aggregate adhesion [22]. Polymer modified bitumen may increase the resistance of bitumen to acidic water.

4.2. Effects of acidic water on bitumen properties

Fig. 3 shows the test results. Fig. 3a shows that the penetration value of the bitumen specimens after being immersed in water was only very slightly reduced compared with the original value. This reduction may be caused by the reheating of the specimens to form samples for testing the penetration value. Fig. 3b shows no change in the softening point between bitumen specimens in acidic water and neutral water after 11 months. Fig. 3c shows that the ductility of bitumen specimens in acidic water and neutral water after 11 months did not significantly change. It should be noted that the test method for ductility unavoidably gives some scatter in the results, and the maximum range of the ductilimeter was 150 cm. In conclusion, the acidity of water (pH = 2) did not cause significant changes in the bitumen penetration value, softening point and ductility during the 11-month testing period.

4.3. Mass change of asphalt materials by acidic water corrosion

Fig. 4 shows the top face of the specimens after 16 months in the acidic water with pH = 2. Fig. 3a shows that the surface brightness of the two kinds of bitumen specimens had been reduced after being immersed in the acidic water for 16 months. The face of the Z bitumen specimen looked brighter than the K bitumen specimen, which might imply that the reaction or corrosion of the acidic water with the Z bitumen was stronger than with the K bitumen.

Fig. 4b,c,d show that tiny pinholes had developed in the faces of the asphalt specimens with different ratios of bitumen to filler, i.e., 1:1, 1:2, and 1:3 by weight, respectively, after being immersed in the acidic water for 16 months. The size and number of pinholes on the specimen faces increased with time. The number of pinholes on the face of the asphalt mastic specimen increased with increasing filler ratio from 1:1(bitumen: filler) to 1:2 to 1:3.

Fig. 4e shows that pinholes had also developed on the faces of sandy asphalt mastic specimens. The size of some pinholes was as large as 2–3 mm in diameter affected by the maximum size of the sand particles of 2.36 mm.

The observations on the specimen faces indicate that acidic water reacted with the bitumen and the limestone filler and with the sand by penetrating the thin bitumen films covering the mineral particles.

Fig. 5 shows the mass change of the bitumen, asphalt mastic and sandy mastic specimens with time in the acidic water. Mass change is defined as specimen weight after immersion minus original weight, divided by original weight.

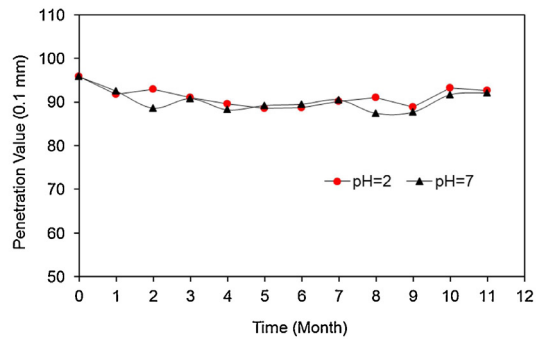
Mass increase or loss of bitumen in acidic water depends on the mass changes of the four components of bitumen (Table 1). As discussed by Wang [10], when bitumen is immersed in acidic water, esterification and alkylation reactions take place between bitumen and sulfuric acid and produce isomeric alkanes with longer chains that cause the increase of saturated hydrocarbon in bitumen. Oxidative condensation of thioether and mercaptan compounds takes place and produces sulfoxide compounds and sulfuric dioxide that causes the increase of asphaltene. The increases of saturated hydrocarbon and asphaltene increase the mass of bitumen. However, solution and ionization of carboxylic acids, phenols, and other acidic substances in bitumen take place to some extent in acidic water, which causes the decrease of gel and a decrease in the mass of bitumen (Wang 2004). Total mass increase or loss of bitumen is determined by the sum of the increases in saturated hydrocarbon and asphaltene and the decrease in gel.

For limestone, sulphuric acid reacts with calcium carbonate and other alkaline substances and produces sulphate, which causes mass loss of limestone [10].

