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Investigation into the effect of high expansion, high stability foaming material on auto oxidation of coal using thermo gravimeteric technique

Spontaneous heating is a nagging problem in coal mines. It results in heavy economic losses and often precious human life. A number of techniques are practiced in various coal producing countries to control spontaneous heating and fire problem in underground coal mines. Among the different techniques, uses of high expansion foam have been found as an effective tool to inertize the fire affected area and thus quenching the fire. In this technique, the foam generated using nitrogen gas at elevated pressure, remains stable for long time. Thus foam blankets the burning coal mass and provides inertization of the surrounding environment as well as cooling effect. The role of foam as inhibitor has not been studied in detail.

This study deals with determination of efficacy of three different foaming compounds in retarding spontaneous heating characteristics of coal using thermo gravimetric analysis technique. The findings have indicated that coal samples treated with foam compound have visible impact on retardation of spontaneous heating characteristics of coal.

Introduction

It is well known that the interaction between coal and air can take place at ambient temperature. Coward (1957), Banerjee (2000) studied the spontaneous heating phenomenon in coal and reported that it is an oxidation reaction and librates heat, which if allowed accumulation would progressively enhance the rate and could ultimately lead to fire, known as spontaneous combustion of coal. Mukherjee (1988) carried out the analysis to the causes of fire in coal mines and revealed that the incidences of fire in mines are mostly due to spontaneous combustion of coal. Oxygen plays vital role in initiation and propagation of spontaneous heating in mines. The problem is particularly acute in India, with its vast resources of low grade thick seamed coal. It will not be out of place to mention here that in India, the losses due to spontaneous combustion of coal amounts to several millions of rupees, every year. Herwig Öttl (2002), Stefan (2004) have reported that in China also the fire causes serious losses in their mines. Special attention to this problem is hence, needed.

From the critical analysis of the various techniques adopted to reduce/control spontaneous heating or any combustion process, it is evident that cut off the oxygen supply is the primary aim of these techniques, either by isolation of the area, surface blanketing, mud flushing or by injection cement or sealant application.

Bhowmick (2000) found that in addition to above, removal of heat and inertization of the affected area by cryogenic fluids is also commonly practiced for quick recovery of the affected area. All these techniques mentioned above have proven efficacy but are associated with limitations.

Application of a number of foaming compounds have been used in coal mines in coal producing countries for various purposes viz. dealing fire, construction of mine seals, filling of voids and rib support etc. Use of high expansion and high stability nitrogen foam has also been found significantly effective in dealing with fires due to its smothering action, by cutting off air feed to the burning fuel as well as acting as coolant.

Development of high expansion nitrogen foam technique in recent past has opened new ways for quick displacement of oxygen from fire affected areas along with removal of heat. Additionally, the technique also guaranties inertization of the area for a protracted period. Amalgamation of the above properties in one has made the technique an extremely useful tool for quick control of fire even in working mines. Trevits (2006) have discussed results of the experiments and provides valuable insight into mine fire deployment strategies for gas-enhanced foam technology.

In this study, an attempt have been made to present brief review of the subject, physical properties of three foaming compounds selected for the study and experimental procedure and results of the investigation. The findings on the basis of therograms have indicated that all the three foaming compound namely protein, inorganic and aqueous film foaming foam (AFFF) have inhibiting effect on auto oxidation of coal.

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Brief review

There are different types of foams namely rigid foam, semi rigid foam and high stability, high expansion foam compounds used in mines depending upon the specific requirement. Glenn (2004) presented the fire problem in coal mines and techniques used to deal them. Neath (1948) discussed the experiences of application of foam extinguishers to control fire at Griff colliery. Ray (2007) discussed various fire suppression techniques like infusion of liquid nitrogen, injection of high pressure high stability nitrogen foam, and water mist on open fire. In this study, emphasis has been laid on high stability, high pressure foams which is used for dealing heating and fire problem in coal mines. Some of the significant work carried in this vital area is as disused as under.

The foam

Thrope (1949) described that foam is a system of laminae which capsulate gas bubbles in the inteterstics of solution or suspensoids containing highly capillary active substances. It is a homogeneous mass of tiny air or gas filled in bobbles of low specific gravity which, when applied in the correct manner and in sufficient quantity, form a compact fluid and stable blanket. Also it is capable of blanketing completely the burning mass and thus preventing atmospheric air to reach the burning source. It is produced by mechanically mixing a gas or air to a solution of a foam compound (concentrate) in water.

