

Chapter I

Introduction

1.1. General

Pollution prevention is a significant task in present era throughout the world of industrial development. In India, air pollution due to sulfur dioxide (SO₂) and nitrogen oxides (NO_x) were pondered to be highly hazardous for our ecosystem as they have explicit influence over all living beings and non-living things. Their concentration in air is an increasing threat to living beings and the natural environment throughout the world. The presence of these highly toxic substances in the atmosphere causes death or health issues to living beings. These toxic substances are generally present in the atmosphere but they tend to be as pollutant when the concentration of substance in a known zone becomes high compared to the actual requirement. It means SO₂ and NO_x can be considered as air pollutants when their concentration in the atmosphere can affect adversely humans and the environment. These toxic substances were released in to the atmosphere due to man-made and natural sources. As the atmosphere is a mixture of highly complicated natural gaseous system which essentially supports life on earth

we must have the responsibility to protect it. The adverse effect on ecosystem due these contaminants is the area of concern in the current era. In recent years, the Indian government laid great importance to air pollution control also has enacted various environmental laws and regulations for the prevention and control of air pollution.

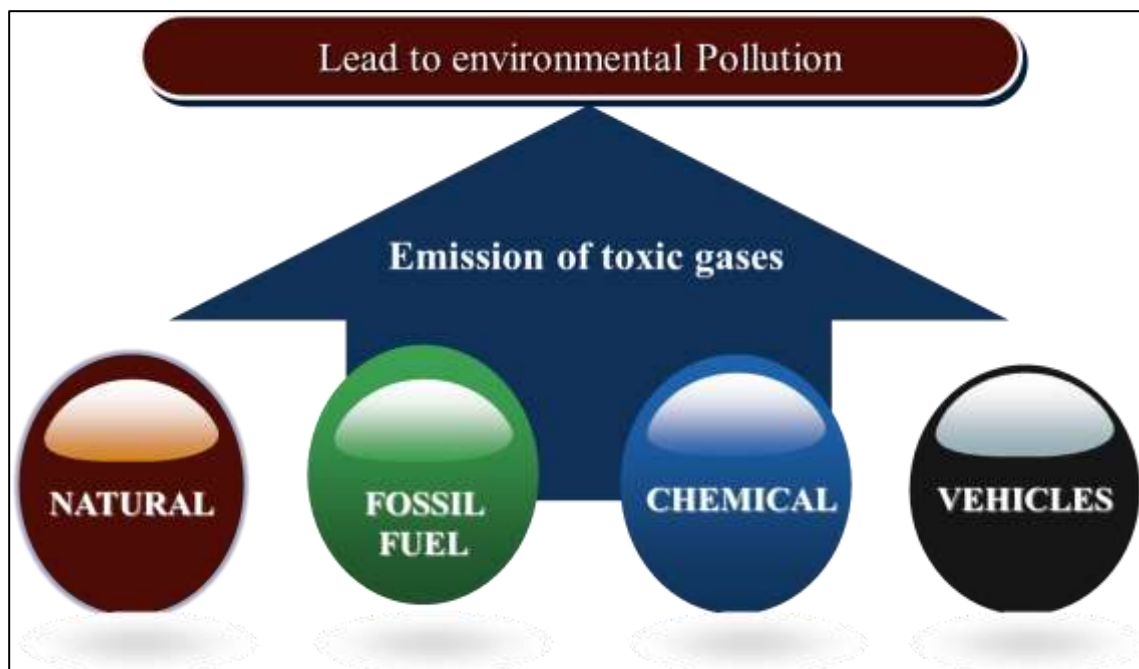


Figure 1.1. Emission outline of SO_2 and NO_x

1.2. Sources of SO_2 and NO emission

Sources of air pollutants SO_2 and NO_x can be classified as natural and anthropogenic. These lethal air pollutants escape into the atmosphere by natural, anthropogenic and industrial activities. Due to burning of fossil fuels in natural, fuel, industrial and traffic

sources, these toxic gases are emitted into the environment. Figure 1.1. shows the emission outline view of these toxic gases into the environment. These gases are the main pioneers for the haze.

1.2.1. Natural sources

Bulk bio-mass from agricultural burning, forest fires, photochemical smog, pollen grains, from gases agricultural lands and weeds, soil erosion, storms, volcanic eruption and other reactions occurring in the atmosphere naturally contributes some contaminant into the ambient air. Control of these natural reactions is beyond the human capability. But control of anthropogenic sources (man-made sources) is the current challenge throughout the world to keep the eco system safe for the future.

1.2.2. Man-made sources

Man-made air pollutants may be classified on the basis of their type of discharge into the environment. In these they are majorly divided into two types, as stationary sources and as mobile sources. The major stationary sources were further classified into two types as point sources and as area sources. Industrial processing plants, power plants, municipal incinerators for solid waste, fuel combustion in iron, steel, coal, oil and natural gas industries are the major considerations of point sources. Residential heating, on-site incineration, open burning, industrial and commercial heating are the area sources. In the category of mobile sources, the division was further classified into line sources and area sources. High way vehicles and rail route locomotive were the major line sources. Mobile vehicles (Light, medium and heavy duty) and railcar motive were the mobile sources in category of mobiles sources.

1.2.2.1. Sulfur oxides (SO_x)

Sulfur oxides refers to several types of sulfur and oxygen containing compounds such as sulfur monoxide (SO), sulfur dioxide (SO₂), sulfur trioxide (SO₃), di-sulfur monoxide (S₂O), di-sulfur dioxide (S₂O₂), etc. Predominantly SO₂ is considered to be major composition in SO_x. It is colorless, inflammable and non-explosive gas with suffocating odor. SO₂ is generated by volcanoes and in various industrial processes due to the burning of a sulphur-containing fuel such as coal, oil, etc. The percentage distribution of SO₂ emission from various industries, is given in Figure 1.2. The major contributors were found out in power generation sector.

