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Research of the Formation of Foamed Gel with Fly Ash

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A new type of technology of foamed gel with fly ash is developed to prevent and extinguish fire so as to overcome the existing shortages of fire prevention technologies. As a complex multi-component foam system, the foamed gel with fly ash is mainly formed by putting foaming agent, thickener and crosslinker into fly ash slurry, introducing nitrogen and stirring physically and mechanically. The experiments were done to investigate the microstructures of foamed gel with fly ash and theoretically analyze its gelation process and mechanism. The results show that the foaming agent is one of the key factors of forming foamed gel. And when the thickener dissolved in water, the helical mesh polymer or double helix cluster are formed by molecular chains, besides, active group in polymer or cluster fully collide with that in the main chain structures of crosslinker, thereby the three-dimensional network structures are formed, making the scattered polymer and cluster form a uniform continuous phase.

1. Introduction

Coal spontaneous combustion, seriously threatening the personal safety of miners and causing heavy property and economic losses to the country, is one of the serious natural disasters in coal mine. According to statistics, more than 51% of mines in China key state-owned coal mines exists the danger of spontaneous combustion, and the fire caused by spontaneous combustion accounts for over 90% of total fire accidents (Singh et al., 2007). Moreover, the fire in goaf accounts for 60% of all the spontaneous fire (Wang et al., 2014). Especially in recent years, with the popularization and application of fully mechanized sublevel caving mining technology, the coal output and the production benefit significantly increase. However, this mining method has the characteristics of high output, large falling height and serious air leak, making the spontaneous combustion of left coal in goaf happen frequently. In order to prevent spontaneous fire in coal mines, since 1950s, the technologies of grouting, nitrogen, inhibitor, gel, foam and so on have been used (Stracher and Taylor, 2004; Xu et al., 2012). Although those techniques have supplied an important guarantee for the mine safety production, due to the extremely complex condition of coal mines, all of them can not completely meet the need of fire prevention and extinguishing. When grouting, slurry can only flow to the low-lying areas and can not cover the coal in higher places in goaf. While nitrogen, it is easy for gas to spread with air but difficult to stay in the infuse area and thereby the effect of fire extinguishing and cooling is not ideal. If inhibitor, it is hard to evenly disperse on the coal and has corrosive action, which may threaten both equipment and the health of workers. When gel, it is difficult to be applied to put out the fire in large areas of goaf. If foam, foam can't realize curing and its normally stability is 8~12h. Thus, the work of fire prevention and extinguishing in coal mine is still an arduous task for scholars at home and abroad to study.

In order to overcome the deficiencies in conventional fire prevention and extinguishing technologies, foamed gel with fly ash, for first time, is developed to prevent the spontaneous combustion of coal. The foamed gel with fly ash formed by adding polymers and foaming agent into water and stirring physically and mechanically under the function of nitrogen, is a complex mixed system. After a while, different polymers take crosslinking reaction with each other in foam liquid films and form three dimensional network structures, which constitute the rigid backbone of foamed gel with fly ash (Lv et al., 2006; Zhang and Qin, 2014). The foamed gel with fly ash not only has the property of gel but also has the characteristic of foam. Furthermore, it can also overcome their shortages, significantly improving the effect of fire prevention and extinguishing.

At present, few researches have been conducted on foamed gel with fly ash. In petroleum exploitation industry, foamed gel is preliminarily investigated and mostly used as plugging agent and profile control so as

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to increase the mining rate of petroleum (Ramyadevi and Rajan, 2015; Miller et al., 1995; Miller and Fogler, 1995; Chen et al., 2007). However, the foamed gel used in petroleum exploitation does not contain the solid particle of fly ash and is formed only by aqueous solution, whereas the foamed gel with fly ash contains solid particle, difficult to investigate and with more complex influencing factors. In this paper, fly ash of Datun Coal and Electricity Corporation (China), lab-made type F3 foaming agent, thickener and crosslinker are used as the raw materials. Moreover, D/Max-3B x-ray diffractometer and Bruker (Veeco) atomic force microscope are adopted to carry out studies on the foaming reasons of fly ash slurry and the crosslinking mechanism of compounding between thickener and crosslinker so as to provide a reference for the application of foamed gel with fly ash in preventing and extinguishing fire.

2. Foaming Reasons of Fly Ash Slurry

The development of foaming agent is closely related to the constitution of fly ash, which is made of crystals such as SiO_2, $Al_6Si_2O_{13}$, CaO and so on. With the different environments during combustion, some crystals such as Fe_3O_4, Fe_2O_3 and so on might be appeared. Type D/Max-3B x-ray diffractometer is adopted to analyze the fly ash of Datun Coal and Electricity Corporation, as shown in Table 1.

