Biodesulfurization of Coal and Petroleum Coke

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ABSTRACT-*The sulphur content in coal is up to 10% or more by weight, which exists in inorganic and organic forms. Sulfur in coal associated with coalmines like petroleum wastes can occur as organic sulfur, sulfate sulfur and pyritic sulfur. The oxidized form of sulfur contributes largely into acid rain, the burning environmental issue.*

Chemical process involves high temperature and pressure, which is lengthy and affects coal quality. The removal of organic sulphur from coal/coke/metcoke while retaining its fuel value is most difficult. On the other hand, biological processes need mild reaction conditions. Organic sulphur occurs as an integral part of the molecular coal and the petroleum waste matrix and so not available to microbes. Desulphurization by microbial technique or degradation of sulfur compounds by microorganisms is comparatively better than the conventional physical and chemical processes as the process has no harmful reaction products and the value of coal remains unaffected.

In the present study the lignite coal from upper seam lignite shale, over burden sample and petcoke sample was taken and all the samples were undergone the microbial culture treatment of thiobecillus species in different amount and for different time slot. The study shows the significant amount of sulfur was reduced in both coal and petcoke.

Key words: Acid rain, Chemical/physical/biological desulfurization, organic sulfur, Thiobacillus species, Lignite, Petcoke

1. INTRODUCTION

1.1 Coal

Coal is one of the primary sources of energy, accounting for about 67% of the total energy consumption in the country . Also called brown coal , a large amount of lignite is extracted in India (38Mt); Gujarat (34.6%) second after Tamilnadu (61.3%); majority of which has very high sulfur . Coal/lignite/pet coke contains up to 10% sulfur, although values of 1-4% are more typical depending on the region of its extraction.

Hydro desulfurization, a physicochemical technique, has been applied as a conventional method for sulfur removal worldwide. Process occurs at high-pressure (10-17 atm) and high temperature (200-425 ®C) in which sulfur forms hydrogen sulfide (Monticello, 1998). Although high reaction rates of chemical or hydro desulfurization processes are costly, hazardous and the structural integrity deteriorating.

In addition, the processes do not work well on organo sulfur, particularly the polyaromatic sulfur heterocycles. This has tempted researchers to move to the biological methods, which offer many advantages. The processes are performed under mild conditions with no harmful reaction products and the value of coal is not affected (Monticello, 1998).

The organic sulfur in coal is covalently bound into its large complex structure and is difficult to remove physically or chemically, in contrast to pyritic or inorganic sulfur (Constanti et al., 1994).

1.2 Pet coke

Pet coke is a carbonization product of high-boiling hydrocarbon fractions obtained in petroleum processing (heavy residues). Petroleum coke is produced through the thermal decomposition of heavy petroleum process streams and residues. It is a product of extreme temperature and pressure treatments that convert heavy petroleum feed stocks into a solid substance composed predominately of carbon (US EPA, 2007). Pet coke is a hard, brittle, porous material with honeycomb structure. It is solid, fairly inert, low toxic material with higher oil content. It is considered as low temperature coking product at 900^0-1200^0F. Pet coke is *used as a refinery and commercial fuel, in the manufacture of electrodes, abrasives, artificial graphite, and calcium carbide and as a metallurgical fuel* ***(Thomas, 1951).***

Low sulfur content is required if petroleum coke is to be used in the manufacture of electrodes or as a metallurgical fuel.

1.3 Analysis of Coal and Petcoke

There are two methods: ultimate analysis and proximate analysis. The ultimate analysis determines all coal component elements, solid or gaseous and the proximate analysis determines only the fixed carbon, volatile matter, moisture and ash percentages. . Fixed carbon refers to carbon in its free state, not combined with other elements. Volatile matter refers to those combustible constituents of coal that vaporize when coal is heated.

Typical proximate analysis of Various coals (in percentage) : Table 1			
Parameter	Upper Seam Coal	Over Burden Coal	Shale Coal
Moisture	35-40	50-52	23-24
Ash	8-10	6-8	12-14
Volatile matter	20	30	28
Fixed Carbon	28	15	20

Petroleum coke basically comes in two types named the fluid coke and delayed coke. Fluid coke is typically left with / contains about 5 % volatiles and because of its small particle size is not generally very suitable for combustion in CFB boilers. There are a few important aspects which should be taken into consideration when petroleum coke is to be fired in CFB boilers.

