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CHEMICAL CLEANING OF COAL USING PEROXYACETIC ACID-A STUDY OF DESULFURIZATION, ASH REDUCTION AND EFFECT ON GROSS CALORIFIC VALUE IN MIANWALI COAL

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Abstract

Background: *Leaching of Mianwali coal was carried out by using peroxyacetic acid as leaching agent. The effect of peroxyacetic acid concentration at different particle size of coal was investigated. The peroxyacetic concentration was varied from 80ml, 100ml, 140ml and 200ml and particle size of coal from 60 mesh, 100 mesh, 150 mesh and 200 mesh. The effect of peroxyacetic acid onto the particle size was determined by washing the coal with water and HCl respectively. The findings of this investigation have shown that acetic acid concentration has direct relation with sulfur reduction (%) and ash reduction (%). Accordingly, maximum reduction in sulfur and ash was obtained at 100ml and 200ml concentrations of peroxyacetic acid respectively and 200 mesh particle size. The total reduction in ash and sulfur contents after leaching was found to be 62% and 78% respectively. The clean coal can be used in various energy recovery*

Objectives and scope of the study: *Though many oxidative reagents have been used by different researchers, the selection of peroxyacetic acid is highly capable because this reagent is an excellent and essential chemical in the establishments of various industries. It is used for bleaching process of pulp (Borah [5] and wood chips in presence of acid, to form volatile substances, in sugarcane industry [6], in the paper making process. Therefore, due to large utilizations of peroxyacetic acid in various industrial sector, and as an oxidizing reagent used by Palmer [7] to desulphurize coal, it is measured that it could be an excellent oxidizing reagent for the removal of sulfur and ash content present in Mianwali coal.*

The objective of this study is to reduce the amount of sulfur and ash contents present in Mianwali coal by chemical cleaning of coal. Coal contains several trace elements and metals which may be related as mineral matter or bonded with organic matter. During desulphurization process some metals could be leached out from coal particles which may also affect sulfur and ash removal process. The presence of metal ions in the *oxidative desulphurization of pyritic sulfur by hydrogen peroxide has been observed. The present investigation is an attempt to understand the possible pathways for the formation of oxidized sulfur species responsible for desulphurization. Moreover, the formation of silicates and aluminates of trace metals, present in the coal matrix which may be responsible for the addition of some extra ash content in the leached coal, have also been discussed.*

Significance of work: *Researches have been shown that Peroxyacetic Acid is a better oxidizing agent for the desulfurization of coal having high sulfur content than acetic acid and hydrogen peroxide. This is an upgraded technology in the field of chemical cleaning of coal for the improvement of coal technology because it is simple with low cost and easily available chemical, and therefore, has significant technological interest.*

INTRODUCTION

Many coals hold as much as 50% organic sulfur, which cannot be detached by physical coal cleaning methods Edelstein [1], Abdul [2]. Removal of the organic sulfur requires chemical desulfurization practices, many of which can also remove inorganic sulfur and ash-forming minerals. Recent research in this zone has expressed chemical desulfurization processes accomplished by reducing the sulfur content of high sulfur coal thus meeting New Source Performance Standard (NSPS) Nowak and Meyers [3].

Chemical reaction can break down and remove a portion of the coal along with the associated organic sulfur, while leaving inert ash forming minerals behind. When this happens, the sulfur content expressed as weight percent of the product will decrease because of increased dilution of sulfur the carbonaceous material with ash forming materials, but the actual quantity of sulfur present per unit energy content of the product might be the same as or even higher than in the original feed. To be sure that a process is truly selectively removing organic sulfur, it is necessary to perform a complete materials balance (including gaseous and dissolved product) to account for the dilution effect. At a minimum, the sulfur content of the desulfurized product must be reported as sulfur per unit heat content and not simply as sulfur per unit weight. If this is not done, sulfur removals reported on a mass basis are almost meaningless Meyers [4]

Literature Review

Palmer [7] studied the effect of desulfurization of two high sulfur Illinois Basin coals using selective oxidation with a mixture of hydrogen peroxide in acetic acid, which is known as peroxyacetic acid. The experimental parameters were coal type, particle size, method of coal preparation, reaction time and reaction temperature. In general, all inorganic sulfur and some of the organic sulfur could be removed from these coals using very mild conditions.

Stephen R [8] investigated the effect of desulfurization of pyrolysis on oxidized and unoxidized Indiana coals. Both coals were pretreated with peroxyacetic acid as the pretreatment process and then treated with various hydroxide and carbonate bases, such as water, methanol, ethanol as the solvent. The reaction variables were used temperature, time, and pressure. Sulfur removal was 95% were obtained in some cases.

Jorjani [9] worked out the effect of desulfurization by combination of microwave irradiation and peroxyacetic acid washing on Turkish Tabas coal. The effect of time, power, and temperature and particle size on reduction of sulfur was investigated. The 86.6% sulfur was removed in this study.

Doskočil [10] studied the effect of oxidation with H_2O_2 for Mir mine lignite coal. The experimental parameters were time 1-4 h and temperature 30- 50 °C. Thus, Malonic acid and succinic acid were produced.

Levent [11] carried out investigation on sulfur removal by H_2O_2/H_2SO_4 solutions for lignite from Artvin/Yusufeii, Turkey. He used different parameters including reaction temperature 10-60 °C, solid to liquid ratio 0.01-0.08 g/ml, reaction time 15-120 min, stirring speed 200-300 rpm and particle size 710-120 microns. According to analysis it was seen that all parameters were effective in removal of pyritic and total sulfur.

