Emissions of SO_2, NO_x and PMs from Cement Plant in Vicinity of Khoms City in Northwestern Libya

Hesham G. Ibrahim[1], Aly Y. Okasha[2], Mokhtar S. Elatrash[2] and Mohamed A. Al-Meshragi[1]

1. Chemical Engineering Department, Faculty of Engineering, Mergheb University, Khoms City, Libya

2. Earth and Environmental Science Department, Faculty of Science, Mergheb University, Khoms City, Libya

Abstract: Estimated emissions of gases and particulate matter from two Portland cement plants near Khoms city in northwestern Libya by computer simulation reveal that the SO_2, NO_x and dust emissions exceed selected international standard limits. The results highlight the need for improved operational procedures to minimize emissions and avoid any possible adverse environmental effects.

Key words: SO_2, NO_x, PMs, air pollutants, emissions, simulation, Libya.

1. Introduction

Emissions from natural gas combustion and raw cement burning can cause negative effects on public health and lead to degradation of the surrounding environment. Several health problems such as respiratory disorders and allergies are attributed to such emissions [1]. Inhalation of NO_x interferes with the function of the human respiratory system and worsens the health condition of asthma patients even at low concentrations [2, 3]. Increased SO_x levels in the atmosphere are blamed for degradation of agricultural productivity and death of some plants in early stages [4-6]. Similar impacts on human health and agricultural productivity are linked to high level of cement dust in the atmosphere [1, 7]. Accumulation of cement dust on leaves of plants prevents photosynthesis and respiration, and reduces the process of transpiration [2].

Spread of emissions is affected by climatic conditions that determine the deposition sites. Several studies indicate that air born particulate matter emissions are transported and deposited within 11 miles to 47 miles from the source [1]. This study aims to calculate the concentrations of emissions from both cement factories using advanced mathematical models.

1.1 Types of Industrial Flue Gas Emissions and Their Sources

Stack emissions vary according to the type of industrial processes and the used fuel. There are two types of emissions, particulate and gaseous.

First, gaseous emissions are products of fuel combustion and include oxides of sulfur (SO_3, SO_2, SO), hydrogen sulfide (H_2S), nitrogen oxides (NO, NO_2, N_2O), carbon oxides (CO, CO_2) and volatile organic compounds (VOCs). Second, particulate matter emissions are fine dust measured in micrometers that includes cement dust and carbon particles emitted from steel plants and power plants as well as different types of heavy metals.

1.2 Emissions Covered by the Study

1.2.1 Sulfur Oxides (SO_x)

Sulfur oxides are emitted from sulfur containing fuels in a form of SO_2 and SO_3. Sulfur dioxide dissolves in water vapor in the atmosphere yielding

Corresponding author: Hesham G. Ibrahim, Ph.D., main research fields: modeling and simulation of chemical processes, transport phenomena, air pollution control. E-mail: hesham.ibrahim80@gmail.com.

sulfite acid H_2SO_3. Sulfur trioxide is either emitted directly from the source or produced from the transformation of sulfur dioxide in the air. The occurrence of the sulfur dioxide is more common than other sulfur compounds in the lower atmosphere. Sulfur dioxide is a colorless gas with a foul odor and its presence in the surrounding air can be sensed by smelling at concentrations within 1,000 to 3,000 µg/m³ [1].

1.2.2 Nitrogen Oxides (NOₓ)

Nitric oxide (NO) and nitric dioxide (NO_2) are regarded as major pollutants in the lower atmosphere, in addition to nitrous oxide (N_2O) that transforms into NO and NO_2. Nitric oxide is a colorless gas with a pungent odor, varies in color from orange yellow to reddish-brown and it is a powerful oxidizing agent converts in the air to nitric acid (HNO_3).

Sources of NOₓ are either natural such as volcanoes or industrial such as electric power stations, automobile engines, industrial boilers, burners, and factories producing nitrogenous compounds such as nitric acid. Nitrogen oxides emitted from industrial sources such as fixed industrial furnaces contribute about 30% of nitrogen oxides emissions, and 70% are attributed to power plants [1, 8].

1.2.3 Particulate Matter Emissions (PMs)

Particulate matters include dust, soot, and liquid droplets (except pure water droplets) and consist of fine particles that can remain suspended in the air. The physical properties of such particles determine the extent of their effect on human health.