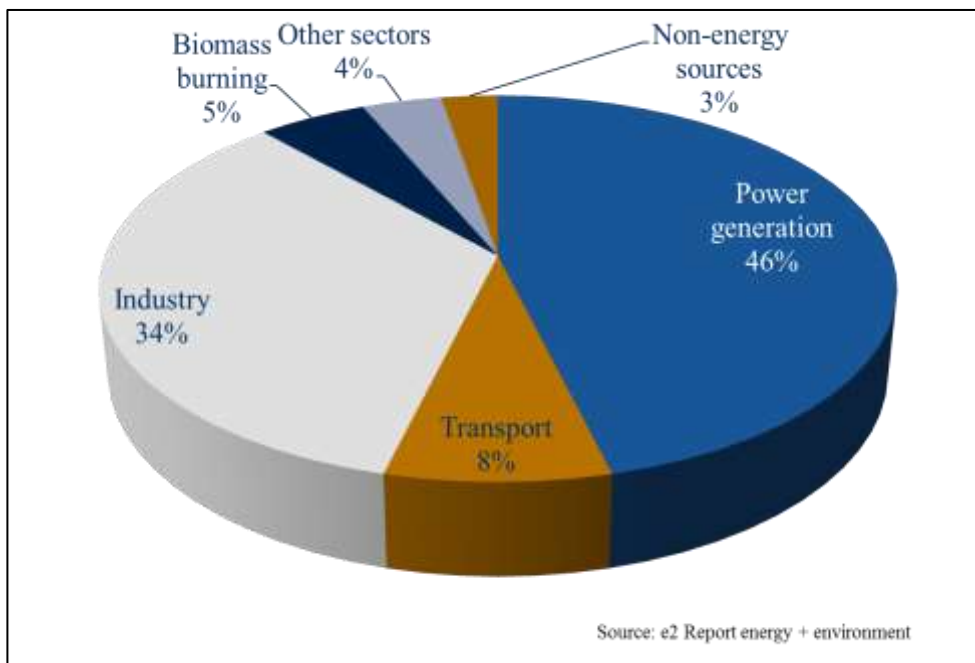


Figure 1.2. Sources of SO₂ emission

1.2.2.2. Nitrogen oxides (NO_x)

Nitrogen oxides mostly refers to nitric oxide (NO), nitrogen dioxide (NO₂), nitrous oxide (N₂O), dinitrogen trioxide (N₂O₃), dinitrogen tetroxide (N₂O₄) and dinitrogen pentoxide (N₂O₅) and trinitro-amide N(NO₂)₃. These are produced especially at high temperatures during the reaction between nitrogen (N₂) in fuel and oxygen (O₂) in the air while combustion. The major sources of NO_x are thermal power plants, transportation sector, bio-mass burning, industrial boilers, etc. The emission contribution of different sources of NO_x is given in the Figure 1.3. NO_x contains 90-95 % NO, which is partially soluble in water, and hence the key attention is given to NO.

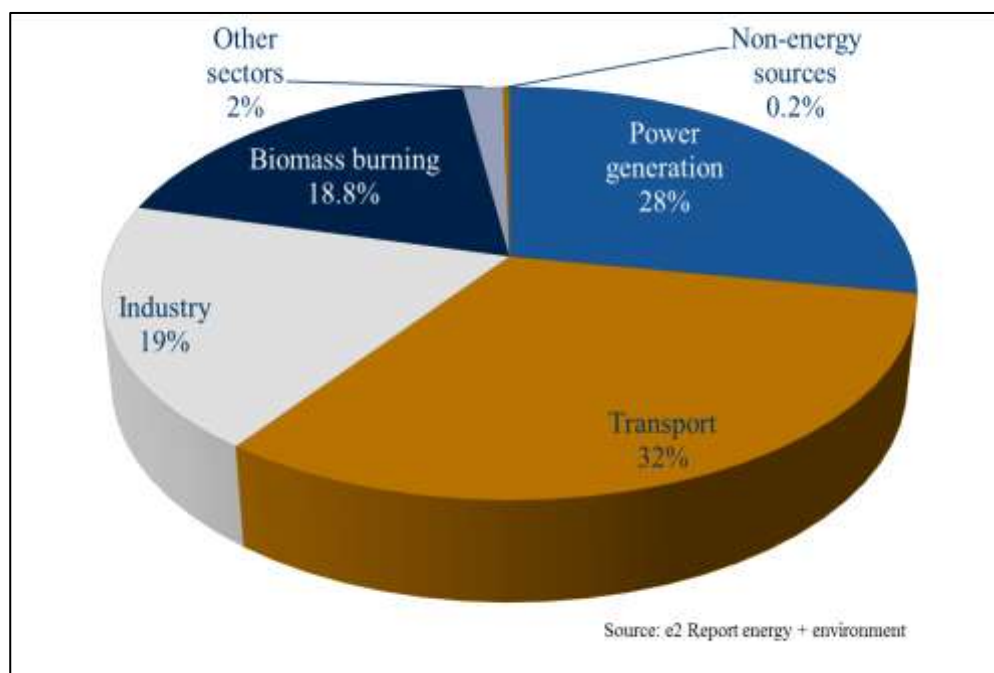


Figure 1.3. Sources of NO_x emission

1.2.2.3. SO₂ and NO_x

The current importance on the environmental impact of combustion process and the progress in national energy production approaches, suggest that extensive use of fossil fuels will require to high efficiency clean stack technology. Its cleaning by seclusion becomes beyond human effort unless the pollutants are controlled at the source itself. SO₂ and NO_x were majorly emitted from fossil fuel combustion. Abatement of SO₂ and NO_x assumes significant importance due to its toxic effects on the living systems. From these various sources, we selected reduction of SO₂ and NO_x from coal fired thermal power plant stack gases as our major concern. Coal is the leading energy resource in fossil fuels worldwide. Throughout the world 30 % of total energy and 40 % of electrical energy was supplied from consumption of coal (Li et al. 2015). Coal combustion has 60 % in man-made sources of sulphur oxides.

1.3. Fuel burning and stack compositions

Fuel adulteration, the burning of high sulphur content fossil fuels can discharge harmful toxic gases into the air and consequently pose significant environmental problems. Coal, oil and natural gas are major energy resources available in the environment where as fuel combustion processes and power plants are the major contributor of SO₂ and NO_x in the form of flue gas (the gas discharges into the environment through a flue a channel for transmitting exhaust gases from a steam generator, inglenook, furnace, oven or boiler etc.). The uncertain change in atmospheric concentration because of toxic gases such as SO₂ and NO_x, due to burning of the coal leads to environmental problems and health effects to living beings. Due to the presence of high sulphur compounds in

natural fuels like petroleum & coal, combustion of these fuels generates SO_2 , except the sulphur compounds are separated prior to post combustion of the fuels. The term “flue gas” refers to the exhaust gas generated after combustion of fossil fuels in fuel industries such as thermal power plants and oil industries etc.

