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Research Article

Desulfurization and Parametric Study of Bituminous Coal via Froth Flotation Technique

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ABSTRACT

Mineral components and pyrite sulfur contents, which are present in varying amounts in bituminous coal, are the major concerns in utilization of coal as in place of alternative fuel. The effect of parameters like pH, air flow rate, composition of feed and separation time with the aid of frother used as pine oil on desulfurization and de-ashing was investigated. At pH =1, very little separation efficiency almost 26% of sulfur removal, and 16% of ash removal were recorded, then with the increase of pH value with respect to time, its value increases reaches at a optimum point of pH=7,where sulfur removal with context to separation becomes maximum almost 54% and ash removal becomes 39 %. Then both values decrease with the further increase in the pH value ranging from 7 to 14. The trend of separation time indicates that both desulfurization and deashing increases with the increase in time. The results showed that with the increase in separation time, Sulfur recovery also increases. The sulfur removal was optimum at the separation time= 55 min. There is also increase in ash removal with the increase in separation time and it reaches to optimum level at separation time= 55min. In third stage, effect of air velocity on the separation efficiency of the pyrite sulfur was studied by keeping the pH, separation time and composition of the feed constant. At pH=07 & Separation time=40 mins, Optimum results in terms of sulfur recovery was achieved for air flow rate of 90 square cubic feet of height of column. Similarly, the ash removal was also increased with the increase in air flow rate and becomes optimum at 90scfh. All parameters of these experiments were performed under the presence of wetting agent (Polyvinyl Alcohol), and Pine oil act as a frothing agent. Never organic sulfur could be completely removed by froth flotation. Hence after playing with all three parameters the total sulfur, ash and volatile matter contents was reduced by 57 %, 43% and 45.2% respectively.

Key words: - Frothers, Wetting Agent, Ultimate & Proximate Analysis.

INTRODUCTION

Coal is carbonaceous solid material formed by the result of decay of vegetation in the biological sense. It has different amounts of Sulfur, Nitrogen, Hydrogen, Carbon and Oxygen as these occurs as traces contents along with radioactive elements too. The physical properties of coal vary as the characteristic of the rank, based on carbon content. Coal is located on very large landmasses of earth. Whenever in the past coal is burned to produce heat, the results come in the production of sulfur and carbon dioxide as pollutants. The pollutants are sulfuric acid, which react with water and converts into acid rain. On the other hand, coal is the important source of renewable energy for hundreds of years. The revolution of industry in the 10th century and the launch of electricity in the 20th century corporate it to a vital fuel. Till 1960's, coal is considered to be most important source of power generation. Although, it was overtaken by oil in the late 60's, this is projected that coal will dominate all other fossil fuels as important source of energy by the first half of this century.

The physicochemical properties of coal depend upon location, shape and colour of coal. Moreover, the rank of coal indicates different carbon contents, which exhibits different kinds of coal found in nature. The highest rank of coal is Anthracite and it is a source of heat energy for commercial and residential purposes. It is hard coal and it contains containing high percentage of fixed carbon and a low percentage of volatile elements. The calorific value of anthracite ranges from 22 to 28 million Btu/ ton. Bituminous coal is usually black, sometimes dark brown, used as fuel for the production of electricity and it is also used in metallurgical processes. The heat content of bituminous coal ranges from 21 to 30 million Btu/ ton. Major types of coal whose properties are between lignite to those of bituminous coal called Sub - bituminous coal and these are also used as fuel for the generation of power. The calorific value of sub-bituminous coal ranges from 17 to 23.5 million Btu per ton. Lignite is the lowest rank of coal and it is also referred as brown coal that is used exclusively as fuel for the production of electricity. The calorific value of lignite ranges from 9 to 17 million Btu/ ton.[1, 2].Several methods such as thermal treatment, electrochemical technology,carbonization, extraction/leaching, microwave energy technology, ox desulfurization via oxidation, microbialdesulfurization and froth flotation are available in literature.Thermal treatment shows a relationship of coal characteristics with their rank as lower ranks coal are more hydrophobic and higher ranks coals are hydrophilic in nature.As the higher rank coals are very difficult to float at high feed rates of emulsifiers. The lignite coal behavior was under observation with the floatability using low temperature heat treatment using a column flotation in a Denver flotation cell. The floatability and hydrophobicity of the coal was done by heating up the coal at 105 °C. After heating, It was clearly observed that the separation efficiency, hydrophobicity and floatability of lignite enhanced dramatically.