Presence of metallic elements in heavy dust emitted from crushing, grinding and burning of raw materials in cement manufacturing includes lead, chromium, nickel, aluminum and barium that are reported to have serious health impacts on human health and animal wellbeing. There are numerous sources of particulate emissions, some are industrial and others are natural. Natural PMs such as sea spray, and airborne dust are generally dominated by coarser particles in comparison to emissions from combustion stacks.

2. Cement Production

Cement is made by heating a mixture of calcareous and argillaceous materials to a temperature of about 1,450 °C. In the process, partial fusion occurs and nodules of so-called clinker are formed. The cooled clinker is mixed with very small quantities of gypsum, and sometimes other additives, and ground into a raw meal. A brief overview of cement manufacturing process is illustrated in Fig. 1 [9-11].

2.1 Modeling Process

Modeling is carried out by using Aspen Plus v10.2 to calculate mass balances of compounds involved in chemical reactions. In order to control any chemical processes and relevant changes in a kiln system better,
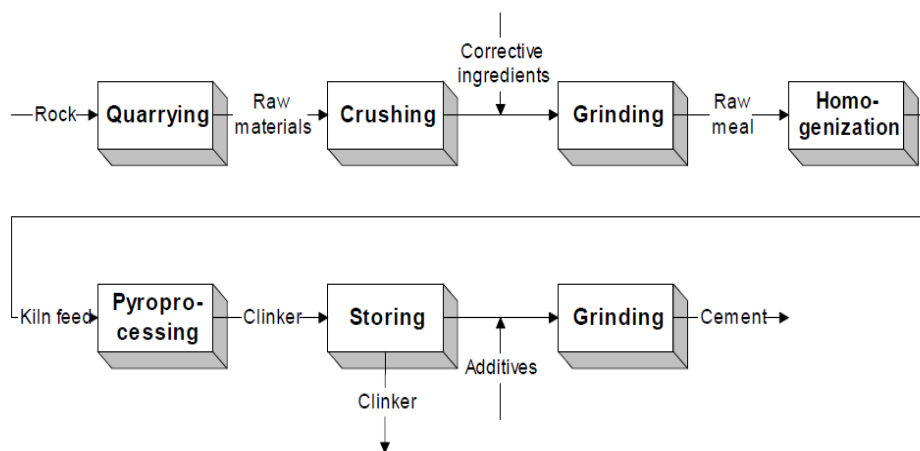

Fig. 1   Principle drawing of the cement manufacturing process [12].

it is necessary to study the state of incoming and outgoing compound flows [13, 14]. The objective of modeling is to find out how well a certain type of reactors or separators can describe a certain function in a process and a behavior of kiln process in a realistic way. A modeling process involves vital information about chemical changes under effect of heat transmission in a kiln, and other parameters controlling clinker burning process. Chemical analyses of the kiln feed and fuel are essentials for a simulation process as they determine chemical composition of emission gases.

Generally, NO_x emissions are generated during fuel combustion by oxidation of chemically-bound nitrogen in the fuel and by thermal fixation of nitrogen in the combustion air. The amount of thermally generated NO_x increases as flame temperature increases. Emissions of SO_2 are generated from sulfur compounds in the raw materials and, to a lesser extent, from sulfur in the fuel [15].

2.2 Gas Pollutants in Cement Rotary Kiln

Since formation of NO from nitrogen and oxygen takes place only at high temperatures, NO level gives an indication of the combined feed and flame temperature. Sulfur dioxide (SO_2) is formed by thermal decomposition of calcium sulfate in clinker and it gives an indication of clinker temperature [16]. SO_3 is present as anhydrite and can easily be decomposed to SO_2 and O_2 [17].

Nitrogen oxides NO, NO_2 and N_2O are produced in the combustion flame of a rotary kiln, enter the atmosphere with the exit gases, and undergo many reactions in the atmosphere [9].

#### 2.2.1 NOₓ Formation in Kiln Systems

Nitrogen oxides in kiln are made up of 90% NO and the remainder is NO_2 [18, 19]. NO is a long lived and not highly reactive gas rapidly converts into NO_2 and N_2O [20]. There are three formation mechanisms of NO_x production. Each depends on the composition of the combustible matter and combustion temperature.

