

CHEMICAL TREATMENT OF COAL BY ALKALI USING LEACHING PROCESS

Faisal Rehman¹, Shahid Raza Malik², Abdul Mateen Khan², Muhammad Shahzad Zafar³, Sharjeel Waqas¹

¹ School of Chemical Engineering, The University of Faisalabad, (Amin Campus) Canal Road, Faisalabad

² Department of Chemical Engineering, NFC Institute of Engineering and Fertilizer Research, Jaranwala Road, Faisalabad

³ Department of Chemical Engineering, University of Engineering and Technology Lahore (Faisalabad Campus), Faisalabad

Corresponding author: faisalrehman_23@yahoo.com, Tel: +923346320610

ABSTRACT: The high contents of sulfur and ash forming components present in the salt range coal (Punjab, Pakistan) are necessary to remove prior to its industrial utilization. The present work reports the desulfurization and demineralization of coal by chemical treatment with sodium hydroxide (5% w/v). The effect of parameters like time, temperature and particle size on sulfur and ash removal are, hence, found to be significant. Orthogonal array experimental design with the above mentioned factors was used to optimize the experimental parameters by the analysis of means (ANOM). The results indicated that the treatment time had the most significant effect on desulfurization efficiency followed by temperature and coal particle size. It was further supported by the significance factor test. The demineralization behavior disturbed by the formation of sodium aluminosilicates precipitates. The confirmatory experiments were performed at the optimum conditions obtained for desulfurization as time: 60 min, temperature: 60°C, particle size: 0.177mm, and for demineralization as time: 40 min, temperature: 40°C, particle size: 0.297mm and examined 41.74% and 35.56% reduction in sulfur and ash content respectively.

Keyword: Coal beneficiation, desulfurization, demineralization, Leaching

INTRODUCTION

In recent years, ecumenical energy industries have been fixating on expediting the advancement of coal chemical industry due to the shortage and elevating rates of natural gas and crude oil. Coal reserves are very vital and dispersed in all over the world. Pakistan with more than 186 billion tons of coal deposits stands at 6th position in the world [1]. But the electricity generated with local coal reserves has not been commenced yet due to many reasons out of which the poor quality of coal is one.

Pakistani coal possesses high ash and sulfur contents which restrict its utilization in many industrial applications. Therefore, elimination of impurities from coal prior to its application is required. The SO_x emission, arise from combustion of high sulfur coal can cause rigorous harm to public health, soil, marine life, ozone and metal structure etc. The problems like handling and disposal of ash, fouling and corrosion of equipment and environmental issues arise due to the presence of high ash contents in coal.

Hence, the presence of sulfur in coal is also intricate as its chemistry affects the extraction of sulfur from coal. Sulfur is present in both organic and inorganic forms (sulfate and pyritic form). However, organic sulfur is structurally bonded and its removal is arduous by physical coal beneficiation process.

For coal beneficiation, a number of physical, microbial and chemical methods have been investigated by various researchers. Physical methods, such as magnetic separation and froth flotation can only remove a part of pyritic sulfur but cannot reduce the portion of organic sulfur. The microbial method mostly used *T. ferrooxidans* and *T. thiooxidans* bacteria, only effective for inorganic sulfur and not remove organic portion of sulfur [2]. Coal was treated with nitric acid solution at different operating conditions of time (5-12 min), temperature (10-90°C), concentration (5-30 % by wt.) and particle size and observed about 90% inorganic sulfur reduction [3]. Coal from northern Thailand was treated with 7% potassium hydroxide and 2% methanol at 150°C for 90 minutes and noticed the 62% elimination in total sulfur [4]. Tabas coal was treated with 5% sodium butoxide for 90 minutes at 120°C and noticed 52% and 13% reduction in