The optimum conditions for sulfur removal from coal by electrochemical reduction technology flotation in an aqueous NaCl solution were determined from orthogonal experiments. Again in this method effect of electrolytic conditions on the desulfurization ratio was under experimentation. Their research works results indicate that the conversion of hydrophobic pyrite of coal into hydrophilic compounds by electrochemical reduction. This results in the increase concentration of hydroxyl groups and decrease in carboxyl group which increases the desulfurization rate [3, 4].

There is a process that governing the process route involving low temperature carbonization along with magnetic separation at the second phase. The process involved with the desulfurization and de-ashing of coal with respect to its ranking of low rank lignite coal. Under the conditions used in this research work, (particle size= 23 mm, low temperature carbonization 600.8°C for 15 minutes), the remarkable results are observed with the decrease in organic sulfur and ash contents. But the serious problem is that the combustion of low rank coal produces large level of combustion of these coals produces large air pollution. [5]

The leaching effect on the coal samples was investigated with acids and bases solutions at varying temperature range. It was followed by desulphurization and de-mineralization of the coal samples using solution of acids and bases.

Many improved results was seen in the present research. Potassium hydroxide solution leads to 15-29% desulphurization and 3-20% demineralization at 96.7°C . The desulphurization rate increases to 25–44% by increasing the temperature to 151.7°C and de-mineralization of coal decreases by 1-11%. There is decrease in demineralization was due to the precipitation to the decrease in potassium alumino-silicates. The coal demineralization rate may be enhanced to 27-45 and 37-66% at 96.7 °C and 150.8°C respectively, by leaching with the 10% hydrochloric acid and potassium hydro-oxide solution. The treatment of acids and bases give the remarkable results to remove elemental sulfur and other impurities from coal. High amounts of elemental sulfur and ash are unsuitable for high combustion rate of the coal samples as per our objective. [6, 7]. The experiments of micro wave energy were studied by the many researchers and improved results of de-sulfurized coal have been observed. The purpose of this research is to observe the HI concentration effect on desulfurization rate. When the chemical reaction was preceded, the desulfurization rate was increased with the increase in concentration of HI. There were used many samples of coal with respect to their ranking and series of experiments was conducted. The main experiment results were that the microwave heating extremely enhanced the desulfurization rate. When the coal samples were subjected to the micro-wave leach treatment, there is increased in removal of elemental sulfur due to the die-electric properties of organic matrix of the coal and mineral matter present in coal. The concentrated HI usage in present research to remove organic sulfur, inorganic sulfur and sulfates from coal samples by using the reactors system at the given optimum temperatures. But the biggest drawback of this research was that after treatment coal was not suitable to be used as alternative fuel. [8].

Ox desulfurization research work includes the oxidation treatment using air acetic acids for desulfurization with sodium but-oxide in a batch reactor. The effects were studied which governing the main parameters like air oxidation temperature, air oxidation temperature, sodium but-oxide reaction, solvent concentration and particle size. The air oxidation treatment is the most elective method for increasing sulfur removal. This procedure indicates that pyritic sulfur has 16% and organic sulfur removal by 19% in treatment with sodium but oxide.

By increasing the temperature, the air oxidized sample increases the sulfur reduction for organic and inorganic by a favorable level. The temperature increases which decreased the sulfur removal. The research shows air oxidation pretreatment can be used as an method that increases of organic and inorganic sulfur from coal. but again the chemical desulfurization of coal is not economical method.[9]. Microbial desulphurization procedure used to indicate the inorganic and organic sulfur reduction from coal mixture by ferric oxide species. The effect of particle size shaking rate, initial pH, pulp density and leaching time were used as inputs to the microbial desulfurization network. The outputs of these models have relatively higher percentages in reduction of organic and inorganic sulfur contents. Again this research only emphasize on the microbiological impurities present in coal. [10, 11,12]Froth flotation among all these above mentioned techniques is best unit operation for desulfurization and deashing of selected lignite coal. In this method, the air bubbles selectively come into contact to the mineral surfaces in a mineral/ water slurry system. The particles are attached to the air bubbles and then come or float to the surface and removed.

