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DESULPHURIZATION OF LIGNITIC COALS USING AQUEOUS CUPRIC CHLORIDE

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Desulphurization of lignitic coal of Pakistan, using an aqueous solution of cupric ions as an oxidant at different temperatures was accomplished in sealed tubes. Desulphurization occured as reaction started. At the early stage of reaction, reduction of sulfur was rapid and thus with the passage of time it became slow. Increment in the level of desulphurization occurred with the increasing concentration of cupric ions and temperature. Reduction of sulfur drops of the levels of ash contents and enhances the value of Clorific Value (CV) .

Key words: Desulphurization, Cupric ions, Reduction, Oxidant, Lignitic coal.

Introduction

There are over 185 billions of tonnes of coal reserves in Pakistan. Most of these are lignitic with high sulfur and ash contents. These coals due to their inherent proportions of sulfur and volatile materials emit toxic, corrosive oxide of sulfur and sulfur and fumes which have horrible effects on the environment. It is thus very necessary to remove these impurities partially or completely to make them environment friendly. Presently, there is no economical and suitable method for washing of these coals physically or chemically for the reduction of sulfur and ash contents. Physical coal cleaning is limited in that it can only reduce the mineral sulfur contents of the coals. Chemical coal cleaning is the method which may help in reducing both inorganic and organic sulfur contents partially or even completely (Cough and Candle 1967; Wheelock 1977; Palmer *et al* 1994).

Researchers are making efforts to remove sulfur chemically though experience shows that this method will not be economical. Treating coal at elevated temperature with gases such as hydrogen, nitrogen and chlorine (Huang and Pulsifier 1977; Sinke 1978; Singh *et al* 1985) reduce the sulfur content. Hydrogenation of coal which is the process of aqueous inorganic acids like HCl, H_2SO_4, HNO_3, HBr, Hl etc. removes only a portion of the recoverable sulfur combined as pyritic sulfur. Organic sulfur may be separated by solvent extraction. Krenkler (1950) extracted first with a powerful solvent before precipitating with a weaker one. The same process has also been adopted by other of ferric sulfate removes 90-95% pyritic sulfur (FeS_2) but it does not remove organic sulfur (Meyers 1977). However a process to remove both pyritic and organic sulfur upto 100% by treating the coal with aqueous cupric chloride was suggested by Lompa-Krzmine (1982). This method may be used in desulphurization of coal to different level of sulfur. But subject requires some more study in detail. This paper describes the desulphurization of coal using aqueous cupric chloride as an oxidant. It also encircles the effects of oxidant, coal, temperature and reaction time on the reduction of sulfur content in the coal samples.

Experimental

Materials. Lakhra coal samples with high sulfure contents (6.21%) were collected. The ultimate and proximate analyses of coal samples are as follows:

Moisture %	Volatile matter%	Ash %	Fixed carbon%	CV* (Btu/lb)	C %	H %	N %	S %
28.05	29.96	12.56	29.93	8873	63.30	5.09	1.87	6.21

*Calorific or Heating value; Btu, British thermal unit.

All the coal samples were finaly ground upto 100 mesh sieve and dried. Analytical grade cupric chloride was used without further purification.

Procedure of desulphurization. All experiments were accomplished in sealed Pyrex tubes, 30 cm long and 2 cm internal diameter. Known quantity of coal sample and aqueous solution of cupric chloride were transferred through a long stem funnel into reaction tube. The tubes were sealed at construction. Finally, the tubes were placed in an oven controlled at required temperature. After required reaction time, the tubes were cooled and the sealed were broken open. The contents were washed on filter paper with 1% diluted HCl and then with water until the washings collected were neutral. The coal was dried and weighed. The dried samples were

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analyzed for sulfur, CV and ash. Sulfur was estimated on LECO-1325, CHNS-600, whilst ash and CV were determined on LECO MAC-400 and parr Bomb Calorimeter respectively.