Foaming agent and application techniques

Glasstone (1951) in the beginning believed that formation of foam is facilitated in solutions, where surface tension is lowered, e.g. in lypophilic solutions. However, now it is known that any substance producing change in surface tension, increase or decrease, will facilitate foam formation. Foaming agents are also of various types. Eisner (1956) suggested a method/technique consists of fitting fabric net across roadway was developed for continuously sprayed with dilute solution of wetting agent; ventilation current through wetted net forms bubbles on side of net next to fire, foam is driven down roadway by ventilation until it reaches either fire itself of length of burnt out roadway sufficiently hot to convert water content of foam into steam.

Linacre (1959) reported a materials and equipment for preparation the foam plug of mine fire fighting at Great Britain and performance was found satisfactory. Nagy (1960) reported results of controlled experiments of foam on fires showed that high expansion foam containing at least 0.2 oz. of water per cu. ft. of foam is effective; ammonium lauryl sulphate has many desirable qualities as foaming agent where heat, roof falls, and smoke prevent direct approach to fire, somewhat more involved procedure of using foam plug may be effective. Robert (1985) and Nakano (1963) also described that the application of foam plug proved itself to be capable of controlling coal mine fire in western Pennsylvania; intermittent operation of foam fire generator enabled fire fighters to attack fire directly with water; use of foam generator during sealing operations permitted same seals to be constructed within 200 ft. of fire. Studies of high expansion-foam plugs show that conversion efficiency is only slightly affected by spraying rate; conversion efficiency is reduced by unduly low air speed, but in small model roadway condition it would normally be 70%; effect of air speed on wetness of foam plug. Wilde (1965) mention that use of high expansion foam for fighting mine fires was effective in controlling the fire during rescue operation in underground mines. Mitchell (1966) studied the uses of urethane and related hazards and reported that associated hazard with the product is heat due to the exothermic reaction during formation of the foam. Nacquet (1993) evaluated Mariflex compound for spray-applied rigid urethane foams and a methodology was developed for the application of Mariflex compound. It is a two component compound and explained the methodology for proper mixing of two component resin and revealed that two components resin and catalyst may be pushed by a pump through two different tubes up to a mixing nozzle for better performance. Geyer (1969) found that the expansion ratio of the foaming material was depending upon the air-water ratio.

Fubao (2006) reported that three-phase foam, which was composed of mud, nitrogen, and water, was used to fight the underground fire. It was injected into the fire zone through boreholes on the ground surface. Due to the simplicity and reliability of this technology, the fire was successfully extinguished.

Experimentation

Physical parameters of different types of foams

Protein, inorganic and aqueous film foaming foam (AFFF) were investigated for their physical parameters including colour, odor, pH, density, viscosity, surface tension, skin irritation and water solubility. Results of the investigation are shown in Table 1.

Table 1: Physical parameters of different types of foaming material

Properties/ parameter	Foaming compound		
	Protein	Inorganic	AFFF
1. Colour	Blackish brown	Slight turbid	Light brown
2. Odor	Rotten protein odor	Mild amonia smell	Light sweet smell
3. Skin irritation	Nil	Nil	Nil
4. pH	6.2-6.9	6.2-8.5	6.2-7.2
5. Density (g/cc)	0.88-1.10	1.01-1.03	0.96-1.00
6. Viscosity (cps.)	42-45	21-25	16-20
7. Surface tension (dyne/cm)	34.28	37.46	32.65
8. Solubility in water	Excellent	Excellent	Excellent

Sample preparation

Coal sample was collected from a coal mine (Haripur colliery, ECL) situated in Raniganj coalfield, India. The coal of this mine is highly susceptible to spontaneous heating. Coal sample was grinded and sieved for -72 mesh BS. 100 g sample of -72 mesh size coal powder was treated with 150 ml of 2.5%, 5% and 7.5% and mother solution of protein, inorganic and AFFF foaming material and stirred well with glass rod and left for 24 hour to complete the reaction. The treated coal samples were dried in a desiccator.

TG analysis

20 mg sample of finally grinded powder of treated and untreated coal was taken in sample holder with the help of balance Model Mattler Toledo and evaluated for their thermal decomposition using thermo gravimetric analyzer (TGA) Model TG-50 and TA processor TC-11 Mattler (Fig.1). Rate of heating was 20°C per minute in air atmosphere. All the samples were run in dynamic mode. The detail experimental and step analysis parameters are given in Table 2. The thermograms and differential thermograms for untreated and treated coal samples are shown in Figs.2-14.