The particles which do not attached to the air bubbles remain in the liquid phase. The simplicity of this method and low operating cost should be the additional features of the froth flotation. In froth flotation technique, the difference in surface wet ability produced by the surfactant on selective coal surface is taken as basis for separation of sulfur/coal mixture. Surface properties of coal can be varied with the help of suitable wetting agent. [12, 13, 14].

MATERIALS AND METHODS

1. CHEMICALS & REAGENT REQUIRED

Utilities and Accessories required for experimental work are as follows,

1. Polyvinyl Alcohol (0.5%PVA, as wetting agent).
2. Hydrochloric Acid (HCl, as pH regulator).
3. Coal samples (60% coal by wt.).
4. Pine oil, (Frothing agent pine oil used at 3.33 ml per liter of solution).
5. Potassium Hydro-oxide (KOH, as pH regulator).
6. Tap water to prepare 1Molar solution of HCl and KOH.
7. PH meter, weigh balance, beakers, volumetric cylinders.

2. PREPARATION OF COAL SAMPLE

Coal sample was obtained from Chamlakh mines Quetta. The shredding of coal was done to the size of 170 microns. The shredded material was then dried at room temperature. The chemicals were used KOH and HCl as pH regulator.

Polyvinyl Alcohol was used as wetting agent and pine oil were used as frothing agent. The samples of coal samples were treated with 1Molar HCl and 1Molar KOH solution using a stirrer for 10 minutes at room temperature to minimize the hydrophobicity of coal samples.

3. FROTH FLOTATION CELL SETUP

A Perspex type glass cylinder of length 1-meter-high and inner diameter of 8 inches was used as a reactor cell. There is a sparger fitted at the bottom of cylindrical column for bubbling of air using an air compressor. Rota meter is installed at bottom to measure air flow rate.

Conditioning of coal samples was carried out in a column of 1m in length and 8in diameter with stirrer for 40 minutes in the solution of wetting agent Polyvinyl Alcohol (.5% solution) to enhance the selective affinity of the bubbles for different coal samples under same condition. Pine oil was fed at dosage rate of 3.33ml per liter of solution.

(FIG.1.1 Froth Flotation Cell Used for Experimental Investigation**)**

Main operation parameters that effect the frothier cell are Feed rate, Mineralogy, Particle size, pulp density and temperature.

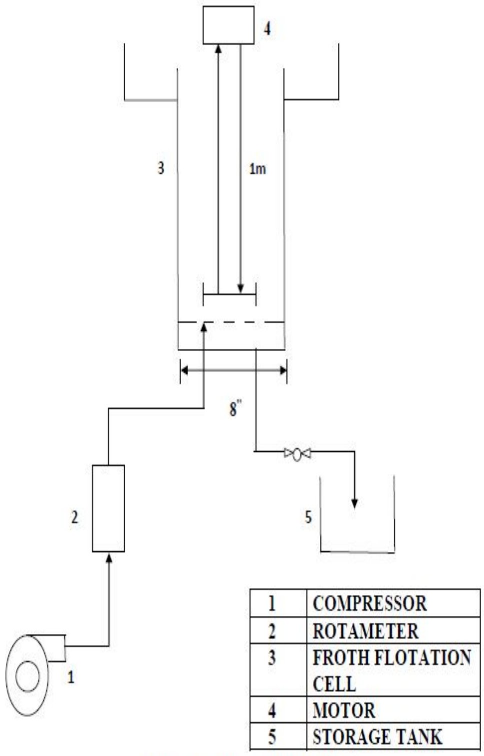


Figure1.2. Schematic Flow Diagram.

Figure1.2. Schematic Flow Diagram.

Pretreatment of feed was done using 1M potassium hydro-oxide and 1M Hydrochloric Acid. Solution of wetting agent was prepared and poured into it. Polyvinyl Alcohol and Pine oil was added in the column. Conditioning of coal samples was performed to selectively suppress hydrophobic properties of coal samples. The air was passed from bottom and froth was collected from the top. Sink mainly containing the coal was collected from the bottom and dried out. The froth was collected from the top. Pyrite sulfur and coal was separated from each other to calculate the separation efficiency of the experiments.