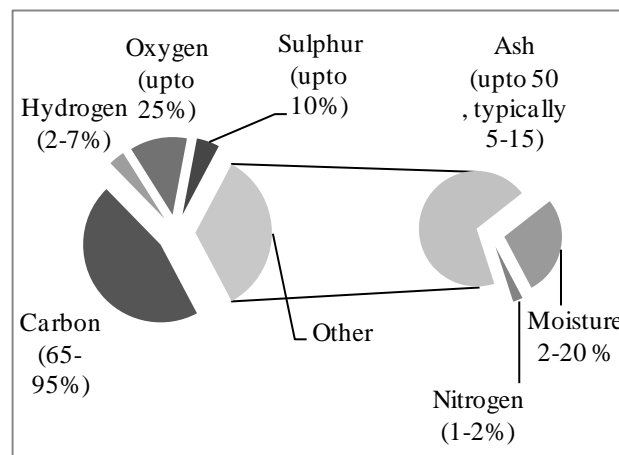


Figure 1.4. Coal composition in mass percent (Source Bueno-Lo´pez and Garcı´a-Garcı´a, 2005)

Flue gas contains numerous air pollutants including carbon, CO , CO_2 , NO_x , particulate matter (PM), and SO_2 in a notable percentage. Flue gases emitted in post combustion of natural energy carrier such as coal in thermal power plants typically contains SO_2 in an amount of 500–2000 ppm (Sumathi et al., 2010a), NO_x in an amount of 125 ppm (Sumathi et al., 2010a; Tsuchiai et al., 1995), O_2 in an amount of 5.2 % (Tsuchiai et al., 1995) CO_2 in an amount of 13 % (Tsuchiai et al., 1995) and H_2O in an amount of 7.8 %

(Tsuchiai et al., 1995). Whereas Figure 1.4 shows the characteristic compositions of the elements normally found in coal referring from Bueno-Lo'pez and Garcí'a-Garcí'a, 2005. Pre-treatment of the stack gases before releasing into the environment can reduce these toxic effects on living beings and meet stringent effluent discharge limits.

1.4. Effects of SO₂ and NO

Acid rain and photo chemical smog due to emission of SO₂ and NO has been identified as one of the most serious threats to the global environment ever faced by humans in the history.

1.4.1. Effects of SO₂

1. Fossil fuels such as coal and petroleum regularly contains sulfur compounds, and their combustion produces sulfur dioxide.
2. Once released to the atmosphere, SO₂ reacts slowly through photo-chemically initiated reactions and reactions with cloud and fog droplets. Further oxidation of SO₂, generally in the existence of a catalyst such as Nitrogen dioxide (NO₂), forms sulphuric acid (H₂SO₄), and thus acid rain.
3. These atmospheric reactions also yield inorganic and organic sulphate compounds.
4. A major fraction of SO₂ is captured on vegetation and soil surfaces because of adsorption and absorption. These processes are collectively termed deposition. Rates of deposition are not accurately quantified and vary both regionally and seasonally. This is the major cause for concern over the environmental impact of the use of these fuels as power sources.

5. During the combustion of sulphur-containing fuels, approximately 94 to 95 % of the sulphur is converted to SO₂. Generally, 0.5 to 2 % of the fuel sulphur is converted to SO₃. SO₃ remains in the vapor state until temperatures decrease below approximately 600°F (300°C). At this temperature, SO₃ reacts with water, as indicated in equation (1.1). In the atmosphere, a part of SO_x is converted into aerosol and sulphuric acid. The latter is washed down to the earth as acid rain. The reaction was given below in equation (1.1).



6. Because of its corrosiveness, it is important to keep gas streams at temperatures above the sulphuric acid dew point.
7. Damage to air pollution control equipment, ductwork, and fans can occur if the gas temperature is below the sulphuric acid dew point in the localized areas.
8. More than 18 million metric tons of SO_x are emitted into the atmosphere each year from man-made sources. Approximately 98 to 99 % of the SO_x emissions are in the form of SO₂. These emissions can cause health problems and contribute to acid rain. Over two-third of all anthropogenic SO_x emissions result from fossil fuel combustion in utility and industrial boilers.
9. Coal and fuel-oil boilers are responsible for most of the utility and industrial boiler SO_x emissions because these fuels have moderate-to-high fuel sulphur levels.
10. The largest non-combustion sources are copper smelters, followed by petroleum refining operations. Other small SO_x sources include residential, commercial, institutional heating furnaces and mobile sources.

1.4.2. Effects of NO_x

1. The high temperature oxidation reactions involve the conversion of atmospheric nitrogen (N₂) to NO and NO₂ in portions of the burner flame having temperatures exceeding 1400 °C and high localized oxygen concentrations. Predominantly among these oxides NO and NO₂ were released in to the atmosphere at significant amount.
2. NO and NO₂ were emitted from high temperature combustion, and are also produced during thunderstorms by electric discharge. Being heavier than air NO₂ is readily soluble in water forming nitric acid (HNO₃) or nitrogen dioxide.
3. They can be seen as a brown haze dome above or a plume downwind of cities. One of the most prominent air pollutants, this reddish-brown toxic gas has a characteristic sharp, biting odor. These two gases have significant role in the formation of photo chemical smog and acid rain.
4. NO_x reacts with ammonia, moisture, and other compounds to form nitric acid vapor and related particles.
5. In presence of sunlight NO_x reacts with volatile organic compounds to form Ozone. Ozone is destroyed by NO_x in the stratosphere and which leads to ozone layer depletion. This is due to the rapid photo chemically initiated reactions and liquid phase reactions (clouds and fog droplets) that result in the conversion of nitrogen oxides to secondary reaction products. In fact, NO₂ is the main chemical compound responsible for the absorption of the ultraviolet light responsible for driving photochemical reactions.

6. NO_x emissions are formed by three complex chemical processes during combustion via, thermal fixation of molecular nitrogen oxidation of organically bound nitrogen contained in the fuel, and formation of NO_x due to the presence of partially oxidized organic species present within the flame. These three separate reaction mechanisms are usually referenced to as: thermal, fuel, and prompt NO_x.
7. More than 20 million tons of NO_x are emitted into the atmosphere each year as a result of burning fossil fuels (EPA, 1996). These emissions can create local ambient levels that are 10 to 100 times greater than the NO_x emitted by natural sources (EPA, 1996).
8. Controlling NO_x is important because of their involvement in the formation of ozone and other photochemical smog compounds that have harmful effects on public health.