Delayed coke contains

Moisture 2 - 10,0%
Ash 0,3 – 5,0 %
Volatiles 8,0 – 15,0 %
Sulfur 3,0 – 8,0 %
Vanadium 500 – 3000 ppm

2. MATERIALS AND METHODS

2.1 Sample collection

The samples will be collected from different depths (seams) of coal/lignite mines of GMDC Matanomadh, Kachchh. Where as samples of petroleum waste (Pet coke) collected from Navanagar Metcoke Ltd, Jamnagar .

Source of collection of organisms

From Institute of Microbial Technology (IMTECH). Sector 39-A. Chandigarh-160036 (India)
Media (9K) composition For the growth of *Thiobacillus* species 9K media (pH 2.5) was used.

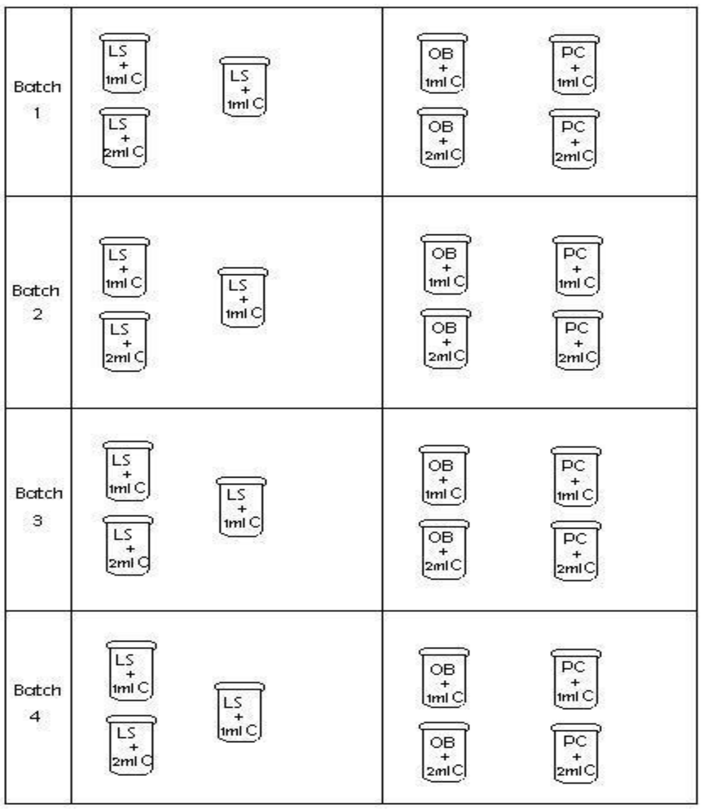
2.2 Experiment setup

The samples then taken into plastic jar with lid in 4 batches. The culture of Thiobecillus species was added in 2 sets of 1ml and 2ml in different coal samples and petcoke sample .
The samples then analyzed after different time slot. The set up was arranged for 32 days maximum.

- In the first set up, 99 ml of 9K media & 1 ml and 2 ml of bacterial culture were added to the weighed amount of coke sample in two separate flasks respectively.

- In control set up, 100 ml of 9K media was added along with the weighed amount of sample. This set up was without bacterial culture.
- After proper labeling, the set ups were kept in the incubator for certain interval of days.
- After incubating the samples for 8 days, 16 days, 24 days and so on, upto 32 days, the samples were filtered with Whatman filter paper no.40
- The residue was allowed to air-dry and was analyzed with respect to total sulfur estimated by Eschka's method.

