

## Unsafe Petrochemical Refinery Air Pollution And Its Environmental Impact Assessment

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*Abstract:* - This research paper discusses various air pollution problems and solutions from petrochemical refineries and their environmental impact assessment (EIA). High levels of carcinogens have been determined from petroleum and chemical refinery air emissions. Unsafe emissions may be due to improper production process, poor maintenance practices and internal operational process problems. Many of the chemicals discharged in to the atmosphere during the leakage periods were found particularly severe to children. It was observed that the concentration of discharge might be varying 150-to 300-mg/ m<sup>3</sup> that is discharged during the production process petrochemicals. High volume air sampler with cascade impactors have been used for measurements and sampling indoor and atmospheric air quality. National ambient air quality monitoring standard (NAAQMS) and American Public health Association standard (APHA) have been applied for the determination of air pollution levels. Petrochemical air sampling measurement reports show that during the course of gas leak there were about thirty toxic chemicals get discharged into atmosphere. These are common refinery chemicals such as benzene and bromo methane, which have been identified and monitored by using high volume air samplers after the gas leakages. Chemicals such as hydrogen sulfide, carbon disulphide, bromo methane, Methyl Ethyl Ketene, Benzene, Toluene, h-Hexane, Methylbenzene, m, p-xylene and n-Nonane were found above safe limits. Benzene and hydrogen sulfide were 36 times and 33 times higher than safer levels prescribed by the pollution control standards of about 5000 µg/ m<sup>3</sup>. A specific case study on air emission and its EIA conducted in a Petrochemical plant at Chennai, India have been presented below. As per EIA carried out, it is recommended that air pollution control systems must be adopted in all

petrochemical industries to mitigate petrochemical emissions [3].

Petrochemical air pollution effects severe health problems to the public who are exposed in the vicinity particularly children. They suffer from chemical based chronic/acute diseases such as ulcer, allergic dermatitis, lung cancer, liver necrosis, brain damage, and premature death, liver and kidney problems. The clinical symptoms of acute toxicity are vomiting, diarrhea, blood loss into the gastrointestinal tract causing cardiovascular diseases. Toxic effects are produced by prolonged contact with airborne or solid or liquid petrochemical carcinogenic compounds even in small quantities. Prolonged exposure causes ulcers, skin irritation and allergic dermatitis. Exposure to chemical dust emissions may cause perforation of nasal septum, corrosion of bronchopulmonary tract and lung cancers. In the kidneys, it causes tubular necrosis and may also damage the liver. These carcinogenic substances produce adverse health effects on the workers and result occupational health hazards. Public get affected non-occupational health hazards especially, those people who are exposed in the vicinity. Several countries have initiated regulatory measures to control chemical pollution. Indian Government and companies do not have even database on EIA nor they take actions. It is essential to evolve control and preventive measures which are to be taken at the planning stages in these industries as prevention is better than cure, very little or nothing can be done if the toxic chemicals reaches the air, water and soil environment. Workers must be provided personal protection equipments, adequate safety guards and machine guard protection devices. It is to be ensured that worker's compensation law and occupational disease law must be enacted. The enactment of worker's compensation and

occupational-disease laws will increase materially the cost of insurance to industry. The increased cost and the certainty with which it is applied have put a premium on accident-prevention work. This cost can be materially reduced by the installation of safety devices. EIA has shown that by implementing proactive measures approximately 80% of all environmental disasters are preventable [9]. Several countries have initiated regulatory measures. For example, the Federal Republic of Germany has enacted an emission protection law and a technical guidance for clean air (TA –Luft). As per TA-Luft, the mass of carcinogenic substances, in respiratory form is restricted to  $1 \text{ mg/m}^3$  (class II) [ $1000 \text{ }\mu\text{g/ m}^3$ ]. The total dust concentration in emissions is limited to  $20 \text{ mg/ m}^3$  [ $20000 \text{ }\mu\text{g/ m}^3$ ] and other inorganic material in dust form (Class III) to  $5 \text{ mg/ m}^3$  [ $5000 \text{ }\mu\text{g/ m}^3$ ]. The maximum allowable concentration (MAK) of carcinogens in air of workplace is  $0.1 \text{ mg/ m}^3$  [ $100 \text{ }\mu\text{g/ m}^3$ ]. Databases and EIA reports that consider all sources of petrochemical carcinogens in the environment, the likelihood of its exposure to humans and post consequences to man and lower organisms from its absorption are reported and presented in this paper.