pyretic sulfur and organic sulfur from coal [5] 25% nitric acid solution used and observed that almost total portion of inorganic sulfur was eliminated when coal (Turkish Lignite) was treated at 103°C for 30 minutes [6]. Oxygen and 1% ozone were used as a reagent at 25°C for 1 hour and resulted the 20% reduction in sulfur from coal [7]. The complete elimination of sulfur from coal was noticed when 10% (vol) aqueous calcium chloride used for 48 hours at 200°C [8]. Sodium benzoxide used at 205°C for 90 minutes and resulted in the 45.9% reduction in sulfur [9]. The desulfurization of Gediz lignite investigated and found the 45% elimination in sulfur when lignite treated with Peroxy acetic acid for 72 hours [10]. 24% reduction in ash content along with 58% reduction in total sulfur was observed when coal was treated with methanol/H₂O and methanol/KOH at 150 °C [11]. 45% removal in total sulfur along with a 45 % reduction in ash was noticed when the coal sample was treated with 15% (vol) Hydrogen peroxide and 0.1N sulfuric acid for 4 hours [12]. Complete removal of pyritic and sulfate sulfur, 30% removal of organic along with 15% reduction in Ash from coal was achieved when coal was treated with chlorine solution at ambient temperature and pressure [13]. A new oxidative method was developed in which peroxyacetic acid used for 1 hour at 21°C and observed 24-37% elimination in total sulfur [14]. The use of Sodium borohydride as a reagent to eliminate the sulfur content from coal was studied. Reaction parameters investigated include pH, time, temperature, stirring rate, solvent concentration and coal particle size [15].

Table 1: Analytical results of coal feed

	Air dried	Dried
Moisture (%)	0.262	-----
Ash (%)	36.3327	36.4281
Volatile Matter (%)	34.5975	34.6883
Fixed carbon (%)	28.8078	28.8843
Sulfur (%)	5.03	5.0432

EXPERIMENTAL SETUP:

The sample of coal utilized in this research work was amassed from Choa Saidan Shah Coal mine (salt range coal field), Punjab, Pakistan. The required particle size of air dried coal for experimentation was achieved by applying the

sequence of unit operations such as crushing, grinding and sieving. Chemicals such as, sodium hydroxide, magnesium oxide, sodium carbonate and barium chloride of pure grade were used in this study. The proximate analysis was performed according to the ASTM standard methods (ASTM D3173 to D3175) and total sulfur content was calculated by ESCHKA method (ASTM D3177). The observed values were twice reiterated to confirm reproducibility and a mean value of tests are hereby reported. Analytical results of coal feed are presented in Table 1.

Table 2: Experimental factors and levels chosen for leaching of coal sample.

Parameter	Parametric levels		
	Level 1	Level 2	Level 3
Time (Min)	20	40	60
Temperature (°C)	40	60	80
Particle size (mm)	0.125	0.177	0.297

Orthogonal experimental design (L_9) provides a systematic and simple approach for optimization of design for performance, quality and cost. The selection of parametric conditions is very important phase in the experimental design. In order to shorten the experimentation time and cost, three factors, i.e., treatment time (20, 40, 60 min), temperature (40, 60, 80°C) and particle size of coal (0.125, 0.177, 0.297 mm), was examined in three-factor, three-level, orthogonal array.

In each test run, 200 ml Sodium Hydroxide solution of 5% w/v concentration and 30 gram of coal sample was added to the 500ml beaker, which kept on a magnetic stirring plate. The temperature was applied by a heating rod and a thermocouple was placed to control the temperature. All the experiments were performed with their corresponding combination of time, temperature and particle size of coal as defined by L_9 experimental scheme. After alkali treatment, the leached coal was cooled, filtered, washed with distilled water, dried in an oven and analyzed by using ASTM standard methods, and total sulfur was estimated by ESCHKA method.

RESULTS AND DISCUSSION:

Optimization of temperature, treatment time and coal particle size by L_9 orthogonal array

Experimental design and results are shown in Table 2 and 3 of orthogonal array for sulfur and ash removal from coal. Analysis of means (ANOM) utilized in this study, shown in Table 4. For each factor in the X_i row, the mean value of X_i was calculated by adding the experimental results of level I and then divided by 3. For example, in terms of sulfur removal the value of X_1 for the factor Sb was $(26.1183 + 28.7159 + 28.0616)/3 = 27.63$

For each factor the range value was calculated by the difference of corresponding maximum and minimum values of X_1 , X_2 and X_3 rows. The higher range values of Sa and Ac implying that these factors had the most significant influence on sulfur and ash removal from coal respectively.