1.5. Abatement of SO₂ and NO_x

There are numerous control technologies and environmental prediction strategies available to reduce these air pollutants. Commonly used air pollution control devices can either destroy contaminants or remove them from an exhaust stream before it is emitted into the atmosphere. At its most basic level land use planning is likely to involve zoning and transport infrastructure planning. In most developed countries, land use planning is an important part of social policy, ensuring that land is used efficiently for the benefit of the wider economy and population as well as to protect the environment. Desulfurization and de-nitrification removes elemental sulphur and

nitrogen and its compounds from solids, liquids, and gases. Several studies have been carried out for the individual removal of NO and SO₂ in wet and dry processes.

1.5.1. NO_x reduction technologies

In the past, NO_x control efforts have focused primarily on combustion system modifications that limit the formation of emissions. These design modifications have been very successful for many sources, such as gas turbines and gas-and oil-fired boilers. There has also been an increased need for add-on NO_x controls for certain types of sources. Accordingly, a variety of add-on control devices and systems have been developed for use in addition to combustion system modifications. It is apparent that utility and industrial combustion systems are very important sources of NO_x. Control techniques have been developed primarily for this broad category of sources. Some basic information concerning the characteristics of these sources and discussions concerning NO_x control techniques are given as pulverized coal-fired boilers, oil and gas-fired boilers, gas turbines, municipal waste incinerators, coal and wood-fired spreader stoker boilers. Emission of these gases into the atmosphere as air pollution can be significant. Thus, numerous researches were carried out regarding the aspect NO_x controlling technologies. Whereas NO is the major contributor in NO_x (90-95 %) many researchers studied the effective removal of NO. Low NO_x burners, selective catalytic reduction (SCR), selective non-catalytic reduction (SNCR), NO_x scrubbers, exhaust gas recirculation and catalytic converter were some of the successful technologies for NO_x reduction in literature. Ozonized catalysts with nanostructured cerium and titanium mixed oxides (Ding et al., 2016), use of Cu-precursors as selective catalysts (Kang and

Choi, 2016), TiO₂/graphene as photo catalyst (Trapalis et al., 2016) , Ag-C₃N₄ photo catalysis by Ag nanoparticles decoration (Sun et al., 2015) and VO_x species supported on TiO₂ catalyst (Gallastegi-Villa., 2015) were some of the recent catalysts used for selective catalytic reduction (SCR) in dry process for removal of NO. Wet process in recent studies had done by using some specialized absorption equipment of capillary pneumatic nebulizer expanded with graphite demister (Li et al., 2014) and process intensification in manufacture of nitric acid with enriched and pure oxygen (Kakani et al., 2015) for NO_x absorption. In case of SO₂ removal, absorption is the most successful technique carried out by researchers.

1.5.2. SO₂ reduction technologies

There are several individual techniques which are successful in the process of removal of elemental sulphur. The major contributors were carried out in wet and dry basis. Wet scrubbers, dry scrubbers and flue gas desulphurization, catalytic and non-catalytic techniques are the important techniques opted for SO₂ reduction. SO₂ absorption with use of fulvic acid solution (Yang et al., 2016), peroxy-di-sulfuric acid oxidant in electro-scrubbing process (Balaji et al., 2015) amino acid salt aqueous solutions such as sodium-lysinate and sodium-glycinate (Rahmani et al., 2015) are some of the recent wet process as for SO₂ removal available in literature. Mn-based activated carbon catalysts (Qu et al., 2013), γ -Al₂O₃, Pt/-Al₂O₃ based adsorption (Hamzehlouyan et al., 2016), Low-temperature SCR activity of Ce-modified V₂O₅-WO₃/TiO₂ catalyst (Ma et al., 2015) are the recent dry processes available in literature for SO₂ removal. Mondal et al.

(2013) successfully studied the solubility of SO_2 with use of sodium citrate/sodium hydroxide blend for absorption of SO_2 .

1.5.3. Simultaneous removal of SO_2 and NO

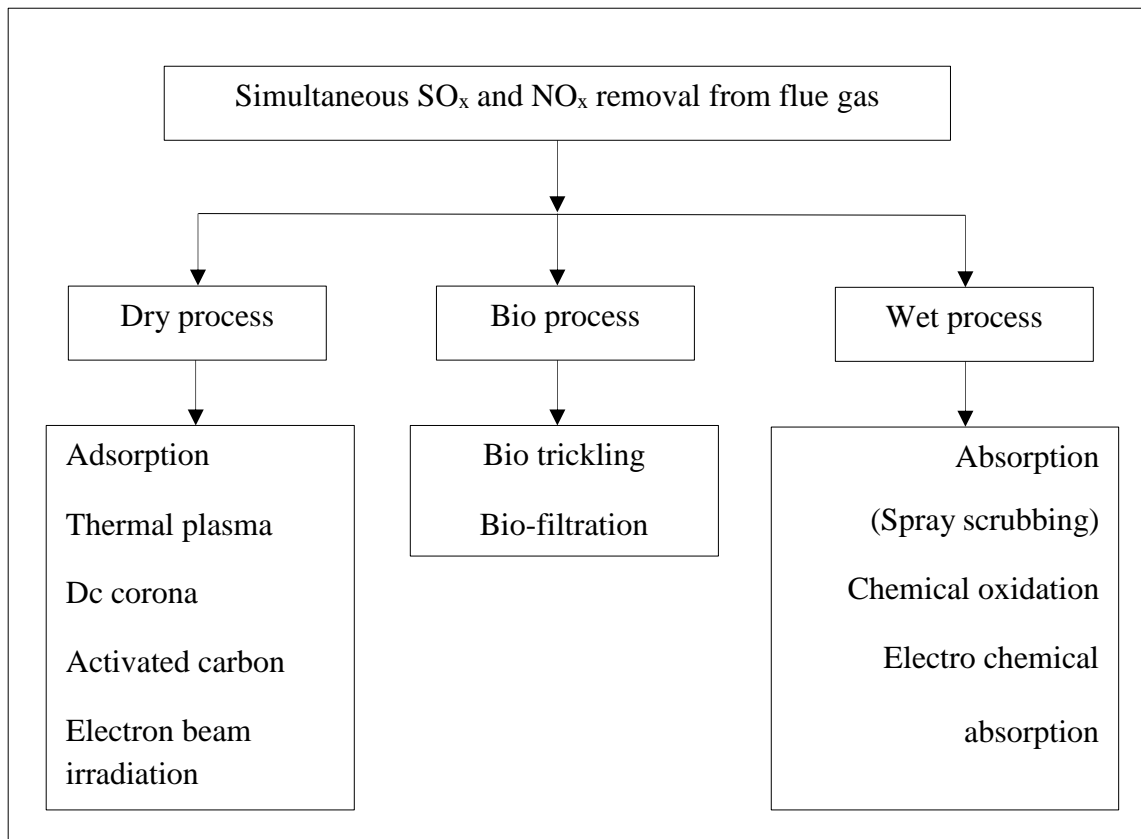


Figure 1.5. Classification of the process

Individual treatment of SO_2 and NO_x by these technologies lead to escalated investment and operating costs. In consideration of cost and area occupancy we have a responsibility to develop a pre-treatment process of these gases simultaneously implementing the process to the industrial scale. The simultaneous removal of NO and

SO₂ is an emerging process for flue gas cleaning up in coal fired, oil fired power plants and related chemical industries. Wet, dry and bio treatment technologies were the leading contributions during the co-capture of SO₂ and NO_x.

