Durability Test of Gangue Paste Filling Material

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Abstract

In order to study the durability of gangue paste, the cement, fly ash and gangue were mixed with the proportion of 1:4:6 to compose paste and the mass concentration was 74%. Anti-erosion， anti-permeability and heat stability of filling body after 28d's maintenance were tested. The results showed that filling body had a good anti-erosion for alkali while the acid and salt had large influence on initial strength of filling body. Filling body's anti-permeability grade was P6 which stood for weak grade. Under the temperature of 30℃ and 60℃, compressive strength of filling body increased slightly while it declined greatly under the temperature of 90℃，120℃ and 150℃, heat stability was bad. The paste was suitable for north mines and deep mines with higher temperature.

Keywords: gangue paste; filling material; durability; anti-erosion; anti-permeability; heat stability

With the reducing of recoverable coal reserves in China, coal mining under buildings, railways, water-bodies and above confined aquifers has become one of the major problems that face the coal companies in China especially in the central and eastern area.

As an important part of green mining, gangue paste filling method is the ideal way to solve the problem of mining under buildings, railways, water-bodies and above confined aquifers. After the goaf was filled with filling materials, it was in an sealed condition that had a high temperature and humidity and no air in the effect of rock's temperature, air compression and expansion, oxidation heating and so on. Filling material could react a series of physical, chemical and physiochemical reactions which could reduce the stability of filling body. Based on the above reasons, it is necessary to study the durability of filling body in the laboratory before the filling material was applied to the mine spot. Considering that the filling body was an kind of "lean concrete", the test method was same with the test of concrete's durability including anti-erosion， anti-permeability and heat stability.

1 Preparation of gangue paste and test standard

In the test, the cement was the kind of ordinary Portland cement, the Ⅱ fly ash of light gray was from the power plant of Huangdao, the gangue was from the Daizhuang Mine after secondary crushing which the main components were SiO_2, Al_2O_3. The proportion of cement, fly ash and gangue aggregate was 1:4:6, the mass concentration was 74%, and the time of maintenance was 28d. The initial strength of filling body mainly came from C-S-H, CH, AFt from the cement reaction while the long-term strength mainly came from the fly ash and $Ca(OH)_2$'s reaction product of C-S-H, C-A-H, C-A-S-H, AFt. The durability of filling body was tested by GB/T50082-2009.

2 Anti-erosion Test

2.1 Test Method

The filling body specimens after 28d's maintenance were divided into four groups including 5 test specimens each. Every group was separately reacted with 2% HCl, 2% Na2SO4, 2% NaOH and distilled water. The compressive strength was tested after 15d, 30d, 60d and 150d erosion and the anti-erosion coefficient F could be gotten based on the strength before and after erosion:

$$F=R_{f浸}/R_{f标} \quad (1)$$

In the formula, $Rf_{浸}$ stood for the filling body's strength after erosion while $Rf_{标}$ stood the original strength.

2.2 Test Results

Table 1 The relationship between compressive strength of the filling body in different erosion solution and time

Erosion days/d	2%Na_2SO_4 Compressive strength /MPa	2%Na_2SO_4 Corrosion factor	2%NaOH Compressive strength /MPa	2%NaOH Corrosion factor	2%HCl Compressive strength /MPa	2%HCl Corrosion factor	H_2O Compressive strength /MPa	H_2O Corrosion factor
0	3.93	1	3.70	1	3.69	1	3.86	1
15	3.09	0.78	3.84	1.04	2.21	0.59	3.92	1.01
30	3.16	0.81	3.98	1.07	2.56	0.69	3.69	0.96
60	2.87	0.73	4.23	1.15	2.29	0.62	3.88	1.01
150	3.04	0.77	4.82	1.29	2.33	0.63	4.02	1.05

Relationship between compressive strength of filling body in different erosion solution and age was in the Table 1.

From the Table 1, it could be gotten obviously that the compressive strength of filling body in the distilled water remained the same so that the strength could be the original strength. The compressive strength declined 21% after the 15d erosion in the Na2SO4 solution while it remained unchanged in the condition of keeping erosion and its final loss ratio was 25%. When the filling body was in the NaOH solution, the strength had been growing with the age and the final strength increased 30%. When the filling body was in the HCl solution, the strength declined obviously and its loss ratio reached 40% in the 15d. But it could keep stable with increasing erosion time.

2.3 Analysis of test results

2.3.1 Na_2SO_4 Erosion

The compressive strength's variation trend of filling body after the erosion of 2% Na_2SO4 solution in different age was shown in Figure 1. A certain amount of $Ca(OH)_2$ in the filling body could react with Na_2SO4 to generate CaSO4 which also could react with C-A-H to AFt. The products made the volume of filling body expansive and some of specimens had been cracked.