2.3 Experimental Layout:



Where:
LS: Lignite Shale, OB: Over Burden, PC: Pet Coke,
C: Culture of (Thiobacillus thiooxidans + Thiobacillus Ferrooxidans) Consortia.
Batch 1: Kept for leaching period of 8 days
Batch 2: Kept for leaching period of 16 days
Batch 3: Kept for leaching period of 24 days
Batch 4: Kept for leaching period of 32 days

Procedure for determining total S: 1gm of sample is taken in crucible and 3gm of Eschka mixture is mixed in to it. The mixture is covered with 1gm of Eschka mixture. The crucible is kept inside the furnace at 800.C for 1½ hr. 4 to 5 washings of crucible are taken in beaker (aprox.150 to 200ml) and 15ml of HCl is added in to it. The mixture is boiled for 5min and was filtered through 40no. Filter paper. The washings of filter paper are done with hot water until it becomes acid free. the mixture (filtrate) is boiled to reduce it up to 300ml.to the mixture,1ml of $BaCl_2$ (10%) is added and the solution is left over night. the filtrate is filtered through watt man filter paper no.42. a few drops of silver nitrate($AgNO_3$) solution are added to 4-5dropes of filtrate in a test tube to check whether the solution has become chloride free. The precipitate along with filter paper was kept in crucible and burnt in the furnace at 800.C for 15min. after cooling; weight of the crucible is taken.

Take 1 gm sample + 3 gm Eschka mixture in crucible . Cover it by 1 gm Eschka mixture.

↓

Keep crucible in muffle furnace at 800· for 1.5 hour.

↓

4-5 washings of crucible are taken in a beaker (approx 150- 200 ml).

↓

Add 15 ml HCl. Boil the mixture for 5 min.

↓

Filter with 40 no filter paper & thoroughly wash it with hot water (For making filter paper acid free).

↓

The mixture (filtrate) is boiled to reduce it up to 300 ml.

↓

Add 10ml $BaCl_2$ (10%) in that 300 ml filtrate. Keep solution for overnight.

↓

Then filter solution with filter paper no 42.

↓

Add 4-5 drops of $AgNO_3$ taking the solution in test tube (for checking whether solution is Cl^- free or not).

↓

Crucible along with filter paper kept in crucible & Burnt at 800· for 15 minutes.

↓

Calculate the weight.

Result and Discussion

Experiment with media in lignite shale and in over Burden					
Days	**C.C (ml)**	**LS.S(gm)**	**LS.S (%)**	**OB.S(gm)**	**OB.S(%)**
0	0	0.4893	6 .7181	0.4433	6 .0865
8	1	0.4680	6 .4256	0.3021	4 .1464
	2	0.4320	5 .9313	0.242	3 .3226
16	1	0.4180	5 .7391	0.1290	1 .7712
	2	0.3960	5 .4370	0.1035	1 .4210
24	1	0.3680	5 .0526	0.1170	1 .6064
	2	0.2040	2 .800	0.1002	1 .3757
32	1	0.325	4 .4622	0.1031	1 .4156
	2	0.200	2 .746	0.099	1.3592

Experiment with Distilled water in lignite shale			
Days	**c.c (ml)**	**LS.S(gm)**	**LS.S (%)**
8	1	0.2778	3.8141
16	1	0.2660	3.6521
24	1	0.2653	3.64
32	1	0.2600	3.5698

For Lignite:
The result shows that the range of removed sulfur in lignite shale in 32 days
Total sulfur removed by 1ml culture from lignite shale sample found: 32.65%
Total sulfur removed by 2ml culture from lignite shale sample found: 59.23%
The result shows that the range of removed sulfur in Over burden in 32 days
Total sulfur removed by 1ml culture from Over burden sample found: 76.75%
Total sulfur removed by 2ml culture from Over burden sample found: 87.6%7

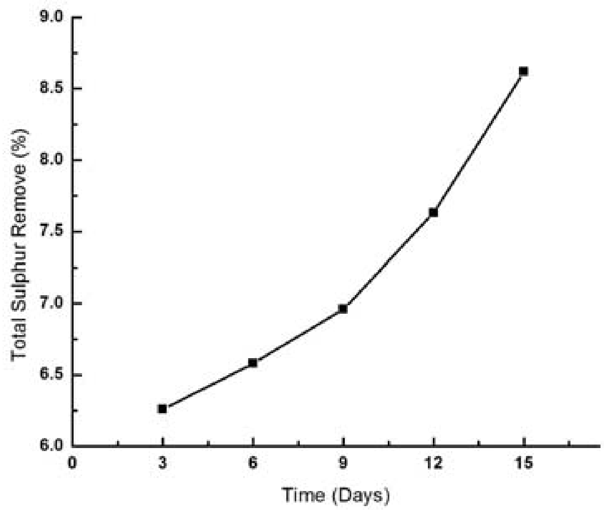
Experiment with media in Pet coke			
Days	C.C. (ml)	PC.S(gm)	PC.S(%)
0	0	0.4603	6.32
8	1	0.4502	6.1812
	2	0.3674	5.044
16	1	0.3950	5.4235
	2	0.3100	4.2563