Percentage of Sulfur removal was calculated by using this formula;

$$\textbf{\% SulfurRecovery} = \frac{\text{Sulfur in concentrate (C)}}{\text{Sulfur In feed (F)}} * 100$$

Sulfur Removal (%) = 100 – Recovery %

RESULTS AND DISCUSSIONS

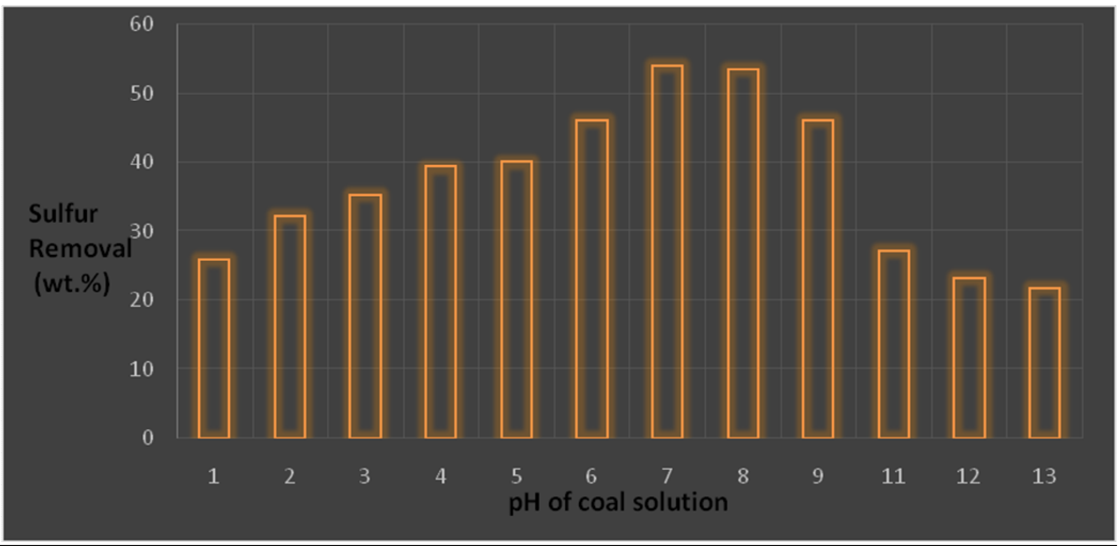
1. Effect of pH of solution on separation efficiency:-

The composition of feed was 60% basis received from the literature review separation time was used as 40 minutes and air velocity=13square cubic feet per hour. The stirrer was rotate at 25 revolutions per minute for all the experimental runs.

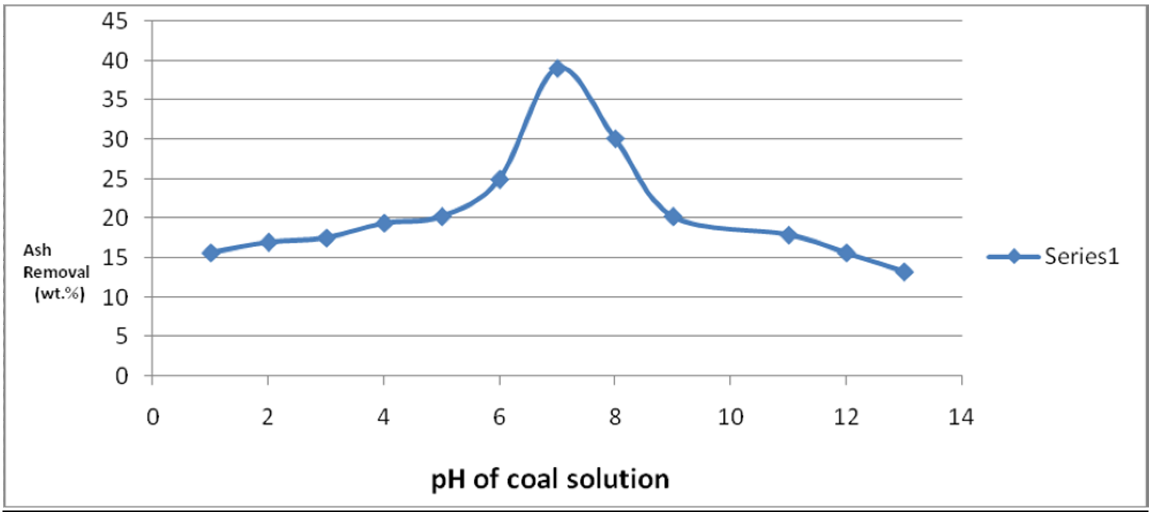
Table 1.1: Effect of pH on impurities removal

pH	Sulfur wt %	Sulfur removal %	Ash wt. %	Ash Removal %
1	5.5	25.87	18	15.65
2	5	32.165	17.7	16.98
3	4.8	35.30	17.6	17.52
4	4.5	39.35	17.2	19.41
5	4.4	40.07	17	20.26
6	4	46.09	16	24.95
7	3.1	54	13	39
8	3.3	53.52	14.9	30.11
9	4	46.09	17	20.26
11	5.4	27.22	17.5	17.91
12	5.7	23.18	18	15.65
13	5.8	21.83	18.5	13.23