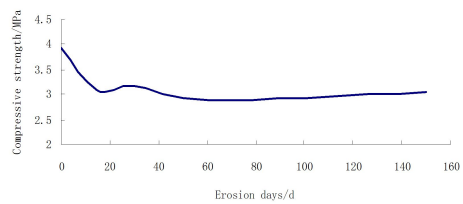

Fig. 1 The relationship between compressive strength of the filling body in 2% Na_2SO_4 solution and time

2.3.2 NaOH Erosion

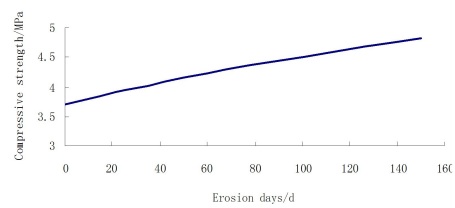

Fig. 2 The relationship between compressive strength of the filling body in 2% NaOH solution and time

The compressive strength's variation trend of filling body after the erosion of 2% NaOH solution in different age was shown in Figure 2. In the initial erosion age, the filling body's compressive strength changed slightly. However, it changed obviously with the increasing erosion time because the substances like C-S-H, AFt in the filling body could still keep stable in the high alkaline solutions. And

also the rise of pH was useful for the maintenance of hydrate products and the increase of filling body's strength.

2.3.3 HCl Erosion

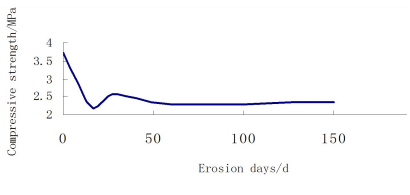

Fig. 3 The relationship between compressive strength of the filling body in 2% HCl solution and time

The compressive strength's variation trend of filling body after the erosion of 2% HCl solution in different age was shown in Figure 3. When the specimen was put in the HCl solution, the reaction was fiercely that it produced some bubble and a large area of surface had dropped with the aggregate outside and produced a foul odor. The phenomenon indicated that HCl and filling body occurred a series of chemical reaction.

H+ from the HCl solution could occur a series of reaction with C-S-H, AFt that resolve the hydrate products. So the essence of all the acid substances reacting with filling body was the H+ reaction.

The reaction of HCl and filling body included two parts:

(1) $H^+ + OH^- \rightarrow H_2O$

(2) $3Cl^- + Al^{3+} \rightarrow AlCl_3$

$2Cl^- + Ca^{2+} \rightarrow CaCl_2$

It could be seen that the smaller of pH, the larger amount of H+ and OH- of the neutral reaction from part 1. When the concentration of H+ reached a certain value, the solution would immediately occur the reaction with solid silicate, aluminate and lime to generate destruction of internal structure. In respect of Cl-, $CaCl_2$ that has a highly soluble in water could aggravate the erosion of HCl. However, the amount of HCl solution in the test was certain so that the pH was increasing with the time of erosion. So the filling body's compressive strength kept stable after the solution building up a new balance.

From the erosion test results, it was gotten that filling body had a good erosion resistance. And the acids and salts had a large effect on the initial strength while slightly on the final strength with the time of erosion.

3 Impermeability Test

3.1 Test Result

Materials resistant to water penetration pressure called anti-permeability, or called impermeability. Material impermeability is usually expressed by permeability coefficient. The physical meaning of Permeability coefficient is : A thickness of the material, under certain water pressure, the amount of water per unit area in unit time through. Expressed by the formula:

$$K_S = Qd_{渗}/AtH \qquad (2)$$

In the formula, K_S stood for the permeability coefficient of the material ,cm/h; Q stood the amount of water by penetration,cm^3 ;d is the thickness of the material, cm; A is the water seepage area, cm^2;t is time water seepage, h ; H is the hydrostatic pressure head, cm.

K_S higher the value, the more water permeable material indicates that the anti-Permeability worse, Anti - permeability is one of the main indicators determine the durability of the material.

At present, China's ordinary stowing body's impermeability indicators assessed using anti-permeability grade .GB 50164 — 2011 《Standard for quality control of concrete》According to the impermeability of concrete at the time of the test specimen can withstand the maximum water pressure, anti-permeability grade of concrete divided five grades :P4,P6,P8,P10,P12.corresponding representation resistant to 0.4MPa, 0.6MPa, 0.8MPa, 1.0MPa and 1.2MPa of hydrostatic pressure without water seepage. That is when

the concrete impermeability test a group of six specimens four largest specimen water seepage water pressure does not appear when.

During the experiment, take catchy diameter of 175mm, under the port diameter of 185mm, height 150mm frustum-shaped test pieces,6 in1 group. From the bottom of the test block 0. 2MPa water pressure began to test every 8h increased 0. 1MPa.It was found that: pressure reaches 0. 8MPa time,3 in 6 filling body were pressure by water penetration. According to the computing standard of anti-permeability grade,0. 7MPa is the calculated indicators of the filling body. anti-permeability grade is calculated as follows:

$$P=10H-1 \quad (3)$$

In the formula, P stood for stowing body's anti-permeability grade ; H stood the water pressure when the third specimen top surface of the specimen start water seepage, MPa.