Liu [12] reported the effect of desulfurization leaching by alkaline solution (NaOH) combined with atmospheric oxidation at low temperature on coal. The result statistics indicate that reduction in organic sulfur, sulfide, pyritic sulfur was 66%, 44% and 15% respectively under the conditions 0.25M NaOH, 90 °C temperature, and 0.136 m3/h air flow rate. When this treated coal was further treated with acidic solution of HCl at pH 1 for 60 mints the reduction increased to 73% for organic sulfur, 83% for sulfide sulfur. Thermodynamic analysis of treated coal shows that unlike other oxidizing techniques did not affect the pyrolysis and burning properties of coal.

Saikia [13] studied the effect of desulfurization leaching by ionic liquids on sub-bituminous coal of India. Different liquids were used for the desulfurization in presence of $HCOOH/H_2O_2$ and V_2O_5. The final data represents that maximum reduction in total sulfur occurred around 50.26% along with ash reduction of 70%. The ionic liquids were recovered and reused for further processing.

Mukherjee and Borthakur [14] conducted research on effect of potassium hydroxide leaching on demineralization and desulfurization of sub bituminous coal of Makkun coal fields Asam, at 90 and 150 °C along with mild acid oxidation of previously treated coal. After leaching with potassium hydroxide and 10% hydrochloric acid, the demineralization was increased to 68% and desulfurization to 53% respectively. The overall treatment indicates that it removed all pyritic and sulfide sulfur and 37% of organic sulfur.

Bolat [15] studied the effect of demineralization by leaching with different acids (HCl, HF, HNO_3 and H_2SO_4) alone and 0.5 N aqueous in combination with one or two of the acids on Amasra bituminous coal from Turkey. Demineralization with NaOH followed by leaching with HCl proved useful for removal of sulfur and the maximum of sulfur removed was ˜ 46.78%.

Rodríguez [16] investigated the effect of demineralization of coal by leaching with nitric acid on Mequinenza coal. This process was specially arranged to target on organic sulfur which reduced by being soluble at high temperature. This process also proved effective for inorganic sulfur as it was attacked very fast. Solubility of organic sulfur was far slower than attack on inorganic sulfur. Overall removal of organic and inorganic sulfur was achieved to great extent.

Wang [17] investigated the effect of demineralization of coal by leaching with calcium hydroxide and washing with dilute HCl. They used light reflecting microscope and scanning electron microscope along with energy dispersive X-ray analysis. All analytical technique results showed that with the increment in the calcium hydroxide concentration the amount of mineral matter reduced. Extensive leaching of coal led to the about 90% reduction of inorganic mineral matter.

Ratanakandilok [18] examined the effect on desulfurized of Mea Meh Coal from Thailand by leaching with methanol/water and methanol/KOH. The investigation was carried out on methanol concentration, coal particles, reaction temperature and reaction time by observing their impact on sulfur and ash reduction. The removal of undesired contents was observed as follows: pyritic sulfur 36-74%, organic sulfur 20-42% and total sulfur 33-62%. Addition of methanol/KOH promoted the efficiency of the process by increasing desulfurization of organic and inorganic sulfur.

Shen [19] studied the desulfurization of high sulfur coal prior to use by dry ash chlorination under various conditions. They used different condition including particle size, chlorination temperature and many others. Two conditions, particle size and chlorination temperature proved greater influence with optimum statistics 48-75 microns and 350 °C respectively. The reduction was examined as in total sulfur 67.7%, in pyritic sulfur 93.0%, in sulfide sulfur 65.6% and in organic sulfur 61.6%.

Wu and Steel [20] carried out investigation on effect of demineralization by two stage leaching process on a bituminous coal from UK. The first stage was undertaken at 65 °C with HF which removed sulfur by 74%. The second stage was carried out with ferric ions which decreased the ash content to 990 ppm by removing the pyrites and fluorides formed during the HF leaching.

Wang and Tomita [21] studied the effect of demineralization and desulfurization by leaching with calcium hydroxide at 300 °C and then washing with dilute HCl on Australian coals. Out of those four-coal reductions in three coal occurred from 8.8-15.4 % to 1 % and in fourth coal took place from 14.9% to 2.8%.

Pietrzak and Wachowska [22] studied the effect of desulfurization by leaching with nitric oxides on Mequinenza and Labin coals. It was found that nitric acid efficiently desulfurized the coal by oxidizing pyritic sulfur. Nitric acid enhanced oxidized organic sulfur species content on the coal surface.

Karaca and Ceylan [23] studied the effect of desulfurization and demineralization by leaching with aqueous hydrogen peroxide or 0.1 N acid of sulfur on two Turkish coals. The effect was observed under various conditions including concentration, time and temperature with their optimum set at 15 wt. % 60 min and 30°C respectively. The reduction in ash, pyritic sulfur and total sulfur was noticed as follows: 70% ash reduction, 95% pyritic sulfur reduction and 58% of total sulfur reduction. Reduction in organic sulfur [21] was relatively low. Excessive amount of hydrogen peroxide did not improve the desulfurization of coal.

Material and Methodology

Collection of samples

A representative 20kg coal sample was collected from stockpiles present outside the Mianwali coal mine. In collecting the bulk samples ASTM standard D-2234 was followed.

Preparation of Represented Samples

The Bulk Sample collected from stockpile was thoroughly mixed and then crushed by using hammer mill up to size of 1-2 inches. The material was shoveled to the apex. These apexes are on the cone and allowed to flow down carefully. In this case mixing is better achieved. After this, the top was flattened out and was divided into four equal quarters. Opposite quarters were removed and remaining two mixed again. The mixed material was again piled and above procedure was repeated until 5 kg is remained. This 5-kg coal was brought to end runner mill for grinding.

Sieving of Sample

The ground sample was sieved by using sieve shaker. Four different sieves including 60#, 100#, 150#, 200# and pan were fixed in the sieve shaker and covered with lid as shown in figure 1. Time was set for 10 minutes, as machine was automatically stopped.