(**Figure.1.1.** Effect of pH of solution on sulfur removal**)**



(Figure.1.2. Effect of pH of solution on ash removal**)**



The minimum composition of coal samples was taken as basis to see the effect of pH on separation efficiency. At pH=1, acidic media, although some purity of the coal sample was achieved but it was at low level. It removes that the hydrophobicity of pyrite sulfur was alive in acidic media. As pH of solution was further increased moved towards the pH=7, the results was Improved due to change in the hydrophobic nature to hydrophilic nature of pyrite sulfur. Surface Properties of coal samples were completely changed at pH=7.From pH=7 to pH=13 and pH=7 To pH=13 and the hydrophobicity increases and hydrophobicity decreases. So, it shows that the Optimum level of pH is 7 where sulfur removal becomes the maximum.

Similarly ash rejection or removal decreases and increases with the sulfur removal. Ash removal Was maximum at pH=7, wherehydrophobicity suppresses the hydrophobicity nature of the pyrite sulfur particles.

2. Effect of Separation time Vs Separation efficiency:-

In the second stage, effect of separation time on the separation efficiency was studied while keeping the composition of feed, pH and air velocity constant as shown in table. The experiments were performed for both the wetting agent Polyvinyl Alcohol and pine oil as frothing agent under above mentioned operating conditions. The effects of separation time on the sulfur removal are shown below.

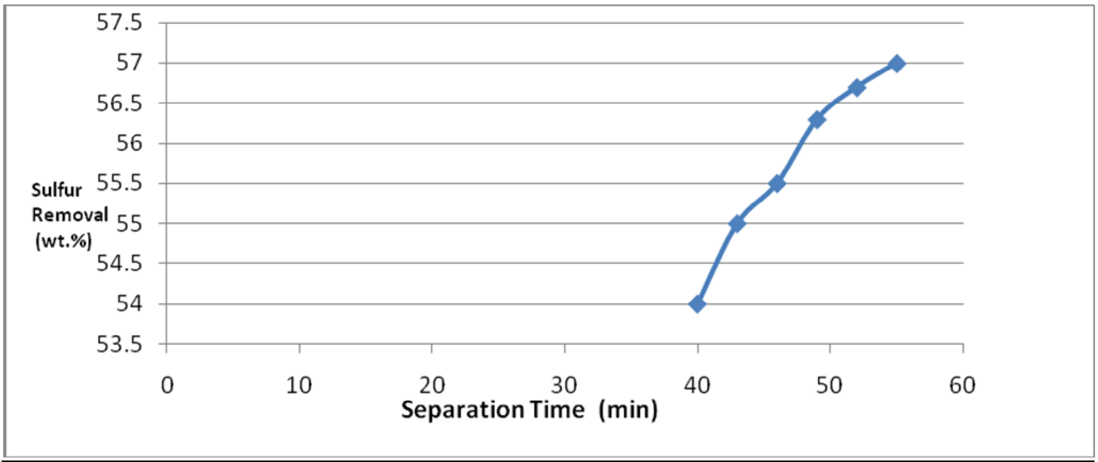
(Following values are taken from the experimental runs)