As the time of leaching up is from 20 to 40 min, the total sulfur removal increased by 26.05%. Further increase in time from 40 to 60 minutes resulted in 20.37% removal of total sulfur from coal. The increase in temperature had the direct influence on the sulfur removal from coal. As the temperature increased from 40 to 60°C the total sulfur removal increased by 25.22% and further increase in temperature up to 80°C resulted in a 12.1% reduction in total sulfur from coal. It can be seen from the results depicted in Table 4 that by decreasing the particle size from 0.297 to 0.177 mm, the sulfur removal was enhanced by 22.32%. Further reduction in particle size of coal to 0.125mm resulted in 9.73% elimination in total sulfur from coal.

Table 3: Experimental design and results for leaching process according to orthogonal array L_9

Test Run	Time	Temp	PS	% Sulfur removed	% ash removed
1	1	1	1	26.1183	20.5048
2	1	2	2	27.5460	34.7049
3	1	3	3	26.5546	28.9141
4	2	1	2	28.7159	33.8541
5	2	2	3	30.3220	33.0670
6	2	3	1	42.0804	28.3925
7	3	1	3	28.0616	32.9383
8	3	2	1	45.9272	23.8189
9	3	3	2	47.7514	18.3738

In case of ash removal, the increment of 13.30% ash removal was observed by increasing the reaction time from 20 to 40 minutes. Further increase in time had an adverse effect on ash removal from coal due to the formation of sodium aluminosilicates precipitates. As the temperature of leaching increased from 40 to 60°C, the ash removal slightly increased by 4.9% but further increase in temperature had the negative impact on ash removal. The maximum ash removed with the coal particle size of 0.297mm, further reduction in particle size of coal lead to the minimum removal of ash forming components from coal.

Sulfur removal:

Sodium hydroxide is very effective to reduce all forms of sulfur, organic, pyretic as well as sulfate sulfur from coal (16). Figure 1 shows the effect of time, temperature and particle size the mean values of sulfur removal from coal.

Effect of time: Time is a very important factor in leaching process. According to the significance factor analysis shown in table 5, time (with maximum f-value i.e. 40.67) is very important factor in desulfurization process. The sulfur removal from coal increased as the treatment time increased because more time was available to interact the solvent with sulfur present in coal.

Table 4: Response Table for Mean

Xi	For % Sulfur Removal			For % Ash Removal		
	Time Sa	Temperature Sb	Particle Size Sc	Time Aa	Temperature Ab	Particle Size Ac
X1	26.74	27.63	38.04	28.04	29.10	24.24
X2	33.71	34.60	34.67	31.77	30.53	28.98
X3	40.58	38.80	28.31	25.04	25.23	31.64
Range	13.84	11.16	9.73	6.73	5.30	7.40

Effect of temperature: The elimination in sulfur rate increased with the increasing temperature due to more easily diffusion of alkali into the coal particles to remove sulfur from it which enhanced the reaction rate. However, the sulfur removal rate at the temperature range of 40 to 60°C was greater than that at a temperature range of 60 to 80°C.

Effect of particle size: The particle size of coal plays an important role in the sulfur reduction. The decrease in coal particle size produces more surface area to react with alkali, so that more impurities can dissolve in solution. The decrease in coal particle size favors the sulfur removal rate from coal.

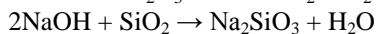
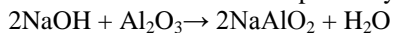
Table 5: Significance factor/process factor test using Minitab 17:

Source	DF	Adj SS	Adj MS	F-Value
For Ash removal				
Time	2	68.16	34.08	0.69
Temperature	2	45.17	22.58	0.46
Particle size	2	84.32	42.16	0.86
Error	2	98.22	49.11	
Total	8	295.87		
For Sulfur removal				
Time	2	287.340	143.670	40.67
Temperature	2	190.772	95.386	27.00
Particle size	2	146.451	73.225	20.73
Error	2	7.065	3.532	
Total	8	631.628		