Thus formed NO_x are categorized into three different types.

2.2.1.1 Thermal NOₓ

Thermal NO_x are products of natural gas combustion that occur in high temperature environment of the main combustion zone (burning zone) of a kiln. Most NO_x are formed by thermal oxidation of atmospheric nitrogen at high temperatures.

Threshold temperatures for thermal NO_x formation fall in between 1,200-1,600 °C (2,200-2,900 °F) [18, 19, 21]. Since kiln flame temperature falls within that temperature range, considerable amounts of thermal NO are generated in the burning zone. The thermal reaction between oxygen and nitrogen to form NO is known as Zeldovic reaction which is simplified as follows [21]:

$$N_2 + O \rightarrow NO + N \qquad (1)$$
$$N + O_2 \rightarrow NO + O \qquad (2)$$
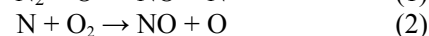
NO formation increases exponentially as temperature increases, and increases as excess oxygen increases. Small changes in temperature, above 1,400 °C, produce large changes in concentrations of NO at a given oxygen concentration. Gas temperatures in kiln burning zones are significantly above clinker material temperatures which must reach about 1,450 °C to form some clinker compounds. Conditions in the burning zones of cement kilns favor formation of thermal NO_x. Further formation of thermal NO_x in secondary zones (calciner, preheater riser ducts and mid-kiln firing zone) is insignificant as such zones operate at temperatures below 1,200 °C [22].

Formation of thermal NO_x in the burning zone is the major contributor to NO_x emissions from the kiln. The main thermal NO_x formation reaction is summarized in Eq. (3) [23];

$$N_2 + O_2 \rightarrow 2NO \qquad (3)$$

Produced NO converts to NO_2 at the exit of the chimney at atmospheric conditions according to Eq. (4) and appears in brown-yellow color:

$$NO + 1/2O_2 \rightarrow NO_2 \qquad (4)$$
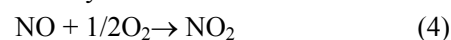
Typically, the amount of O_2 in kiln exit gases is held in the range of 1%-2% for optimum kiln performance

and product quality. This is equivalent to about 5%-10% excess air in the combustion zone, an amount sufficient to enhance NO_x formation [24].

2.2.1.2 Fuel NO_x

Combustion of nitrogen-bearing fuels such as certain coals produces N_2, or NO. Fuel NO_x can contribute as much as 50% of total emissions when combusting oil and as much as 80% when combusting coal [25]. Although the complete mechanism is not fully understood, there are two primary paths of formation. The fact that the amount of Nitrogen compounds in natural gas is insignificant suggests that fuel NO_x mechanism is a minor NO_x contributor.

2.2.1.3 Feed NO_x

It is reported that nitrogen concentrations in various kiln feeds are very small and the potential contribution of feed NO_x to total NO_x emissions is negligible [26]. Furthermore, oxygen concentration in the flame as well as the kind and velocity of the mixing of oxygen with the fuel are of a great importance for approaching a proper temperature convenient for NO formation. The mixture depends to a large degree on the kind of fuel, and on the content of volatile matters. An increase in material temperature in the combustion zone causes an increase in the formation of NO_x. A hotter combustion zone and a shorter and a sharper flame create better conditions for NO_x formation.

2.2.2 SO₂ Formation in Kiln Systems

Sulfur is present in all cement raw materials. Investigations of 21 German preheater kilns show that the amounts of sulfur introduced with the raw mix vary from 0.5 to 11 g of SO_3/kg clinker [27, 28]. As a result of combustion, sulfur in raw mix and in fuel evaporates in the burning zone as SO_2. Excess of SO_2 in the preheater reacts with the $CaCO_3$ and returns to the kiln as $CaSO_4$ which decomposes again in the burning zone and thus increases the SO_2 circulation of the kiln gas, however, some of $CaSO_4$ remains undecomposed in the clinker. A higher sulfur content can result in increased SO_2 emission with the exit gases that leads to chocking and suspension of preheater as well as formation of kiln coating rings [9].

