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AIR POLLUTION CAUSED BY INDUSTRIES

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Summary

Our activities affect the environment and. the environment affects our health. As the number of humans on earth increases, our agricultural and industrial activities have a greater impact on the environment, particularly on the atmosphere. As our most precious resource, the atmosphere has been polluted, so it is imperative to take measures to control air pollution. It becomes necessary to know what the sources have been and how they operate. In this chapter, we first introduce five main air pollutants: carbon monoxide (CO), hydrocarbons, particulate, oxides of sulfur (SO_x), and oxides of nitrogen (NO_x). We then present the industrial emissions inventory. Finally, we analyze the character of air emissions from five main industrial sectors that are combustion sources: the petroleum industry, chemical industry, metallurgical industry, construction material industry, and paper and pulp manufacturing. The emission factors are based on the present processes. With the innovation of processes and the implementation of clean production, the factors will decrease gradually.

1. Introduction

Before we examine air pollution from industries, we need to understand the natural conditions and constituents of the atmosphere. The atmosphere, or air, is normally composed of about 79 percent nitrogen, 20 percent oxygen, and 1 percent mixture of carbon dioxide, water vapor, and small quantities of several gases. A list of these contents is given in Table 1 along with their average concentrations and approximate residence time. Based primarily on temperature, the atmosphere is divided into four layers: (I) *Troposphere* is the layer between the ground and a height of approximately 15km at the equator and 10 km at the poles. In the troposphere, the temperature

typically decreases at the rate of 6.5°C/km, the air is relatively well mixed, and thermally driven convection is relatively strong. The troposphere is the layer that contains most of our air pollutants (II) *Stratosphere* is the layer between the troposphere and approximately 50km. There is little bulk mixing in this layer. The temperature is relatively constant except in the upper stratosphere, where the absorption of UV radiation by ozone causes the temperature to rise to approximately 0 °C. (III) *Mesosphere* is the layer between 50 and 85 km within which the temperature decreases almost linearly to approximately 175K. (IV) *Thermosphere* is the uppermost layer of the atmosphere. The temperature increases to approximately 1500K, but it cannot be measured with a thermometer because the molecular concentrations are very small--about 10^{13} molecules/cm³ by comparison to the molecular concentration of 2.5×10^{19} molecules/cm³ at the earth's surface (Table 1).

Pollution, as we discussed in the former chapter, is something produced by human beings that interferes with our well being. There are several natural sources that degrade the quality of the air, such as gases and particles from volcanoes, dust from natural sources or odors from decomposition of dead plants and animals. However, human beings do not control these phenomena, and they do not fit our definition of pollution. We will focus on the air pollutants from automobile emissions, chemical odors and factory smoke and their controls.

2. Main air Pollutants and Industrial Emissions Inventory

2.1 Major Air Pollutants

Air pollutants can be divided into two main groups—particulate and gaseous. The former group includes solid airborne particulates such as dust, fly ash, smoke, fog, soot, and fumes. Gaseous pollutants include carbon monoxide, hydrocarbon, oxides of sulfur, and oxides of nitrogen. These pollutants are known as primary air pollutants (see Table 2). These materials may interact with one another in the presence of an energy source to form new secondary air pollutants such as ozone and other very reactive materials. Secondary air pollutants also form from reactions with natural chemicals in the atmosphere.

Species	Average concentration /ppm	Approximate residence time	Species	Average concentration /ppm	Approximate residence time
Major species		10 ⁶ yr	Trace species		
N ₂	780840	10yr	CO ₂	350	15yr
O ₂	209460		CH ₄	1.72	10yr
H ₂ O	Variable		H ₂	0.58	10yr
Inter gases			N ₂ O	0.33	150yr
Ar	9340		CO	0.05-0.2	65days
Ne	18		NH ₃	0.01	20days
He	5.2		NO/NO ₂	0.00004-0.001	1 day
Kr	1.1		O ₃	0.02-0.05	
Xe	0.09		H ₂ O ₂	0.001	
Sulfur			HNO ₃	0.001-0.0001	

compounds			HC	0.001-050	
SO ₂		40 days	CFC11	0.003	65yr
CS ₂	0.0002	>1.8 × 105h			
H ₂ S	0.00001-0.0002	53h			
Free radicals					
OH.	1-10×10 ⁶ mol./cm ³				
HO ₂ .	1×10 ⁹ mol./cm ³				

Source: Seinfeld (1986)

Table1: Composition of Atmosphere

Pollutants	Sources
Carbon monoxide(CO)	Incomplete burning of fossil fuels Tobacco smoke
Hydrogen Carbon	Incomplete burning of fossil fuels Tobacco smoke, Chemical processes
Particulate	Burning fossil fuels, Construction operations Industrial waste
Oxide of sulfur (SO _x)	Burning fossil fuels, Chemical processes Smelting ores
Oxide of nitrogen(NO _x)	Burning fossil fuels, Oxide of N ₂ in atmosphere

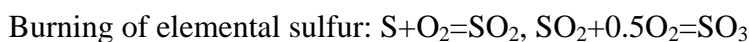
Table 2: Sources of primary air pollutants

The quality of sulfur dioxide emission from both natural sources and man-made sources shows in Table 3.

Source	Discharging quantity	Source	Discharging quantity
Man-made	103.8	Natural source	147
Coal burning	62	Marine	94
Petroleum burning	25.5	Land	48
Petroleum refinery	3.7	Volcano	5
Metallurgy	10.7	Total	250.8
Other industry	1.9		

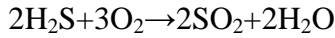
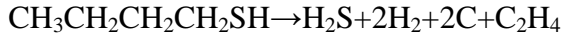
Table 3: Sulfur dioxide discharge 106t/a

Oxides of Sulfur (SO_x): Oxides of sulfur (SO_x) are compounds of sulfur and oxygen that are mostly produced when sulfur-containing fossil fuels are burned. Coal and oil were produced from organisms that had sulfur in their living structure. When the coal or oil was formed, some of the sulfur was incorporated into the fossil fuel. The sulfur is released as sulfur oxide when the fuel is burned. Simultaneously, a large quantity of sulfur oxides is released along with the exhaust gas in metallurgy and vitriol producing process. The reactions involved are as follows:



Burning of iron sulfur ore: $4\text{FeS}_2+11\text{O}_2=2\text{Fe}_2\text{O}_3+8\text{SO}_2$, $\text{SO}_2+0.5\text{O}_2=\text{SO}_3$

Burning of organic sulfur compounds:



Oxides of nitrogen (NO_x): As a category of primary air pollutants, oxides of nitrogen (NO_x) emitted from industries are a mixture of nitrogen oxide (NO) and nitrogen dioxide (NO₂). About half of NO_x, or up to 5.21×10^6 t/a, is produced by human activities such as fossil free burning, production of nitric acid and nitrogenous fertilizer, and other industrial processes. Table 4 shows the quantity of NO_x discharged estimated by Stedman (1983) and Logan (1983).