Simultaneous desulfurization and de-nitrification is most revolutionary technology for reduction of major pollutant emitted from stack gases SO₂ and NO_x respectively which leads to increasing the investment and operating costs. During these reduction processes, major contributions were carried out in wet, dry, bio treatment processes. Although many researches have been carried out regarding this aspect of simultaneous desulfurization and de-nitrification, wet processes with the use of sorbent have a leading role due to cost effectiveness and optimistic in percentage yield of removal. Whereas bio treatment processes will be considered as one of the emerging technologies in spite of being slow. Absorption, adsorption, chemical oxidation, fluidized catalytic reduction, membrane processes, selective catalytic and non-selective reduction, radiation, electrochemical processes, fluidized bed combustion, nanotube operations, thermal and non-thermal plasma are the effective separation operations for these processes. A simple classification of the available processes is presented in Figure 1.5. Some of the technologies were classified in both processes, like flue gas desulfurization (FGD) involves wet or dry scrubbing with calcium-compounds such as lime, limestone, or slurries of these solids, which are injected in the high-temperature boiler gases. A brief discussion of the available processes is given below.

1.5.3.1. Dry process

In the past few years, approaches for the instantaneous removal of NO_x and SO₂ have been receiving exceptional attention and numerous technologies have been investigated, maximum of them are laboratory scale dry process. The extensively used reducing approaches are FGD and SCR. Several non-regenerable sorbents have also been considered for SO₂ and NO_x removal, such as KOH-impregnated activated carbon (Lee et al., 2003), calcium magnesium acetate (Tokunag et al., 1985) which retains SO₂ and reduces NO_x, limestone-urea/ammonia (Wang et al., 1995), FeO/CuO (Gao et al., 1996), Na- γ -alumina powder (Wilde and Marin 2000) and so on. Several attempts such as non-thermal plasma technology, electron beam irradiation technology and adsorption technology were done to remove SO₂ and NO_x simultaneously, but only few commercial applications are noticed (Mok and Lee 2006). Activated carbon and activated coke act simultaneously as an adsorbent and catalyst at low temperatures (Qiang et al., 2005). The literature shows that CuO/Al₂O₃-based catalysts (Xie et al., 2004; Jeong and Dim 2000) and activated carbon-based catalysts (Lee et al., 2003; Wang et al., 2004) were actively efficient for simultaneous removal of these toxic gases. The activated carbon-based studies (Zhu et al., 2001; Wang et al., 2004) showed a favorable future to remove SO_x and NO_x instantaneously however these experiments were done at elevated temperatures (300°C and above). V₂O₅ is believed capable of improving CuO dispersion on activated carbon and Al₂O₃, therefore used broadly as a catalytic component of carbon and Al₂O₃-based catalysts for SCR of NO/SO₂ removal (Liu et al., 2009). Biomass based activated carbon i.e. palm shell activated carbon (PSAC) (Sumathi et al., 2010) which has also reported the sorption characteristics to

remove SO₂ and NO_x. Numerous studies reported the usage of metal oxides for SO₂ and NO_x removal. Some of the studies considered the collective removal of both SO₂ and NO_x in a dual bed of calcium-containing pellets and potassium-containing coal-pellets (Bueno-Lo'pez and Garcí'a-Garcí'a, 2005). Apart from these, the instantaneous removal of SO₂ and NO_x at lower temperature, are selected moderately because flue gas temperature at stack burners range at lower temperature, i.e. from 120 to 250°C. The major contributions are carried out in wet processes were adsorption, thermal plasma, ozone injection, advance oxidation, dc corona, activated carbon and electron beam irradiation.

Adsorption

Adsorption is the capability of an adsorbent to attract molecules of gases through a film of the adsorbate on the surface of the adsorbent. Adsorption majorly includes all dry processes mentioned above. The major steps in this process are preparation of active adsorbents, followed by the passage of the gas stream through the adsorbent and finally the results are characterized with different techniques X-ray diffraction (XRD), Brunauer-Emmett-Teller method (BET), X-ray photoelectron spectroscopy (XPS), transmission electron microscope (TEM), scanning electron microscope (SEM) and temperature programmed desorption (TPD). These results are compared as the pre- and post-adsorbent characteristics. The mechanisms of adsorption of SO₂ and NO by activated carbon fibers (ACFs) have been commonly investigated (Guo et al., 2015; Li et al., 2016) however maximum of them are simulated feed streams. Rare studies have been carried out in the adsorption process in real complex flue gas from sources. Major types of ACFs in their origin states and after pretreatment with HNO₃, NaOH, and KOH

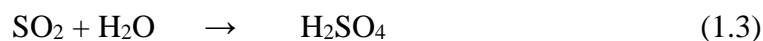
(Lee et al., 2003) were investigated. The removal efficiencies of SO₂ and NO were determined experimentally at designated SO₂ and NO concentrations, at temperature ranges between of 150 - 260 °C. Biomass from AC and impregnated AC's are new addition in the field of adsorption for simultaneous removal of SO₂ and NO_x. The catalytic techniques were also considered in adsorption process. (Tang et al., 2017; Zhou et al., 2016; Xie et al., 2016).