TABLE 2: EXPERIMENTAL PARAMETERS OF TG ANALYSIS

	Step analysis parameters	Screen parameters
1.	Dyn/ISO 1 or 2	1
2.	Autolimit 0 or 1	1
3.	Start temperature °C	25
4.	End temperature °C	800
5.	Baseline type	1
6.	Plot cm	10
7.	Plot mode	2091
8.	Mole mass gas	0
9.	Mol mass init.	0
10.	Sample ID. no.	As per the sample taken
11.	Rate of heating °C/minute	20
12.	Weight mg	As per the sample taken
13.	End screen temperature °C	795-796

Result and discussion

From the thermograms shown in Figs.2-14 for different foams, the following points have emerged.

PROTEIN FOAM

Peaks available in thermograms and differential thermograms for untreated (Fig.2) and treated (Figs.3-6) coal samples with protein foam indicated that peak characteristics of moisture removal at elevated temperature were significantly changed. Results also indicated that burning behaviour was affected upon application of protein in different concentrations..

Results of step analysis shown in Figs.3-6 revealed that moisture content available in untreated coal was released from 25 to 122°C and coal sample decomposed from 261.3 to 587.5°C with 13.08% residual matter at 798.5°C. The results of investigation shown in Figs.3-6 revealed that moisture retention property of coal was enhanced from 122.5°C to 149.0°C, 165.0°C, 161.0°C and 177.0°C upon application of protein foam in 2.5%, 5%, 7.5% and mother solution respectively. Results of moisture content indicate that the susceptibility of auto oxidation of coal was inhibited upon application of protein foam.

Results of decomposition of coal sample at elevated temperature indicated that treated coal samples decomposed at higher temperature and peak ignition temperature and end decomposition temperature was increased. The peak ignition temperature and end decomposition temperature of untreated

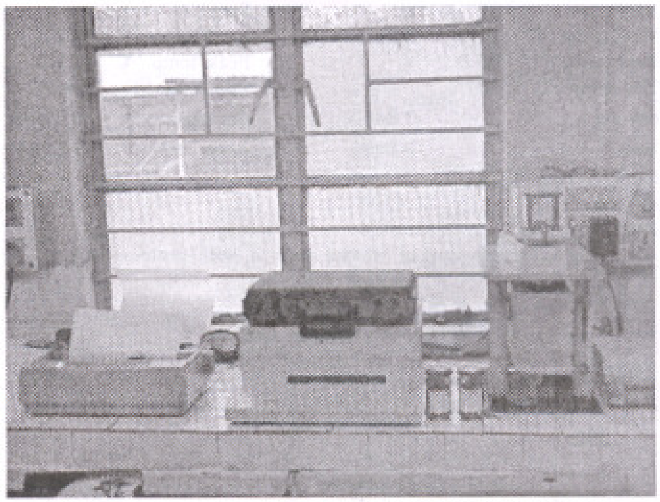
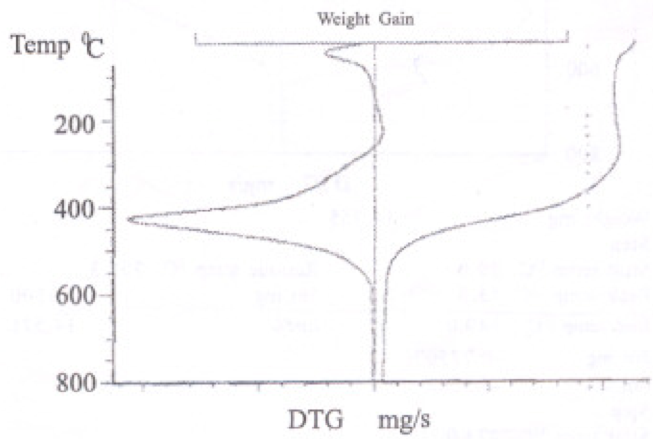