Figure 1: Sieve Shaker

Proximate analysis of Representative Sample

Proximate analysis of representative sample of coal was made by analyzing its constituent's volatile matter, ash, moisture, and fixed carbon. Two further elements were included in proximate analysis which were total sulfur and Gross Calorific value. These two elements were also analyzed by using following methods.

Determination of Total Moisture

About 1 g of coal sample was taken in pre-tarred and pre-weighed petri dish and put in hot Air Oven as shown in figure 2 for 1 hour at 100-110 °C temperature. Then loss in weight of coal sample was measured to determine the moisture content according to ASTM D-3173 standard method.

Figure 2: Moisture Oven

% Total moisture of coal sample was measured by using formula:

$$\% \text{ Total Moisture} = \frac{W_1 - W_2}{W_3} \times 100$$

Where,
W1 = weight of sample and petri dish before heating
W2 = weight of sample and petri dish after heating
W3 = weight of sample

Determination of Ash content

Approximately 1 g of coal sample was taken in pre-tarred and pre-weighed crucible. It was put into muffle furnace as shown in figure 3 specially designed for ash analysis for 3 hours at 750±50 °C. After three hours, the loss in weight measured to determine the ash content according to ASTM D-3174 standard method.

Figure 3: Muffle Furnace

% Ash in coal was measured by using Ash formula

$$\% \text{ ash} = \frac{W_1 - W_2}{W_3} \times 100$$

Where,
W1 = weight of crucible and sample after heating
W2 = weight of empty crucible
W3 = weight of sample

Determination of Volatile Matter

The 1 g of coal sample was taken in pre-weighed and pre-tarred crucible and covered with lid. The crucible was put into muffle furnace as shown in figure for 4 minutes at 950±50 °C according to ASTM D-3175.

Figure 4: Muffle Furnace for VM

The percentage of volatile matter was measured as loss in weight according to equations given below:

% Volatile Matter in coal was measured by formula

$$\% \text{ Volatile Matter} = \frac{W_1 - W_2}{W_3} \times 100$$

Where
W1 = weight of crucible, lid and sample before heating
W2 = weight of crucible, lid and sample after heating
W3 = weight of sample

Determination of Fixed Carbon

After determination of volatile matter, ash and moisture fixed carbon was measured according to the following formula.

$$\% \text{ Fixed Carbon} = 100 - (\text{Volatile Matter} + \text{Ash} + \text{Moisture}) \%$$

Determination of Total Sulfur

Around 1 g of coal was mixed with Eschka mixture (mixture of magnesium oxide and sodium carbonate) and taken in crucible. This mixture was covered with 1 g of Eschka Mixture and put in muffle furnace as shown in figure at 800±50 °C until burn to white ashes. This mixture 5 was poured into hot 100 ml water and filtered. The volume of filtrate was made up to 250 ml and few drops of methyl orange and 2 ml of concentrated hydrochloric acid were added. Then 10 ml of 1 % sodium hydroxide solution was added and mixed it well. The solution was put on hot plate and let it heat. During heating 10 ml of 1% barium chloride solution was added which cause the formation of precipitates. Let the solution was stand over the night and next day it was filtered. Precipitate was washed and along with filter paper was put into pre-tarred and pre-weighed crucible. The filter paper was burnt in muffle furnace at 900±50 °C and residue left in the crucible was measured to determine the total sulfur.

Figure 5: Muffle Furnace

The % of total sulfur was measured by using formula:

$$\%\,\text{Total Sulfur} = \frac{W_1}{W_2} \times 13.73 \times 100$$

Where,
W1 = weight of residue
W2 = weight of sample

Determination of Gross Calorific Value

Bucket of bomb calorimeter was filled with 2 kg of water. Fuse wires were fitted into the holes of bomb sleeves. Pellets were weighed and the crucible was fitted into the sample holder of bomb. Bomb assembly was closed. Oxygen was filled to 25 bar pressure. Bucket was put into the jacket and then bomb assembly into bucket. Lid was closed and thermometer and stirrer was placed for 5 mints. Red button was pressed 3-4 second. First value of initial temperature measured and then the final value where the maximum temperature reached per ASTM D-5865.

GCV can be determined by using formula

$$\text{GCV} = M_2 + W \times C_p \text{of water} \times \frac{T}{M_2}$$

Where,
T = initial temperature – final temperature
Cp of water = 1 (Cal/g)
Water equivalent of calorimeter = 321.4 grams

Leaching experiments

Experiments were carried out in a three-neck flask containing magnetic stirrer and hot plate. In each experimental run, 20g of coal sample was taken into three necked round bottom flasks and added various concentration of acetic acid (80mL, 100mL, 140mL, and 200mL) and fixed concentration of hydrogen peroxide 30% (V/V). Reflux condenser was fitted at the top of the flask neck. Thermometer was fitted to maintain the temperature at 70 °C for reaction time 30 min. The flask contents were filtered and washed with hot distilled water and then HCl. The filtered residue was dried at 110 °C and subjected to analysis for determining the total sulfur and ash contents. The tests were carried out according to the following diagram.