*Key-Words:* - carcinogens, petroleum, refinery, sampling, and standards

## 1 Introduction

Environmental impact assessment in petrochemical industries is defined as an identification and evaluation of potential effects or impacts to the total environment and their mitigation. Petrochemical

refineries release often-toxic chemicals into the air during the processing of petrochemicals. This chemical air emission produces adverse health effects on public and workers exposed in their vicinity. There are chemicals and carcinogenic gases namely, benzene and bromo methane, which have been identified and monitored by using High volume air samplers after the gas leakages during 2007-2008. Chemicals such as hydrogen sulfide, carbon disulphide, bromo methane, Methyl Ethyl Ketone, Benzene, Toluene, h-Hexane, Methylbenzene, m, p-xylene and n-Nonane . Air pollution control systems have been developed and used to mitigate petrochemical emissions in the environment [3] namely wet chemical scrubbers. The present study has been done to present the research investigations pertaining to petrochemical refinery emissions and their environmental health effects. A health survey has been carried out to characterize and assess chemical pollution [3]. A model has been presented to assess the potential impacts due to emissions from petroleum refineries [6]. Research investigations are provided pertaining to source of chemicals, health effect and its environmental impact assessment (EIA). As per survey conducted, research inputs must be needed with respect to environmental modeling to solve the petrochemical pollution problems. It is important to have a database and EIA reports on petrochemical industries, which is one of the hazardous industry classified by Environmental protection agency, USA. This paper provides EIA conducted in order to assess the environmental impacts of petrochemical industries. A specific case study on air emissions from a petrochemical refinery plant, Chennai, India has been presented.



**Figure 1 , Environmental Impact Assessment Carried Out In A Petrochemical Refinery Plant Located At Chennai, India**

## 2 Problem Formulation

### 2.1 An Environmental System Modeling Approach For Finding Health Impacts

EIA on human by petrochemical emissions can be assessed by a simple modeling, which is given below [2]. An approach for explaining the combined *synergistic (augmentative)* health effect is given in a formal model. Model is a simplified formulation that mimics real-world phenomena so that complex situations can be comprehended and prediction made. It is designed to simulate some real situations for decision-making purpose regarding impact of the natural environment on man. In simplest form, models may be verbal or graphic, that is, consisting of concise statements or picture graphs. There are informal and formal models. Formal models are such formulations going to play an increasing role in decision-making problems [6].

### 2.2 Overview Of Environmental System Modelling

In its formal version a working model of a synergistic and health effects of refinery emissions situation would, in most cases, have four components, as listed below (with certain technical terms listed in parentheses)[6].

1. Properties (state variables)
2. Forces (forcing functions), which was outside energy sources or casual forces that drive the system
3. Flow pathways, showing where energy flows or materials transfers connect properties with each other and Forces
4. Interactions (interacting functions) where forces and properties interact to modify, or amplify or control flows.

On this model were shown six properties  $P_1, P_2, P_3, P_4, P_5$  and  $P_6 \dots 30$  toxic chemicals, which interacted at 'I' to produce or affect the fourth property  $P_n$ , when the system was driven by forcing function, 'E'. Flow pathways were shown with  $F_1, F_2 \dots$  and so representing input and output flow-paths respectively for the system overall [2].

Where,  $P_1, P_2, P_3, P_4, P_5$  and  $P_n \dots 30$  toxic chemicals emitted from the refinery emission. Under the driving force of four factors namely sunlight (photo energy), temperature, humidity and air movement, these interacted and 'Pn' is the interacting function 'I' was a synergistic or augmentative one, which was more serious as a pollutant than  $P_1, P_2, P_3, P_4, P_5$  and  $P_n \dots 30$  toxic chemicals acting independent of each other. Hence, it has been evaluated by using a mathematical modeling that the potential impacts are thirty five times than normal atmospheric condition. It is essential that air pollution control systems may be equipped in all petrochemical industries to mitigate petrochemical air emissions.

## 3 Problem Solution

### 3.1 Environmental Impact Assessment

Chemicals in refinery atmosphere act on human in three ways such as (1) local action as dermatitis or absorption through skin, (2) direct inhalation and (3) ingestion or absorption into the stomach. Toxic effects are produced by prolonged contact with airborne, solid or liquid chemical compounds even in small quantities because of their properties such as carcinogenicity, mutagenicity and corrosiveness [2]. Complications do arise due to the reducing nature of these carcinogenic chemicals that affect organic tissues of body. Health survey is in progress.

