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Reaction Mechanism of Formation of $CaSO_4$ in AFBC

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Abstract

Attempts have been made to investigate and predict the reaction mechanism of formation of calcium sulphate ($CaSO_4$) in Atmospheric Fluidized Bed Combustor (AFBC). Formation of NO_x, from nitrogen content to coal has been found beneficial for the oxidation of sulphur dioxide to sulphur trioxide.

Introduction

Huge deposits of coal about 185 billion tonnes, although lignitic in nature, an economical source of energy, cannot be ignored and let them remain dormant.[1] Presently, hardly, 3 million tonnes of coal is, annually, mined.[2] Most of coal mined is used in brick kilns and less than 0.5 % is being used for power production. No significant literature is available on R & D on Pakistani lignites. Attempts were made to produce coke from Sharigh coal in early 1970's. About ten thousand tonnes of coal had been, annually, used for the production of the briquettes at Briquetting Plant, Quetta, for the last fifty years (1942-92).

Attempts have been made to predict the reaction mechanism of formation of calcium sulphate ($CaSO_4$). It is also observed that formation of NO_x is from nitrogen compounds of coal and not from nitrogen of atmospheric air used as primary and second ary air for combustion of coal in AFBC. NO_x is also found beneficial as it acts as catalyst for the oxidation of sulphur dioxide to sulphur trioxide.

Materials and Methods

Equipment

Atmospheric Fluidized Bed Combustor (AFBC) has been used for the combustion of Lakhra lignite the analysis being given in Tables I and II. The AFBC has been provided with thermocouples, water circulating tubes, in-bed and over-bed feeding faclities, cyclones and bag house. The AFBC has been preheated from the flue gases of natural gas to a temperature of 800^{O} C in excess air so that coal may get ignited. The mixture of coal and limestone has been thoroughly mixed before feeding as it remained in fixed proportion during combustion. In a conventional

AFBC, coal and limestone are separately fed; (the rate of feeding is pre-set). It is worth to mention here that the heat transfer is through convection in AFBC from preheated sand to the mixture of coal and limestone.

Lakhra coal, used in AFBC for combustion, has been analysed on CHN 600 LECO, USA for ultimate (Elemental) analysis and Mac 400 LECO, USA for proximate analysis. Sulphur was determined on Sulphur Determinator SC - 132 LECO, USA. Heating (calorific) value has been determined of Parr Oxygen Adiabatic Bomb Calorimeter. Results have been given in Tables I and II.

Table I. Ultimate (elemental) analysis of Lakhra coal used in AFBC (on moisture-ash free basis)

Element	Percentage
Carbon	46.5
Hydrogen	6.9
Nitrogen	0.7
Sulphur	7.9
Oxygen	38.0

Table II. Proximate analysis of Lakhra coal used in AFBC

Constituents	Percentage
Moisture	21.1
Volatile matter	28.2
Ash	25.6
Fixed carbon	25.1
Heating value (Btu/1b.)	7920

Results and Discussion

About 30-50 % excess air was used in Atmospheric Fluidized Bed Combustor (AFBC) for combustion of Lakhra lignites with 40 % limestone of the coal to trap / fix sulphur of the coal. The temperature of the bed was maintained around 800^{O} C by controlling feed (coal and limestone) and circulating water in the water tubes used for steam production and transmission to electricity turbine.[5]

The reaction mechanism of sulphur fixation is discussed here as during combustion of Lakhra lignites, NO_x was formed from oxidation of nitrogen compounds of coal as atmospheric nitrogen of air is inert and is not oxidised to NO_x at 800^{O} C. NO_x is produced from oxidation of nitrogen compounds and not from nitrogen of air. (As has been done in the production ammonia and nitric acid). However, at very high temperature above 2000^{O} C, NO_x is formed during combustion of fuels as observed in the exhaust of vehicles etc.