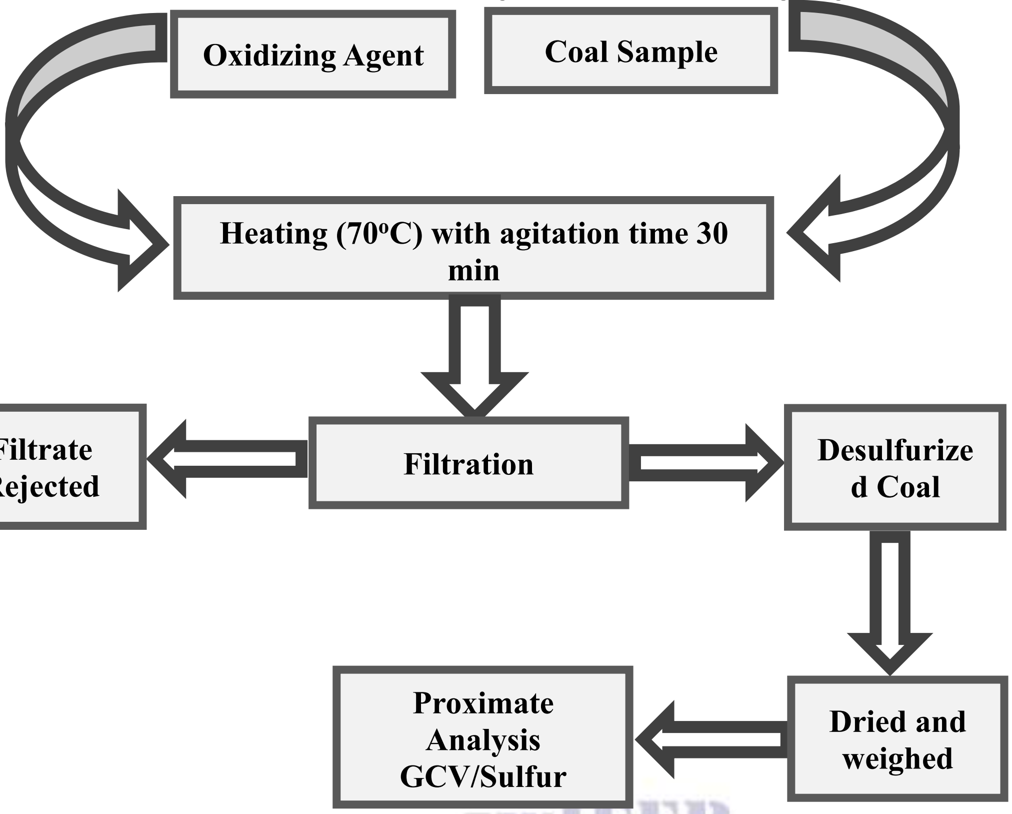

Figure 6: Schematic diagram showing desulphurization of coal

Results and Discussions

Proximate analysis of sample

A high sulfur coal obtained from Mianwali (Punjab Pakistan) was used in this study. The coal was ground to size 60 mesh, and stored in air-tight plastic bag. Table shows the proximate and ultimate analysis of the coal sample.

Table 1: Summary of detailed proximate analysis of the bulk sample

Proximate and Ultimate Analysis		
Serial No	Component	Value in wt. %
1	Total Moisture	6
2	Volatile Matter	25
3	Fixed Carbon	51

4	Ash Content	18
5	Sulfur Content	5
6	Gross Calorific Value (GCV)	5900 kcal/kg

Effect of acetic acid concentration on ash reduction

Figure 7 and Table 2 show the effect of acetic acid concentration on ash reduction of Mianwali coal using hot water washing and HCl washing options at different particle sizes. As shown in Figure 7a, the contents of ash were actually increased significantly by leaching with acetic acid at lower particle size of +60 mesh and +100 mesh with hot water washing. However, the ash reduction was observed in case of finer particles sizes i.e. 150 mesh and 200 mesh. The maximum of ash reduction of 53.0% was observed for 150 mesh particles at 200 ml concentration of acetic acid. Moreover, the lower concentration of acetic acid was found to be useful, since it gave higher ash reduction in each case of particle size. It was observed that the ash content of coal was actually increased for low particle size and ash contents were actually double in the leached coal compared to its original coal content. This might be due to the dissolution of organic and inorganic contents in the form silicates and aluminates. As shown in Equations 1 & 2, the peroxyacetic acid produces strong electrophile, hydroxyl cation (OH+) that has strong electrophilic properties [7]. It is very much expected that the ash contains oxides such as SiO_2, Al_2O_3, Fe_2O_3 and oxides of trace elements along with sulfates and pyrites converting these to soluble aluminates, silicates and ferrates [14]. Many of these products are water sparingly soluble in water and or soluble in organic solvents. Therefore, the rise in ash contents of the leached coal can be expected during leaching with peroxyacetic acid. Furthermore, the acidic or basic washing may require during the cleaning process to remove insoluble for of silicates or aluminates.

$$CH_3COOH + H_2O_2 \Leftrightarrow CH_3COOOH + H_2O \quad (1)$$

$$CH_3COOOH + H^+ \Leftrightarrow CH_3COOH + OH^+ \quad (2)$$

Figure 7b shows the effect of HCl washing on ash reduction in acetic acid treated Mianwali coal. The washing of HCl was found to be very effective in reducing the ash contents. The maximum of ~60% ash was reduced using acetic acid and HCl washing option. The effect of acetic acid concentration on ash reduction was found to be similar i.e. the lower concentration of acetic acid was more useful in reducing the ash contents from coal compared to concentrated acetic acid concentration. The maximum removal of ash for 60 mesh particle size was 26.7%, for 100 mesh particle size was 37.0%, for 150 mesh particle size was 53.0% and for 200 mesh particle size was 62%. The increased removal of ash in case of HCl washing is attributed to the carbonates and sheet silicates that are insoluble or sparingly soluble in water. Acidic washing is useful in removing un-oxidized components of mineral matter such as pyrites [15].