2.3 Natural Gas as a Fuel

In recent years, natural gas has become the most favored fuel due to its lower sulfur content. The main components of natural gas are methane, ethane and other hydrocarbons as shown in Table 1. Some natural gas may also contain up to 10% inert gases such as carbon dioxide, nitrogen and helium. Sulfur presence in natural gas occurs in a form of hydrogen sulfide.

2.4 Chemical Reactions in Rotary Kiln and Pollutants Formation

The amount of combustion gases generated from the same amount of thermal units of natural gas is 18.5% and 12.2% higher than that generated from coal and fuel oil respectively [9]. Higher volumes of combustiongases released from natural gas combustion are attributed to air requirement. Combustion of fuel oil requires lesser amounts of air than natural gas.
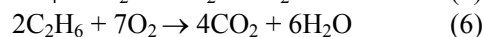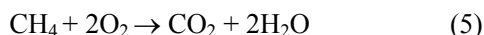
The increased air requirement for combustion results in lower flame temperature from natural gas as compared to others fuels, higher gas velocities inside the rotary kiln resulting in a lower heat exchange rate from the gas to the kiln charge, and higher kiln exit gas volumes and thus higher heat losses with the exit gases. The recommended flame temperatures for optimum use are within 1,200-1,600 °C in cement industry by dry process in Libya [30]. This range of flame temperatures corresponds to excess air within 90%-30% for natural gas combustion as reported [31].

Table 1   Composition of natural gas used as fuel [29].

Composition	Unit	Value
N_2	mol.%	0.593
CO_2	mol.%	2.023
CH_4	mol.%	86.482
C_2H_6	mol.%	10.392
C_3H_8	mol.%	0.496
i-C_4H_{10}	mol.%	0.014
Total	mol.%	100
M.Wt.	kg/kgmol	18.282
Density	kg/Nm³	0.77519
T.S.	g/Nm³	0.0009

2.4.1 Combustion of Natural Gas

The main reactions associated with natural gas (Table 1) combustion are as follows [9]:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad (5)$$
$$2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O \qquad (6)$$
$$2C_3H_8 + 10O_2 \rightarrow 6CO_2 + 8H_2O \qquad (7)$$
$$C_4H_{10} + 6.5O_2 \rightarrow 4CO_2 + 5H_2O \qquad (8)$$

With conversion rate of 100% at operating conditions [9], the main reactions are accompanied the following side reactions:

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O \qquad (9)$$
$$N_2 + O_2 \rightarrow 2NO \qquad (10)$$

The reactions are with conversion rates of 100% of H_2S and 0.5% of incoming nitrogen to the kiln [3].

2.4.2 Combustion of Feedstock

The main reactions of feedstock are as follows [9]:

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (11)$$
$$MgCO_3 \rightarrow MgO + CO_2 \qquad (12)$$
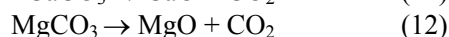
These chemical reactions tend to initiate formation of complex compounds through a chain of reactions that lead to formation of clinker.

Emissions of SO_2 from modern cement plants are relatively low (as investigated in Al-Burg Cement Plant at Zliten/Libya) as sulfur contained in the kiln fuel input and for any calciner is very effectively bound in a form of sulfate embedded in the clinker. However, some emissions from the preheater may occur if the utilized raw materials contain sulfide such as pyrite and marcasite. If pyrite is present in the raw materials, there is a risk that about one half of the sulfur content may escape in the form of SO_2 [32].

It is suggested that all SO_3 emitted from feed stock converts into SO_2 and half of the sulfur content emits with combustion gases as follows [16, 17];

$$S + O_2 \rightarrow SO_2 \qquad (13)$$

2.5 Simulation Process and Operating Conditions

Since the main sources of NO_x, SO_2 and dust in cement plants are rotary kilns, the simulation in this study is dedicated for the rotary kilns and based on the operating conditions for process using ASPEN Plus. Building a simulation model requires knowledge of kiln process and sufficient information regarding design and operation of the cement plants under study [13]. The data from Mergheb and Lebda cement plants correspond to steady state conditions.

2.5.1 Mergheb Cement Plant

The plant was built in the late 1960s, located only few kilometers west of Khoms city and the neighboring ancient Roman city of Lepits Magna and surrounded by forming areas.