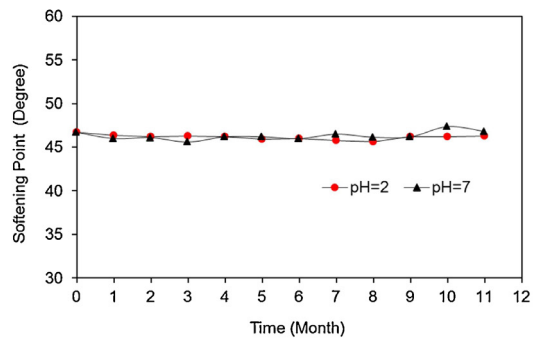
Fig. 5 shows the mass increase of pure K and Z bitumen specimens with time in acidic water and that the mass of K bitumen specimens increased more than Z bitumen specimens. This is in agreement with the observation in Fig. 4a in which the reaction of the acidic water with the Z bitumen seemed stronger than with the K bitumen. For the asphalt mastic and sandy asphalt mastic specimens the acidic water caused mass increase of bitumen but caused mass decrease of limestone. The mass changes of asphalt mastic and sandy asphalt mastic specimens depend on the volumetric ratio of bitumen to limestone. Table 8 shows the volumetric ratio of bitumen to limestone based on the mass ratio of bitumen to limestone (filler and sand) and the densities of bitumen and limestone.

Based on the test results shown in Fig. 5, the mass changes of the bitumen, asphalt mastic, and sandy asphalt mastic specimens versus time were assumed to be approximately linear. Using linear regression for all the test results, the mass change rate of bitumen and limestone in the acidic water was 0.065 %/month for the K bitumen, 0.033 %/month for the Z bitumen, and -0.115 %/month for the limestone in the asphalt and sandy asphalt mastic specimens.

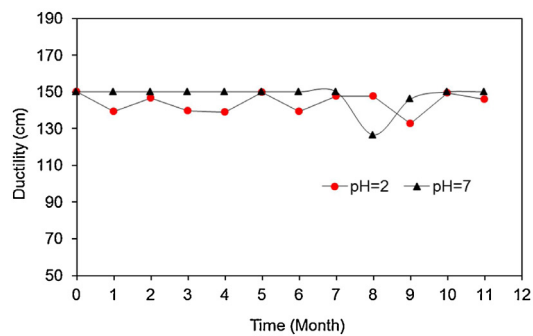
The test results with linear “fitting” lines are compared and shown in Fig. 6. It should be noted that it was only one face of the bitumen and asphalt mastic specimens in contact with the acidic water, while it was two faces for the sandy asphalt mastic specimens. Therefore, the calculations for the sandy asphalt mastic specimens were made for only one face to directly compare with the bitumen and asphalt mastic specimens.



(a) Penetration value



(b) Softening point



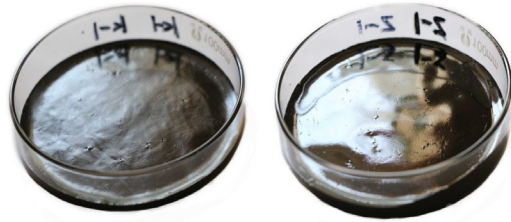
(c) Ductility

Fig. 3. Comparison of penetration value, softening point, and ductility of K90 bitumen specimens in acidic water with pH = 2 and in neutral water with pH = 7.

4.4. Effects of acidic water on the tensile strength of asphalt concrete

(1) Effects on porous (pavement) asphalt concrete

The neutral water (pH = 7) had insignificant effect on the asphalt tensile strength with time, and the test results for the specimens in the neutral water were taken as reference values for the specimens in the acidic water (pH = 2). Fig. 7 shows the strength ratios of asphalt specimen in the acidic and neutral water with time. The strength ratio is defined as the tensile strength of the specimen immersed in acidic water divided by the strength of the specimen in neutral water. Fig. 7 also shows the corresponding ratio between tensile strain across the specimen diameter at failure when the specimen failed in tension (splitting).