Source	Discharging quantity	
	Stedman(1983)	Logan(1983)
Natural source	65	96-126
Lighting	10	26
Stratosphere input	3	2
Oxide of NH ₃	3	3-33
Burning of biomass	16	39
Discharge of soil	33	26
Man-made sources	66	108

Table 4: NOX discharge 106t/a

There are two kinds of NO_x from fuel combustion: one is thermal NO_x, from N₂ and O₂ reaction when burned at high temperature, and the other is fuel NO_x, which is the decomposed and oxidized compounds of nitrogenous compounds in fuel such as pyridine (C₅H₅N), piperidine (C₅H₁₁N) and carbazole (C₁₂H₉N) at high temperature. Most of fuel NO_x is NO, less than 10% NO is oxidized to NO₂ in flue gas.

Carbon Monoxide (CO): Carbon monoxide is produced when organic materials, such as gasoline, coal, wood, and trash, are incompletely burned. The reactions are following:



Due to the lack of oxygen, the oxidation rate from CO to CO₂ is very slow. Improvements in combustion equipment and technology cause the discharge of CO from stationary sources to decrease gradually. Table 5 shows the contribution of CO from different sources.

Source	Discharge	Source	Discharge
Industry	300-500	Oxidization of methane	400-1000
Burning of biomass	300-700	Oxidization of other	
Activity of creature	60-160	Hydrocarbon	200-600
Discharge of sea	20-200	Total	1800-2700

Table 5: CO discharge 106t/a

Hydrocarbon (HC): Hydrocarbons are a large family of compounds, which include

most organic compounds with less than about 12 carbon atoms. They are either evaporated from fuel or are remnants of fuel that did not burn completely. Table 6 shows the contribution of hydrocarbon from different sources.

Source	Discharge	Source	Discharge
Coal	2.9	Dissolvent	10
Thermal power	0.2	Burning of rubbish	25
Industrial	0.7	Burning of lumber	0.7
Resident and commerce	2.0	Forest fire	1.2
Petroleum	48.4	Total	88.2
Petroleum refinery	6.3		
Gasoline	34		
Diesel oil	0.1		
Heavy oil	0.2		
Evaporation of oil	7.8		

Table 6: Hydrocarbon discharge 106t/a

Particulates: Particulates, small pieces of solid materials dispersed into the atmosphere, constitute the third largest category of air pollutants. Smoke particles from fires, bits of asbestos from brake linings and insulation, dust particles, and ash from industrial plants contribute to the particulate load.

2.2 Industrial Emissions Inventory

Due to the wide variety of industrial processes, reliable determinations of industrial emissions have been found to depend on individual types of treatment. This is expensive and time-consuming, as it involves detailed study and testing of specific plants and processes. In some cases, data on industrial emissions could be obtained by means of questionnaires sent to the individual plants requesting information on processes, types and quantities of process exhaust, air cleaning equipment and fuel consumption. Frequently, the industries themselves do not have on-line data of this sort. Consequently, insufficient or incomplete results can be expected. Information on air emissions can also be obtained by using engineering estimates which are based on the raw materials or fuel consumed in a given process and reported figures on types and rate of pollutants emitted per unit weight of raw material or fuel used in a particular process. Unfortunately, there does not exist a sufficient body of readily available and reliable information on process emissions derived from actual tests, so it is difficult to obtain satisfactory results. The detailed procedure for making an industrial survey involves the use of a computer card identifying each establishment and its location. A detailed questionnaire sent to each establishment to collect information, which includes data on plant size, operating schedule, fuel usage, processes, and solvent usage. This procedure may provide more reliable results.

Emission factors, which have been applied to source data to yield emission data for SO_x, NO_x, HC, CO, particulates and so on, exist for a wide variety of industrial processes such as fuel burning, chemical production, manufacturing processes, and solvent usage.

Classification of air pollution sources and emissions are showed in Table 7.

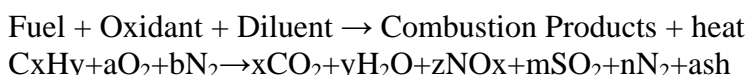
Source type	Category	Examples	Pollutants
Dust production Process	Crushing, grinding screening, demolition milling	Road mix plants Urban renewal Grain elevators	Mineral and organic particulates
Combustion	Fuel burning	Home heating unit Power plants	SO _x , NO _x , CO, smoke, fly-ash organic vapors,
	Motor vehicles	Autos, buses and trucks Community and apartment	metal oxide particles and odors
	Refuse burning	house incinerator, open burning dums	
Manufacturing processes	Metallurgical plants	Smelters, steel mills, aluminum refineries	Metal fume, fluorides SO _x
	Chemical plants	Petroleum refineries, pulp mills, super phosphate fertilizer plants, cement plants	H ₂ S, Sox, F, organic vapor, particle, odors
	Waste recovery	Metal scarp yards, auto body burning, rendering plants	Smoke, soot, organic vapor, odors
Solvent	Spray painting	Furniture and appliance finishing	Organic phosphates, chlorinated
	Inks	Photogravure and printing	hydrocarbons, As, Pb
	Solvent cleaning	Dry cleaning, degreasing	

Table 7: Classification of air pollution sources and emissions

3. Combustion Sources and their Emission Characterization

Combustion refers to the rapid oxidation of substances (usually referred to as fuels) with the evolution of heat. Most fuels are a mixture of chemical compounds referred to as hydrocarbons, such as coal, fuel oil and natural gas, which, when burned, are converted into final products of carbon dioxide and water. The reaction products of the combustion process are collectively called combustion products, and include CO₂, H₂O, CO, HC, SO₂, SO₃ and NO_x. In the case of fuels containing halides (usually chlorine and fluorine), the combustion products may contain hydrochloric or hydrofluoric acids (HCl, HF) and trace quantities of organohalides such as dioxins and furans.