Results and Discussion

Effect of time, concentration of oxidant ($CuCl_2$), temperature and coal concentration on desulphurization of coal (Sulfur, CV and ash content) are discussed in the following paragraphs:

1) Effect of time. Table 1 illustrates the effect of time on desulphurization of lignitic coal using 20% $CuCl_2$ solution at 150°C. The results indicate that desulphurization began as the reaction started. At the early stage of the reaction, the rate of desulphurization was rapid (Fig 1) and slowed down with the passages of time. The increase in the rate of desulphurization results in the reduction of ash contents and enhancement in CV of the treated coal, where as the CV of untreated cool was 8873 Btu /lb. The reduction in ash content was probably due to simultaneous dissolution of mineral and organic part of the coal. Further, the enhancement in CV could be attributed to the reduction of ash content. The decrease or increase in CV and ash content were consistant not with increase of time which might be due to the quantities of pyritic sulfur left unaffected in treated coal. Similar results were also reported by Palmer *et al* (1994), who accomplished selective oxidation with per oxyacetic acid to study desulphurization of two Illionois basis coals. According to this investigation, desulphurization was quite rapid at the early stages of the reaction, but slowed down towards the latter stages, These results suggest that the desulphurization reaction may be dependent on the reaction time.

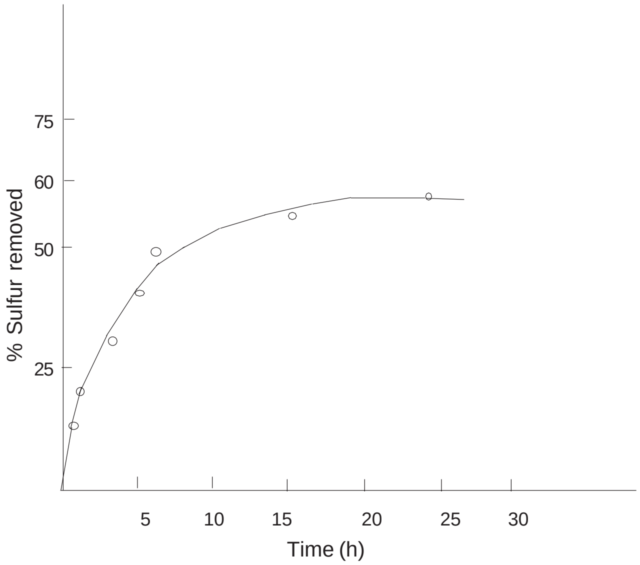

Fig 1. Effect of time on desulphurization of coal.

2) Effect of amount of $CuCl_2$. Table 2 includes the data obtained at different concentrations of aqueous $CuCl_2$ solution keeping temperature (200°C) and time (1-5h) constant. From the results, it is evident that the increasing concentration of $CuCl_2$ solution tended to increase the level of desulphurization of coal. Total sulfur reduced from 6.21% to 2.42%. In Fig 2, % desulphurized sulfur is plotted against amount of $CuCl_2$ solution which inferred that the amount of desulphurized sulfur got increased with increasing amount of $CuCl_2$ solution.

At 20% $CuCl_2$ concentration, the maximum sulfur (61%) was removed at 200°C in 5h, whereas in 1h. 44.0% reduction of sulfur occured. It further showed that with the increasing concentration of $CuCl_2$ solution, the value of CV got increased but at 5% of $CuCl_2$, it was decreased. Further more, the ash contents of treated coal reduced with the increasing concentration of $CuCl_2$. The decrease or increase in CV and of ash content of treated coal are not regular with increasing concentration of $CuCl_2$. It is probably due to some quantity of pyritic sulfur was left unaffected in treated coal samples after desulphurization. The presence of pyritic sulfur in coal samples

Table 1

Effect of time on desulphurization of lignitic coal using aqueous cupric chlorides as desulphurizing agent

S.No.	Time (h)	Wt. of coal (g)		Ash (%)	Total sulfur (%)	Desulphurized sulfur (%)	CV (Btu/lb)
		Before reaction	After reaction				
1	½	5.00	4.3544	09.58	5.42	12.72	9843
2	1	5.00	4.7450	08.00	4.98	19.81	10066
3	3	5.00	4.8772	09.98	4.34	30.11	9869
4	5	5.00	4.8020	11.30	3.72	40.10	8960
5	7	5.00	4.8078	10.85	3.11	49.92	9565
6	15	5.00	4.7858	11.50	2.73	56.04	9600
7	24	5.00	4.7884	11.90	2.48	60.06	8956

20% $CuCl_2$, 20 ml; Temp, 150°C.

increases ash contents and organic sulfur has no contribution in the decrease or increase of ash content. These results suggest that required level of desulphurization may be achieved by using different concentrations of $CuCl_2$ solution. The concentration of $CuCl_2$ may also be more than 20%.