(a) Bitumen, left, K-1; right, Z-1



(b) Asphalt mastic (bitumen: filler = 1:1), left, KF1-1; right, ZF1-1



(c) Asphalt mastic (bitumen: filler = 1:2), left, KF2-1; right, ZF2-1



(d) Asphalt mastic (bitumen: filler = 1:3), left, KF3-1; right, ZF3-1



(e) Sandy asphalt mastic, left, KFS; right, ZFS

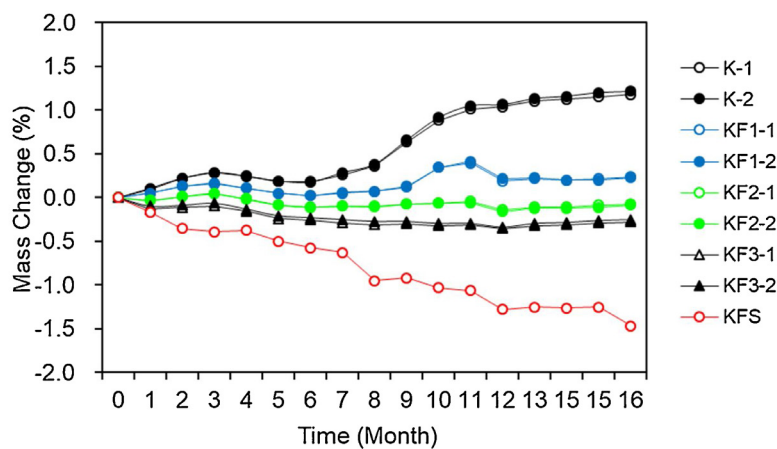
Fig. 4. Top faces of bitumen, asphalt mastic, and sandy asphalt mastic specimens after 16 months in the acidic water with pH = 2 at 20 °C. The label meaning is shown in [Table 5](#).

Fig. 7 shows that the strength ratio was reduced by about 40% during the first 9 months in the acidic water (pH = 2). After that time the strength ratio stayed nearly constant. The strain ratio showed some scatter, but there was an about 20% increase after 9 months.

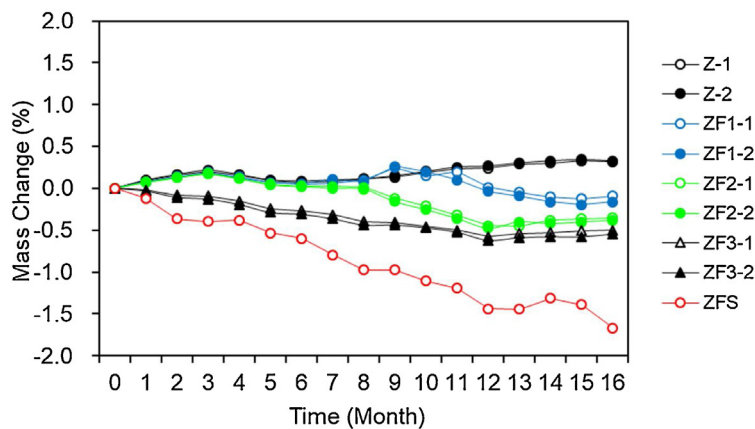
The acidic water penetrates into the voids in the asphalt specimens with void porosity about 5% and thus reacts with the bitumen and the limestone. In addition to degrading the property of bitumen and limestone, the acid reacts with the suboxide in the limestone and produces an emulsifying agent causing the bitumen film to peel off the limestone particles [10]. This would cause the decrease in strength ratio during the first 9 months. After 9 months the strength ratio stayed nearly constant, probably because the acid in the water in the voids would be consumed with time due to the chemical reaction with bitumen and limestone. The acidity of the water in the specimen voids would therefore reduce although the acidity in the acidic water in the container surrounding the specimens was kept constant. The water in the voids with reduced acidity had insignificant effects on the asphalt concrete strength after the first 9 months. The reduction of acidity in acidic water is illustrated in Fig.2b and is discussed in reference [16].

(2) Effects on impervious (hydraulic) asphalt concrete

Fig. 8 shows the corresponding strength and strain ratios for the impervious asphalt specimens in the acidic water (pH = 2, 4, and 6).