In general, the combustion process can be represented by the following equation.



Most combustion systems operate with an overall excess of air to ensure complete combustion. The excess air would then function as an additional diluent, contribute to the combustion products and result in the emission of gaseous or particulate pollutants.

Based on the physical states in which they are found in nature, fuels can be classified as solid, liquid, or gaseous, with coal, fuel oil, and natural gas being the three most common examples of each. The following sections describe these three fuels and their emission characteristics.

3.1 Coal Combustion

Coal is the most readily available energy source throughout the world. While coal is important to the development of industry, it results in air pollution when burned. During combustion, the coal is subject to either or both oxidizing and reducing conditions because of the presence of oxygen, carbon, and carbon monoxide in the bed. The air pollutants from the combustion of coal include particulates, SO_x, NO_x, HC, and CO. Amounts of each are highly dependent on the type of coal, combustion process, and operation of the process. The particulates consist mostly of ash particles. They also include unburned coal blown out during the turbulent combustion. Typical pulverized coal-fired boiler flue gas contains 2-10ppm CO, 3.9-5.1% O₂, and 14.3-15.3% CO₂. Gaseous emissions of sulfur oxides in the process of coal combustion are largely SO₂ and to a much smaller extent, SO₃ and gaseous sulfates. These compounds form as the organic and pyritic sulfur in the coal is oxidized during the combustion process. On average, 98% of the sulfur present in bituminous coal will be emitted as gaseous sulfur oxides, whereas somewhat less will be emitted when sub-bituminous coal is fired. Generally, boiler size, firing configuration, and boiler operations have little effect on the percent conversion of fuel sulfur to oxides of sulfur. Nitrogen oxides are produced in the combustion process by at least two different mechanisms: one source is from the molecular nitrogen in the combustion air (thermal NO_x), the other is from the nitrogen in the fuel being burnt (fuel NO_x). Generally, the amount of nitrogen in the fuel is relatively small compared with that in the combustion air, therefore, fuel NO_x is only a small part of total NO_x. The relative contributions of these two formation pathways depend on the combustion conditions, the type of boiler, and the type of fuel being burnt. Large coal-fired boilers emit more NO_x than any other combustion source. The combustion paradox is that the size increase of boilers will increase nitric oxide but decrease CO and HC. The reverse is true. Volatile organic compounds (VOCs) and carbon monoxide (CO) are unburned gaseous combustibles that are also emitted from coal-fired boilers, but generally in quite small amounts. However, during start-up, temporary upsets, or other conditions preventing complete combustion, unburned combustible emissions may increase dramatically. The VOC and CO emissions per unit of fuel that is burned are normally lower from pulverized-coal or cyclone furnaces than from smaller stokers and hand-fired units where operating conditions are not as well controlled.

Table 8 lists the uncontrolled emission factors from the different types of furnaces discussed for particulate, SO_x, NO_x, CO, and HC.

Furnace			Uncontrolled Emission, g/kg coal				
Boiler category	Heat input 10 ⁶ kcal/hr	type	Particul atematte r ^a	SO _x ^b	CO	HC ^c	NO _x ^d
Utility or large		Pulverized	8A	19S	0.5	0.15	9

industrial	> 25	Cyclone	1A	19S	0.5	0.15	27.5
Commercial or industrial	2.5-25	Underfeed & crossfeed	2.5A	19S	1	0.5	7.5
		Overfeed	6.5A	19S	1	0.5	7.5
Small commercial or domestic	< 2.5	Overfeed	1A	19S	5	5	3.0
		Hand fired	20	19S	45	45	1.5

^aA = Weight percent ash in coal.

^bS = Weight percent sulfur in coal, pollutant weight is reported as SO₂.

^cPollutant weight is reported as CH₄.

^dPollutant weight is reported as NO₂.

Table 8: Typical Uncontrolled Emission from Coal Combustion

3.2 Oil Combustion

The most common liquid fuel used in utility processes is fuel oil derived from crude petroleum. Fuel oils are broadly classified into distillate kerosene and residual fuel oils. The former is mostly used for domestic and small commercial applications; the latter is used in utility and industrial boilers. Emissions from fuel oil combustion depend on the grade and composition of the oil, the type and size of the boiler, the firing practices used, and the level of equipment maintenance. Properly designed and operated oil-fired boilers produce less uncontrolled air pollution emission than coal-fired boilers but more than gas-fired boilers.

Boiler	Fuel oil	Uncontrolled Emissions, g/l of Fuel				
		particulate	SOx ^a	CO	HC ^b	NOx ^c
Utility or large						
Industrial	Residual	1	19.2S	0.4	0.25	0.12
Commercial or industrial	Residual	2.75	19.2S	0.5	0.35	0.12
	Distillate	1.8	17.2S	0.5	0.35	0.25
Small commercial or domestic	Distillate	1.2	17.2S	0.6	0.35	0.25

^aS = weight percent sulfur in oil; pollutant weight is reported as SO₂.

^bPollutants weight is reported as CH₄

^cPollutants weight is reported as NO₂; use one-half this value for tangentially fired boilers.

Table 9: Typical uncontrolled emission from oil combustion

Horizontal firing and tangential firing are the two basic arrangements used in oil combustion systems. The oil is directed toward the center of the furnace in a horizontally fired system resulting in a hotter flame and the formation of about twice the NOx as is formed by tangentially fired oil furnaces. Large boilers burn hotter and produce more NOx than small one. About 0.65% of sulfur dioxide converts to sulfur trioxide in an oil-fired boiler. Table 9 lists typical uncontrolled emissions for horizontally fired oil furnaces.