The results showed that: filling body's anti-permeability grade was P6 which stood for weak grade.

3.2 Impermeability mechanism analysis

The Anti - permeability of the material depends primarily on the internal porosity of the material, including the void size distribution and continuity. Judging from the microstructure, filling body is a non-homogeneous pore structure of the porous structure of concrete. Including the matrix pores in slurry , the pores in the aggregate matrix and bone interface transition zone pore. The body has many different size distribution of the fine pore. With respect to the concrete used in construction, the cementation performance of the filling body is poor. That grout matrix porosity is more, waste rock aggregate quantity is larger. That is the pore between the substrate and the aggregate interface transition zone. Compactness is lower, after crushing the internal microcracks in waste rock aggregate is more. These factors stowing body's anti-permeability grade was weak grade.

4 Thermal stability test

4.1 Test Methods

First of all, Process the good filling body specimens after 28d curing under standard conditions by low temperature drying, Due to evaporation and gas expansion at high temperatures, a density of the filler mass will change. Water is the raw material of filling body, in the filling body will inevitably contain some bound water and free water, water may be present in a combination form of the compound down, and free water will condense filling body with a gradual decrease. Because the body is filled with uneven particle size composition of raw materials, it is inevitable there will be a gap, hat caused there is gas in the filling body. Under high temperature, the water will evaporate violently, the gas will expand rapid. This will cause a change in the volume of backfill, to avoid experimental errors caused by evaporation, so before the test to make restorations low drying.

The specimens were placed in each group of 30 ℃, 60 ℃, 90 ℃,120 ℃, 150 ℃ and would l be conserved under , 2h,5h, 10h, 16h, 24h range. The uniaxial compressive strength of filling body were measured after each temperature at different curing time .

4.2 Test Result

Table2 Compressive strength of the filling body under different temperature and time

Time/h	Compressive strength/MPa				
	30℃	60℃	90℃	120℃	150℃
0	3.59	3.86	3.71	3.82	3.91
2	3.62	4.02	3.62	3.37	3.48
5	3.75	3.81	3.54	3.21	3.11
10	3.76	4.03	3.68	3.14	2.93
16	3.71	4.07	3.47	3.32	3.08
24	3.75	4.05	3.41	3.25	2.89

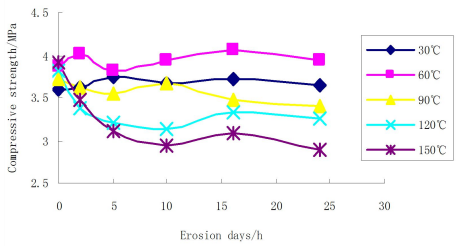

Fig. 4 Compressive strength of the filling body specimen under different temperature and time of the diagram

Filling uniaxial compression test results are shown in Table 2.Backfill specimens at various temperatures shown in Figure 4 the relationship between curing time.

4.3 Analysis of the mechanism of thermal stability

It could be seen from Figure 4,At a temperature of 30 ℃, 60 ℃,a slight increase in the compressive strength of filling body with the increase of curing time. At a temperature of 90 ℃, 120 ℃, 150 ℃,when the curing time of 2h,its compressive strength is more obvious decline; when 10h,its compressive strength declined to lowest point. So filling body strength at elevated temperatures dropped more obvious. Its compressive strength remained stable when continue heating.

Because the strength of the filling body depends on the adhesive Properties of C-S-H and ettringite. As the curing temperature increased slightly, Backfill conducive to the continued hydration reaction, the proportion of polymerization degree of C-S-H gel silica tetrahedron and C-S-H gel alumina tetrahedron. At this time for ettringite, there is no significant impact on its temperature, but after curing temperature reaches 60 ℃ ,conservation under continuous high temperature the water loss rate of specimen increases. The initial hydration generated ettringite of backfill specimen easily decomposed. Prone ettringite and sulfur-type single crystal transition sulphoaluminate, cause varying degrees of damage restorations, lower compressive strength. The C-S - H gel did not change with increasing temperature. Therefore, when the post-heating was continued, substantially no change in compressive strength

5 Conclusion

Due to the low compactness of the specimen, more aggregate internal microcracks, led to poor filling body impermeability, filling body's anti-permeability grade was P6 which stood for weak grade. Since the filling itself is an alkaline material, stowing sample had good anti-erosion for alkali，acid and salt had large influence on initial strength of stowing sample. At room temperature continues to heat up, helps to increase body strength filling, but filling body strength at high temperature decreased more significantly, heat stability was weak. According to backfill Performance, this paste was suitable for north mines and deep mines with higher temperature.

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