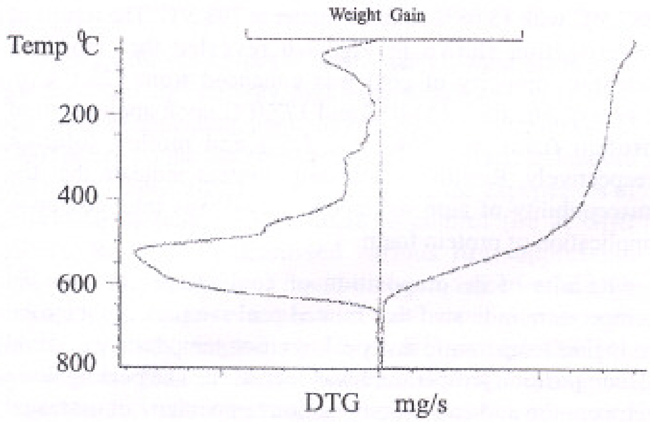
Fig.1 Thermo gravimetric analyzer (Model TG-50, Mattler)



Weight mg 15.675

Step		Step	
Strat temp °C	25.0	Strat temp °C	261.3
Peak temp °C	43.8	Peak temp °C	426.3
End temp °C	122.5	End temp °C	587.5
δm mg	-1.0600	δm mg	12.715
δm%	-6.7624	δm%	81.116
Residue temp °C	798.5		
δm mg	2.0500		
δm%	13.078		

Fig.2 Thermogram of untreated coal

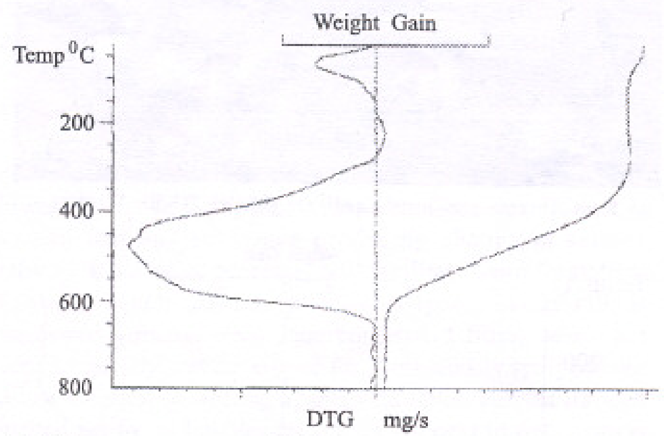


Weight mg 19.570

Step		Step	
Strat temp °C	29.0	Strat temp °C	177.0
Peak temp °C	65.0	Peak temp °C	525.0
End temp °C	177.0	End temp °C	669.0
δm mg	-0.8400	δm mg	-8.1900
δm%	-7.9470	δm%	-77.483

Residue temp °C 795.7
δm mg 1.4200
δm% 13.434

Fig.3 Thermogram of treated coal of with protein foam (mother solution)



Weight mg 14.755

Step
Strat temp °C 29.0
Peak temp °C 65.0
End temp °C 149.0
δm mg -0.78500
δm% -5.5202

Step
Strat temp °C 273.0
Peak temp °C 481.0
End temp °C 653.0
δm mg -11.880
δm% -80.515

Residue temp °C 795.3
δm mg 2.1500
δm% 14.571

Fig.4 Thermogram of treated coal with protein foam (2.5% solution)

coal sample was 426.3°C and 587.5°C and for treated coal sample with 2.5%, 5%, 7.5% solution and mother solution of protein foam it was 481°C and 653°C, 485°C and 665°C, 481°C and 729°C, 525°C and 669°C respectively. Results revealed that protein foam showed the suitability in inhibiting the spontaneous heating of coal.

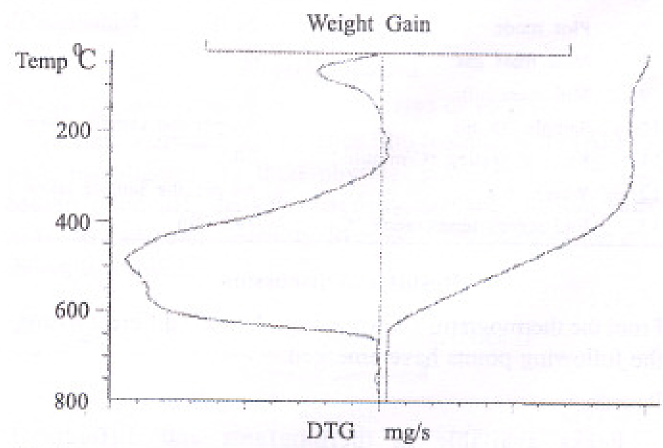
Results of residual matter indicated that residual matter was increased slightly upon application of coal with protein without affecting burning characteristics of coal.