Irradiation with an electron beam

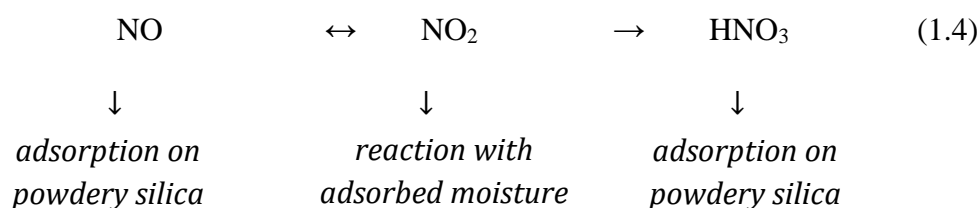
Irradiation with an electron beam was a technique for eliminating NO_x and SO₂ from stack gases in industries like chemical plants, power stations and steel plants. In this treatment, the irradiation renovates NO_x and SO_x to aerosols and are further accumulated by an electrostatic precipitator (ESP); the method is a capable technique for instantaneous removal of NO_x and SO₂ from stack gases (Tokunag et al., 1985). This process is accomplished without catalysts and it can transform heavy oil combustion gases NO_x and SO₂ into aerosol which is removable by an ESP. (Kawamura et al., 1977). During the analysis, a linear correlation occurs between p/q and P for both NO_x and SO₂. Where p/q is the ratio of NO_x or SO₂ concentration in gas phase at equilibrium (p) to the amount of NO_x or SO₂ adsorbed on powdery silica (q). This signifies that the adsorption isotherms of NO_x and SO₂ can be denoted by the resulting equation (1.2) of Langmuir:

$$\frac{p}{q} = \frac{1}{ab} + \frac{p}{b} \quad (1.2)$$

Here 'a' is constant, and 'b' indicates the saturated quantity of NO_x (or SO₂) adsorbed on powdery silica, respectively. The adsorbed SO₂ might react with moisture which is adsorbed on the surface of powdery silica as the following equation (1.3).



The pathway of NO removal in the irradiation of the blend with powdery silica can be represented in equation (1.4):



Catalytic process

Catalytic processes accomplish the use of unique catalysts which effectively destroys NO and SO₂ using effective material such as zeolitic materials and activated carbon. As discussed above the catalytic techniques are also considered in the adsorption process. Here nitrogen oxides are removed most efficiently by SCR technology with 80 to 95% removal efficiency. Modern improvements in SCR involve copper-based zeolitic catalyst (CuZSM-5) and iron-supported zeolitic catalyst (FeZSM-5) involving nanoparticles to accelerate reactions among NO and NH₃ with oxygen existence (Feng & Hall 1996; Lyon 1987) and some of the catalysts were graphene based (Tang et al., 2017). A well-known technique in catalytic process is using activated carbon (Guo et al., 2015; Li et al., 2016), as some techniques consider the base for V₂O₅ catalyst which can be fitted into the boiler technology making the supplement of a multi pollutant control system (Jianrong et al., 2008). In this system a two-stage reactor is used where the SO₂ removal occurs on the activated carbon in the early stage of the reactor and the

NO reacting with NH_3 to produce N_2 in the next stage. These reactions carried out were at a low temperature of $150\text{ }^\circ\text{C}$ results only a sensible removal of SO_2 and NO from the flue gas. The V_2O_5 / activated carbon honeycomb (ACH) catalyst was studied for simultaneous SO_2 and NO removal between temperatures $150\text{--}250\text{ }^\circ\text{C}$ as the NO removal was supported at higher temperatures, while the SO_2 reduction was finest at lower temperatures (Nimmo et al., 2004; Ighigeanu et al., 2004). Even though there are some catalysts such as Ce/TiO_2 (Zhou et al., 2016), made successful attempts for SO_2 and NO absorption at low temperatures.

Thermal plasma

Another revolutionary technic in dry process non-thermal plasma, has been considered as a capable technology for flue gas treatment, ensuring high efficiency and multicomponent-pollution control, which has been significantly examined for instantaneous SO_2 and NO removal. The basic nature of non-thermal plasma is that the gas temperature is considerably lesser than that of the electron temperature. High energetic electrons stimulate molecule excitation, ionization and dissociation, with the attachment of lower energy electrons form negative ions in the discharge area simultaneously. Here the secondary plasma reactions were initiated by dissociated molecules, radicals and ions by radical–molecule reactions. Surface reaction occurs with generated aerosol particle. The surface reaction increases with the increase in aerosol particle density so that the addition of alkaline compounds will enhance the removal of pollutants. Electron beam and electrical discharge induced non-thermal plasma (Ighigeanu et al., 2004), wet scrubbing combined with thermal plasma (Park et al.,

2015), pulsed corona discharge plasma and additives (Onda et al., 1997), non-thermal plasma (Yu et al., 2007) and a non-thermal plasma hybrid reactor using NiO/TiO₂, V₂O₅/TiO₂, TiO₂ as catalysts (Kim et al., 2007), TiO₂ thin film coated by PCVD process (Nasonova et al., 2010), TiO₂ coating on zeolite particles (Nasonova and Kim, 2013) are some of the recent technologies using thermal plasma adapted for simultaneous removal SO₂ and NO.

Carbon nanotube based support

Carbon nanotube (CNT) based support of SCR for SO₂ and NO simultaneous removal has been considered as an effective technology. The sole one-dimensional tubular structure and unique surface make CNT an attractive substrate for numerous applications in catalysis. CNT has stable structures and are resistant to burning, thus predictable to exhibit better properties in the SCR reaction. The uniform structures and clear surfaces of CNTs might be beneficial for empathizing the catalytic functions of carbons. Addition of V₂O₅ (Huang et al., 2007; Bai et al., 2010), TiO₂ (Ma et al., 2013) and doped Cu on TiO₂ (Liu et al., 2014) to the CNT will create a SO₂ and NO reduction catalyst. With this CNT based catalyst the experiments are carried out at effective temperature range 70–190 °C which shows efficient results for SO₂ and NO removal. Here the conversion range increases with increase in temperature. The increase in concentrations of additives such as Cu, V₂O₅, and TiO₂ improves the conversion of SO₂ and NO. The geometry and loading also plays a characteristic role in investigation in the effect of SO₂, H₂O, NO and mechanical properties.

1.5.3.2. Wet process

In wet scrubbing, the gases are repeatedly scrubbed in a column whereas the aqueous phase is circulated continuously in counter-current or co-current operation. The wet scrubbing treatment is concerned with absorption of the gaseous species into the liquid phase endorsed by rapid, irreversible chemical reaction in the liquid phase. Further this gas absorption in the liquid solution is facilitated by the large surface area in the column to provide large gas/liquid interfacial area for larger mass transfer. Thus, numerous varieties of wet scrubbers are in use, among these the most important scrubbers are spray column, packed column, plate column, impingement type scrubber, multi-stage bubble column, multi-jet column and the venturi-scrubbers have been developed to accomplish the combined removal of NO_x and SO₂ from combustion flue gases utilizing strong oxidants.