3.3 Gas Combustion

As the cleanest-burning fuel, gas is used for power generation, and the production of heat/steam for industry. Gas is in great demand for areas with high pollution levels. It is also the choice of an auxiliary fuel for incinerator secondary chambers. Natural gas is the most available fuel. It can be obtained at the refinery or directly from wells. In most cases it consists of almost pure methane (CH₄) with slight amounts of ethane (C₂H₆), nitrogen, helium, and carbon dioxide. It contains trace amounts of substances such as hydrogen sulfide and mercaptans. The average gross heating value varie from 8900-9800 kcal/Nm³. The density is about 7.5×10⁻⁴g/cm³ which gives a specific gravity of about 0.57 when compared to air. Another kind of gas is liquefied petroleum gas (LPG), which is a gasoline-refining byproduct and consists mainly of butane, propane, and trace a mounts of propylene and butylene. Although it is distributed as a liquid under high pressure, it reverts to a gas state when throttled and is burned as a gaseous fuel. Gaseous fuels are normally the cleanest available. The low sulfur content results in very little SO₂ emissions and the capability to be combusted at low excess air results in less NO_x formation and maximized efficiency. Typical emissions from gases-fired boilers are presented in Table 10.

Boiler	Fuel oil	Uncontrolled Emissions, g/l of Fuel				
		particulate	SO _x ^a	CO	HC ^b	NO _x ^c
Utility or large						
Industrial	Natural gas	80-240	20.9	272	16	11200-1920-
Commercial or industrial	Natural gas	80-240	20.9	272	48	3680
	Butane(LPG)	22	0.01	0.19	0.036	1.45
	Propane(LPG)	0.20	0.01	0.18	0.036	1.35
						1280-
Small commercial or domestic	Natural gas	80-240	20.9	320	128	1920
	Butane(LPG)	0.23	0.01	0.24	0.096	1.0-1.5
	Propane(LPG)	0.22	0.01	0.23	0.084	0.8-1.3

Table 10: Typical uncontrolled emission from gas combustion

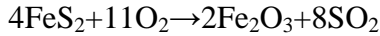
4. The Chemical Industry

The chemical industry is highly complex and its products reach every facet of modern life. Its basic raw materials have been minerals, coal, oil, natural gas, air and water. By various means, these raw materials could be converted to a wide variety of industrial products. Usually the main air pollutants in chemical industrial processes are dusts and odors. Sometime, a few specific pollutants such as SO_x, NO_x, H₂S, florides and acid mist may be produced. Where fossil fuels are used for heat and power, emissions of combustion products result.

4.1 Sulfuric Acid

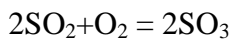
Sulfuric acid is a basic raw material in an extremely wide range of industrial processes and manufacturing operations. Because of its widespread use and relatively low production cost, sulfuric acid plants are scattered throughout the world. The production

of sulfuric acid involves the generation of sulfur dioxide (SO₂), which is obtained from pure sulfur and pyrites (iron sulfide, FeS₂), its oxidation to sulfur trioxide (SO₃), and the reaction SO₃ with water to form sulfuric acid (Figure1). In practice, the reaction of SO₃ with water is accomplished by first absorbing the SO₃ in strong sulfuric acid and then adding water. When pyrites is roasted in air, the reaction is:



When sulfur is burned, the reaction is simply: $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$

The sulfur dioxide from this oxidation process, generally in concentrations between 8 and 14% in air, is then allowed to pass over a catalyst at 450°C. Further oxidation occurs:



The sulfur trioxide is then absorbed in moderately concentrated sulfuric acid to give acid of desired commercial concentration: $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$

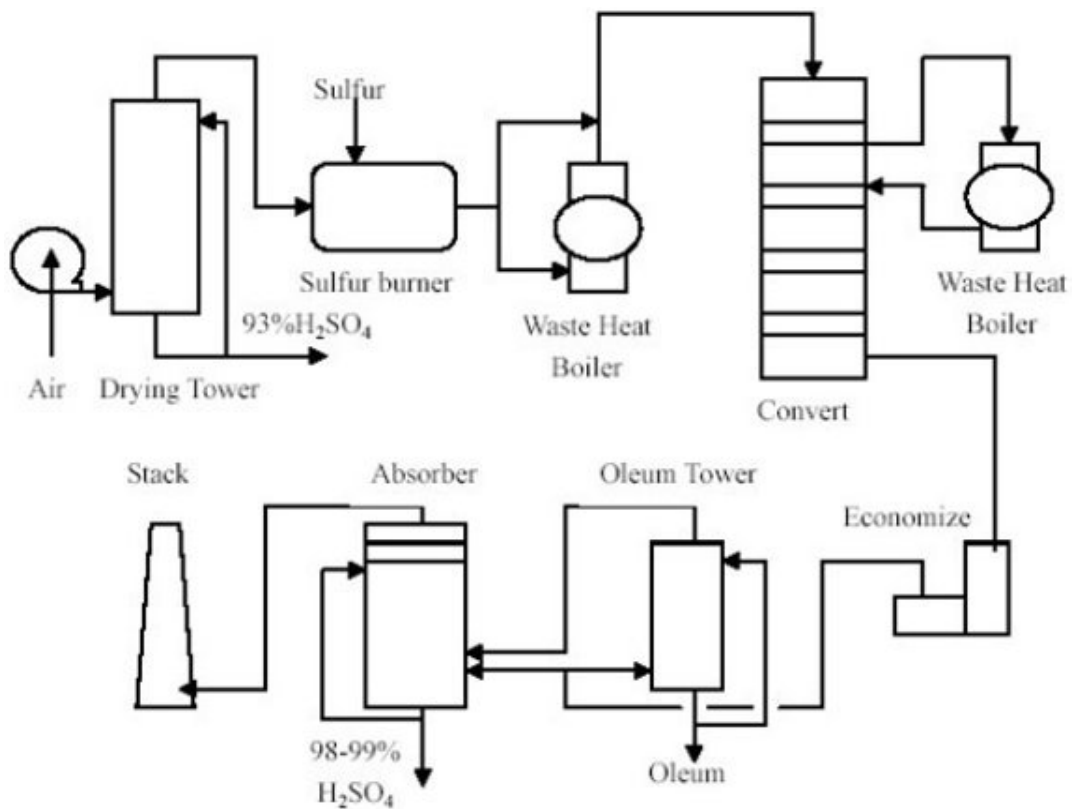


Figure 1: Flow Diagram of a Single-Absorption, Sulfur-Burning Sulfuric Acid Plant

The significant source of air pollutant emissions from a sulfuric acid plant is the tail gas leaving the final absorbing tower. The gas contains small amounts of SO₂ and even a smaller amount of SO₃, sulfuric acid mist. Producing one ton H₂SO₄, the emissions of SO₂ and sulfuric acid mist are 9~18kg and 0.377kg, respectively.