Inorganic foam

Peak characteristics shown in thermograms Figs.7-10 for treated coal samples with inorganic foam indicated that no significant change in the decomposition peaks was observed.

Thermograms and differential thermograms of coal samples treated with inorganic foam shown in Figs.7-10 indicated that moisture retention properties of coal was significantly increased. The moisture was retained up to 205°C, 201°C, 221°C, and 265°C when coal was treated with 2.5%, 5%, 7.5% mother solution of inorganic foam respectively. Result of moisture retention revealed that more the retention of moisture in coal lower the chance of auto ignition of coal in underground mines.

Results of ignition temperature and longevity of burning of coal indicated that peak ignition temperature and end decomposition temperature of treated samples with inorganic foam in different concentration has sifted toward higher temperature in comparison to untreated coal except the coal sample treated with mother solution of protein foam. The peak ignition temperature of coal sample treated with mother solution of inorganic foam was reduced from 426.3 °C to 424.0 °C. It may be due to decomposition of inorganic foam at lower temperature. Results indicated that inorganic foam was quite

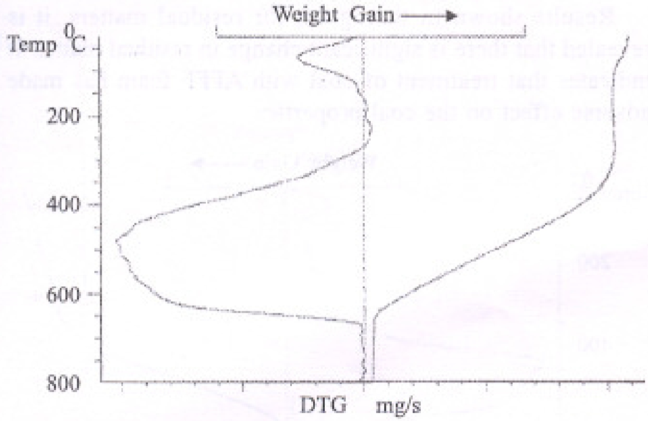


Weight mg 26.910

Step		Step	
Strat temp °C	29.0	Strat temp °C	273.0
Peak temp °C	65.0	Peak temp °C	485.0
End temp °C	165.0	End temp °C	665.0
δm mg	-0.91500	δm mg	-13.385
δm%	-5.4110	δm%	-79.154

Residue temp °C 795.3
δm mg 2.6800
δm% 15.849

Fig.5 Thermogram of treated coal with protein foam (5% solution)



Weight mg	20.030		
Step		Step	
Strat temp °C	29.0	Strat temp °C	273.0
Peak temp °C	69.0	Peak temp °C	481.0
End temp °C	161.0	End temp °C	729.0
δm mg	-1.0250	δm mg	-15.760
δm%	-5.1173	δm%	-78.682
Residue temp °C	795.7		
δm mg	3.3550		
δm%	16.750		

Fig.6 Thermogram of treated coal with protein foam (7.5% solution)

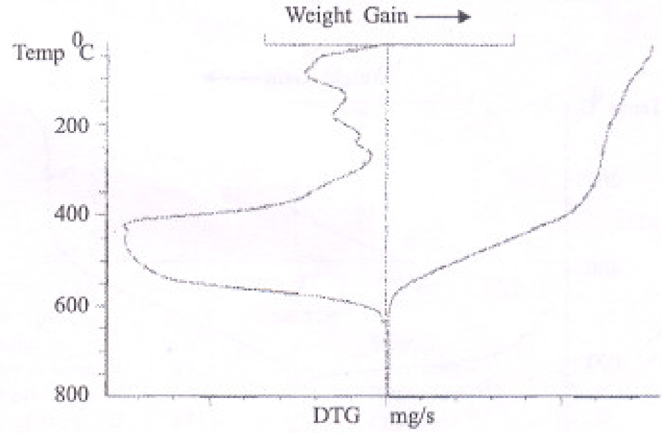
effective in inhibiting the spontaneous heating of coal but impact of inhibiting was lower than protein foam. Residual matter was significantly increased in treated coal samples in comparison to untreated coal sample. It may be due to presence of such chemicals which releases residual matter upon decomposition at elevated temperature.

Results shown in therogram for residual matters, it is revealed that there is no significant change in residual matter. It indicates that treatment of coal with AFFF foam has not made any adverse effect on the coal properties.

