

Chemical Investigations of the Emission of Selected Fertilizer Industries

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(Received 3rd February, 1994, revised 31st July, 1994)

Summary: Samples of gases from selected Urea and phosphate fertilizer industries were collected. These samples were analyzed for nitrogen, oxygen, hydrogen, methane, ammonia, argon and oxides of carbon and sulphur by standard ASTM methods. The results of analysis are presented and its implication discussed.

Introduction

Pollution of the ambient air may result from natural process or anthropogenic. The natural process leading to atmospheric pollution includes volcanoes, forest fires, pollen, decomposition of plants and vegetation, ocean spray and volatile hydrocarbon emission from vegetation. The major anthropogenic routes of atmospheric pollutions are vehicular emissions, burning of fossil fuels and industrial emissions.

Primary air pollutants include oxides of carbon, oxides of nitrogen, oxides of sulphur, and

particulate matter, substantial amount of CO, SO₂, NO, NO₂, NH₃, H₂S, Cl, HCl and HF are added to the atmosphere each year, by human activities. The hazardous effects of these substances are well documented [1-10].

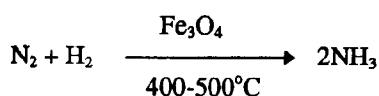
Extensive literature is available for the analysis of N₂, CO₂, O₂, H₂, CO, CH₄, SO_x, Ar and NH₃ in air samples [11-20].

In the present work standard ASTM methods were used for sampling and analysis of the

above mentioned gases in the sample from selected fertilizer industries.

Results and Discussion

The raw material for urea industry is air and natural gas, while phosphatic fertilizer industry is phosphate rocks and sulfuric acid. The natural gas after desulphurization is converted into H₂ which reacts with nitrogen obtained from the air forming ammonia as follow:



The emission from urea fertilizer industries is from four different units, each involving different process or reaction. These gases are (i) stack gases from reforming step (ii) purge gases from synthesis step (iii) off gases from urea plant and (iv) flue gases from the boiler. The emission from phosphatic fertilizer industry is of two types, that is flue gases from sulphuric acid plant and scrubbing gases from fertilizer unit. The analyses of the raw material of the two industries, that is natural gas and phosphate rocks are given in Table-1 and 2. The analyses of the flue gases from the above mentioned four different sections of urea plant are given in Table-3. While the analysis of the flue gases of phosphate fertilizer industry are given in Table-4.

The analysis of the natural gas indicates that it contains traces of both organic and inorganic sulfur and sufficient amount of carbon dioxide, which are continuously pumped into our environment. It is worth mentioning that the same natural gas which contains sufficient amount of CO₂ is used for domestic as well as industrial purposes through out the country. Table-2 indicates, that the local phosphate rocks contain high quantity of Al₂O₃, which may lead to lithospheric pollution but on the other hand contain minimum amount of carbon dioxide as compared to the imported one.

From Table-3, it can be seen that high quantity of carbon dioxide (9.4%) is present in the reforming stack gases. The purge gases are used as fuel for boiler as it is sent to the boiler house. The

analysis of the purge gases and off gases are given in Table-3 section 2 and 3. Ammonia from these gases is recovered in the recovery plant by absorption in water, while the remaining gases are sent to the boiler section, where it is used as fuel. The analysis of the boiler off gases are given in Table 3 section 4. The results also show the absence of CO and CH₄, while it indicates high quantity of CO₂, which is released into the atmosphere.

Table-1: Analysis of natural gas

Chemical species	% composition
Methane (CH ₄)	87.04
Ethane (C ₂ H ₆)	5.79
Propane (C ₃ H ₈)	1.85
Butane (C ₄ H ₁₀)	0.78
Pentane (C ₅ H ₁₂)	0.19
Nitrogen (N ₂)	3.38
Oxygen (O ₂)	0.16
Carbon-dioxide (CO ₂)	0.90
Organic sulphur (C ₂ H ₅ SH)	2.55 ppm
Inorganic sulphur (H ₂ S)	5.56 ppm

Table-2: Chemical analysis of phosphate rock

Chemical species	% composition	
	Imported	Local
P ₂ O ₅	32.33	28.35
CaO	52.40	39.90
SiO ₂	3.00	16.24
Fe ₂ O ₃	1.50	1.50
Al ₂ O ₃	-	2.40%
MgO	0.30	0.25
F	3.4	3.0
CO ₂	4.50	1.40
H ₂ O	1.50	0.16
SO ₃	0.50	0.35
Na ₂ O	-	0.31
K ₂ O	-	0.59
Cl	-	125 ppm