Table 2: Effect of acetic acid concentration at various particle sizes on ash reduction of the coal (water wash)

Particle Size: mesh # (μm)	Acetic acid concentration (mL)	Water Washed		HCl Washed	
		Ash in Treated Coal (Wt. %)	Ash Removal (%)	Ash in Treated Coal (Wt. %)	Ash Removal (%)
60 (250)	80	28.84	-60.22	14.20	21.1
	100	26.46	-47.00	13.86	23.0

	140	24.03	-33.50	13.52	24.9
	200	22.68	-26.00	13.2	26.7
100 (150)	80	26	-44.44	12.96	28.0
	100	24	-33.33	12.42	31.0
	140	23	-23.00	11.88	34.0
	200	21.06	-17.00	11.34	37.0
150 (105)	80	18.26	-1.44	10.26	43.0
	100	16.38	9.00	9.36	48.0
	140	14.94	17.00	8.82	51.0
	200	13.86	23.00	8.46	53.0
200 (74)	80	13.14	27.0	8.64	52
	100	11.88	34.0	7.92	56.0
	140	11.16	38.0	7.38	59.0
	200	10.44	42.0	6.84	62

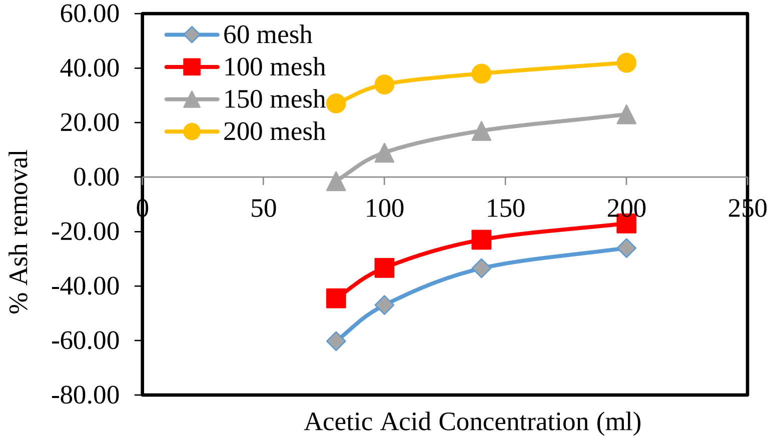

Figure 7(a): Showing % Ash reduction against Coal to Acid Ratio at various particle sizes (water wash)

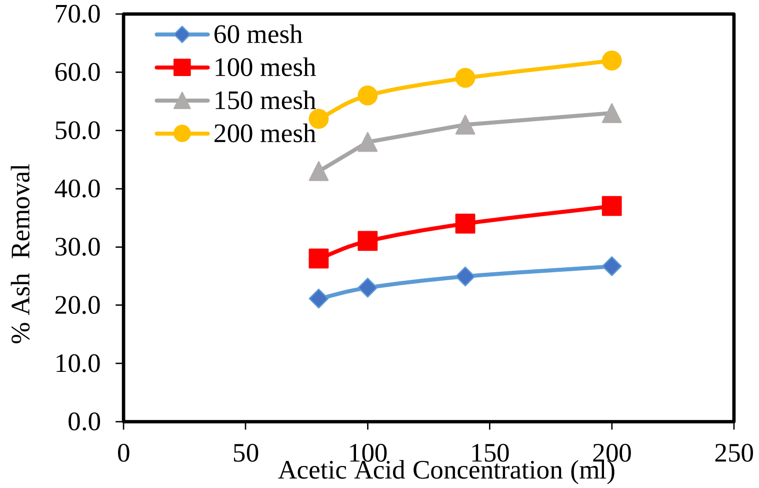

Figure 7(b): Showing % Ash reduction against Coal to Acid Ratio at various particle sizes (HCl wash)

Effect of acetic acid concentration on sulfur reduction

Figure 8 and Table 3 show the effect of acetic acid volume on sulfur reduction of Mianwali coal using hot water washing and HCl washing option at different particle sizes. As shown in Figure 8a, the contents of sulfur were actually increased significantly by leaching with peroxyacetic acid at lower particle size of +60 mesh and +100 mesh. However, the sulfur reduction was observed in case of finer particle sizes i.e. 150 mesh and 200 mesh. The maximum of sulfur reduction of 78% was observed for 200 mesh particles at 100 ml concentration of acetic acid. Moreover, the lower concentration of acetic acid was found to be useful, since it gives higher sulfur reduction in each case of particle size. According to Gilbert [24], oxidized sulfur compounds when reacted with water, desulfurization happens by hydrolysis of sulphonic acids. Such a behavior in the oxidized coal effected the organic sulfur content, usually decreasing the organic sulfur content, usually decreasing the organic sulfur level [25]. Equation 3 shows that if pyrite is present, it would strongly affect the rate of oxidation process [26]. The particle size was found to decrease due to increase in external surface area per unit mass of coal the rate of sulfur removal increased with decreasing of particle sizes from 250μm to 105μm.

$$\text{Coal - Sulfur} + \text{Oxidant} \rightarrow \text{Coal} + \text{S.Oxidant} = \text{Sulfur Removal}$$

(3)The desulphurization was lower in case of particle size 60 mesh i.e. 250μm because sometimes in the center of bulk coal organics, the oxidant may oxidize the other species such as carbon etc. instead of oxidizing the sulfur which may lead to limited oxidation of sulfur. The extent of desulphurization for particle size 74μm decreases because the oxidized sulfur species are strongly solvated in acetic acid hence they would be bulky and oxidant may not be completely accessible towards oxidation despite having high collision [27]. Alternative way of low level of desulphurization is the holding of soluble sulphate in the system because sulphate acts as a bidentate, monodenate and chelating ligand [28]. Chemical desulphurization procedures involve the conversion of organic sulfur to sulphate [27] which may form sulphuric acid. Also, the oxidation reaction of coal and hydrogen peroxide makes phenyl sulphoxide, which makes sulphoxidonium ion with peroxyacetic acid in the presence of sulphuric acid. It suggests that as soon as sulphate arises in the system, it bans further oxidation of sulphoxide. Figure b shows the effect of HCL washing on a sulfur reduction in peroxyacetic acid treated Mianwali coal. The washing of HCl was found to be very effective in reducing the sulfur contents. The maximum of 78% sulfur was reduced using acetic acid and HCl washing option. The effect of acetic acid concentration on sulfur reduction was found to be comparable i.e. the lower concentration of acetic acid was more useful in reducing the sulfur content from coal compared to higher concentration of acetic acid. The maximum removal of sulfur for 60 mesh particle size was 52%, for 100 mesh particle size was 64%, for 150 mesh particle size was 73% and for 200 mesh particle size was 78%. Borah and Baruah [29] have shown that smaller molecules are much more prone to attack by the leaching solution for the rapture of C-S as well as S-S bonds. Also, the low temperature oxidation form S=O and -SO_2 [30]. In this way, the aliphatic sulfur as well as aromatic disulphide compounds can also be leached out. Due to increase in external surface area per unit mass of coal the rate of sulfur removal increased with decreasing of particle sizes from 250μm to 74μm. So, these results show that grinding to small particle size is necessary to enhancing the level of desulfurization. Furthermore, researches have shown that he effectiveness of peroxyacetic acids as oxidants is the result of strong polarization due to their dissymmetry about the O-O bond so that a peroxyacetic acid separates more readily than any other parallel oxidants.