AFFF FOAM

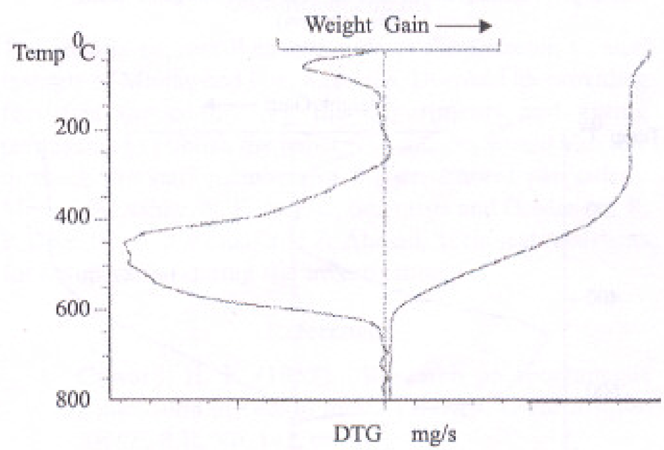
The peak characteristics of different treated and untreated samples shown in Figs.11-14 revealed that the peak height and peak width of treated samples have changed compared to untreated sample. The moisture retention properties of coal were increased upon increasing of concentration of AFFF foam. Moisture retention temperature was 161°C, 165°C and 181°C upon treatment of coal sample with 2.5%, 5% and 7.5% AFFF foam solution respectively. It is evident from the peaks that moisture retention properties have improved significantly in case of the treated samples. Thus it will decrease the self ignition property of the exposed coal without affecting the coal characteristics.

Decomposition peaks indicated that ignition temperature of coal samples treated with AFFF foam was significantly changed in comparison to untreated coal. The decomposition start temperature and decomposition end temperature of untreated coal was 261.3°C and 587.5°C. Whereas it was 273°C and 669°C, 269°C and 701°C, 277°C and 641°C after



Weight mg	12.345		
Step		Step	
Strat temp °C	29.0	Strat temp °C	265.0
Peak temp °C	85.0	Peak temp °C	424.0
End temp °C	265.0	End temp °C	641
δm mg	-2.0000	δm mg	-8.6540
δm%	-16.201	δm%	-70.271
Residue temp °C	795.7		
δm mg	1.5150		
δm%	12.272		

Fig.7 Thermogram of treated coal with inorganic foam (mother solution)

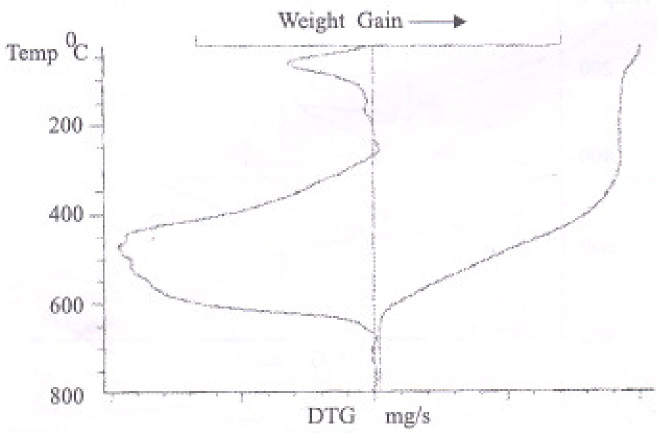


Weight mg	13.690		
Step			
Strat temp °C	29.0	Residue temp °C	795.7
Peak temp °C	65.0	δm mg	1.8050
End temp °C	205.0	δm%	13.185
δm mg	-0.96500		
δm%	-7.0489		
Step			
Strat temp °C	269.0		
Peak temp °C	457.0		
End temp °C	681.0		
δm mg	-10.960		
δm%	-80.058		

Fig.8 Thermogram of treated coal with inorganic foam (2.5% solution)

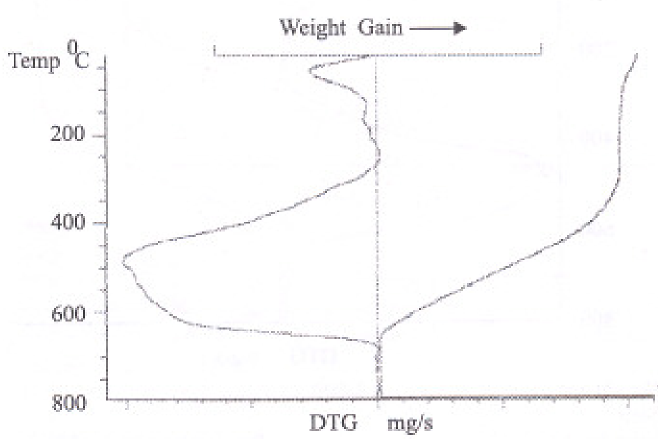
application of coal sample with 2.5%, 5% and 7.5% solution of AFFF foam respectively. The results of AFFF foam were encouraging towards inhibiting susceptibility of auto oxidation of coal.

