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Analysis and Suggestions on the Use of Polymer Materials for Coal Mines

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Abstract: In recent years, polymer materials used in coal mines have been widely used in coal rock reinforcement, grouting and plugging in coal mines, and have played an important role in coal mine disaster management. However, according to the relevant data, more than 100 accidents have occurred in the use of polymer materials in China ' s coal mines, and most of them are used to reinforce coal and rock mass polymer materials. The use and safety management of polymer materials need to be strengthened. This paper summarizes the characteristics of polymer materials used in underground coal mines, analyzes the problems that may arise in the use of polymer materials used in coal mines and the shortcomings of relevant existing standards, and points out that most of the safety accidents of polymer materials are spontaneous combustion of materials, coal seam combustion and poisoning caused by toxic and harmful gases. The main causes of combustion accidents are too high reaction temperature, insufficient flame retardancy, uncontrollable reaction process, imperfect standards and insufficient safety awareness of the material itself. Reasonable suggestions and measures for preventing similar accidents are put forward to provide technical guidance for the safe use of polymer materials for coal mines.

Keywords: Polymer Materials, Flame Resistance, Standard System, Safety, Safety, Scientific Use

1. Introduction

Polymer materials used in coal mines include polyurethane, epoxy resin, urea-formaldehyde resin, etc., which are mainly poured into the cracks of coal and rock mass through pressure or chemical infiltration. They can be consolidated in a short time and achieve high strength, so that the loose and broken surrounding rock is cemented into a continuum. Polymer material is a kind of chemical grouting material, mainly by AB two components through the grouting pump in accordance with a certain proportion of mixing [1-3].

Grouting technology in China has been applied since 1950s and developed rapidly. It has been widely used in various geotechnical engineering. The earliest chemical grouting technology is epoxy resin grouting and methanation, followed by acrylamide. In the late 1970 s, polyurethane began to be used as grouting material. In the 1980 s, with the development of new materials and new technologies, some new polymer grouting technologies have been introduced into China and developed rapidly. Acrylate, urea-formaldehyde resin, unsaturated resin and other varieties have been widely promoted and applied [4, 5].

Polymer materials used in coal mines have the characteristics of high infiltration permeability, fast setting speed, short curing time, small shrinkage after grouting, good bonding and compressive properties, strong durability and impermeability, which are more and more widely used in coal mines. According to incomplete statistics, the relevant production units have more than one hundred, the use of more than 2000 mines, the annual use of 40000-50000 tons. Reinforcement and filling materials account for 90% of the total polymer materials. In recent years, polymer materials have been increasingly widely used in coal mining, ventilation, gas, water prevention and control, and have achieved significant economic and social effects, and made significant contributions to mine safety production and emergency rescue. However, with the extensive application of this technology in coal mines, serious disasters such as smoke and fire occur almost every year in polymer materials [6]. The process of polymer mixing in the underground belongs to chemical exothermic reaction, and there are many uncontrollable factors. Therefore, the use and safety

management of polymer materials need to be strengthened.

2. Basic Application of Polymer Materials

Polymer materials used in coal mines are mainly used in underground coal mines. Two liquid components, A and B, are mixed by grouting pump in underground coal mines and then grouting operation is carried out. After a period of solidification, the product of material C that needs to be used is finally generated, commonly known as AB material.

According to the use, there are mainly four types: polymer materials for water plugging, polymer materials for spraying air plugging, polymer materials for reinforcing coal and rock mass, and polymer foam materials for filling and sealing. By composition classification, mainly includes: polyurethane, phenolic resin, uraldehyde resin, acrylic salt, unsaturated polyester, lignin, etc [7].

At present, the implementation standards include: AQ 1087-2011 «Polymer materials for water plugging in coal mines» [8], AQ 1088-2011 «Polymer materials for air plugging by spraying in coal mines» [9], AQ 1089-2011 «Polymer materials for coal and rock reinforcement in coal mines» [10], AQ 1090-2011 «Polymer Foaming Materials for Sealing Filling in Coal Mines» [11].