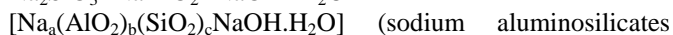
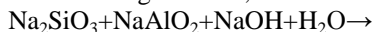
DF: Degree of freedom, Adj SS: Adjusted sum of square, Adj MS: Adjusted mean square

ASH removal:

The behavior of ash removal from coal with alkali treatment is different from sulfur removal from coal. The coal has high content of ash forming components. Alumina and Silica are the two major components of mineral matter present in the coal. NaOH reacted with these two impurities to form soluble aluminates and silicates respectively.



In the presence of NaOH, silicates and aluminates react each other and form sodium aluminosilicates precipitates (17). By the following reaction;



precipitates) These precipitates can only dissolve with acid treatment after alkali leaching. Figure 2 shows the effect of parameters on the mean value of ash removal from coal.

Effect of time: As the treatment time increased from 20 to 40 minutes, the ash removal increased, but further increase in time had the negative impact on ash removal.

Effect of temperature: The increase in temperature from 40 to 60°C had only marginally effect on increasing the ash removal rate, but further increase in temperature up to 80°C decreased the ash removal rate.

Effect of particle size: The reduction in coal particle size leads to the minimum removal of ash forming components from coal due to the presence of high mineral matter, which lead to the sodium aluminosilicates precipitates.

Confirmatory experiment:

At last, confirmatory experiment was performed based on the predicted optimum conditions. The objective was to verify the improvement in the removal efficiency at the optimum conditions suggested by the orthogonal array experimental scheme. Results showed 41.74% removal of total sulfur by alkali leaching at the optimum conditions. And 35.56% ash removal observed at the optimum conditions, which is the highest in comparison to all other experiments. It showed that observed results and the suggested optimum values were indeed compatible

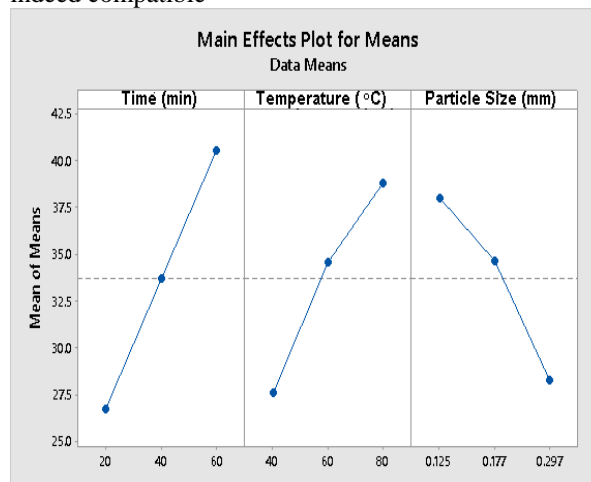


Figure 1: Effect of time, temperature and particle size on mean of % sulfur removal using Minitab 17

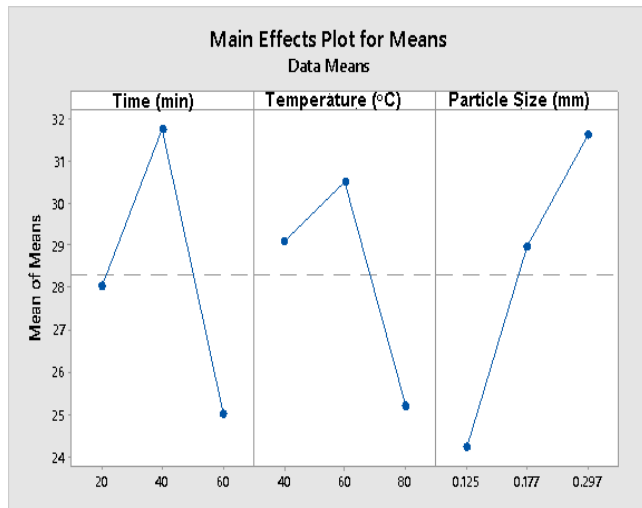


Figure 2: Effect of time, temperature and particle size on mean of % ash removal by using Minitab 1