NO_x, so formed, in the AFBC, was observed beneficial for the oxidation of sulphur dioxide to sulphur trioxide. It may be termed as NO_x acts as catalyst[4] :

$$SO_2 + NO_x \longrightarrow SO_3 + NO_x$$

It is observed that sulphur trioxide (SO_3) takes two routes. Either SO_3 directly combines with CaO, which was obtained from the calcination of calcium carbonate (limestone fed with coal in AFBC). Formation of calcium sulphate may be due to direct action of freshly produced quicklime (CaO) from calcination of limestone in AFBC and sulphur trioxide (SO_3)

$$CaCO_3 \xrightarrow{\text{Calcination}} CaO + CO_2$$

$$CaO + SO_3 \longrightarrow CaSO_4$$

or sulphur trioxide reacts with water vapors produced during combustion of coal as coal contains water in two forms such as inherent water content and surface water content (absorbed due to porosity), forming sulphuric acid (H_2SO_4). This formation of sulphuric acid is same as commonly termed as "Acid Rain"

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

Now this sulphuric acid reacts in two ways

i) $CaO + H_2SO_4 \longrightarrow CaSO_4 + H_2O$

ii) $CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2$

Water vapors so formed in two above mentioned reactions, react with SO_3 formed during combustion of coal as explained above, produce sulphuric acid in AFBC. In this way, sulphur of coal, in any form, is fixed as calcium sulphate which appears in fly ash and as well as in bottom ash.

Formation of calcium sulphate is explained as the coal used in the experiment contains 7.9 % sulphur. CaO formed due to calcinations of $CaCO_3$ captures sulphur as discussed above. As obvious from Table III, total SO_3 of $CaSO_4$ is 7.34 % (3.49 % from bottom and 3.85 from fly ash). Without going into detailed stoichiometric calculations, as pure substances are not used and produced in AFBC, 93 % sulphur is fixed as $CaSO_4$.

The temperature of bed of AFBC is maintained around 800^{O} C for two reasons.

I. Ash produced in AFBC during combustion of coal (high ash Lakhra lignite) should not fuse to form agglomerates.

Table III. Comparison ash of Lakhra coal and bottom / Fly ash of AFBC plant

Constituents	Ash of Lakhra coal	Bottom ash	Fly ash
Silica	39.76	40.30	45.20
Alumina	20.18	25.85	22.30
Iron oxide	30.23	10.00	14.85
Calcium oxide	4.55	10.52	7.33
Magnisum oxide	2.28	2.53	3.03
Sodium oxide	1.18	0.66	0.53
Potassium oxide	0.62	0.10	0.30
Sulphur trioxide	16.9	3.85	3.49

Agglomeration may choke nozzles of air of AFBC and deposition of ash on boiler tubes, reducing heat transfer to water forming steam and deposition of coal ash on the walls of AFBC (scaling).

II. The formation of NO_x at 800^O C is minimum. It is formed from the oxidation of nitrogen compounds of coal and not from atmosphere nitrogen as atmospheric nitrogen is inert and does not react with oxygen of air at 800^O C. However, nitrogen compounds react with atmospheric oxygen of air to form NO_x. But as mentioned above, NO_x is beneficial for the oxidation of SO_2 to SO_3 (NO_x acts as catalyst). However, formation of NO_x during combustion of fuels is kept minimum as it is not favorable and creates environmental problem. It is, therefore, in AFBC, temperature of bed is kept below / around 800^O C to minimize the formation of NO_x.

Above mentioned observations and discussions are based on experience and yet to be further physically and chemically verified and need further R & D work on well equipped / instrumented AFBC.

Conclusion

It is concluded that formation of NO_x is mainly due to the nitrogen content of the coal and not from nitrogen of air as 800^O C is maintained in AFBC. The formation of $CaSO_4$ in AFBC reduces the quantity of hazardous emission of SO_2 and SO_3. It is therefore, high sulphur coal could be used in AFBC provided $CaSO_3$ is used as sorbent.

References

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