Several successful sorbents were introduced in this wet scrubbing technology. Some of them independently remove these toxic gases and preferred researchers have proceeded for mixture of gases to obtain optimal results. Absorption using KMnO₄ based solutions such as KMnO₄/NH₃ (Pan et al., 2015), Urea/KMnO₄ (Fang et al., 2013), KMnO₄/NaOH (Chu et al., 2001), absorption using sodium humate solution (Hu et al., 2010), absorption using NaClO₂ based solutions in batch (Chien and Chu 2000), spray (Chien et al., 2003), packed (Chen et al., 2005), wetted wall column (Lee et al., 2005), NaClO₂ scrubbing with use of electro static precipitator (Park et al., 2015), absorption with use of blends such as NaClO₂/Urea (Wei et al., 2009), NaClO/NaClO₂ (Zhao et al., 2010), advanced oxidation with use of UV/H₂O₂ (Liu et al., 2010), iron based sorbents such as Fe(II) EDTA (Wang et al., 2007), ferrate (VI) (Zhao et al., 2014), wet scrubbing

with urea (Fang et al., 2011), ClO_2 (Jin et al., 2006), per acids (Littlejohn and Chang 1990), metal chelates (Harriott et al., 1993; Xu and Chang 2007), chloric acid (Kaczur 1996), hexamine cobalt (II)/iodide (Long et al., 2005), and etc. were the available literature in wet process of removal of SO_2 and NO . A maximum wet removal method described in the literature considered together an oxidizing agent and an essential reagent initially oxidize NO to NO_2 and then to neutralizes the acids formed by NO_2 dissolution. Several strong oxidizing agents are added into removal process to obtain the convincing NO removal efficiency as that of SO_2 in wet process. Ozone has showed to be an effective gas phase oxidant with advantages of selectivity, high oxidation efficiency, fast oxidation speed and nonpolluting decomposition products, etc.

Absorption

Absorption is a process in which gaseous molecules enter bulk liquid phase due to physico-chemical reactions. Absorption is the most effective technique for simultaneous desulfurization and denitrification. Wet process, advanced oxidation, absorption oxidation, chemical oxidation, electrochemical process, irradiative electron beam are the major techniques employed for simultaneous desulfurization and denitrification with use of absorption. Several practical methods for re eliminating SO_2 and NO_x from exhaust gases with the use of absorption are presently operating all over the world. $\text{FeSO}_4/\text{H}_2\text{SO}_4$, $\text{KMnO}_4/\text{NaOH}$, Fe(II)EDTA , Na_2SO_3 , $\text{FeSO}_4/\text{Na}_2\text{SO}_3$, H_2O_2 , urea, per acids, metal chelates, chloric acid, $\text{KMnO}_4/\text{NaOH}$, hexamine cobalt (II)/iodide, ClO_2 and NaClO_2 , with NaClO_2 are the absorbing agents studied for simultaneous absorption of SO_2 and NO_x .

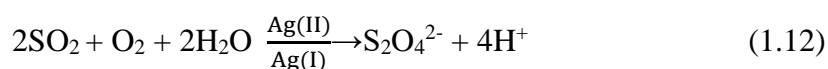
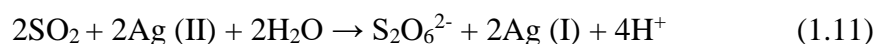
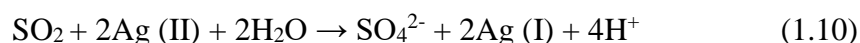
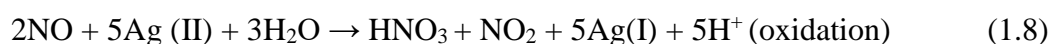
Chemical oxidation

Chemical oxidation is an approach to remove toxic gaseous pollutants using oxidation process. Absorption is the major unit process carried out in this technique. These approaches are divided into absorption–oxidation process and oxidation–absorption process. In absorption–oxidation process, liquid oxidants with strong oxidation capacity are used as absorbent, such as sodium chlorite, hydrogen peroxide, potassium permanganate, Na_2SO_3 , urea and etc. Here both gases were directly subjected to liquid absorption. While oxidation–absorption process is carried out in two steps with gas phase oxidants, such as hydrogen peroxide and ozone, are injected into flue gas first to oxidize NO to NO_2 which is highly soluble in water, and then NO_2 and SO_2 can be removed simultaneously by wet removal process. Here initial process was a dry process and the next process was wet oxidation. Major contribution carried out for this technique was using ozone as an initial oxidant.

Electro chemical absorption

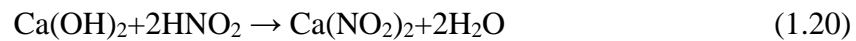
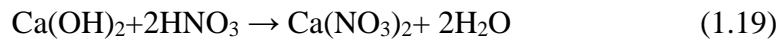
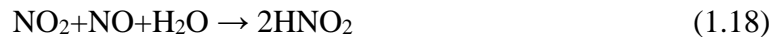
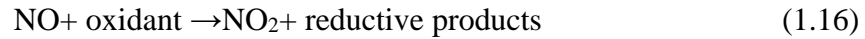
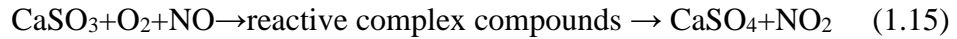
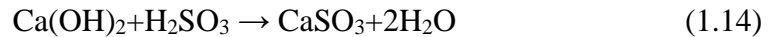
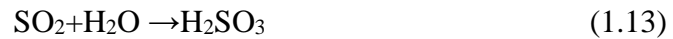
An immersive attention has been dedicated to electrochemical methods in recent years as a potential option (Pillai et al., 2009) which could prevent the problems related to chemical absorption. Mediated electrochemical oxidation (MEO) process is an emerging electrochemical technique fit for the NO_x and SO_2 removal from industrial exhaust gases. It is incorporated with use of metal ion based redox systems, identical to Ag(II)/Ag(I) , Ce(IV)/Ce(III) , Co(III)/Co(II) , Mn(III)/Mn(II) , produced in an electrochemical cell and equipped to a scrubber column in a closed loop for thorough mineralization of pollutants in a shorter duration of time. The MEO based treatment has also been extended for flue gas abatement (Hoffmann et al., 1997). The absorption

equations during this process for oxidation of NO, NO₂ and SO₂ in the scrubber solution by Ag (II) (Pillai et al., 2009) are given below:



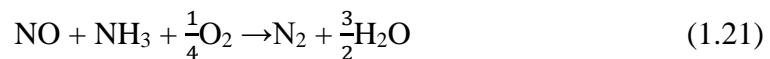
Fluidized bed reduction

Fluidized bed approaches make use of circulating fluidized bed (CFB) (Zhao et al., 2007) and fluidized-bed combustors to remove NO and SO₂. Nitrogen oxides are removed efficiently by catalytic reduction with an efficiency of 60 to 70% whereas sulphur oxides are also removed most successfully with an efficiency of 80 to 95%. Reducing agents like lime slurry and NH₃ were used for this technology. The key point for simultaneous SO₂ and NO removal technique in CFB is to convert NO into NO₂ rapidly in the exhaust gases. The reaction mechanism (Zhao et al., 2007) in flue gas CFB can be deduced as follows for lime slurry:



Reduction in NO by ammonia is completed via a complex radical chain reaction.