3) Effect of temperature. Table 3 includes the observations obtained at variable temperature while the concentration of $CuCl_2$ and reaction time was fixed i.e. 20% and 5h respectively. These results show that the level of desulphurization increased by increasing the temperature and as a result of this ash contents got reduced whereas CV enhanced. In Fig 3, graph indicates that at 200°C, the level of desulphurization was higher and it was lowest and slows down with decreased temperature. The removal of sulfur at 100°C is 9.0%, whereas at 125°C, 150°C and 200°C, the level was produced as 21.10%,

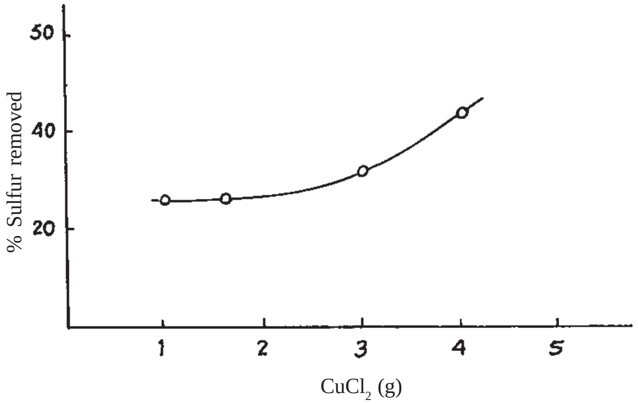

Fig 2. Effect of cupric ions on desulphurization of coal.

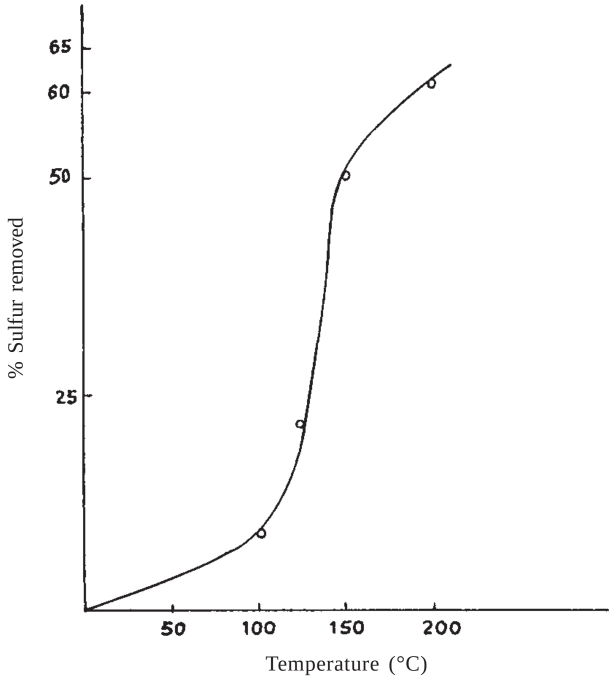

Fig 3. Effect of temperature on desulphurization of coal.

Table 2

Effect of cupric chloride amount on desulphurization of lignitic coal using aqueous cupric chloride as desulphurizing agent

S.No.	20% $CuCl_2$	Wt. of coal (g)		Ash (%)	Total sulfur (%)	Desulphurized sulfur (%)	CV (Btu/lb.)
		Before reaction	After reaction				
8	5.0^a	4.9968	4.2120	12.80	4.62	25.60	7482
9	8.0^a	5.0339	4.3144	11.19	4.57	26.40	9081
10	15.0^a	5.0282	4.4620	12.00	4.28	31.10	9876
11	20.0^a	5.0147	4.2926	11.49	3.48	44.00	8942
12	20.0^b	5.0041	4.2860	11.80	2.42	61.00	9948

Time, a = 1h, b = 5h; Temp, 200°C.