Particle Size: mesh # (μm)	Acid Concentration (mL)	Water washed		HCl washed	
		Sulfur in treated coal (Wt. %)	Sulfur Removals (%)	Sulfur in treated Coal (Wt. %)	Sulfur Removal (%)
60 (250)	80	4.3	14.8	2.51	49.8
	100	4.2	17	2.38	52.4
	140	4.4	12	2.5	50

	200	4.7	6	2.7	46
100 (150)	80	3.9	23	1.91	61.8
	100	3.7	25.5	1.8	64
	140	3.8	23.1	2	60
	200	4.2	16.8	2.17	56.6
150 (105)	80	3.5	31	1.4	72
	100	3.4	32	1.31	73.8
	140	3.5	30.5	1.42	71.6
	200	3.7	27	1.71	65.8
200 (74)	80	3.2	35.5	1.28	74.4
	100	3.1	38.5	1.1	78
	140	3.2	36.2	1.2	76
	200	3.2	35.6	1.52	69.6

Table 3: Effect of Coal to Acid Ratio at Various Particle Sizes on Desulfurization of the Coal

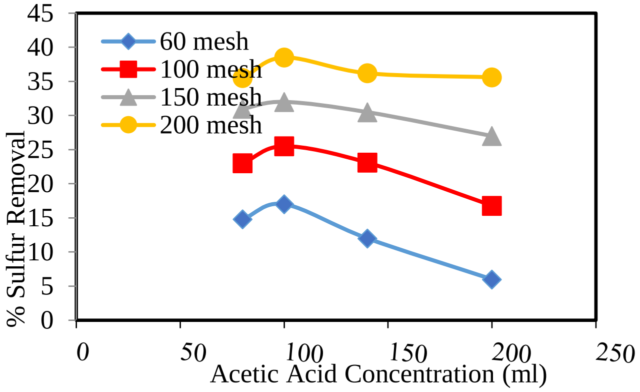

Figure 8(a): Showing % sulfur reduction against Coal to Acid Ratio at various particle sizes (water wash)

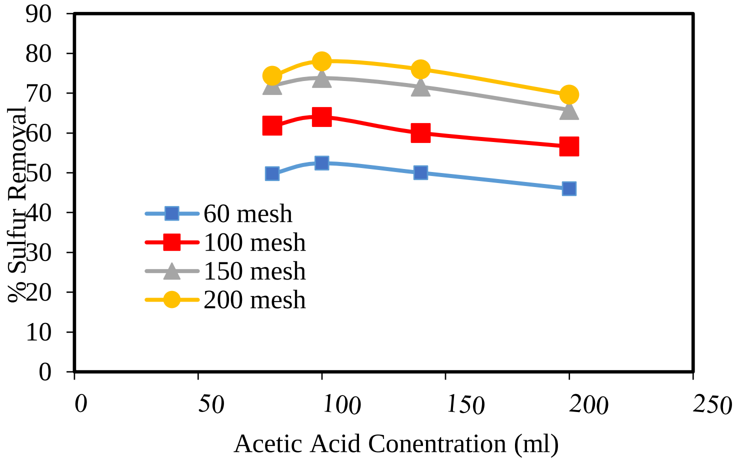

Figure 8(b): Showing % sulfur reduction against Coal to Acid Ratio at various particle sizes (HCl wash)

Effect of Acetic Acid Volume on Gross Calorific Values

Figure 9a and Table 4 shows the effect of acetic concentration on gross calorific value of the Mianwali coal using hot water washing and HCl washing option at different particle sizes. As shown in Figure 9a, the gross calorific values were decreased seriously by leaching with peroxyacetic acid at lower particle sizes of +60 mesh and +100 mesh. However, the increase in GCV was noticed in case of finer particle sizes i.e. 150 mesh and 200 mesh. The maximum increase in GCV of 223 kcal/kg was observed for 200 mesh particles at 200 ml concentration of acetic acid. Moreover, the smaller particle sizes were found to be useful, as they give higher heating values. The trend of decrease in gross calorific values was because of decrease in mineral matter or ash contents present in peroxyacetic acid leached Mianwali coal. The ash contents were higher in 60 mesh and 100 mesh particle sizes and hence the gross calorific values were lower for those particle sizes. As the particle size shifts from 150 mesh to 200 mesh, the gross calorific values enhanced in a similar manner.