However, the overall reaction can be written as:



Under favorable conditions, oxidation of NH₃ to NO can also occur by the following equation (1.22)

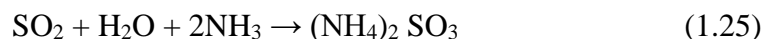
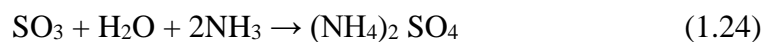


The reduction reaction proceeds in the existence of oxygen over a temperature range of 827–1127 °C. At temperatures, less than 830 °C, the reaction rate for both cases is very low (Dean 1985).

Decomposition of SO_x by ammonia

Lucas and Brown (1983) NH₃ injection does not affect SO₂ and SO₃ emissions, whereas some researchers (Zhao et al., 2007; Shale 1971) reported that ammonia reacts with SO₂ and SO₃ to form either ammonia sulphite and ammonium sulphate or ammonium bisulphate and ammonium bisulphate via equations (1.23) to (1.26) given below:





1.5.3.3. Bio process

Implementation of bio treatment processes will be considered as one of the emerging technologies in spite of being slow for simultaneous desulfurization and denitrification. Regarding this process natural adsorbents and absorbents are used for reduction of SO₂ and NO_x. Bio processes can be adaptable for both wet and dry process. It can be considered as natural treatment which efficiently removes both these toxic gases. The requirements used in bio process are bio scrubber, bio filter and bio trickling. Some of the findings clearly indicate that absorbents are prepared from waste oyster shells can be considered as substitutes for limestone and applied directly to industries endeavoring to reduce the emissions of SO₂ and NO_x (Jung et al., 2007). Activated carbon based natural adsorbents are also used in bio treatment such as PSAC made from oil palm fruit waste (Sumathi et al., 2010a, b). Recent studies have been carried out in bio process using bio trickling towers to study the effect of oxygen (Wang et al., 2015) in simultaneous removal of SO₂ and NO. This process has obtained efficient results in terms of removal efficiency.

1.6. Technical difficulties of various processes

Although the approach using chemical oxidants has been showing good results for many years, there are certain drawbacks in the wet scrubbing utilizing various chemicals. The scrubbing processes concern the fact that the processes require

continuous usage of large amounts of expensive oxidizing agents. In addition, it also presents special disposal problem because of the high concentration of the spent scrubbing solution. Solid circulation and the loss of sorbent during regenerative fluidized bed are major drawbacks of the rapid process. Performance of the SCR largely decreases as the temperature decreases. SCR combined with non-thermal plasma process may not be applicable to the exhaust gases containing both SO₂ and NO_x, because coexisting SO₂ and ammonium salts formed during the treatment can ultimately deactivate the catalyst. Catalysts are severely poisoned by H₂O and SO₂. When the reacting temperature is higher than 200 °C, SO₂ improves the SCR activity, while it is lower than 200 °C; SO₂ deactivates the V₂O₅/CNT catalysts. In addition, chemical complication techniques, which uses ferrous chelating agents for simultaneous removal of NO and SO₂ have the disadvantage of being irreversibly poisoned by oxygen. Strong oxidizing agents can improve NO_x removal efficiency but there are certain drawbacks, such as high cost of oxidizing agents, disposal problems of absorption solution, high water usage, undesirable products (e.g., nitrites, nitrates, chlorides), and variable SO₂ removal. Wet scrubbers also include corrosion.

1.7. Origin of the problem

Absorption, adsorption, chemical oxidation, electrochemical processes, fluidized bed combustion and nanotube operations are the leading separation options in recent years for simultaneous removal of SO₂ and NO. Removal efficiency of the pollutants is the major parameter focused by researchers. As the dry and bio processes have proven themselves as emerging techniques for this simultaneous removal, wet process will help

in commercializing it from industrial point of view and reduce the operating cost. Numerous successful sorbents were introduced in wet scrubbing technology to remove these toxic gases to obtain optimum results. Recently, considerable attention has been focused on simultaneous removal of SO₂ and NO_x in the single reactor considering the capital investment operating cost and space for equipment. Space and cost limitations require techniques capable of removing NO and SO₂ simultaneously which is a commercial implementation of individual desulfurization and denitrification. A minor adjustment of individual desulfurization and denitrification may provide sufficient removal efficiency for simultaneous SO_x/NO_x removal system. Absorbing agents currently used can remove SO₂ effectively, so research will be concentrated on NO_x removal efficiency. All these wet processes have done tremendous job in terms of removal efficiency but the disposal of spent absorbent is still a problem. Hence the treatment of SO₂ and NO using wet absorption process in a single absorption was concentrated to produce valuable products as they may be treated as fertilizers.

1.8. Objective of the present work

Among the various technologies for simultaneous removal of SO₂ and NO from the gas stream, wet scrubbing with use of the absorbent has shown a leading role due to its cost effectiveness and optimistic results. The objective of the present work aimed to evaluate efficient removal of simultaneous absorption SO₂ and NO from simulated gas stream by using semi-batch and continuous mode of operation. To achieve this, the research work was predicted and analyzed with the following problems:

1. To study the effect of operating parameters (initial SO₂ and NO concentrations, absorbent concentration, temperature, initial pH, etc.) in a semi batch column on feasibility of the absorbents, NaClO, Ca(OCl)₂ and NaClO/NaOH for combined removal of SO₂ and NO,
2. To select suitable absorbent for combined removal of SO₂ and NO,
3. To see the kinetics and thermodynamics of the process over best suitable absorbent,
4. To study the combined SO₂ and NO removal efficiencies for the continuous spray column,
5. To study the effect of additives NaOH and NH₃ in the suitable absorbent for combined SO₂ and NO removal efficiencies for environmental solution.