4.2 Hydrochloric Acid

The production of hydrochloric acid involves the generation of hydrogen and chlorine, which are electrolyzed from the chlorine alkali aqueous solution. Hydrogen and chlorine are mixed proportionally and burned in synthesis furnace to form chlorine hydride gas. Chlorine hydride gas is cooled and reacts with water to form hydrochloric acid. The main pollutants are chlorine hydride and chlorine, whose quantities are 1.4 and 0.9 kg per ton hydrochloric acid, respectively.

4.3 Synthetic Rubber

Two types of polymerization reaction are used to produce styrene butadiene copolymers, the emulsion type and the solution type. Volatile organic compound (VOC) emissions from the manufacture of copolymers of styrene and butadiene are made by emulsion polymerization process. Emissions factors are presented in Table 11.

Process	VOC* /g.kg ⁻¹	Process	VOC* /g.kg ⁻¹
Emulsion		Emulsion latex Monomer	
Monomer recovery, uncontrolled	2.6	removal condenser vent	8.45
Absorber vent	0.26	Blend tank uncontrolled	0.1
Blend/coagulation tank uncontrolled	0.42		
Dryers	2.51		

* Non-methane volatile organic compounds, mainly styrene and butadiene. Expressed as units per unit of copolymer produced.

Table 11: Emission factors for emulsion styrene-butadiene copolymer production

4.4 Fertilizer Manufacture

With regard to air pollution control, fertilizer manufacture is a varied industry, ranging from ammonia plants with little or no manpower allocated to air pollution control to phosphatic fertilizer plants with their highly publicized dust and fluoride problems.

Fertilizer & process	Emission Factors/ kg.t ⁻¹ product						
	NH ₃	Hg	NaOH mist	CO	HC	fluoride	clorine
Calcined Soda (Na ₂ CO ₃)	3.5						
Caustic soda (NaOH)							
Electrolysis by mercury		0.025	4.55	22.7	24.3		
Electrolysis by septum							9-45
Nitrogen fertilizer							
NH ₄ NO ₃	22.7						
(NH ₄) ₂ SO ₄	3-68						
Phosphate fertilizer						0.07	

Table 12: Emission Factors for Fertilizer Manufacture

In the manufacture of ‘superphosphate’ fertilizer, sulfuric acid is mixed with crushed phosphate rock in enclosed mixers called ‘dens’. Some of the constituents in the phosphate rock react and are emitted, the most notable air pollutants from this process being hydrogen fluoride and fluosilic acid. Emissions factors in manufacturing processes of different fertilizers are presented in Table 12.

5. Metallurgical Industry

5.1 Smelting of Non-Ferrous Ores

As a dominant industry, the metallurgical industry has made a substantial contribution to the development of the world. However, it has been responsible for the discharge of large quantities of many kinds of air pollutants from different processes such as aluminum smelting, copper smelting, metallurgical coke, lead smelting, zinc smelting, steel and iron smelting. The most concentrated sources of sulfur dioxide and particulate pollution are from the roasting of non-ferrous sulfide metal ores, the most common being copper, lead and zinc. In the smelting of non-ferrous ores, there are two stages. The first stage is the concentration of the valuable ore fractions. The second stage is the ‘roasting’ of the ore in a stream of air, which oxidizes the sulfide to the metal oxide and sulfur dioxide.

Copper smelting			Lead smelt		Zinc smelting	
Source	Particulate	SO ₂	Source	Particulate	Source	Particulate
Roaster calcine			Ore storage	0.012	Roasting	Negligible
Discharge	1.3	0.5	Ore mixing	1.13	Sinter plants	
Smelting furnace	0.2	2	Sinter machine		Wind box	0.12-0.55
Converter	2.2	65	Machine leakage	0.34	Discharge	
Converter slag			Sinter return		and screens	0.28-1.22
Return	no data	0.05	handling	4.5	Retort	
Anode furnace	0.25	0.05	Blast		building	1.0—2.0
Slag cleaning surface	4	3	Lead pouring to ladle, transferring	0.47	casting	1.26
			Slag colling	0.24		
			Zinc fuming			
			furnace vents	2.30		
			Reverberatory			
			furnace leakage	1.50		
			Silver retort	0.90		
			Lead casting	0.44		

Note: unit, kg per ton of product

Table 13: Fugitive emission factor for primary copper, lead and zinc smelters

In the *copper* smelting process, the roaster, smelting furnaces, and converters are sources of both particulate matter and sulfur oxides. Copper and iron oxides are the primary constituents of the particulate matter, but other oxides, such as arsenic, antimony, cadmium, lead, and zinc, may also be present, with metallic sulfates and sulfuric acid mist. Fuel combustion products also contribute to the particulate emissions

from multiple-hearth roasters and reverberatory furnaces. Table 13 presents the potential fugitive emission factors for these sources.

Lead is usually found naturally as a sulfide ore containing small amounts of copper, iron, zinc, and other trace elements. It is usually concentrated at the mine from an ore of 3-8% lead to a concentrate of 55-70% lead that can contain up to 30% free and uncombined sulfur. Processing involves three major steps—sintering, reduction, and refining. Each of these three processes generates substantial quantities of SO₂ and/or particulate. Nearly 85% of the sulfur present in the lead ore concentrate is eliminated in the sintering operation. In handling fugitive off-gases from the process, either a single weak stream of gases is taken from the machine hood at less than 2% SO₂, or two streams are taken, a strong stream (5-7% SO₂) from the feed end of the machine and a weak stream (less than 0.5%SO₂) from the discharge end. Particulate emissions from the sinter machine ranges from 55 to 20% of the concentrated ore feed. In terms of product weight, typical emissions are estimated to be 106.5kg/t of lead product. This value, and other particulate and SO₂ factors, are presented in Table 13.