At constant pH=7 and air velocity=13scfh,

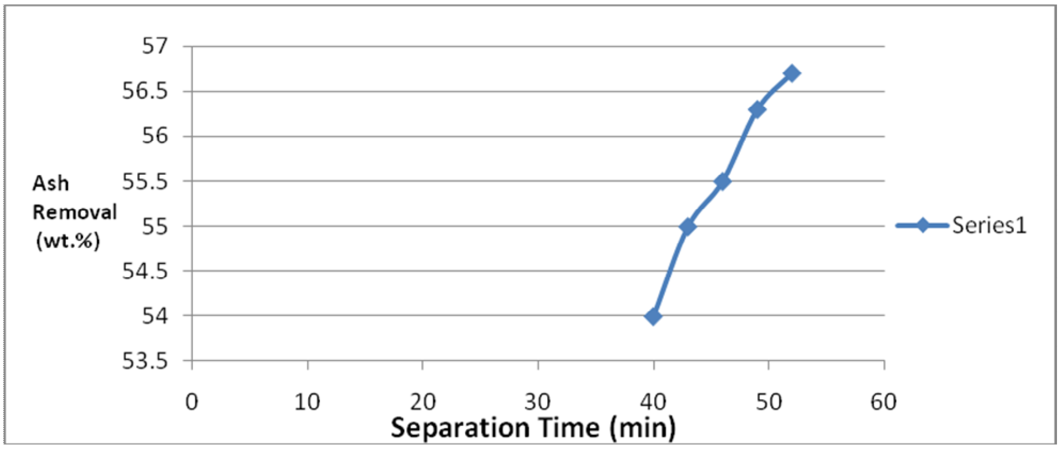
Table 2.1: Effect of separation time on impurities removal

Time = min	Sulfur Removal %	Ash wt. %	Ash Removal %
40	54	13	39.024
43	55	12.8	39.96
46	55.5	12.7	40.43
49	56.3	12.6	40.90
52	56.7	12.4	41.83
55	57.0	12.0	43.21

(Figure.2.1 Effect of separation time on sulfur removal**)**



(Figure.2.2 Effect of separation time on ash removal**)**



The Results indicate that with the increase in separation time sulfur removal was increased. It was observed that with the increased in time, Separation efficiency was increased with the time.

After every 3 minutes, The experimental runs are carried out and here we see the increased in the separation efficiency of pyrite sulfur. The results showed that with the increase in separation time, Sulfur recovery also increases. The sulfur removal was optimum at the separation time=55 Min.There is also increase in ash removal with the increase in separation time and it reaches to Optimum level at separation time= 55min.

3. Effect of Air Velocity Vs Separation Efficiency

In third stage, effect of air velocity on the separation efficiency of the pyrite sulfur was studied by keeping the pH, separation time and composition of the feed constant. The experiments are performed under the same operating conditions. The effect of air velocity on the sulfur removal is shown below.

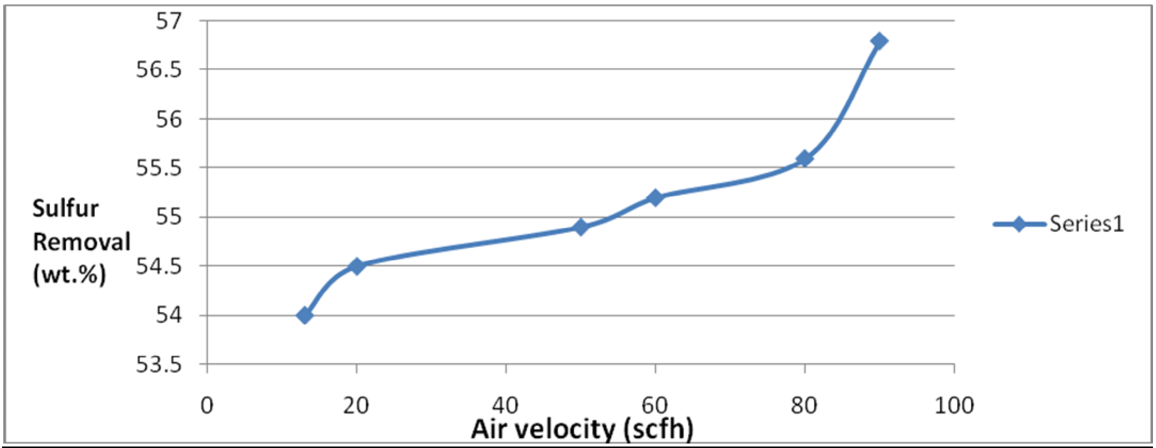
At pH=7 and Separation Time=40 min

(Following values are taken from the experimental runs)