For pet coke:
The result shows that the range of removed sulfur in Pet coke in 16 days
Total sulfur removed by 1ml culture from Pet coke sample found: 14.19%
Total sulfur removed by 2ml culture from Pet coke sample found: 32.65%

4. Discussion

This suggests that pyrite oxidation in coal to a large extent must rely on the indirect mechanism. In the indirect mechanism, the bacteria oxidize ferrous iron (Fe2+) to ferric iron (Fe3+); the regenerated Fe3+ ions are then used for chemical oxidation of pyrite. Equations 2 describes the indirect oxidation mediated by Fe3+ and *T. ferrooxidans*(Larsson *et al*., 1994): The oxidation of ferrous iron in the absence of microorganisms is a slow process. It is considered to be the rate-limiting step for the oxidation of pyrite with ferric iron. Another option for the indirect mechanism is that the ferric iron oxidizes the ferrous iron in the pyrite, leaving elemental sulfur behind as in Equation 3. The elemental sulfur is then oxidized to sulfate by the microorganisms as shown in Equation 4.

$2FeS_2 + 7O_2 + 2H_2O \xrightarrow{\text{bacteria}} 2FeSO_4 + 2H_2SO_4$
$4\,FeSO_4 + O_2 + 2H_2SO_4 \xrightarrow{\text{bacteria}} 2Fe_2(SO_4)_3 + 2H_2O$
$FeS_2 + Fe_2(SO_4)_3 \rightarrow 3FeSO_4 + 2S$
$2S + 3O_2 + 2H_2O \xrightarrow{\text{bacteria}} 2H_2SO_4$



Result of Experiment among time gradient:
Along with increasing time gradient the microbial activity increases. So sulfur is consumed in much amount by microbes. So sulfur concentration is decreasing in coal.

Result of Experiment among culture gradient:
Compared with that of oil, biodesulfurization of coal is more difficult as permeation of highly polymeric material into the bacterial cells is fairly hard. The efficiency of microbial oxidation of pyrite depends on a number of parameters, for example the particle size of the pulverized coal, the pyrite content, nutrient media composition, pH, temperature, aeration and reactor design.

The removal of sulfur from coal before combustion by biological method is a technically feasible process. Several different microorganisms have been suggested for the process and these microorganisms behave differently. Desulfurization activities of the current desulfurizing bacteria are still too low for an economical desulfurization process. More active microbial cultures with improved desulfurization efficiency toward a wide variety of sulfur compounds are needed for process development. Advancement in genetic engineering could perhaps fulfill the need for microbial cultures that present more complete and more rapid sulfur removal activities. To assess desulfurization processes more correctly, accurate and convenient analytical methods for measuring sulfur in coal are required.

Other barriers to the scale up to commercial application of biodesulfurization processes are the logistics of sanitary handling, shipment, storage, and use of living bacterial cells. However, transporting the bacterial cells as freezedried bacteria or using the bacteria inherent in the coal and running desulfurization at the coal sites could reduce the risk assessment of the processes.

It can be seen that a wide range of further studies on coal biodesulfurization process is required, e.g. investigation in sulfur removal mechanisms and rate enhancement; and investigation of the effects of many parameters, such as substrate type in the growth medium, substrate concentration, type of reactor, type of coal, initial pH, growth temperature, shaking rate, and aeration rate on the process efficiency. In addition, the key engineering issues include reactor design, separation processes, by-product disposition and product quality. Therefore, the co-operation of scientists and engineers is certainly needed for the process improvement.

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