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Desulphurization of Coke Oven Gas

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ABSTRACT

Coke oven gas is used in the industries for power/energy generation. Coke oven gas consists of many impurities. Sulphur is also present in the composition of the coke oven gas as an impurity. Sulphur pollutes the environment. So it is necessary to remove the sulphur from the coke oven gas. There are several methods for purification of coke oven gas. In this paper the Iron oxide process used for desulphurization of coke oven gas is emphasized. Coke oven gas contains hydrogen sulphide (H₂S) and other sulphuric compounds like carbon disulphide (CS₂), carbonyl sulphide (COS), mercaptans etc. The separation of these pollutants is strongly required by environmental protection.

Generally the processes suitable for desulphurization of coke oven gas can be subdivided into different methods:

- Dry oxidation processes
- Wet oxidation processes
- Absorption/stripping processes

Coal gas contains several impurities, in particular dust and H₂S are the most important ones. Gas cleaning is not only necessary to prevent pollution of the environment, but also to protect the equipment against corrosion. Hence there are not only environmental requirements for desulphurization of coke oven gas there are also technological and safety requirements.

KEYWORDS

Coke oven gas purification; H₂S Removal from COG; Clean coke oven gas; Sulphur removal from COG; Cleanup of COG; COG desulphurization.

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INTRODUCTION

The sulfur content of many coals is too high to comply with the EPA standard for power plant fuels. The Coke Oven Gas is produced during the carbonization of coal. Coke Oven Gas is used in the iron and metallurgical industry. Coke Oven Gas contains many impurities. The Coke Oven Gas typically contains appreciable quantities of hydrogen sulphide, organo sulphur compound such as thiophene, tetrahydrothiophene, thionin, and inorganic carbon sulphur compounds such as carbon disulphide and carbonyl sulphide^{1, 2,3,4,5}. The removal of H₂S is a very important gas cleanup process which is closely related with the product quality, environment protection needs, as well as safety and stability of production process^{6, 7}. The current alternatives for utilizing coal as a fuel include either complete gasification of the coal with the sulphur removal effected by conventional gas treatment, or direct combustion of the coal with stack gas scrubbing. Development of improved desulfurization process is very important that accomplishes the required sulfur reduction^{8,9}.

Despite the long held reputation of coke oven gas (COG) as a "clean" fuel, enactment of stringent ambient airquality standards for SO₂ in 1969 forced reexamination of the emissions potential of this fuel^{10,11}. In 1971, as part of their implementation plans, a number of states (Alabama, Kentucky, New York, Ohio, Pennsylvania, and West Virginia) enacted regulations sharply limiting the allowable sulfur content of COG used as fuel. In addition, Allegheny County, PA, with the largest density of coke plants in the world, wrote a stringent regulation limiting COG sulfur content^{10, 12, 13, 14}.

Enactment of emission regulations limiting the sulfur content of COG has stimulated considerable interest in the development of new technologies for its desulfurization. Such activity has, in turn, raised questions regarding prospects for increasingly restrictive regulations in the future as more advanced desulfurization technologies become available^{15, 16, and 17}.

However, increased desulfurization could be dictated by fuels management policies at integrated facilities using several fuels. Also, the need to maintain an efficient and reliable COG distribution system completely free from corrosion and plugging may also dictate the substantial removal of sulfur from COG^{18, 19}.

Table-1: properties of coke oven gas^{20, 21, 22}

SL. NO.	PROPERTIES	RANGES
I.	Calorific value	4200 kcal
II.	Density at 0°C and 760 millimeters of mercury (mm Hg)	0.45–0.50 kg/m
III.	Explosive concentration in air	6–30 %

Coke-oven gas is toxic and explosive.

Table-2: coke oven gas composition^{20, 21, 22}

SL. NO.	COMPONENT	DRY BASIS(% VOL)	ACTUAL COMPOSITION (% VOL) (WATER SATURATED AT 176 ^o F)
I.	Water vapor	-	47%
II.	Hydrogen	55%*	29%*
III.	Methane	25%	13%
IV.	Nitrogen	10%	5%
V.	Carbon Monoxide	5%	3%
VI.	Carbon Dioxide	3%	2%
VII.	Hydrocarbons (Ethane, Propane etc.)	2%	1%

* alters on A/C of the impurities

Table-3: coke oven gas impurities^{20,21, 22}

Sl. No.	Impurities	Range (g/m ³)
I.	Tar	60.0 – 120.0
II.	H ₂ O	350.0 - 450.0
III.	NH ₃	8.0 – 10.0
IV.	H ₂ S	5.0 – 10.0
V.	S (organic)	0.3 – 0.4
VI.	HCN	1.0 – 1.5
VII.	Benzene, Toluene, Xylene	25.0 – 40.0