1. To study the health effects and socio-economic impact of environmental pollution in refineries, an endeavor was made. Local ESI centers, State Government hospitals, private clinics and nursing homes were contacted to assess physiological disorders and diseases.
2. Field studies and rough estimates of the morbidity rates, hospital admissions and absenteeism with normal values, ESI beneficiary records and workers health records have shown that there was high risk of health damaging potential in and around the refineries. This was readily gauged from the fact that there were large number of private clinics and nursing homes in and around the above towns. The incidence of refinery emissions based diseases and related

health effects on the people around this refinery was noticeable.

3. The percentage incidence of refinery emission based diseases and related health effects on the people around these refineries were noticeable. They were noted based on the field study made on chemicals based diseases as per epidemiological evidences [2].

Suspended particulate chemical matter (SPM) and Respiratory particulate chemical matter (RSPM) in indoor refinery and out door air with respect to various carcinogenic chemicals such as hydrogen sulfide, carbon disulphide, bromo methane, Methyl Ethyl Ketene, Benzene, Toluene, h-Hexane, Methylbenzene, m, p-xylene and n-Nonane found in RSPM and SPM which are above safe limits. Total chemical air pollution levels ranging 15000-30000  $\mu\text{g}/\text{m}^3$ . Chemical particulate size diameter (PSD) varying from 1 to 100 microns.

Sl. No.	Quantity of chemical concentration in ambient air	$\mu\text{g}/\text{m}^3$
1	SPM Collected-While HVAS run outside the refinery at full swing	883
2.	SPM Collected-While HVAS monitored when full swing	6723
3.	RSPM below 1 microns-HVAS Monitored	57
4.	RSPM 1 to 3 microns	142
5.	RSPM 3 to 5 microns-HVAS monitored	153
6.	RSPM 5 to 7 microns – HVAS run	86
7.	RSPM 7 to 10 microns	95
8.	RSPM below 1 microns	173
9	RSPM 1 to 3 microns	119
10	RSPM 3 to 5 microns	121
11.	RSPM 5 to 7 microns	545
12	RSPM 7 to 10 microns	6141
15	RSPM below 1 micron–HVAS monitored inside refinery	190
16	RSPM 1 to 3 microns-HVAS monitored inside refinery	132
17	RSPM 3 to 5 microns–HVAS monitored inside refinery	295
18	RSPM 5 to 7 microns–HVAS monitored inside refinery	448
19	RSPM 7 to 10 microns	4232
20	RSPM below 1 microns	51
21	RSPM 3 to 5 microns	123
22	RSPM 3 to 5 microns	68
23	RSPM 5 to 7 microns-HVAS monitored without refinery in operation	56
24	RSPM 7 to 10 microns-HVAS monitored without refinery in operation	2133

During 2007-2008, twenty-four samples were analyzed using HVAS with cascade impactor. SPM and RSPM and Chemicals were reported as alarmingly very much high against the safe limits for the dust samples below 10 microns that is 5 mg/cubic meter. SPM, RSPM and chemical RSPM concentrations were documented. According to Environmental protection agency (EPA), USA and national ambient air quality standards / central pollution control board (CPCB/NAAQS), the concentration of dust in ambient air should not be 1. SPM at chemical particle size diameter (PSD), PSD cut off to about 40 to 45 microns  $2495\mu\text{g}/\text{m}^3$ ;

more than  $150\mu\text{g}/\text{m}^3$  as 24 hours time weighed average (TWA) for industrial area. The safe limit of chemical dust concentration in ambient air as TWA for industrial area is  $1\text{ mg}/\text{m}^3$ . Chemicals such as hydrogen sulfide, carbon disulphide, bromo methane, Methyl Ethyl Ketone, Benzene, Toluene, h-Hexane, Methylbenzene, m, p-xylene and n-Nonane were found above safe limits. Benzene and hydrogen sulfide were 36 times and 33 times higher than safer levels prescribed by the pollution control standards of about  $5\text{ mg}/\text{m}^3$ . Chemical content in dust collected was 1994 ppm; chemical concentration in air was  $4975\mu\text{g}/\text{m}^3$ .

2. RSPM was 9 to 4232  $\mu\text{g}/\text{m}^3$ . Chemical content in dust collected was 173 ppm; Chemical concentration in air was 554 $\mu\text{g}/\text{m}^3$ . PSD < 10 microns.

Results are provided by Using Atomic Absorption Spectrophotometer, Colorimetric Method and X-ray Fluorescence Diffraction Method]. Chemical

pollution levels documented that is air chemicals emitted from refineries were analyzed by using AAS method, x-ray florescence method, spectrophotometer-colorimetric method, chemical precipitation method while following American Public Health Association (APHA) method.