(a) K bitumen series-see Tables 4 and 5



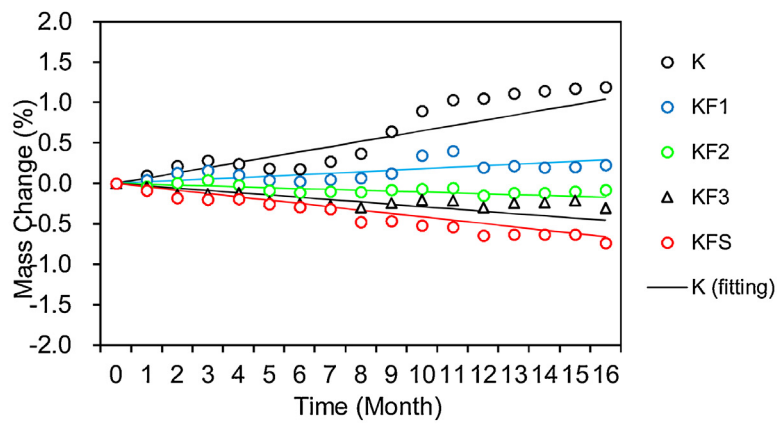
(b) Z bitumen series-see Tables 4 and 5

Fig. 5. Mass change of bitumen, asphalt mastic and sandy mastic specimens with time in acidic water with pH=2 at 20 °C.

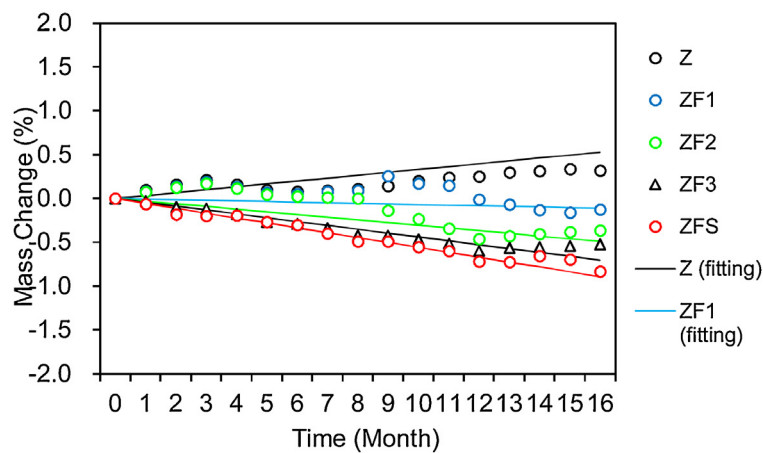
Table 8
Volumetric ratio of asphalt material specimens.

Name	Sample	Mass ratio (bitumen: filler: sand)	Volumetric ratio (bitumen: limestone)
Bitumen	K	1:0:0	1:0
	Z		
Asphalt mastic	KF1	1:1:0	0.74:0.26
	ZF1		0.73:0.27
	KF2	1:2:0	0.58:0.42
	ZF2		0.57:0.43
	KF3	1:3:0	0.48:0.52
Sandy asphalt mastic	ZF3		0.48:0.52
	KFS	1:2:2	0.41:0.59
	ZFS		0.40:0.60

Note: Sample meaning is shown in Table 5.



(a) K bitumen series.



(b) Z bitumen series.

Fig. 6. Comparison of test results and linear fitting lines for mass changes of bitumen, asphalt mastic, and sandy mastic specimens with time in acidic water with pH = 2 at 20 °C.