3. Cause Analysis of Polymer Material Accidents in Underground

Because the mixing process of material A and B in the underground belongs to chemical exothermic reaction, if the product quality is poor (such as the flash point of material A and B is low), the grouting process control is improper, the reaction temperature is too high, and the product C material is not flame retardant, it may cause carbonization failure, spontaneous combustion, explosion, fire, combustion, and toxic and harmful gases lead to poisoning and corrosion accidents [12].

3.1. Roof Accidents

4238 fully mechanized working face in + 1030 m level four mining area of a coal mine in Sichuan Province occurred fire accident in the process of using organic polymer filling reinforcement material to deal with the top high caving area of 18#~26# support, resulting in the closure of the whole mining area.

Direct cause of the accident: 4238 fully mechanized mining face 18#~26# support section of the high-rise area filled with 20 t solid material reaction heat release caused by the internal temperature of the material increased, fire, ignite wood stack, ignite coal wall and return air side combustible and coal seam, fire.

The indirect causes of the accident are as follows:

(1) Security technology management confusion.
(2) Mixing different polymer materials.
(3) Poor air circulation environment. Since the front is a closed falling space, which is almost not circulated, and the volume of the falling space is limited, a large amount of heat cannot be, forming a heat accumulation area.
(4) Spontaneous combustion of materials. Water injection cooling is not enough, the head of the water and water pressure is not large, can not inject a large number of cooling water at high temperature point, resulting in the combustion of polymer material itself, and then cause coal combustion.

3.2. Smoke Accidents

A large amount of yellow smoke was released by chemical reaction of polymer materials filled in 5 # drilling site of 7118 working face in a coal mine in Huaibei, producing toxic and harmful gases. A worker was smoked down at the bottom of the drilling site door and died after rescue was ineffective.

The direct cause of the accident: the filling material is not qualified, after filling the high temperature and toxic and harmful gas caused by poisoning death.

Accident indirect causes:

(1) The procurement of filling materials is random. Not in accordance with the provisions of the company, from the normal channels of regular manufacturers import, acceptance.
(2) The material acceptance personnel in the ventilation area failed to work, only received quantity and did not check the quality.
(3) Poor hazard identification ability. Ventilation area gas inspectors in the third inspection smell, see yellow smoke but not informed.
(4) Unclear job responsibilities. Institution adjustment, the outburst prevention area has just been listed and has not been properly operated; The construction personnel directly used the filling material without identification, resulting in the chemical reaction of the filling material and producing high-level and toxic and harmful gases.

4. Problems in Current Standards

Four standards for polymer materials used in coal mines were issued and implemented in 2011. From the existing situation, the practical application effect of the series of standards is not ideal, and there are great objections to the standards. The current standards only regulate the flame retardant and antistatic ability and mechanical properties of polymer materials under normal temperature conditions, but the important contents such as the reaction characteristics of polymer grouting materials for mining, the safety of reaction exothermic itself, the possibility of coal spontaneous combustion caused by reaction exothermic, the smoke toxicity after combustion and the safety construction technology for exothermic problems have not been involved, and have not been standardized by indicators.

4.1. The Main Problems in the Standards of Reinforcement and Water Plugging Polymer Materials Are as Follows

(1) In AQ1089 - 2011, according to the different parts of reinforcement materials in coal and rock mass, it can be divided into C (coal reinforcement) and R (rock reinforcement). In the practical application process, it is difficult to distinguish in most cases.

(2) The anti-aging performance index is expressed as ' no change in surface and no loss in mass ', which is problematic. In the aging process, the volatilization of some solvent molecules will reduce their mass, but generally will not affect their mechanical properties.

(3) The expression of " hazardous substance limit " in the standard is relatively vague. It should be concretized according to the material type, increase the flue gas toxicity test of the material, and quantitatively detect the content of toxic and harmful gases (HCN, NO, CO, halogen acid gas, etc.).