Table 1: X-ray analysis of fly ash of Datun Coal and Electricity Corporation.

Components	Percentage/%
SiO_2	13
$Al_6Si_2O_{13}$	6
CaO	7
$CaSO_4$	5
$CaCO_3$	2
Fe_3O_4	2
Fe_2O_3	3
$(Na,Ca)AlSi_3O_8$	2
$Al_x(OH)_mSi_yO_z{\cdot}nH_2O$	4
Others	56

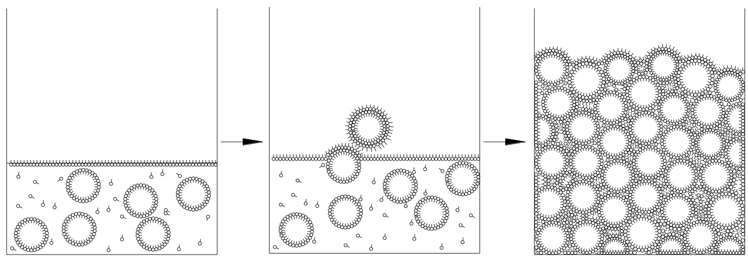

Figure 1: Solution of foaming flow chart

From Table 1, it can be known that the fly ash is composed of SiO_2, CaO, $Al_6Si_2O_{13}$, $CaCO_3$, Fe_2O_3, $(Na,Ca)AlSi_3O_8$, etc., which all have very strong hydrophilicity. After fly ash was dispersed into water and formed slurry, the soluble calcium salt ionizes slightly and produces some Ca^{2+}. According to the adsorption law of ions, the ions having the same chemical elements with original compound are absorbed preferentially. Therefore, for fly ash particles having the elements of $(Na,Ca)AlSi_3O_8$ and $CaCO_3$, those Ca^{2+} are preferentially absorbed on the surface of fly ash particles, making them have positive charge. In order to make the system stable, the foamed gel with fly ash is electrically neutral and thus there must be some anions to make it balance. The foaming agent added has the ability of changing the physicochemical characteristics of fly ash particles. Adding type F3 foaming agent into water, they dissociate into charged ions, which, on the one hand, make the fly ash particles with positive charge produce electrostatic attraction with anions and electrostatic repulsion with cationic. Thus, the anions will enrich on the surface of fly ash particles and cationic keep far away from them, forming electric double layer. At the same time, under the function of electrostatic repulsion, the anions on the surface of the particles repel with the anions on the other surface, making the fly ash particles separate from each other. Hence, with the help of repulsion, fly ash particles will not aggregate and sink, but under the function of electrostatic attraction, they will not apart from each other, ensuring that fly ash particles evenly and uniformly added to the surface of foam particles. On the other hand, type F3 foaming agent can be equably absorbed on the gas-liquid interface. The hydrophobic C-H chains insert gas phase of foam and the hydrophilic polar head insert water, forming monolayer foams. Thus the interfacial tension between foams and liquid is reduced and the stabilized of foams is strengthened. When foams rise above water and contact with air, surfactant molecular layer exists between air and slurry interface, thus two stable layers including foams surfactant monolayer and slurry surfactant monolayer are formed. Under the protection of two stable layers, the stability of foams significantly increases. As the continuous gas injection or stirring vigorously, the foams in slurry constantly flock to the surface. Gradually, those foams accumulate on the surface of slurry and form foams aggregation. The solution of foaming flow chart is shown as Figure 1.