Primary production of *zinc* is somewhat similar to primary production of copper and lead. Zinc ores are processed into metallic zinc slabs by two basic methods—the electrolytic process and a pyrometallurgical smelting process. Electrolytic processing involves four major steps: roasting, leaching, purification, and electrolysis. Pyrometallurgical processing involves three major steps: roasting (as above), sintering, and retorting. Each of the two zinc-smelting processes generates emissions at the various stages. Although the electrolytic reduction process emits less particulate than does pyrometallurgical reduction, small quantities of acid mist are generated during electrolysis that are exhausted directly to the atmosphere. Fugitive emission factors have been estimated for the zinc smelting industry and are presented in table14. These emission factors are based on similar operations in the lead and copper industries. Emission factors for point sources within a zinc smelting plant appear in Table 14.

Lead smelting			Slab zinc smelting		
Process (uncontrolled)	Particulate	Sulfur dioxide	Process	Particulate (uncontrolled)	Particulate (controlled)
Ore crushing	1.0	no data	Roasting		
Sintering	106.5	275.0	Multiple hearth	113	no data
Blast furnace	180.5	22.5	Suspension	1000	4
Reverberatory furnace			Fluidized	1083	no data
Materials handling	10.0	negligible	Sinter plant		
			Uncontrolled	62.5	no data
	2.5	5.0	With cyclone	NA	24.1
		no data	With cyclone&ESP	NA	8.25
			Vertical retort	7.15	no data
			Electric retort	10.0	no data
			Electrolytic process	3.3	no data

Note: unit, kg per ton of product

Table 14: Emission factors for primary lead smelting and slab zinc processing

5.2 Manufacture of Iron and Steel

The process of manufacturing iron and steel is composed of mining, separating, sintering, smelting, rolling, coking and other associated operations. About 6-7 tons of raw materials are consumed to produce 1 ton of steel. Eighty percent of the raw material, which includes iron ore, coal, limestone, manganese ore, and so on, are transformed into various kinds of waste material and then exhausted into the environment. The main air pollutants are dust, SO₂, CO, NO_x, fluoride and chloride. Unlike other industries, there are many fugitive emissions entering the atmosphere from other than a stack, chimney, or similar devices, and these are classified as either process or non-process emissions. Potential sources of fugitive emissions and particulate emission factors from iron and steel mill operations are indicated in tables below.

Iron production sources		Steel production sources
Iron ore unloading	Sinter machine discharge	Scrap steel unloading,
Limestone unloading	(breaker and screen)	transfer, and storage
Iron storage	Sinter cooler	Ore and flux material
Iron ore handling and transfer	Sinter storage	unloading, transfer, storage
Limestone storage	Sinter handling and transfer	Molten pig iron transfer to
Limestone handling and transfer	Blast furnace charging	charge ladles
Coke storage	Blast furnace upsets(slip)	Basic oxygen furnace
Coke handling and storage	Blast furnace tapping-iron and	Open hearth furnace
Blast furnace flue dust storage	slag	Electric arc furnace
Blast furnace flue dust handling and transfer	Slag handling	Molten steel reladling
	Slag storage	Continuous
Sinter machine wide box discharge	Slag crushing	casting/conventional teeming Scarfing

Table 15: Identification of potential sources of fugitive emission from iron and steel production

Source	Emission factor	Source	Emission factor
Sinter wind box		Electric arc furnace	
Uncontrolled leaving grate	5.56	Melting and refining	
After coarse particulate removal	4.35	Uncontrolled carbon steel	19.0
Controlled by dry ESP	0.8	Melting, refining, charging,	
Controlled by wet ESP	0.085	tapping and slagging	
Controlled by venturi scrubber	0.235	Uncontrolled	
Controlled by cyclone	0.5	Alloy steel	5.65
Sinter discharge (breaker and hot screens)		Carbon steel	25.0
Uncontrolled	3.4	Controlled by	
Controlled by baghouse	0.05	Building evacuation to	
Controlled by venturi scrubber	0.295	baghouse for alloy steel	0.15
		Direct shell evacuation	0.0215

Blast furnace		Open hearth furnace	
Slip	39.5	Melting and refining	10.55
Uncontrolled cast house roof monitor		Controlled by ESP	0.14
Basic oxygen furnace (BOF)	0.3	Roof monitor	0.084
Top blown furnace melting and refining			
Uncontrolled			
Controlled by open hood vented to:	14.25		
ESP	0.065		
Scrubber	0.045		

Note: unit, kg per ton of product

Table 16: Particulate emission factors for iron and steel mills

6. Construction Material Industry

With regard to air pollution, the construction material processing industry has many potential sources: Portland cement, glass manufacturing, lime manufacturing, and stone and gravel processing. In each of these industries, nonmetallic minerals are processed at high temperature to produce the desired products. The chief air pollution problem is usually the emission of dust from various points in the process, particularly from high-temperature operations. In all of these industries, the mining, crushing and transport of the materials are associated with the generation of large amounts of dust, both coarse and relatively fine, which contains silica and, in some instances, asbestos, so worker exposure is a concern.

6.1 Hot-mix Asphalt Mixing Facilities

Hot mix asphalt (HMA) paving material is a carefully proportioned mixture of graded aggregates and asphalt cement. The aggregates, which include stone, sand, and mineral dust, and can include reclaimed asphalt pavement (RAP), make up about 92-96% of total mixture by weight. In addition to serving as paving materials for roadways, parking lots, race tracks, etc., HMA can also be used as a cushion for reservoirs, landfills and other containment purposes. The process of producing HMA involves drying and heating the aggregates to prepare them for the asphalt cement coating. There are four kinds of processes: recycle mixing, batch mixing, parallel-flow drum mixing and counter-flow drum mixing processes. The air pollutants from these processes are particulate, CO, NO_x, HC, SO_x and HC.

6.2 Portland Cement

Portland cement is a fine powder, usually gray in color, which consists of a mixture of hydraulic cement minerals, dicalcium silicate, tricalcium silicate, and tetracalcium aluminoferrite, to which one or more forms of calcium sulfate have been added. There are more than 30 raw materials that are known to be used in the manufacture of Portland

cement which can be divided into four categories: lime, silica, alumina, and iron. The production is a four-step process: acquisition of raw materials, preparation of the raw materials for pyroprocessing, pyroprocessing of the raw materials to form Portland cement clinker, and grinding of the clicker to Portland cement. Figure 2 is a basic flow diagram of the Portland cement manufacturing process.