Results shown in therogram for residual matters, it is revealed that there is significant change in residual matter. It indicates that treatment of coal with AFFF foam has made adverse effect on the coal properties.



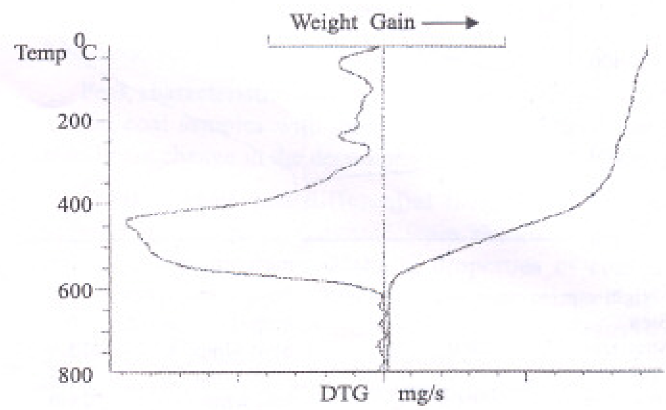
Weight mg	16.630		
Step		Step	
Strat temp °C	25.0	Strat temp °C	273.0
Peak temp °C	61.0	Peak temp °C	469.0
End temp °C	201.0	End temp °C	669.0
δm mg	-1.1300	δm mg	-13.160
δm%	-6.7950	δm%	-79.134
Residue temp °C	795.3		
δm mg	2.4300		
δm%	14.612		

Fig.9 Thermogram of treated coal with inorganic foam (5% solution)



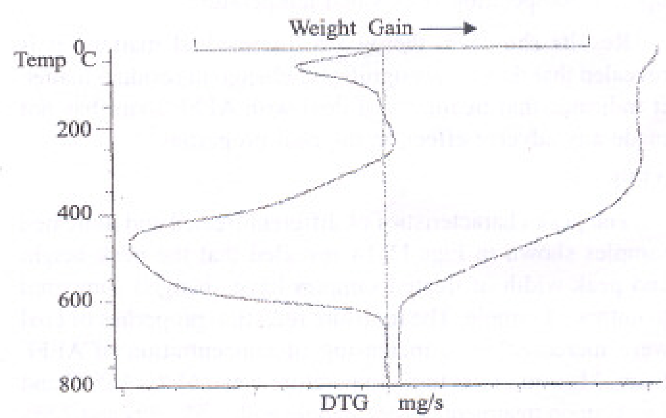
Weight mg	18.970		
Step		Step	
Strat temp °C	29.0	Strat temp °C	269.0
Peak temp °C	57.0	Peak temp °C	485.0
End temp °C	221.0	End temp °C	677.0
δm mg	-1.1000	δm mg	-14.7500
δm%	-5.7986	δm%	-77.754
Residue temp °C	795.7		
δm mg	2.9750		
δm%	15.683		

Fig.10 Thermogram of treated coal with Inorganic foam (7.5% solution)



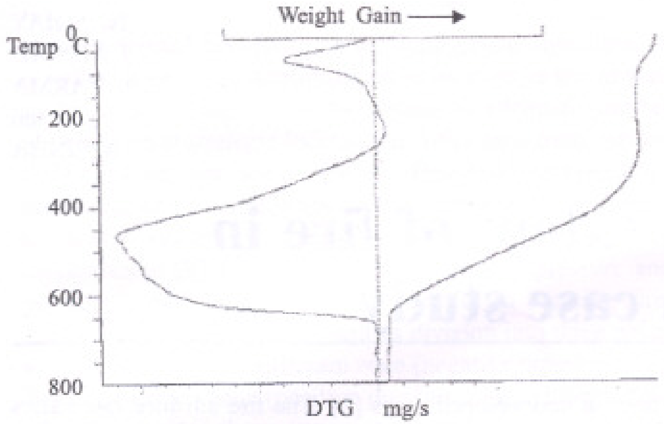
Weight mg	13.285		
Step		Step	
Strat temp °C	29.0	Strat temp °C	273.0
Peak temp °C	61.0	Peak temp °C	437.0
End temp °C	121.0	End temp °C	621.0
dm mg	-0.5500	dm mg	-9.7050
dm%	-4.1400	dm%	-73.052
Step			
Strat temp °C	121.0	Residue temp °C	795.7
Peak temp °C	233.0	dm mg	2.1600
End temp °C	273.0	dm%	16.259
dm mg	-0.7300		
dm%	-5.4949		