• Plant design capacity = 1,100 tons of clinker/day (300 day/year) [33];

• Furnace operational capacity = 1,000 tones clinker/day [34];

• Amount of feeding into the furnace = 1,680 tons/day [34];

• Type of fuel: natural gas [33];

• Fuel supplier: Sirte Oil & Gas Company [29];

• Sulfur content in fuel = 0.0009 g/m³ [essentially is representative of the gas hydrogen sulfide] [29];

• Combustion furnace temperature = 1,500 °C [34];

• Amount of excess air = 40% [9].

The chemical composition of raw material feeding the furnace is shown in Table 2.

2.5.2 Lebda Cement Plant

The plant was built in 1981 about 15 km southeast Khoms and 10 km south of Souk Elkamis, a coastal farming strip inhabited by about 100,000 people.

Table 2   Chemical composition of the raw material feeding the furnace of Mergheb and Lebda cement plants [34, 35].

Component	Kiln feed of Mergheb cement plant (wt.%)	Kiln feed of Lebda cement plant (wt.%)
SiO_2	14.43	14.69
Al_2O_3	3.9	2.57
Fe_2O_3	2.27	1.97
CaO	42.61	42.22
MgO	1.09	1.57
SO_3	0.1	0.11
K_2O	0.9	0.5
Na_2O	0.09	0.07
Cl	00	0.01
LOI	34.61	36.29
Total	100	100
$CaCO_3$ content	76.09	77.02

• Plant design capacity = 3,000 tones clinker/day (300 day/year) [33];

• Furnace operational capacity = 3,000 tones clinker/day [33];

• Amount of feeding into the furnace = 6,000 tons/day [33];

• Type of fuel: natural gas [33];

• Fuel supplier: Sirte Oil & Gas Company [29].

The chemical composition of raw material feeding the furnace is shown in Table 2.

3. Results and Discussion

Computer simulations of both cement plants provide estimates of emission concentrations of SO_2, NO_x and PMs. Tables 3 and 4 contain the results against the standard limits of four international codes, American (USEPA), Canadian (CEPA), European (ECE) and Saudi (KSA).

The (+) sign represents the percentage by which an emission rate of a certain gas or dust exceeding a certain standard limit, and the (-) sign represents the percentage by which an emission rate falls below a standard limit.

Nitrogen oxides and dust emitted from Mergheb Cement Plant exceed all the standard limits set by the USEPA, CEPA, ECE and KSA several times

Table 3 Comparison of NOₓ, SO₂ and dust emissions of Mergheb Cement Plant with four international standard limits [36-39].

Pollutants	Standards	USEPA	CEPA	ECE	KSA
NOₓ	Unit	lb/Ton Clinker	kg/Ton Clinker	mg/m³ (E.G.)*	lb/MBtu
	Standard limit	1.5	2.3	150	0.3
	Estimated value	49.1766	22.326	8,714.298	8.683
	Deviation%	+3,178.44	+870.696	+5,709.532	+2,794.333
SO₂	Unit	lb/Ton Clinker	kg/Ton Clinker	mg/m³ (E.G.)*	lb/Mbtu
	Standard limit	1.33	4.6	300	2.3
	Estimated value	1.4807	0.6723	262.392	0.26
	Deviation %	+11.33	-85.3848	-12.536	-88.6957
Dust	Unit	mg/m³ (E.G.)*	mg/m³ (E.G.)*	mg/m³ (E.G.)*	kg/Ton of feed
	Standard limit	120	50	100	0.2
	Estimated value	12,298.6076	12,298.6076	12,298.6076	18.66321
	Deviation %	+10,148.84	+24,497.215	+12,198.6076	+9,231.605

* E.G.: emitted gases.