Table-3: Chemical analysis of emissions of urea fertilizer industry

Chemical Species	S.L.	1	2	3	4	
N ₂	%	-	72.90	18.72	32.11	84.60
CO	%	0.08	Nil	Nil	Nil	Nil
CH ₄	%	-	Nil	13.33	3.50	Nil
CO ₂	%	-	9.40	Nil	Nil	9.20
Ar	%	-	1.40	9.06	9.00	1.00
O ₂	%	-	5.40	Nil	Nil	3.40
H ₂	%	-	Nil	57.55	24.39	2.60
SO ₂	ppm	8000	1.0	Nil	Nil	1.50
NH ₃	ppm	-	Nil	0.19	29.80	Nil

1. Stack gases:- 25000 NM³/hr

2. Purge gases:- 2000 NM³/hr

3. Off gases:- 1000 NM³/hr

4. Flue Gases:- 500 NM³

S.L.: - Local standard limit

Table-4, shows the analysis of the flue gases of phosphatic fertilizer industry. Though the

analysis indicates that the values of most of the serious pollutants with the exception of SO₂ fall within the loose local standard limits which are in practice in this country.

Table-4: Chemical analysis of the flue gases of phosphate fertilizer

Chemical species	Jan. 1993	Feb. 1993	Mar. 1993	Apr. 1993	May 1993	June 1993	Stand limits
HF(ppm)	25.0	30.3	29.5	19.7	25.5	38.5	150
H ₂ S (ppm)	5.0	4.0	6.0	3.0	6.0	7.0	10
SO ₂ (ppm)	850	925	1506	2300	11105	820	6000
CO (ppm)	306	419	210	591	405	395	800
CO ₂ (ppm)	3.0	1.0	2.4	3.1	2.7	1.3	-

Experimental

Instruments

Recording sulfur analyzer model 286 from ITT Balton USA, Chinese make CO and CO₂ analyzer and Chinese make gas chromatographs (Beijing Analytical Instrument Factory) model SP 2304 with TCD, SP 2305 with TCD and SP 2307 with TCD and FID were used during this work. The type of gas chromatograph with its operational condition are given below:

1. Gas Liquid Chromatograph SP-2304

I	Detector:-	Thermalconductivity TCD
II	Bridge Current:-	200mA
III	Carrier Gas:-	Hydrogen 1.0Kg/Cm ²
IV	Column length:-	2 meter
V	Column Material:-	Dibutylphthanate on support 6201 (40-60 mesh)
VI	Column temp.:-	Room Temperature
VII	Analysis:-	Hydrocarbons

2. Gas Chromatograph: SP 2305

I	Detector:-	Thermalconductivity TCD
II	Bridge Current:-	200mA
III	Carrier Gas:-	Hydrogen 0.5 Kg/Cm ²
IV	Column Length:-	2 meter
V	Column Material:-	Molecular Sieve
VI	Column Temp.:-	80°C
VII	Analysis:-	Ar, O ₂ , N ₂ , CO, CH ₄ , CO ₂

3. Gas Chromatograph:- SP-2307

I	Detectors:-	TCD, FID
II	Bridge Current:-	200mA
III	Carrier Gas:-	Hydrogen 1.5Kg/Cm ²
IV	Column Length:-	1 meter
V	Column Material:-	Carbon Molecular Sieve TDX-01
VI	Column Temp.:-	80°C
VII	Detector Temp.:-	100°C
VIII	Oven Temperature:-	250°C
IX	Dilution Gas:-	Nitrogen
X	Burning Assistant Gas:-	Air
XI	Analysis:-	N ₂ , CO, CH ₄ , CO ₂

Sampling

On line sampling of the flue gases for sulfur, CO and CO₂ was conducted. For other gases below ball sampling technique was used.

Procedure

Sulfur contents in the natural gas was analyzed by the auto analyzer utilizing the Bromine titration method. While the stack, purge, off, flue gases and air samples collected in the vicinity were analyzed using gas chromatographs keeping the conditions given below:

Conclusion

The urea fertilizer industry releases CO₂ and traces of NH₃ into the environment in the form of flue gases, while other serious pollutants are absent in the flue gases. The phosphatic fertilizer industry releases most of the serious pollutants in relatively greater quantity especially SO₂ and CO. This trend if not checked properly in time may eventually lead to problem like green house effect and acid deposition in the surrounding localities.

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