METHODS TO REMOVE SULPHUR FROM COG^{10, 23}

1. Dry Oxidative Process:

- Iron oxide
- Zinc oxide

2. Wet Oxidative Process:

- Stretford
- Perox
- Takahak
- Thylox
- Fumaks
- Lo cat

3. Neutralization Process:

- Sulfiban
- Cyclasulf
- Vacasulf
- Soda lye scrubbing

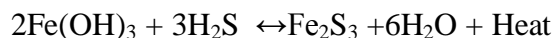
Iron oxide process

The **Iron Oxide Process** was used for the first time in the early 17th century and the process has hardly changed since then. For the absorption of hydrogen sulphide ferric hydroxide mass is utilized. An iron oxide process based plant mainly consists of cleaning, depositing and emptying towers with a certain number of baskets or of boxes with layers of ferric hydroxide^{22, 24, 25}.

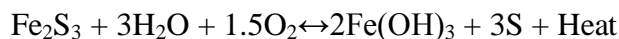
As you can see from Fig.1, oxygen for sulphur forming is required (approx. 1 to 1.5 % vol. of oxygen). That means oxygen has to be added to the coke oven gas. Due to formation of water by the process, the coke oven gas should be slightly overheated before entering the towers/boxes. By this process elemental sulphur is produced and forms a layer on the iron oxide mass and lowers the activity of the mass. Therefore after loading of the mass to a certain extent, this basket tower/box has to be changed to a tower/box with fresh mass. In the beginning in using this process big boxes were used, but later cylindrical towers have been used because of operating the process at higher pressure and because of less necessary space^{24, 25,26,27,28}.

The chemistry involved in absorption and regeneration using iron oxide shows that iron sulphides are produced when H₂S reacts with Fe(OH)₃ with the empirical composition approaching Fe₂S₃. The iron used in this process is called BOG iron^{10, 24}.

H₂S adsorption:



Sulphur forming:



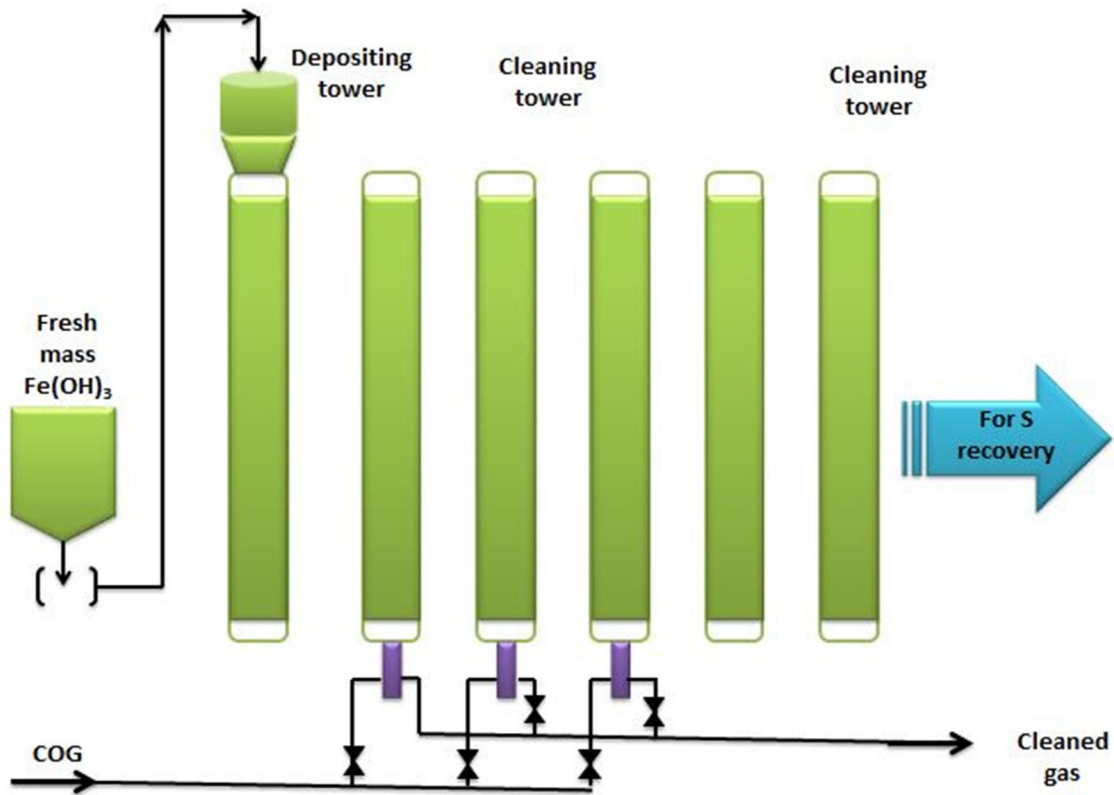


Fig.1: iron oxide process for desulphurization of cog

Material balance for H_2S removal^{29, 30}

- Inlet composition of COG (% vol)^{20,21,22}:

H_2	55%
CH_4	25%
N_2	10%
CO	5%
CO_2	2%
C_nH_m	2%
H_2S	1%

- Flow rate of COG: 42000 m³ /hr
- H_2S in COG = 10 g/m
- Mass flow rate of H_2S = 10 X 42000 =420000 g/hr

- Mol. Wt. of H₂S = 2 X 1+32 =34
- Molar feed rate of H₂S = (Mass flow rate of H₂S)/(Mol. Wt. of H₂S)
- Molar feed rate of H₂S = 420000/34
=12352.9 moles /hr
=12.3529 kmol/hr
- H₂S is 1% of the feed
- So total feed rate=12.3529 X 100
=1235.29 kmol/hr
- Assumed 95% conversion of H₂S²⁵
- H₂S converted=(12.3529 X 95)/100
=11.7325 kmol/hr
- Amount of H₂S in exit stream
- H₂S unconverted= H₂S in feed- H₂S converted
=12.3529-11.7325
=0.6204 kmol/hr
- O₂ supply=0.5 of H₂S mole in feed
=0.5 X 12.3529
=6.17645 kmol/hr
- O₂ used=0.5 of H₂S moles in exit stream
=0.5 X 11.7325
=5.86625 kmol/hr
- O₂ in exit stream
O₂ unconverted= O₂ supplied- O₂ used
= 6.17645- 5.86625
=0.3102 kmol/hr

- Exit stream rate

$$\begin{aligned}
 &= \text{inlet stream without H}_2\text{S} \\
 &\quad + \text{H}_2\text{S unconverted} \\
 &\quad + \text{O}_2 \text{ unconverted}
 \end{aligned}$$

- Exit stream rate

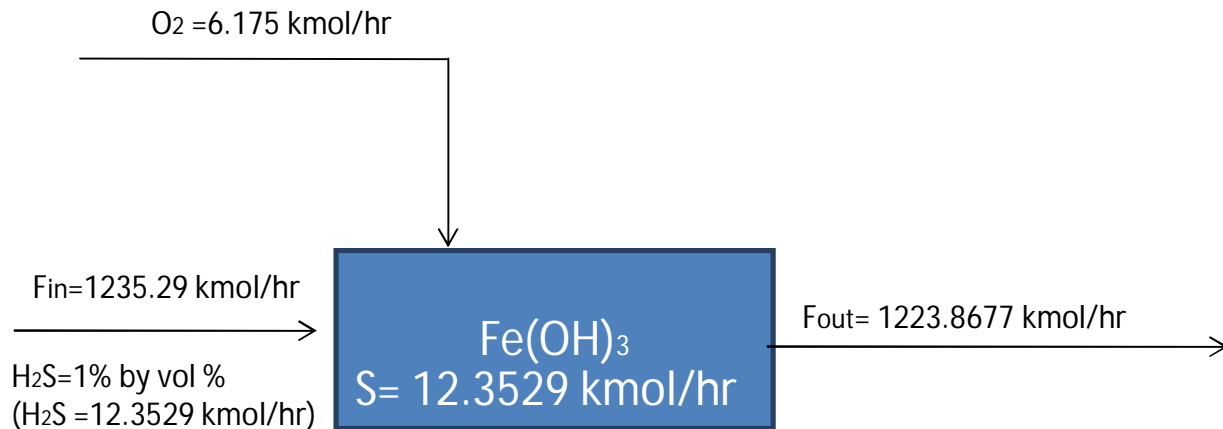
$$\begin{aligned}
 &= (1235.29 - 12.3529) + 0.6204 \\
 &\quad + 0.3102 \\
 &= 1223.8677 \text{ kmol/hr}
 \end{aligned}$$

- According to the reaction

$$\begin{aligned}
 \text{Moles of S formed} &= \text{Moles of H}_2\text{S inlet} \\
 &= 12352.9 \text{ moles/hr}
 \end{aligned}$$

- Amount of S formed

$$\begin{aligned}
 &= (\text{Moles of S formed}) \times (\text{mol. wt of S}) \\
 &= 12352.9 \times 32 \\
 &= 395292 \text{ g/hr} \\
 &= 395.292 \text{ kg/hr}
 \end{aligned}$$



CONCLUSION

Iron oxide process is very effective process for desulphurization of coke oven gas. This process removes 95-98% of the H₂S from the coke oven gas. By this process elemental sulphur is produced and forms a layer on the iron oxide mass and lowers the activity of the mass.

This process is formerly used for desulphurization of coke oven gas. Further research is done for making the process more effective. However this process is not widely used as more developed processes are developed which are more efficient than this process.

Iron oxide process is not more economic and also requires more place but it is more effective than others processes. It also removes the other impurities present in the COG in fewer amounts. Efficiency of the iron oxide process of removing the sulphur from coke oven gas is high this process is widely accepted in the SAIL, plants.

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