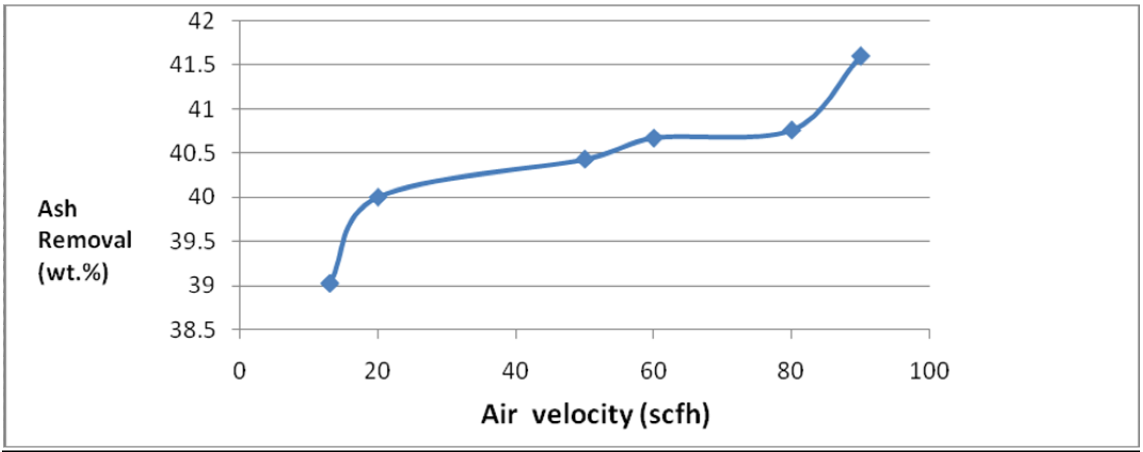
Table 3.1: Effect of air velocity on impurities removal

Air Velocity (Scfh)	Sulfur Removal %	Ash wt. %	Ash Removal %
13	54	13	39.024
20	54.5	12.75	40.0
50	54.9	12.70	40.43
60	55.2	12.65	40.67
80	55.6	12.63	40.76
90	56.8	12.45	41.60

(Figure. 3.1. Effect of air velocity on sulfur removal**)**



(Figure.3.2. Effect of air velocity on ash removal**)**



At low air velocity separation results was moderate showed that air bubbles were at the moderate Level to escape the sulfur particles from column. The wetting and frothing agent almost gave the Same trends. Sulfur recovery was improved with the increase in air velocity as shown in above Figures. An optimum result in terms of sulfur recovery was achieved for air flow rate of 90 scfh.However at high air flow rate, the high velocity accounts for turbulence in the column which Shows that due to high turbulence in the column less pyrite sulfur was captured which results in Decrease in recovery of sulfur in froth flotation column. Similarly, the ash removal was also Increased with the increase in air flow rate and becomes optimum at 90scfh.

Conclusions As Bottom Line & Key Points

The froth flotation test was performed for the separation of pyrite sulfur from coal samples. Experiments showed that pH, air flow rate, composition of feed and separation time are the major factors for the pyrite sulfur removal from the coal samples. Wetting agent Polyvinyl Alcohol PVA and frothing agent Pine oil are used that helps for stabilizing air bubble in the froth flotation column and capturing the pyrite sulfur from the column.

Although Polyvinyl Alcohol had been the focus of many researchers that gave better results.

PVA is used to suppress the surface properties of the selective material from pyrite sulfur and coal mixture. Present research shows that PVA has its role as good wetting agent for the pyrite Sulfur/coal mixture. As the market price of PVA is about 0.0276$/g that helps in making it most feasible for the usage as wetting agent. The pine oil is used as frother or emulsifier. Optimum conditions found for separation of pyrite sulfur from coal mixture after experiments are as follows:

1. Separation was achieved in neutral media (for pH =7) which shows that neutral media helps in suppressing the hydrophobicity of selective (pyrite sulfur) component from coal mixture. Optimum value was pH =7 and no significant separation efficiency was found greater than this value.
2. Separation time is the time used to pass air from column and collect pyrite sulfur from the top. Minimum separation time used in experiment was 40 minutes. By increasing separation time almost high separation efficiency of pyrite sulfur has been achieved.
3. Air velocity was found to be very important parameter in separation of pyrite sulfur from coal mixture. At low air velocity, air bubbles will not capable of capturing pyrite sulfur flakes. Therefore, at moderate air flow rate significant amount of sulfur has been achieved. At very high flow rate turbulence in column starts which results in increase material recovery at the top but purity of the coal sample is decreased. 90 scfh was found to be optimum flow rate of air for separation of pyrite sulfur from coal mixture in the froth flotation column.

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