Table 4 Comparison of NOₓ, SO₂ and dust emissions of Lebda Cement Plant with four international standard limits [36-39].

| Pollutants	Standards	USEPA	CEPA	ECE	KSA
NOₓ	Unit	lb/Ton Clinker	kg/Ton Clinker	mg/m³ (E.G.)*	lb/MBtu
	Standard limit	1.5	2.3	150	0.3
	Estimated value	58.543	26.578	8,663.33	8.6388
	Deviation%	+3,802.897	+1,055.565	+5,675.553	+2,779.6
SO₂	Unit	lb/Ton Clinker	kg/Ton Clinker	mg/m³ (E.G.)	lb/MBtu
	Standard limit	1.33	4.6	300	2.3
	Estimated value	1.939	0.88	286.933	0.2876
	Deviation%	+45.782	-80.8	-4.355	-87.4957
Dust	Unit	mg/m³ (E.G.)	mg/m³ (E.G.)	mg/m³ (E.G.)	kg/Ton of feed
	Standard limit	120	15	100	0.2
	Estimated value	25,386.4122	25,386.4122	25,386.4122	7.6181
	Deviation%	+21,055.34	+169,142.75	+25,286.412	+3,709.35

* E.G.: emitted gases.
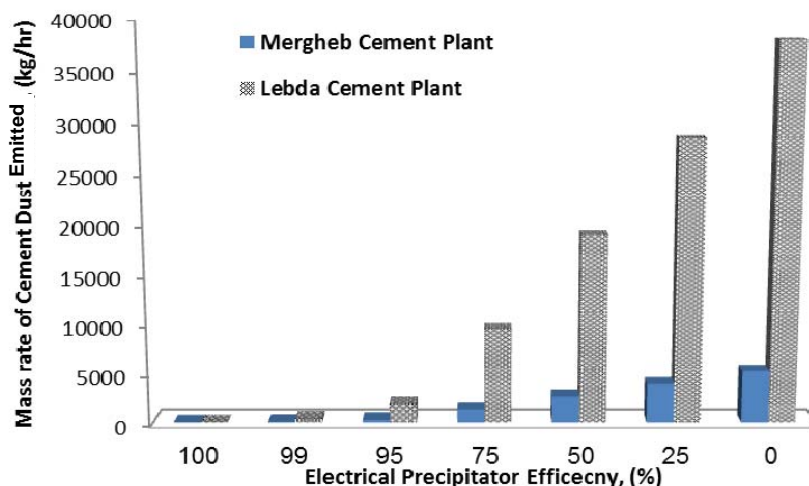
Fig. 2   Performance of electrical precipitators.

corresponding to standard deviations ranging from 870.7% (CEPA) to 5,709.5% (ECE) for NO_x and from 9,232% (KSA) to 24,497% (CEPA) for dust. However, sulfur dioxide emissions remain within the standard limits except the limit set by the USEPA such that the difference between the estimated value and the USEPA limit corresponds to a standard deviation of 11.3%.

Nitrogen oxides and dust emitted from Lebda Cement Plant follow a pattern which is similar to NO_x and dust emission rates from Mergheb Cement Plant. They exceed all the standard limits by differences corresponding to standard deviations within 1,055.6% (CEPA) and 5,675.5% (ECE) for NO_x and standard deviations within 3,709% (KSA) and 169,143% (CEPA) for dust.

Sulfur dioxide emissions from Lebda Cement Plant are in the limits of the CEPA, ECE and KSA, but exceed the USEPA limit by a difference corresponding to a standard deviation of 45.75%.

ESP (electrostatic precipitators) play a key role in controlling cement dust emissions. The relationship between ESP efficiency and dust emissions from each plant is illustrated in Fig. 2. This study is based on the assumption that the average annual efficiency of the ESP of each plant is 75%. Since each electrostatic precipitator in each plant consists of four parallel unit arrangements operation simultaneously, the increased

concentrations of CO can lead to full suspension of the ESP operation. Despite the excessive emission rates associated with the above assumption, the estimated emission rates represent the best case scenario which indicates 75% of possible negative impacts on the biodiversity and public health in the surrounding environment [40-43].

4. Conclusions

Emissions of NO_x from both cement plants can mainly be attributed to large quantity of excess air exceeding the optimum values, however, raw materials form another source of NO_x. Since the used fuel is natural gas high rates of emissions should not occur and high rates of NO_x can not be linked to the fuel. Sulfur dioxide emissions are largely attributed to the raw materials adsorbed by the cold feed in the preheater and the remainder is released with the flue gases in presence of large quantities of excess air.

Occurrence of excessive particulate emissions suggests a presence of high rates of CO in the ESP result from inadequate operational procedures that reduces the performance of each electrostatic precipitator.

Acknowledgments

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