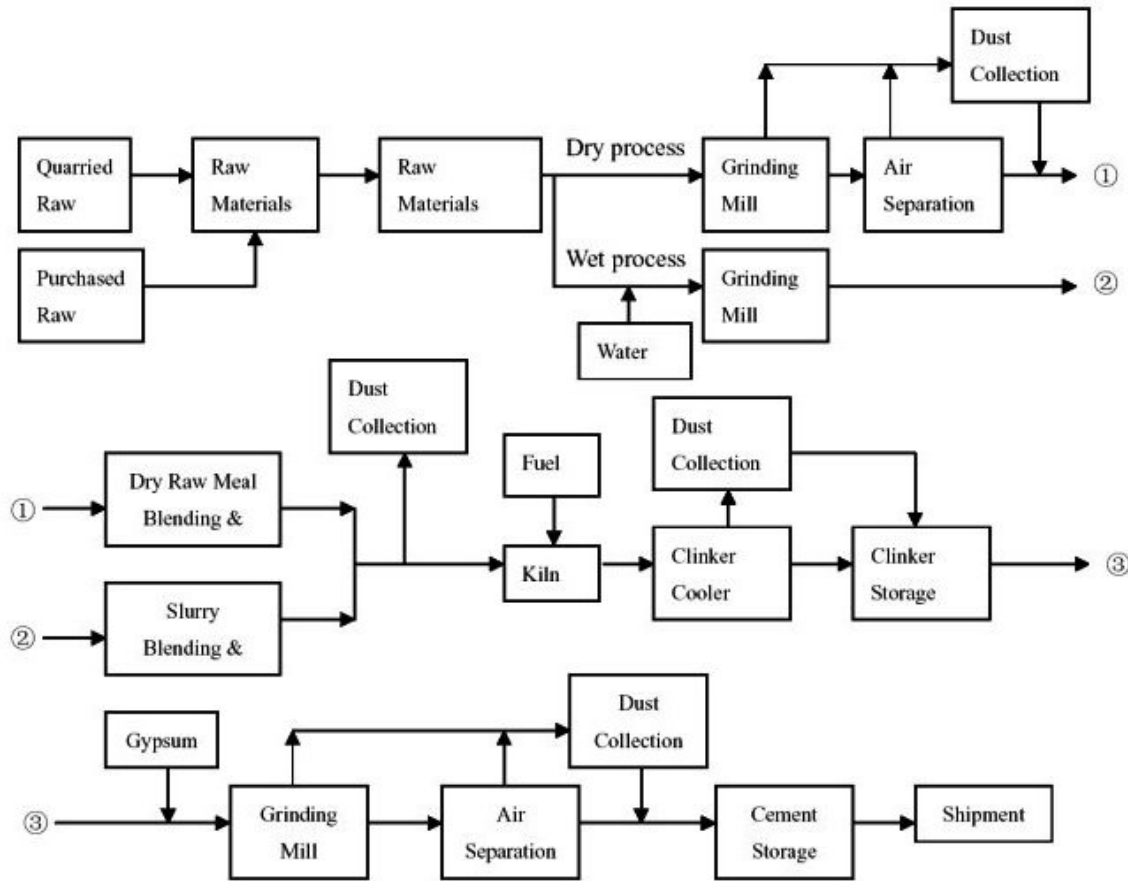
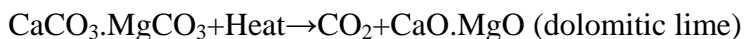


Figure 2: Basic Flow Diagram of the Portland Manufacturing Process

The raw materials are quarried, crushed, ground, mixed intimately, and fed to the cement kiln. During the grinding, blending, and handling operation, dust is emitted at various points. Raw materials can also be the source of some environmentally undesirable emissions from the kiln stack later in the process. If the raw materials contain naturally occurring hydrocarbons, such as petroleum or kerogen, these materials can evaporate in the relatively cooler portions of the pyroprocessing system and appear at the stack exit as a “blue haze”. Nitrogenous constituents of raw materials can potentially contribute to NO_x emissions that are unrelated to combustion. Sulfides in raw materials have been identified as contributors to SO₂ emissions under some operating conditions.

Lime manufacture: lime is the product of the high-temperature calcination of limestone. There are two kinds of lime: high-calcium lime (CaO) and dolomitic lime (CaO-MgO). Lime is manufactured in various kinds of kilns by one of the following reactions.



During manufacturing, pollutants discharge from quarrying, crushing, calcining, and transfer processes. Particulate is the main pollutant of concern from most of the operation; however, gaseous pollutants are also emitted from kilns. The most important source of particulate is the kiln. Of the various kiln types in use, fluidized-bed kilns have the highest uncontrolled particulate emissions. The rotary kiln is next to the fluidized-bed kilns in uncontrolled particulate emissions. The vertical kiln has the lowest uncontrolled dust emissions owing to the large lump-size feed and relatively slow air velocities and slow movement of material through the kiln. Typical dust loadings in effluent gases from vertical kilns are 0.7 to 3.0 g/m³. In rotary kilns, loading could be as high as 50 g/m³. Another source of dust is the hydrator where quicklime can be converted to hydrated lime by the addition of water. Dust emission may be controlled using water scrubbers. Dust loading in the effluent may vary from 0.02 to 2.3 g/m³ depending on collector efficiency.

7. Petroleum industry

The petroleum supplies many of the kinds of fuel used world-wide. As a mixture of liquid hydrocarbons, like alkanes, aromatic hydrocarbons and naphthene, crude petroleum contains from 1 to 4.5% or more sulfur, depending on the source, and a number of inorganic metal compounds. At the refinery, crude oil is converted into a large variety of products, such as hydrocarbon fuels and feedstock for the petrochemical industry. Refining operations include physical separation of the components in the crude oil and chemical conversion and treating processes to generate the desired products. The main processes are air and reduced-pressure distillation and catalytic cracking. The major air contaminants from petroleum-related operations have been hydrocarbons, sulfur compounds, CO, and particulate matter. Crude oil is a heavy, viscous liquid or semi-liquid consisting of a variety of hydrocarbons ranging from light, normally gaseous, materials to normally solid wax-like materials. The crude becomes contaminated with small amounts of sulfur compounds, water and ash. In the handling, separation, purification, and distribution of the crude oil, refinery intermediates, and refinery products, hydrocarbons are lost to the atmosphere principally by evaporation from storage tanks, procession units, pumps and valve compressors, transfer operations, loading and unloading, and waste effluent handling. Sulfur compound losses from the petroleum industry have been usually in the form of hydrogen sulfide, sulfur dioxide, and, a small amount of mercaptans. Crude oils themselves vary widely in their sulfur content, and the emissions of sulfur compounds both in the oil field and the refinery reflect their quantity in the crude. Most of these emissions have been in the form of hydrogen sulfide and mercaptans. In refining operations, particularly stills, separators, and cracking units, the hydrogen sulfide evolved has been accompanied by considerable quantities of hydrocarbon gas which makes the gas highly suitable as a fuel. In burning, any residual hydrogen sulfide is converted to sulfur dioxide and emitted in the flue gases. Estimates of the sulfur emissions from refineries have been based on the sulfur content of the crude oil. The principal source of carbon monoxide and particulate matter in refinery operations has been the catalyst recovery unit operated in conjunction with