4.2. The Main Problems of Filling and Sealing Polymer Materials Standards Are as Follows

(1) The materials in AQ1090 - 2011 were divided into N and P categories. In the actual grouting process, the materials used for hole sealing also need to bear pressure, so there is no need to classify them.

(2) The standard flash point determination problem, generally A material can not measure the flash point, 50 ~ 60°C began to bubble, 80 ~ 90°C overflow pot, 100 ~ 110°C condensation; Material B is an acid without flash point. Substances with low boiling points (foaming agent) may be added in component A. After heating, the gas overflows and expands, and material A will bubble, overflow pot or even condense, which is difficult to measure.

(3) The expansion ratio specified in the standard is not less than 25 times. Due to the different underground environments of coal mines, some need large expansion ratios, and some do not. In general, the higher the expansion ratio is, the lower the mechanical strength of the material is, and the expansion ratio of the material is not less than 10 times.

(4) The expression of ' hazardous material limit ' in the standard is vague and should be specified according to the type of material; The flue gas toxicity test of materials should be added to quantitatively detect the content of toxic and harmful gases (HCN, NO, CO, halogen acid gas, etc.).

5. Preliminary Analysis of Accident Causes of Downhole Polymer Materials

The use of polymer materials for coal mine disaster management has developed rapidly in the past decade. It is not difficult to find that the industry has two significant characteristics by carefully observing the development of the industry. First, the technical source of polymer reinforcement materials is relatively single, and the research and development potential is insufficient. Second, the users of polymer materials do not know enough about the properties of materials and have insufficient participation. It is also these two characteristics of the polymer material industry that have brought some problems in the management of safety production disasters and safety management, and indirectly caused the occurrence of safety production fire accidents. In summary, fire accidents caused by polymer reinforcement materials mainly include the following reasons:

(1) Poor flame retardancy of polymer materials.

Polymer materials are not flame retardant, and additives are needed to meet the flame retardant requirements. However, the content and quality of flame retardants for practical materials are difficult to guarantee. Once the temperature is too high, flame retardant can not meet the requirements, prone to fire smoke accident.

(2) High exothermic temperature of polymer materials.

A large amount of heat will be released during the curing process of polymer materials, and the heat release temperature is directly related to the safety of coal mines, especially in high gas and coal dust mines. Using the test method specified in AQ1089-2011 standard, the maximum reaction temperature and temperature variation with time of polyurethane reinforcement materials and modified polyurethane reinforcement materials were compared, as shown in Figure 1.

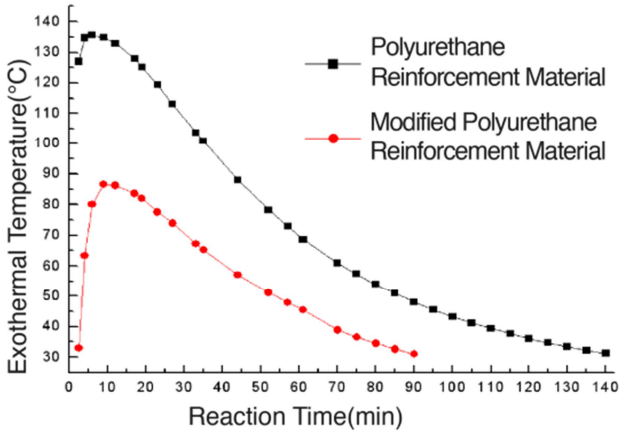

Figure 1. *The maximum reaction temperature of reinforcement material and its variation with time.*

It can be seen from Figure 1 that the polyurethane reinforcement material has a significantly high maximum reaction temperature (>135°C), while the modified polyurethane reinforcement material has a lower maximum reaction temperature (<90°C). In addition, the temperature attenuation of polymer reinforced materials is also significantly better than that of polyurethane reinforced materials (1h polyurethane reinforced material temperature attenuation to 69°C, and modified polyurethane reinforced material temperature is less than 46°C). Therefore, there is

still such a difference under the total volume of 200 mL. If a large volume of polymer reinforcement material is injected into the construction, and the construction environment is complex and humid, the difference will become larger and larger. Some data show that the exothermic temperature of a polyurethane reinforcement material even reaches 340°C after adding 1% water [13].