Given below data on chemical air pollution

RSPM Results By Using Gravimetric Dust Sampler and Total Sampling: Time Weighed Average (TWA) of 24 hrs.

1. Particle size diameter (PSD) found = 10  $\mu\text{m}$
2. Sampling of RSPM = 0.025  $\text{m}^3/\text{min}$  or 2.5 liters/minute
3. RSPM range = 160 to 527  $\mu\text{g}/\text{m}^3$
4. Chemical concentration in RSPM dust = 75 to 2000 ppm as total chromium
5. Chemicals emission refinery air = 19 to 400  $\mu\text{g}/\text{m}^3$

Carcinogenic chemicals determined such as hydrogen sulfide, carbon disulphide, bromo methane, Methyl Ethyl Ketene, Benzene, Toluene, h-Hexane, Methylbenzene, m, p-xylene and n-Nonane which were found above safe limits.

Ten samples were analyzed in refineries by using gravimetric dust air sampler and corresponding total chemical analysis were reported. They were alarmingly very high than the safe limits for the chemical dust samples below 10 microns. Concentration of chemical RSPM was documented. According to national ambient air quality standards (NAAQS/CPCB), the concentration of dust in ambient air should not be more than 5  $\text{mg}/\text{m}^3$  as 24 hours time weighed average (TWA) for industrial area. The safe limits of chemical concentration in ambient air as TWA for industrial area was 1.5  $\mu\text{g}/\text{m}^3$ .

Monitoring of chemical air pollution levels were done by measure and monitoring collecting chemical dust samples using cascade impactor with high volume air sampler and gravimetric sampler emitted from various unit chemical operations. The studies relevant to monitoring the refinery air in terms of total dust levels, worker dose, air pollution levels, duration of exposures, SPM chemical concentration, RSPM chemical concentration, air borne SPM, SPM concentration in ambient air, refinery air, outdoor air, RSPM below 10 microns, its different diameter range and chromium air borne RSPM in different PSD levels ranging below 1  $\mu\text{m}$ ,

1-3  $\mu\text{m}$ , 3-5  $\mu\text{m}$ , 5-7  $\mu\text{m}$ , 7-10  $\mu\text{m}$  were done. Refinery effluent samples were collected to find out total water pollution load.

**3.3 Sources And Health Effects Of Particulate Chemical Matter**

Particulate matter in the air usually refers to small solid particles of material found in the atmosphere in addition to gases. The particles of organic or inorganic composition that is suspended may be individual elements and / or compounds. Chemical particle size diameter (PSD) may be used to classify the types of sources. For example, particles having PSD less than 1  $\mu\text{m}$  are mostly products of condensation and combustion. Large particles having PSD above 10  $\mu\text{m}$  result from physical actions, such as wind erosion and grinding or spraying operations [2]. Those particles between 1 and 10  $\mu\text{m}$  of PSD tend to be fugitive dusts, process dusts and combustion products. Suspended particulate matter (SPM) in the air refers to particles, which are too fine to have an appreciable falling velocity and therefore tend to stay suspended in atmosphere for a considerable time. Metallic fumes, fibrous materials, heavy metals, all micro-organisms, various allergens and many organic carcinogens are present in air in the form of SPM having the PSD up to 100  $\mu\text{m}$ . Air contaminant dust in the size-range of 0.25-10.0  $\mu\text{m}$  is called respirable suspended particulate matter (RSPM). RSPM of different range

series are absorbed forcibly against any surface through the principle of impaction.

SPM chemicals are the dust entirely consisting of coarse particulate, which are quickly eliminated in the respiratory system and hence are not very harmful. The coarser dust collected as part of the SPM creates nuisance, soiling of surfaces and some visibility problems but is unlikely to contribute significantly to respiratory and other health effects associated with air pollution. Generally, health effects are caused primarily by *RSPM* in the PSD range of 0.25-10 microns emissions from industries. Particles having PSD less than 0.25 microns are retained in lung alveolar regions. Particles greater than 10 microns are lodged in the upper tract and do not reach the bronchi. Various chemical air pollution sources produce *lung* damaging size range particles [5].

### 3.4 Health effects of respirable suspended particulate chemical matter

The dangerous dust from the chemical worker's point of view falls under the category of RSPM chemicals. This invisible fine dust enters the air passages and produce physiological changes [7]. Particles size analysis carried out show that the PSD of the chemical *dust* particles varies between 1 to 40 microns and higher. Particles with PSD varying from 5 to 50 microns result in respiratory troubles, as human nose cannot effectively filter the particles and lead to allergic symptoms like asthma. There are diseases called disabling lung disease caused due to inhalation of carcinogen chemical *dust* over long periods of time. It is accompanied by chest tightness with respiratory troubles [1].