the catalyst cracking unit. The quantities emitted have usually been minor in comparison to other sources in the community. Black soot can be emitted occasionally from overloaded flares or the burning of waste residues. Emission factors for petroleum refineries are presented in Table 17.

Processes	Units	Emission factor	Processes	Units	Emission factor
Boilers and process heaters	g HC/m ³ oil burned	0.399	Compressor internal combustion engines	g HC/m ³ of fuel gas burned	19
	g HC/m ³ gas burned	0.416			
	g particulate /m ³ oil burned	2280		g NO ₂ /m ³ of fuel gas burned	13.8
	g particulate /m ³ gas burned	0.32		g CO/m ³ of fuel gas burned	negligible
	g NO ₂ /m ³ oil burned	8265		g HCHO/m ³ of fuel	
	g NO ₂ /m ³ gas burned	3.65		gas burned	1.8
	g CO/m ³ oil burned	negligible		g NH ₃ /m ³ of fuel gas	
	g CO/m ³ gas burned	negligible		burned	3.2
	gHCHO/m ³ oil burned	71.3	Miscellaneous process equipment		
	gHCHO/m ³ gas burned	0.05		g HC/m ³ refinery capacity	
			1.Blowdown system		
			a.with control		14.3
Fluid catalytic units	g HC/m ³ of fresh feed	570	b.without control		855
	g particulate/ton of catalyst circulation		2.Process drains	g HC/m ³ waste water	
		5.1 ^a	a.with control		23
	g NO ₂ /m ³ of fresh feed	180	b.without control		598
	g CO/m ³ of fresh feed	39045	3.Vacuum jets	g HC/m ³ vacuum distillation capacity	
	g HCHO/m ³ of fresh feed		a.with control		negligible
		54	b.without control		371
	g NH ₃ /m ³ of fresh feed	154	4.Pipeline valves and flanges	g HC/m ³ refinery capacity	79.8
Moving bed catalytic cracking units	g HC/m ³ of fresh feed	248	5.Vessel relief valves	g HC/m ³ refinery capacity	31.4
	g particulate/ton of	1814 ^b	6.Pump seals	g HC/m ³ refinery	48.5

	catalyst circulation			capacity	
	g NO ₂ /m ³ of fresh feed	14.3			
	g CO/m ³ of fresh feed	10830	7.Compressor seals	g HC/m ³ refinery capacity	14.3
	gHCHO/m ³ of fresh feed	34	8.Others	g HC/m ³ refinery capacity	28.5
	g NH ₃ /m ³ of fresh feed	14			

^aWith electrostatic precipitator; ^bWith high efficiency centrifugal separator

Table 17: Emission Factors for Petroleum Refineries

8. Paper and pulp manufacture

Paper is made of layers of cellulose fibers obtained from wood and pressed together. Trees, cut from the forests, have first been debarked and chipped. The chips are then treated chemically to free the fibers. One of the most common processes has been the “Kraft” process, where the wood chips are cooked in large steel vessels at comparatively high pressure with an alkaline solution of sodium hydroxide (NaOH) and sodium sulfide (Na₂S). The sodium hydroxide and sulfide interact with the resinous material (lignin) which holds the wood fiber together, and a ‘black liquor’ is formed having small quantities of hydrogen sulfide and organic sulfides. In a process used for hardwoods called the ‘neutral sulfide semi-chemical’ (NSSC) process, the reagent has been a less alkaline solution of sodium sulfide (Na₂SO₃), and sodium carbonate (Na₂CO₃), and a similar pungent smelling black liquor has been produced.

Emission factors for Kraft Pulp process are presented in Table 18.

Source	Gaseous Pollutants			Particulate pollutants	Type of control
	H ₂ S	CH ₃ HS	(CH ₃) ₂ S		
Digester blow system	0.05-0.03	0.4-2.4	0.4-1.7	negligible	untreated
Smelt tank	-	-	-	9	Uncontrolled
				2.3	Water spray
				0.5-1.0	Mesh demister
Lime klin	0.5	negligible	negligible	8.5	Scrubber (E=80%)
Recover furnace	1.6	2.3	1.4	68	Primary stack gas scrubber
	1.6-3.2	-	-	3.2-7.3	Electrostatic precipitator
	0.3	-	-	5.5-11.4	Venturi scrubber
Multiple effect	0.5	0.002	-	negligible	untreated
Evaporator	0.2	0.002-0.015	negligible	negligible	Black liquor oxidation
Oxidation towers	-	-	0.05	-	Black liquor oxidation

Table 18: Emission Factors for Kraft Pulp Process (kg/ton pulp produced)

In the recovery process, the black liquor is dried and then burned in special furnaces, which produces an ash of sodium sulfide and sodium carbonate. Sodium hydroxide can

be recovered by reacting these two products with calcium hydroxide. The vapors given off during the drying, and some of the volatile compounds incompletely burnt during combustion, are composed of the sulfide (H_2S), methylmercaptan (CH_3HS), dimethyl mercaptan ($(\text{CH}_3)_2\text{S}$), and dimethyl disulfide($(\text{CH}_3)_2\text{S}_2$) which have been responsible for the offensive odor associated with paper pulp mills.

The chief air pollution problems of the kraft pulp industry have been related to emissions of malodorous gases from the digesters, evaporates, and the recovery furnace and emissions of particulate matter from the recovery furnace, the lime kiln, and the bark-burning boilers.

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