(3) Insufficient demonstration of polymer material construction scheme Due to the lack of understanding of polymer materials in coal enterprises, the interaction of material construction schemes is not enough in the process of proposing, modifying and finalizing. The lagging or imperfect situation in safety preparation, plan preparation and response in the construction process has hidden dangers for the occurrence of polymer material fire accidents.

(4) Lack of security awareness Fire accidents due to polymer materials occur every year, a problem can not be ignored is the lack of safety awareness. No matter the material production enterprises or coal enterprises, there is a lack of strong sense of security responsibility.

6. Conclusion

In short, the coal industry itself is a high-risk industry, and the two seemingly non-hazardous materials are defined separately. However, the severe chemical reactions in the dangerous coal mines should be highly valued. In fact, there is no absolutely safe material. How to ensure the safe production of coal mines while reasonably selecting polymer materials is the top priority.

Based on the above opinions, combined with the characteristics of polymer materials, in order to further improve the safety of polymer materials and improve the current situation of polymer materials, the following suggestions are put forward:

6.1. Improving the Access Threshold of Product Manufacturing and Enhancing the Level of Product Specialization

The production of such products belongs to the production process of chemical products. Enterprises should establish and improve the safety production responsibility system and related safety production system. During production, it is necessary to do a good job of personal safety protection for production staff, and strictly follow the operation rules and process rules. It is necessary to strictly control the quality of raw materials, and adjust the formula when the raw materials change greatly to ensure effective control in the production process and ensure the production of qualified coal mine polymer materials.

6.2. Scientific Use, Enhanced Maintenance Management

At present, the materials used for reinforcing coal and rock mass in the market are mainly polyurethane and silicate. Phenolic resin, urea-formaldehyde resin because of its performance (such as compressive properties, bonding strength, etc.) can not meet the requirements of reinforcement standards, mainly used in coal mine filling sealing. Polymer grouting materials should be used in underground coal mines in strict accordance with the following requirements:

(1) Accurately grasp the amount of grouting material, A, B component classification shipment, classification storage, underground polymer materials shall not be stored.

(2) Polymer materials and other chemical materials of different types, different properties and different manufacturers shall not be used in the same construction site.

(3) It is strictly forbidden to inject multi-holes simultaneously, and the maximum dose of single-hole injection should not exceed five groups (each group of A and B components should not exceed 125 kg); When grouting, the top side of the face slag and spalling phenomenon immediately stop grouting; The grouting is stopped immediately when the slurry is discharged from the grouting eye and the top end face, and the grouting time of each eye is generally 10-20 min.

(4) It is strictly forbidden to grout into large space such as high-rise area and cavity area, but only to grout into loose coal and rock mass, so as to prevent a large number of accumulated and exothermic reactions of grouting materials.

(5) Before construction, the high-pressure water supply pipeline was extended to the construction site, and the dry powder and CO_2 fire extinguishing equipment were fully equipped; The construction site was set up to monitor the changes of carbon monoxide, oxygen and temperature. During the grouting process, at least once every 10 min was observed, and all operations in the working face were stopped immediately when the coal temperature and carbon monoxide were found to be abnormal, which were processed in accordance with the prepared emergency plan.

(6) After grouting, the changes of carbon monoxide, oxygen and temperature were continuously monitored at the construction site, and the continuous observation time should not be less than 16 h, at least once every 20 min.