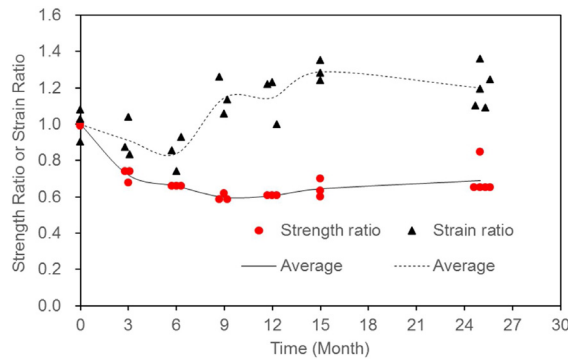
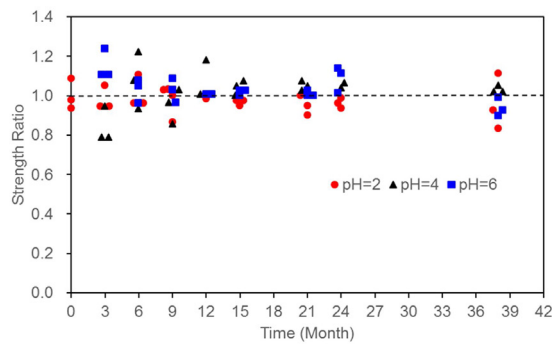
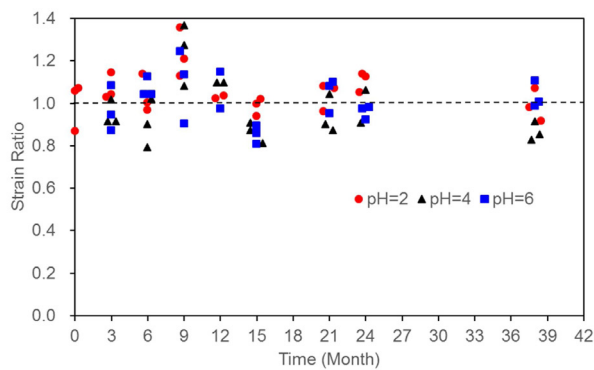


Fig. 7. Strength and strain ratios for porous asphalt specimens in the acidic (pH = 2) water with time at 20 °C.



(a) Strength ratio



(b) Strain ratio

Fig. 8. Strength and strain ratios for the impervious asphalt concrete specimens in the acidic (pH = 2, 4, and 6) water with time at 20 °C.

Fig. 8 shows that the acidity of the water had no significant effect on the cracking resistance and tensile strength. After three years of immersion in strongly acidic water, the tensile strength was about the same as that of asphalt concrete in the neutral water (pH = 7). The main reason for that is that the acid water did not penetrate into the almost impervious asphalt specimens and did not degrade the bitumen and the aggregate-bitumen adhesion (bonding).

5. Discussion of results and practical implications

The effects of acidic water on asphalt concrete depends on the acidity of the water, type of bitumen, type of mineral materials in aggregates and filler, asphalt mix, void content of asphalt concrete, temperature and time. The acidic water affects asphalt concrete in mainly three ways.

(1) Acidic water reacts with bitumen to degrade its properties. The test results in the study show that the acidic water ($\text{pH} = 2$) caused bitumen mass increase of 2-mm thick specimens at a rate of 0.78%/year (0.065%/month) for K90 bitumen and 0.40%/year (0.033%/month) for Z90 bitumen, respectively. If 100% mass increase is assumed to corrode all the bitumen, it would take about hundred years for the acidic water ($\text{pH} = 2$) to corrode all of the 2-mm thick bitumen specimens in the test program.

(2) Acidic water reacts with the mineral materials to degrade the properties of the filler and aggregate materials. The rate of degradation depends on the kind of mineral materials. For the limestone used in the study, the results show that the acidic water ($\text{pH} = 2$) caused limestone mass loss at a rate of 1.4%/year (0.115%/month). It would take about 60 years for the acidic water to corrode all the limestone material in the 5-mm thick specimens in the test program.

(3) Acidic water affects asphalt concrete by reacting with the suboxide in the limestone and producing an emulsifying agent to cause the bitumen film to peel off the limestone particles. This loss of aggregate-bitumen adhesion accelerates the degrading process of the asphalt concrete.

In road and airfield engineering, most of the asphalt pavements are made of porous asphalt concrete. The degrading of asphalt pavements consists of many factors, e.g., vehicle loading, hydrodynamic pressures, abrasion, weathering, etc. Acid rain is only one of the factors degrading asphalt pavements and may not be one of the critical issues as the pavements are designed for a lifetime of only 8–15 years [20].