3. Microstructures of foams

Prepare the first foamed gel mixed by the mass fraction of 0.4% of type F3 foaming agent, the second mixed by the mass fraction of 0.4% of type F3 foaming agent and 0.3% of thickener, the third mixed by the mass fraction of 0.4% of type F3 foaming agent and 0.3% of crosslinker, the fourth mixed by the mass fraction of 0.4% of type F3 foaming agent and both 0.3% of thickener and crosslinker. The microstructures of different foam system are characterized, and some meaningful results are obtained. It can be found the microstructures of foam without thickener and crosslinker are chaotic and irregular. As the adding of thickener or crosslinker, the microstructures of foam system are regular and the films are thick. However, the shortage of crosslinker or thickener makes crosslinking reaction not be taken place, thus the stability of foams is poor, appearing phase separation after standing for half an hour. After adding thickener and crosslinker blends, not only the microstructures of foam system are regular, but also the films become thicker, increasing the stability of foam system. The phenomenon of dehydration stratified can not be seen after standing 24 hours. The stability of different foamed gel system is shown as Figure 2.
From Figure 2, it can be found that the foams seem to be irregular; in fact, the structures are quite regular, following the balance condition of Plateau. From the viewpoint of foam geometry topology, every four foams constitute a group of interactional basic unit. In the unit, every three foams enclose a concave triangle plato channel, whose curvature radius is 1um~1mm, about one third of foams' size and is the channel for liquid flowing. The four plato channels compose one meeting point, every two foams form one film, and four foams form six liquid membranes, whose thickness generally is 10Å~1um, which is the minimum separation distance between foams. The dihedral angle between liquid membranes is 120° while the tetrahedral angle between plato channels is 109.47°. Different additives and fly ash particles store in the liquid membranes, plato channels and meeting points.

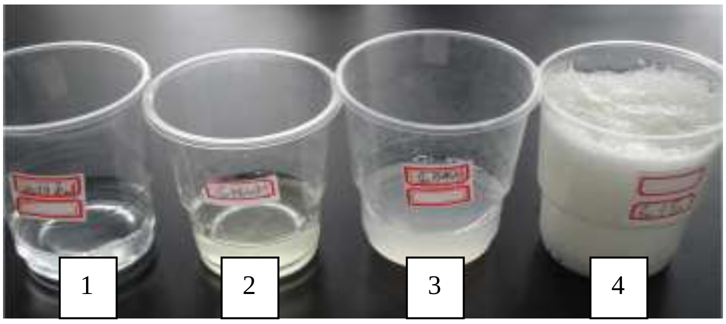

Figure 2: The stability of different foamed gel system after standing 24 hours. 1-both 0% of thicker and crosslinker, 2-0.3% of thicker, 3-0.3% of crosslinker, 4-both 0.3% of thicker and crosslinker.

4. Crosslinking Mechanism

Foams belong to the unstable system, after standing for a while, some slurry in liquid membranes, under the function of mutual extrusion among gravity and capillary force, occur seepage, causing the slurry to accumulate on the plato channels and meeting points. Therefore, in order to keep the stability of foamed gel with fly ash, the thickener and crosslinker is put into slurry. Crosslinking reaction is taken place in liquid membranes and form foamed gel, controlling the displacement of slurry. Thus the foamed gel with fly ash with good stability, high viscosity, no dehydration and consolidating solids, can be formed.
Prepare the thickener and the thicker and crosslinker blends, respectively take 10μL of the two solution samples on mica sheet, and make it spread as can as possible, heating slightly into membranes. Use AFM to observe the microstructures under the scanning range of 500nm, as shown in Figure 3.

From Figure 3, we can see that the microstructures of thickener without crosslinker is chaotic, dispersed into water in granular grape and unable to form three dimensional structures, as represented in Figure 3-1. With the crosslinker, filled in the molecules of thickener, the dispersed thickener molecules aggregate into uniform continuous phase, thus forming three dimensional structures, as shown in Figure 3-2. This is because when the thickener dissolved in water, the helical mesh polymer or double helix cluster are formed by molecular chains, besides, active group in polymer or cluster fully collide with that in the main chain structures of crosslinker, thereby the three dimensional network structures are formed (Montri and Manop, 2006; Mao et al., 2012), making the scattered polymer and cluster form a uniform continuous phase (Juan et al., 2008; Khouryieh et al., 2007). Consequently, under the function of crosslinker, the thickener can react with each other in foam liquid films to form foamed gel and keep the stability of foams.

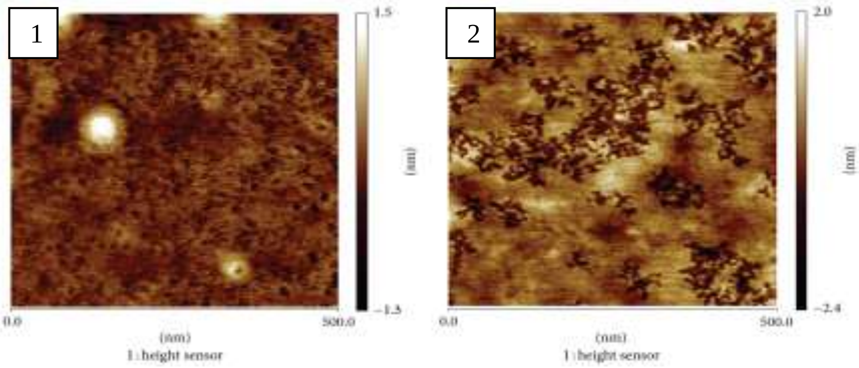

Figure 3: AFM images of foamed gel samples in the scanning range of 500nm. 1-thickener, 2-thickener and crosslinker blends