6.3. Strengthening Standards System Research and Improving Standards and Regulations

The four AQ 1087 ~ 1090 standards issued and implemented in 2011 have played a certain role in standardizing the production and inspection of coal mine water plugging, spraying plugging, reinforcing coal and rock mass and filling polymer materials for sealing. However, in practical use, it is found that there are some unreasonable provisions, such as the provisions of 'flash point' and test methods; Two is the 'maximum reaction temperature' item does not reflect the actual use of safety; Third, the operability of some projects is not strong, for example, 200 cycles are required for ‘freeze-thaw resistance’, and one cycle needs at

least 24 hours; 4 The expression of ' hazardous material limit ' in the standard is vague and should be specified according to the material type; It is suggested that the flue gas toxicity test of materials should be added and the content of toxic and harmful gases (HCN, NO, CO, halogen acid gas, etc.) should be quantitatively detected. The GB / T 20285 - 2006 «Risk Classification of Tobacco Toxicity of Materials» [14] can be used for hazard classification. It is suggested to increase the provisions on the use place of polymer materials in "«Coal mine safety regulations»."

6.4. Strengthening Institutional Construction and Implementing Post Responsibility System

In order to ensure the safety and health of workers and prevent accidents, coal mines should carry out safety and environmental protection assessment before using products, because some polymer grouting materials have stimulating odor, improper operation will endanger the safety and health of themselves and others, and coal seam fire accidents caused by improper grouting construction technology are also common. Coal mine grouting construction personnel and field management personnel need to receive safety technical education and professional training, and obtain the corresponding qualification certificate before they can be employed. At the same time, law enforcement and supervision should be strengthened to eliminate hidden dangers.

References

[1] Qian Sifang. Research on safe use technology of polymer materials for coal mine reinforcement [J]. Shandong coal science and technology, 2016, (10).

[2] Fang Kun. Safety Analysis of Polymer Materials Used in Coal Mines [J]. The Journal of North China University of Science and Technology, 2005, (01).

[3] Cai Ming, Ni Jianming. Research on exothermic characteristics and safety of polymer reinforcement materials for coal mines [S]. Papers of 2013 International Symposium on Coal Mining and Safety. 2013.

[4] Zhang Huzhuang, Xiang Jianfei. Development and Application of New Chemical Grouting Material for Mine [J]. Coal science and technology, 2012, (02).

[5] Song Yanbo, Zhou Yichao. Application of New Polymer Products in Coal Mine Production [J]. Coal science and technology, 2005, (12).

[6] Jiang Shuozhong. The development and prospect of chemical grouting technology in China [J]. The Journal of Yangtze River Academy of Sciences, 2003, 20 (5): 25-27.

[7] Wu Huaiguo, Wei Hongliang, Tian Fenglan. Performance characteristics and research direction of polymer grouting reinforcement materials for mining [J]. Coal science and technology, 2012, 40 (5): 27-29.

[8] National Safety Production Standardization Technical Committee Coal Mine Safety Subcommittee. AQ 1087-2011 «Polymer materials for water plugging in coal mines» [S]. China Coal Industry Press, 2011.

[9] National Safety Production Standardization Technical Committee Coal Mine Safety Subcommittee. AQ 1088-2011 «Polymer materials for air plugging by spraying in coal mines» [S]. China Coal Industry Press, 2011.

[10] National Safety Production Standardization Technical Committee Coal Mine Safety Subcommittee. AQ 1089-2011 «Polymer materials for coal and rock reinforcement in coal mines» [S]. China Coal Industry Press, 2011.

[11] Coal Mine Safety Subcommittee of the National Technical Committee for Standardization of Safety Production. AQ 1090-2011 «Polymer Foaming Materials for Sealing Filling in Coal Mines» [S]. China Coal Industry Press, 2011.

[12] Danger of safety work caused by the use of polymer materials in Fang Aimei Coal Mine [J]. Journal of Huainan Mining University, 02, 1989, ISSN: 1672-1098.

[13] Wu Huaiguo. Experimental study on safety of polymer grouting reinforcement materials for mining [J]. Coal science and technology, 2013, 41 (11): 53-55.

[14] Seventh Technical Committee of the National Fire Standardization Technical Committee. GB / T20285-2006 «Risk Classification of Tobacco Toxicity of Materials» [S]. China Standards Press, 2006.