For mine tailings dams, impervious asphalt concrete may be used as facing or interior core. The asphalt may be subject to strongly acidic water (AMD) erosion. Asphalt facings are usually about 10 cm thick while asphalt cores are more than 50 cm thick [2–4]. The bitumen content is in the range of 6.5–8.0%, and the corresponding volumetric ratio of bitumen to mineral materials is in the range 0.15:0.85 to 0.20:0.80. The test results reported in the section of effects of acidic water on the tensile strength of asphalt concrete show that the mass loss rate (corrosion) of hydraulic asphalt concrete is very low even when subjected to very acidic water. The mechanical test results show no signs of property degradation of impervious asphalt concrete in 3 years even when subjected to water with $\text{pH} = 2$.

6. Summary and conclusions

Aggregate-bitumen adhesion was tested using boiling tests after the bitumen-covered aggregate particles had been immersed in acidic water with $\text{pH} = 2, 4, 6,$ and 7 . The penetration value, softening point, and ductility of bitumen were tested after the bitumen specimens had been immersed in acidic water with $\text{pH} = 2$. Mass changes were measured for two kinds of bitumen specimens and asphalt mastic specimens with different mass ratios of bitumen to filler (1:1, 1:2, 1:3). Furthermore, sandy asphalt mastic specimens were tested after having been immersed in acidic water with $\text{pH} = 2$. Tensile (splitting) tests were carried out on porous asphalt specimens (road asphalt) and on impervious specimens (hydraulic asphalt) after the specimens had been immersed in strongly acidic water. The following findings and conclusions may be presented:

Bitumen specimens that had been immersed in acidic water of $\text{pH} = 2$ for 11 months showed that the acidic water had insignificant effect on the penetration value, softening point, and ductility of the bitumen. Bitumen itself is very acid-resistance.

When bitumen-covered limestone particles were immersed in acidic water for 4 weeks, the acid reacted with the limestone particles to degrade the aggregate-bitumen adhesion (bonding), but not by very much (Grade 5→Grade 4).

Asphalt mastic specimens with different mass ratios of bitumen to limestone filler, and sandy asphalt mastic specimens were immersed in acidic water with $\text{pH} = 2$ for 16 months. The results showed mass change rates of about 0.8%/year for K90 bitumen, 0.4%/year for Z90 bitumen, and -1.4%/year for the limestone material, respectively.

Porous (road pavement) asphalt concrete with void content (air porosity) about 5% was immersed in acidic water with $\text{pH} = 2$. The tensile strength of the specimen in the acidic water was reduced by about 40% compared to that of the specimen in the neutral water ($\text{pH} = 7$) in the first 9 months of immersion. After the first 9 months, there was no further reduction in tensile strength. This is probably because the acidity of the water in the voids in the asphalt concrete specimen undergoes a reduction with time as shown by Wang [10] and in Fig. 2b.

Impervious (hydraulic) asphalt concrete specimens with void content of less than 2% were immersed in acidic water of $\text{pH} = 2, 4, 6,$ and 7 for three years, and tensile (splitting) tests were carried out quarterly. There was no sign of asphalt concrete degradation with time causing reduction in cracking resistance and tensile strength.

Based on the above test results, it may be concluded that the degradation of impervious (hydraulic) asphalt concrete in acidic water is extremely slow. Hydraulic asphalt may be used as impervious facing or central core in tailings dams even for projects requiring storage of very acidic water.

CRedit authorship contribution statement

Shan Feng: Data curation, Investigation. **Weibiao Wang:** Methodology, Formal analysis, Supervision, Writing - original draft. **Hang Tan:** Data curation. **Meng Xue:** Data curation. **Kaare Höeg:** Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The research work for the paper was partly supported by the National Natural Science Foundation of China (No. 51179155 and No. 51779208).