CONCLUSION:

Sodium hydroxide is very effective to dissolve sulfur from coal as well as to react with most of ash forming design shortened the time and cost and the parameter optimized by applying analysis of means. The increased treatment time, reaction temperature and reduction in coal particle size enhanced the desulfurization rate. The ash removal showed the different behavior due to the formation of sodium aluminosilicates precipitates. The results of alkali leaching revealed the following as optimum experimental conditions for desulfurization, time: 60 min, temperature: 60°C, coal particle size: 0.177mm and the optimum conditions for demineralization, time: 40 min, temperature: 40°C, particle size: 0.297 mm. The confirmatory experiments was performed at the optimum conditions and found the compatible results.

REFERENCES:

1. MALKANI, M. SADIQ, "A REVIEW OF COAL AND WATER RESOURCES OF PAKISTAN", Sci., Tech. and Dev., 202-218 (2012)
2. Huan He, Fen-Fen Hong, Xiu-Xiang Tao, Lei Li, Chen-Yan Ma, Yi-Dong Zhao, "Biodesulfurization of coal with *Acidithiobacillus caldus* and analysis of the interfacial interaction between cells and pyrite", s.l.: Fuel Processing Technology, **101**(2012)
3. Ramon Alvarez Rodriguez, Carmen Clemente Jul and Dulce Gomez-Limon, "The influence of process parameters on coal desulfurization by nitric leaching ". Fuel, **75**(1996)
4. S. Ratanakandilok, S. Ngamprasertsith, P. Prasassarakich, "Coal desulfurization with methanol/water and methanol/KOH", Fuel, **80**(2001)
5. E.Jorjani, B.Rezai, M.Vossoughi, M.Osanloo, M.Abdollahi, "Oxidation pretreatment for enhancing desulfurization of coal with sodium butoxide", Minerals Engineering, **17**:545-552(2004)
6. S. Karaca, M. Akyurek, S. Bayrakcheken, "The removal of pyritic sulfur from Ashkal lignite in aqueous suspension by nitric acid", Fuel Processing Technology, **80**, (2003)

7. Steinberg M, Yang RT, Horn TK, Berlad AL, "Desulfurization of coal with ozone: an attempt", : Fuel, **56**, (1977)
8. LL, Krzymien "Complete removal of sulfur from coal using solutions containing cupric ions", Fuel, **61**, (1982)
9. Prasassarakich P, Thaweesri T. "Kinetics of coal desulfurization with sodium benzoxide", Fuel, **75**, (1996)
10. Sonmez O, Giray ES., "The influence of process parameters on desulfurization of two turkish lignite's by selective oxidation", Fuel Process Technol, **70**, (2001)
11. Ratanakandilok S, Ngamprasertsith S, Prasassarakich P, "Coal desulfurization with methanol/water and methanol/KOH". Fuel, **80**, (2001)
12. Mukherjee S, Borthakur PC, "Chemical demineralization/desulfurization of high sulfur coal using sodium hydroxide and acid solutions". Fuel, **80**: 2037-2040 (2001)
13. Ozdemir M, Bayrakceken S, Gurses A, Gulaboglu S, "Desulfurization of two turkish lignite's by chlorinolysis", Fuel Process Technol, **26**:15-23, (1990)
14. S.R. Palmer, E.J. Hippo, X.A. Dorai, "Selective oxidation pretreatment for the enhanced desulfurization of coal", Fuel, **74**:193-200 (1995)
15. Zhiling Li, Tonghua Sun, Jinping Jia, "An extremely rapid, convenient and mild coal desulfurization new process: Sodium borohydride reduction", Fuel Processing Technology, **91**:1162-1167(2010)
16. Samit Mukherjee, "Demineralization and Desulfurization of High-Sulfur Assam Coal with Alkali Treatment", Energy & Fuels, **17**: 559-564 (2003)
17. Samit Mukherjee, "Demineralization and Desulfurization of High-Sulfur Assam Coal with Alkali Treatment ", Energy Fuels, **17** (3): 559-564 (2003)