Figure 9b shows the effect of HCl washing on GCV in peroxyacetic acid treated Mianwali coal. The washing of HCl was found to be very effective in increasing the gross calorific values. The maximum of 1442 kcal/kg of gross calorific values were increased using peroxyacetic acid and water washing option. The effect of acetic acid concentration on GCV enlargement was found to be similar i.e. the higher concentration of acetic acid was more useful in increasing the gross calorific values from coal compared to lower concentration of acetic acid. The maximum increase in gross calorific value for 60 mesh particle size was 429 kcal/kg, for 100 mesh particle size was 621 kcal/kg, for 150 mesh particle size was 756 kcal/kg, and for 200 mesh particle size was 845 kcal/kg. The increase in gross calorific values is due to the lower ash content in leached coal because of using HCl washing option, hence there is no extra addition of mineral matter content which would be responsible for extra addition of ash content in the peroxyacetic acid leached Mianwali coal and therefore, the gross calorific values were higher than the values of untreated fresh Mianwali coal [31].

Table 4: Effect of Acetic Acid Volume at Various Particle Sizes on the GCV of the Coal

Particle Size: mesh # (µm)	Acetic acid concentration (mL)	Water washed		HCl washed	
		GCV in treated Coal kcal/kg	Increase in GCV kcal/kg	GCV in treated Coal kcal/kg	Increase in GCV kcal/kg
60 (250)	80	4571	-1442	6415	221
	100	4843	-1268	6376	243
	140	4923	-1087	6551	345
	200	4803	-975	6598	429
100 (150)	80	4360	-1165	6744	351
	100	4768	-921	6978	425
	140	5034	-756	7035	524
	200	4700	-576	6999	621
150 (105)	80	5323	-462	5929	507
	100	5656	-244	6127	589
	140	5848	-52	6186	658
	200	5997	40	6690	756
200 (74)	80	6170	-113	5954	587
	100	6281	20	6159	667
	140	5940	112	5965	764

	200	6213	223	6342	845

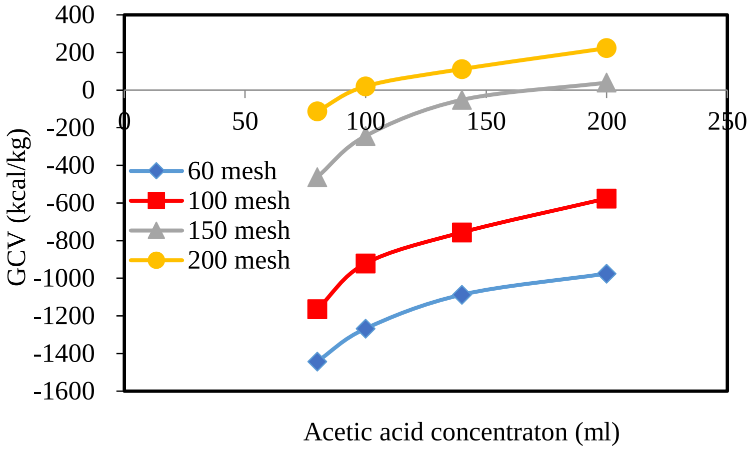

Figure 9(a): Showing increase in GCV against Coal to Acid Ratio at various particle sizes (water wash)

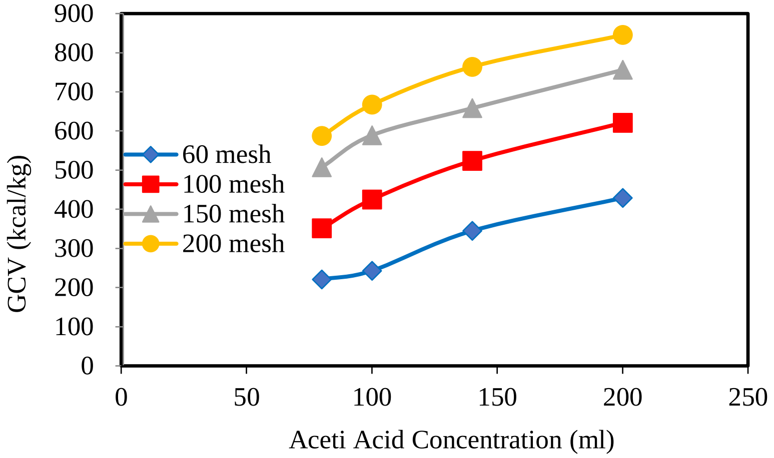

Figure 9(b): Showing increase in GCV against Coal to Acid Ratio at various particle sizes (HCl wash)

Conclusion

Chemical leaching was applied on coal sample of Mianwali to upgrade it to an extent so that it could be suitable as a fuel for cement industry and power plants. Per proximate analysis the coal consisted of 18% Ash, 5% Sulfur and 5900 kcal/kg of gross calorific value. Apparently, it was a low-grade coal and needed cleaning to reduce the sulfur and ash content and to increase gross calorific value. For this study, two oxidizing agents namely CH_3COOH and H_2O_2 as CH_3COOOH were tested under identical experimental conditions for desulfurization and demineralization of Mianwali coal. Based on the optimum experimental conditions the following conclusions have been drawn. CH_3COOOH being very strong oxidizing agent, has reduced 78% sulfur in the bulk coal sample. An ash reduction of 62% has been observed after leaching and washing. There is an increase in the gross calorific value of up to 845 to 1442 kcal/kg. HCl washing option is sufficiently effective for desulfurization and demineralization of Mianwali coal. The particle size reduction had a positive effect on efficiency of leaching process. Pakistani coal with high sulfur and ash contents makes them unsuitable to use as a fuel, producing considerable amount of ash and generating excessive amount of SO_2 that is environmentally harmful. Coal cleaned through CH_3COOOH leaching contains sulfur around 1.1% and ash about 7% that is suitable for cement industry and power generation. The cleaned coal can be used directly or by blending with various high-grade coals in cement industries and power plants.