### 3.5 Enactment of occupational diseases and worker's compensation laws

It has been observed by the author that most of the management of the petroleum refineries in India in both private and Government refineries have not implemented the worker's compensation and occupational diseases Laws. As per research survey study conducted, it has been proved that approximately 80 percent of all industrial petrochemical disasters are preventable [9]. Hence, the worker's compensation and occupational disease laws must be enacted in all refineries. The principle involved Worker's compensation laws and occupational disease law is that the worker injured or

disabled in industry should be enabled, through proper medical treatment, to return to wage-earning capacity as promptly as possible and, while incapacitated, should receive compensation in lieu of wages, regardless of fault. The expenses of medical treatment and compensation should properly be borne by industry and become a part of the cost of its products. The laws generally provide that workers injured in industry shall be furnished the necessary medical treatment, and, in addition, compensation based on a percentage of their average weekly wages, payable periodically. Dependents of employees killed in industry are likewise compensated [9].

Workers may be supplemented worker's compensation and occupational diseases law by providing comparable monetary benefits in cases of incapacity or death due to occupational disease. Management of the industries may provide for compensation benefits in occupational-disease cases either by enlarging the scope of the worker's compensation law, by separate legislative enactment, or by judicial constructions. The enactment of worker's compensation laws has to be followed in many jurisdictions by more stringent provisions relating to refinery inspections for the prevention of accidents in industry and of occupational disease. The enactment of worker's compensation and occupational-disease laws will increase materially the cost of insurance to industry. The increased cost and the certainty with which it is applied have put a premium on accident-prevention work. This cost can be materially reduced by the installation of safety devices [9].

## 4 Conclusion

This research paper discusses various air pollution problems and solutions from petrochemical refineries and their environmental impact assessment (EIA). High levels of carcinogens have been determined from petroleum and chemical refinery air emissions during 2007-2008 in Chennai Petro chemical Industries Ltd., Chennai, India. High levels of carcinogenic chemicals are found with respect to suspended particulate chemical matter (SPM) and respirable suspended chemical matter (RSPM) which have been determined from petrochemical refinery air emissions. Monitoring of chemical air pollution levels were

done by measure and monitoring collecting chemical dust samples using cascade impactor with high volume air sampler and gravimetric sampler emitted from various unit chemical operations. The studies relevant to monitoring the refinery air in terms of total dust levels, worker dose, air pollution levels, duration of exposures, SPM chemical concentration, RSPM chemical concentration, air borne SPM, SPM concentration in ambient air, refinery air, outdoor air, RSPM below 10 microns, its different diameter range and chromium air borne RSPM in different PSD levels ranging below 1  $\mu\text{m}$ , 1-3  $\mu\text{m}$ , 3-5  $\mu\text{m}$ , 5-7  $\mu\text{m}$ , 7-10  $\mu\text{m}$  were done. Refinery effluent samples were collected to find out total water pollution load.

Unsafe emissions may be due to adoption of improper maintenance practices and of internal operational problems. Many of the carcinogenic chemicals discharged in to the atmosphere during the leakage periods were found particularly sever to children. It was observed that the concentration of discharges might be varying 150 to 300  $\text{mg}/\text{m}^3$  that is during the manufacturing process of petrochemicals. High volume air samplers with cascade impactors have been used for measurements and sampling indoor and atmospheric air quality. National ambient air quality monitoring standard (NAAQMS) and American Public health Association standard (APHA) have been applied for the determination of air pollution levels. Petrochemical air sampling measurement reports show that during the course of gas leak there were about thirty toxic chemicals get discharged into atmosphere. These are common refinery chemicals such as benzene and bromo methane, which have been identified and monitored by using high volume air samplers after the gas leakages. Chemicals such as hydrogen sulfide, carbon disulphide, bromo methane, Methyl Ethyl Ketene, Benzene, Toluene, h-Hexane, Methylbenzene, m,p-xylene and n-Nonane were found above safe limits. Benzene and hydrogen sulfide were 36 times and 33 times higher than safer levels prescribed by the pollution control standards of about 5000  $\mu\text{g}/\text{m}^3$ . It has been evaluated by using a mathematical modeling that the potential impacts are thirty five times higher than normal atmospheric condition. A specific case study on air emissions and its EIA carried out in a Petrochemical plant at

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which it is applied have put a premium on accident-prevention work. This cost can be materially reduced by the installation of safety devices.

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