5. Gelling Time

The mass fraction of type F3 foaming agent is fixed at 0.4%, water-cement ratio is 5:1, the ratio of thickener and crosslinker is 1:1, and then prepare the thickener and crosslinker blends with the mass fraction of 0.6%, 0.8% and 1% respectively. To study on the effect of various mass fractions on gelling time, the results are shown as Figure 4.

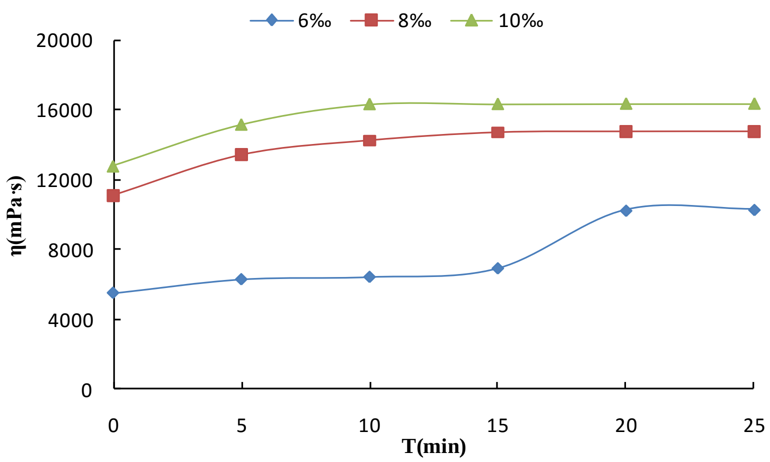

Figure 4: Relationship between mass fraction of blends and gelling time

From Figure 4, it can be seen that when the mass fraction of the blends is 0.6%, the gelling time is 20min. When the mass concentration increased to 1%, the gelling time decreased to 10min. This is because the rise of mass fraction leads to shortening of the distance and increasing of the collision between molecules. The crosslinking reaction between the thickener and the crosslinker becomes stronger, which makes great contributions to forming three-dimensional network structures with strong continuity (He et al., 2001; Matuda et al., 2008). Therefore, the gelling rate increased with the rise of the mass fraction of polymer blends. Nevertheless, on the one hand, if the mass concentration is too high, the reaction rate among polymers

increases, not easy to control the gelling time. On the other hand, the rise of the mass fraction of polymer causes the higher of viscosity of the solution, reducing foaming ability. Therefore, when choosing the mass fraction of the blends is 0.6%, the effect is the best.
The preparation method of the foamed gel with fly ash is that: firstly, in mixing station, a certain proportion of thickener, crosslinker, fly ash and water stir uniformly to form polymerization solution. Then, transport it to the grouting pipeline system by using of pressure pump, at the same time, put foaming agent into grouting pipeline through the quantitative screw pump. The polymerization solution with foaming agent in pipeline flows through foam generator. Finally, nitrogen is introduced into the foam generator and the gas is fully stirred with the mixed solution to form uniform and exquisite foamed gel. The relevant parameters are studied in the laboratory. The results show that the prepared foamed gel could achieve the best performances with the mass ratio of thickener and crosslinker of 1:1, respective concentration of 0.3%, foaming agent concentration of 0.4% and water-cement ratio of 5:1. The picture of prepared foamed gel is shown in Figure 5.

Figure 5: Picture of the foamed gel with fly ash

6. Conclusions

The foamed gel with fly ash, as a new type of fire prevention and extinguishing, not only fully makes use of the advantages of foam and gel, but also overcomes their shortages, thus greatly increase the efficiency of fire prevention and extinguishing.
According to the foaming process of foamed gel with fly ash, the foaming agent is one of the key factors of forming foamed gel. The foaming agent on the one hand changes the physicochemical properties of surface of fly ash particles, making it easy absorb on the foam walls. On the other hand, it can significantly decrease the surface tension of gas-liquid, making slurry foam a lot and maintain the stability.
The microstructures of foamed gel with fly ash have been also investigated. The results show that the thicker and crosslinker in liquid membranes have crosslinking reaction with each other and form three dimensional structures, constituting the rigid bone of foams and enormously increasing the stability of foams.

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