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Reference

[1] S. Edelstein. Adsorption of sulphur dioxide and reduction of sulphate on alumina and alkali-alumina at high temperatures. California Institute of Technology1987.
[2] A. Abdul, S.K. Srivastava, R. Haque. Chemical desulphurization of high sulphur coals. Fuel. 71 (1992) 835-9.
[3] R. Nowak, R. Meyers. Molten-caustic leaching (MCL) process integration. Coal Science & Technology. (1993) 305-.
[4] R.A. Meyers. Interpersonal deception theory. Communication theory. 6 (1996) 203-42.
[5] D. Borah, M.K. Baruah, I. Haque. Oxidation of high sulphur coal. 9 3. Desulphurisation of organic sulphur by peroxyacetic acid (produced in situ) in presence of metal ions. Fuel processing technology. 86 (2005) 959-76.
[6] L.C. Teixeira, J.C. Linden, H.A. Schroeder. Optimizing peracetic acid pretreatment conditions for improved simultaneous saccharification and co-fermentation (SSCF) of sugar cane bagasse to ethanol fuel. Renewable Energy. 16 (1999) 1070-3.
[7] S.R. Palmer, E.J. Hippo, X.A. Dorai. Chemical coal cleaning using selective oxidation. Fuel. 73 (1994) 161-9.
[8] P. Stephen R, H. Edwin J, D. Xavier A. Selective oxidation pretreatments for the enhanced desulfurization of coal. Fuel. 74 (1995) 193-200.
[9] E. Jorjani, B. Rezai, M. Vossoughi, M. Osanloo. Desulfurization of Tabas coal with microwave irradiation/peroxyacetic acid washing at 25, 55 and 85 C. Fuel. 83 (2004) 943-9.
[10] L. Doskočil, L. Grasset, D. Válková, M. Pekař. Hydrogen peroxide oxidation of humic acids and lignite. Fuel. 134 (2014) 406-13.
[11] M. Levent, Ö. Kaya, M. Kocakerim, V. Yiğit, Ö. Küçük. Optimization of desulphurization of Artvin–Yusufeli lignite with acidic hydrogen peroxide solutions. Fuel. 86 (2007) 983-92.
[12] K. Liu, J. Yang, J. Jia, Y. Wang. Desulphurization of coal via low temperature atmospheric alkaline oxidation. Chemosphere. 71 (2008) 183-8.
[13] B.K. Saikia, K. Khound, B.P. Baruah. Extractive de-sulfurization and de-ashing of high sulfur coals by oxidation with ionic liquids. Energy Conversion and Management. 81 (2014) 298-305.
[14] S. Mukherjee, P.C. Borthakur. Effect of leaching high sulphur subbituminous coal by potassium hydroxide and acid on removal of mineral matter and sulphur☆. Fuel. 82 (2003) 783-8.
[15] E. Bolat, S. Sağlam, S. Pişkin. Chemical demineralization of a Turkish high ash bituminous coal. Fuel Processing Technology. 57 (1998) 93-9.
[16] R.Á. Rodríguez, C.C. Jul, D. Gómez-Limón. Evolution of the organic sulfur and other components during nitric acid leaching of Mequinenza coal. Fuel. 76 (1997) 1445-50.
[17] J. Wang, A. Tomita, G.H. Taylor, J.D.F. Gerald. Microscopic observation of coal demineralization by Ca (OH)2 leaching. Fuel. 76 (1997) 369-74.
[18] S. Ratanakandilok, S. Ngamprasertsith, P. Prasassarakich. Coal desulfurization with methanol/water and methanol/KOH. Fuel. 80 (2001) 1937-42.
[19] S. Shen, J. He, M. Pan, Z. Zhou, C. Feng, G. Liang. Effective removal of sulfur from high-sulfur coal prior to use by dry chlorination at low temperature. Journal of hazardous materials. 217 (2012) 116-22.
[20] Z. Wu, K.M. Steel. Demineralization of a UK bituminous coal using HF and ferric ions. Fuel. 86 (2007) 2194-200.
[21] J. Wang, A. Tomita. Removal of mineral matter from some Australian coals by Ca (OH) 2/HCl leaching. Fuel. 77 (1998) 1747-53.
[22] R. Pietrzak, H. Wachowska. The influence of oxidation with HNO 3 on the surface composition of high-sulphur coals: XPS study. Fuel Processing Technology. 87 (2006) 1021-9.

[23] H. Karaca, K. Ceylan. Chemical cleaning of Turkish lignites by leaching with aqueous hydrogen peroxide. Fuel Processing Technology. 50 (1997) 19-33.

[24] E.E. Gilbert. Sulfonation and related reactions. Interscience Publishers1965.

[25] D.J. Boron, S.R. Taylor. Mild oxidations of coal: 1. Hydrogen peroxide oxidation. Fuel. 64 (1985) 209-11.

[26] C.R. Ward. Isolation of mineral matter from Australian bituminous coals using hydrogen peroxide. Fuel. 53 (1974) 220-1.

[27] H.H. Szmant, G.A. Brost. The Cryoscopic Behavior of Organic Compounds in Sulfuric Acid. II. Sulfides, Sulfoxides and Sulfones. Evidence for the Existence of New Sulfur Ions. Journal of the American Chemical Society. 73 (1951) 4175-7.

[28] N.N. Greenwood, A. Earnshaw. Chemistry of the Elements. (1984).

[29] D. Borah, M. Baruah. Electron transfer process. Part 2. Desulphurization of organic sulphur from feed and mercury-treated coals oxidized in air at 50, 100 and 150° C. Fuel. 79 (2000) 1785-96.

[30] D. Borah, M. Baruah, I. Haque. Oxidation of high sulphur coal. Part 1. Desulphurisation and evidence of the formation of oxidised organic sulphur species. Fuel. 80 (2001) 501-7.

[31] A. Mustafa, T. Ahmad, J. Akhtar, K. Shahzad, N. Sheikh, S. Munir. Agglomeration of Makarwal coal using soybean oil as agglomerant. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects. 38 (2016) 3733-9.