Table 3

Effect of temperature on desulphurization of lignitic coal using aqueous cupric chloride as desulphurizing agent

S.No.	Temp°C	Wt. of coal (g)		Ash (%)	Total sulfur (%)	Desulphurized sulfur (%)	CV (Btu/lb.)
		Before reaction	After reaction				
13	100	5.0710	4.1198	8.16	5.65	09.00	9886
14	125	5.0184	4.5879	8.90	4.90	21.10	9673
15	150	5.0000	4.8020	11.30	3.11	49.90	8960
16	200	5.0041	4.2860	11.80	2.42	61.00	9948

20% $CuCl_2$, 20 ml; Time, 5 h.

Table 4

Effect of concentration on desulphurization of lignitic coal using aqueous cupric chloride as desulphurizing agent

S.No.	Wt. of coal (g)		Ash (%)	Total	Desulphurized	CV (Btu/lb)
	Before reaction	After reaction	after reaction	sulfur (%)	sulfur (%)	
17	4.0041	4.2860	11.80	2.42	61.00	9948
18	4.0074	3.5371	9.50	2.13	65.70	9820
19	2.9706	2.5469	10.00	1.95	68.60	8900
20	2.0240	1.6700	6.86	1.64	73.60	8888
21	1.0243	0.9757	5.77	1.05	83.10	8978

Time, 5h; Temp, 200°C; 20% $CuCl_2$, 20 ml.

49.9% and 61% respectively. Ash content and CV of treated coal are also affected with increase in temperature. At comparatively low temperature (100-125°C), the ash contents of treated coal were estimated as 8.16-8.9%, whereas at high temperatures the ash contents were obtained as 11.3-11.8%. Further more, with increasing temperature CV of treated coal were obtained as 9886-9948 Btu/lb whereas the CV of raw coal is 8873 Btu/lb.

4) Effect of coal concentration. Table 4 includes the experiments which were carried out on varying concentrtions of raw coal at constant temperature (200°C), concentration of $CuCl_2$ (20 ml) and time (5 h). These results and our laboratory experience indicate that with decreasing concentration of coal the desulphurized sulfur of treated coal and CV increased whereas ash content droped with decreasing concentration of raw coal.

In brief, when coal samples with aqueous solution of cupric chloride is sealed at construction and heated at elevated temperatures for desired reaction time, cupric ions oxidize pyritic sulfur (FeS_2) to sulfuric acid.

$$FeS_2 + 14CuCl_2 + 8H_2O \rightleftharpoons 14CuCl + FeCl_2 + 2H_2SO_4 + 12HCl$$

The organic compounds of sulfur are also oxidized to water soluble products. The C-S bonds of organic sulfur are also oxidized to water soluble products. The C-S bonds of organic sulfur are broken due to oxidation by $CuCl_2$ and form water soluble compounds which are removed by washing with water. The treated coal is washed until the filtrate collected is neutral, dried and weighed. The estimation of treated coal for chlorine is carried out to ensure that the chlorination of coal does not take place and only the oxidation of sulfur compounds (both organic and pyritic) occurs. It was noted that white crystals of cupric chloride were found in the treated coal which on exposure to air were converted into cupric chloride and removed by washing with water. The estimation of desulphurized coal for sulfur, ash and CV provides the following informations.

Conclusion

1) Chlorination of coal does not take place and copper chloride oxidizes pyritic sulfur and organic compounds containing sulfur functional groups.
2) Desulphurization of raw coal is quite rapid in the early stages of the reaction. Induction period of desulphurization begins as $CuCl_2$ and raw coal come in contact with each other. The results suggest that the desulphurization of coal depends upon time.
3) Raw coal may be desulphurized using various concentrations of aqueous $CuCl_2$ solution. Increment in the leval of desulphurization occurs with increasing concentrations of $CuCl_2$.
4) The increase in temperature enhance the level of desulphurization of raw coal. The sulfur free coal may be obtained at high temperature.
5) Reduction of sulfur content in the treated coal resulted in reduction of ash content and enhancement of CV.

Hence desulphurization of coal in the presence of cupric chloride depends upon their variables i.e. time, temperature and concentrations of cupric chloride.

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