References

- [1] Ministry of Transport of the People's Republic of China, Technical specifications for construction of highway asphalt pavements, Transport Industry Standard JTG F40-2004, China Communication Press, Beijing, 2004.
- [2] ICOLD (International Commission on Large Dams), Embankment Dams with Bituminous Concrete Facing, Bulletin 114, ICOLD, Paris, France, 1999.
- [3] ICOLD (International Commission on Large Dams), Asphalt Cores for Embankment Dams, Bulletin 179, ICOLD, Paris, France, 2018.
- [4] People's Republic of China National Energy Administration, Design specification of asphalt concrete facings and core for embankment dams, State Power Industry Standard DL/T 5411-2009, China Electric Power Press, Beijing, 2009.
- [5] Ministry of Water Resources of the People's Republic of China, Design code of asphalt concrete facings and core for embankment dams, Ministry of Water Resources Standard SL 501-2010, China Water & Power Press, Beijing, 2010.
- [6] E. Schönián, The Shell Bitumen Hydraulic Engineering Handbook, Thomas Telford., London, 1999.
- [7] Q. Zhang, J. Hu, Y. Peng, Analysis of chemical mechanism for aggregates corroded by acid rain in asphalt mixtures, Highway 2 (2004) 104–106.
- [8] Q. Zhang, Y. Peng, X. You, Thermodynamic analysis of corrosion of acid rain on aggregate in asphalt mixtures, J. China & Foreign Highway 24 (2) (2004) 71–73.
- [9] Q. Zhang, X. Jia, Y. Li, S. Tong, Investigation of effect of acid rain on strength and void content of asphalt mixture, J. China & Foreign Highway 25 (1) (2005) 78–80.
- [10] X. Wang, The Research on the Erosion Damage Mechanism of the Acidic Rain on the Asphalt and Asphalt Mixture Master thesis, Changsha University of Science and Technology, Changsha, China, 2014.
- [11] X. Feng, A. Chen, X. Wang, X. Xiong, Research on technical performance and corrosion mechanism of asphalt corroded by acid rain, Highway 4 (2017) 223–228 (in Chinese).
- [12] E. Franzoni, E. Sassoni, Correlation between microstructural characteristics and mass loss of natural stones exposed to simulated acid rain, Sci. Total Environ. 412–413 (2011) 278–285.
- [13] S. Chandra, Hydrochloric acid attack on cement mortar—An analytical study, Cem. Concr. Res. 18 (2) (1988) 193–203.
- [14] Y. Liu, J. Li, Y. Wu, S. Lu, Study on the effect of acidic environment on mechanical properties of rock, Adv. Sci. Technol. Eng. Syst. J. 17 (21) (2017) 196–201 (in Chinese).
- [15] Z. Zhong, W. Lou, X. Liu, H. Li, J. Cheng, X. Hu, Experimental study on mechanical properties deterioration of limestone in acid environment based on nuclear magnetic resonance, J. China Coal Society 42 (7) (2017) 1740–1747.
- [16] Y. Xia, P. Wu, R. Zhang, J. Zhu, Y. Wang, C. Song, L. Li, The effects of acid mine drainage on the erosion of carbonatite in carbonate rocks, Chinese J. Ecol. 37 (6) (2018) 1702–1707.
- [17] A. Mellado, M.I. Pérez-Ramos, J. Monzó, M.V. Borrachero, J. Payá, Resistance to acid attack of alkali-activated binders: simple new techniques to measure susceptibility, Constr. Build. Mater. 150 (2017) 355–366.
- [18] Ministry of Transport of the People's Republic of China, Standard test methods of bitumen and bituminous mixtures for highway engineering, Transport Industry Standard JTG E20-2011, China Communication Press, Beijing, 2011.
- [19] People's Republic of China National Energy Administration, Test code for hydraulic bitumen concrete, State Power Industry Standard DL/T 5362-2018, China Electric Power Press, Beijing, 2018.
- [20] Ministry of Transport of the People's Republic of China, Technical standard of highway engineering, Transport Industry Standard JTG B01-2019, China Communication Press, Beijing, 2019.
- [21] L. Han, Y. Jiang, Y. Wang, Comparison and characterization of ageing-resistance of bitumen under acting of thermal aging, Chem. Eng. 33 (6) (2019) 93–96 (in Chinese).
- [22] W. Wang, Y. Zhang, K. Höeg, Y. Zhu, Investigation of the use of strip-prone aggregates in hydraulic asphalt concrete, Constr. Build. Mater. 24 (2010) 2157–2163.