Fig.11 Thermogram of treated coal with AFFFfoam (mother solution)



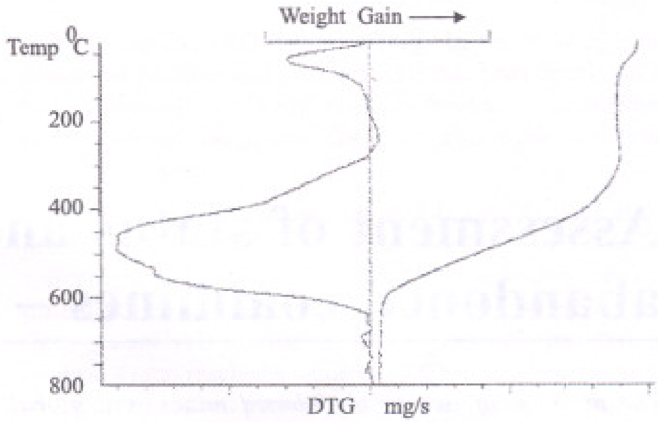
Weight mg	16.530		
Step			
Strat temp °C	29.0	Residue temp °C	795.3
Peak temp °C	65.0	dm mg	3.1100
End temp °C	161.0	dm%	18.814
dm mg	-1.0600		
dm%	-6.4126		
Step			
Strat temp °C	273.0		
Peak temp °C	465.0		
End temp °C	669.0		
dm mg	-12.475		
dm%	-75.469		

Fig.12 Thermogram of treated coal with AFFFfoam (2.5% solution)



Weight mg	20.350		
Step		Step	
Strat temp °C	29.0	Strat temp °C	269.0
Peak temp °C	69.0	Peak temp °C	469.0
End temp °C	165.0	End temp °C	701.0
δm mg	-1.2650	δm mg	-15.825
δm%	-6.2162	δm%	-77.764
Residue temp °C	795.3		
δm mg	3.330		
δm%	16.364		

Fig.13 Thermogram of treated coal with AFFFfoam (5% solution)



Weight mg	14.220		
Step		Step	
Strat temp °C	29.0	Strat temp °C	277.0
Peak temp °C	65.0	Peak temp °C	493.0
End temp °C	181.0	End temp °C	641.0
δm mg	-0.9450	δm mg	-10.735
δm%	-6.6456	δm%	-75.492
Residue temp °C	795.7		
δm mg	2.5600		
δm%	18.003		

Fig.14 Thermogram of treated coal with AFFFfoam (7.5% solution)

Conclusions

The following conclusions are made on the basis of analysis of therograms received from thermo gravimetric analyzer (TGA):

i. Protein foam is giving satisfactory results for moisture retention and increasing the ignition temperature of coal and decreasing the chance of auto oxidation of coal. Protein foam shows encouraging results towards inhibiting the auto oxidation of coal. Therefore, it is suitable to apply protein foam in underground coal mines during fire as well as for the protection of exposed coal from auto oxidation/spontaneous heating.

ii. Treatment of inorganic foam giving satisfactory results. The ignition temperature is increased after application of mother solution of inorganic foam without changing the burning characteristics of coal. The water retention properties of coal are increased and moisture from the coal is releasing at higher temperature in comparison with untreated coal. Application of inorganic solution would give the better results during rescue operation in underground coal mines during fire.

iii. AFFF foam not shows very encouraging results towards inhibiting the auto ignition of coal and increasing the residual matter.

iv. Application of different types of foam is not affecting the quality of coal and residual matter is not changes significantly.

v. It is concluded that application of protein and inorganic foam in underground coal mines will decrease the susceptibility of auto oxidation of coal. AFFF foam is not too much effective in comparison to protein and inorganic foam.

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