

Implementation of the BAT concept in the cement industry

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**UNIVERSITY OF ZAGREB
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**UNIVERSITY OF SPLIT
FACULTY OF CHEMISTRY AND TECHNOLOGY
CHEMICAL AND ENVIRONMENTAL TECHNOLOGY**

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DIPLOMA THESIS

Zagreb/Split, September 2022

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IMPLEMENTATION OF THE BAT CONCEPT
IN THE CEMENT INDUSTRY

DIPLOMA THESIS

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SUMMARY

The BAT concept is defined as well as its implementation in the cement industry. Processes for reducing the emission of hazardous gases in the cement industry, which are also utilized as part of the BAT implementation in other industries, are extensively described. The comparison between selective non-catalytic reduction (SNCR) and selective catalytic reduction (SCR) as secondary processes for lowering NO_x emissions is characterized. Flame cooling, low NO_x burners and staged combustion as the primary NO_x reduction techniques are covered. It is presented how the activated carbon addition and implementation of wet scrubber reduces SO_x emissions. Fabric filters, electrostatic precipitators (ESPs), or a mix of both, known as hybrid filters, are analyzed technologies for reducing dust emissions. The approaches of reducing energy consumption, demands for usage of alternative fuels and optimizing working conditions, as an example of its overall contribution to greater cement production effectiveness and minimizing adverse effects on the environment are highlighted.

Keywords: BAT, cement process, NO_x emission reduction, SO_x emission reduction, dust emission reduction, energy consumption reduction, optimization

SAŽETAK

Definiran je BAT koncept i njegova primjena u industriji cementa. Opširno su opisani procesi za smanjenje emisije štetnih plinova u industriji cementa, koji se također koriste u sklopu implementacije BAT-a u drugim industrijama. Opisana je usporedba između selektivne nekatalitičke redukcije (SNCR) i selektivne katalitičke redukcije (SCR) kao sekundarnih procesa za smanjenje NO_x emisija. Hlađenje plamena, plamenik s niskim sadržajem NO_x i stupnjevito sagorijevanje kao primarne redukcijske tehnike su obuhvaćeni. Predstavljeno je kako dodavanje aktivnog ugljena i primjena mokrog skrubera smanjuje SO_x emisije. Filteri od tkanine, elektrostatski precipitatori (ESP) ili njihova mješavina, poznati kao hibridni filteri, analizirane su tehnologije za smanjenje emisije prašine. Pristupi smanjenju potrošnje energije, zahtjevi za korištenjem alternativnih goriva i optimizacija radnih uvjeta, kao primjer ukupnog doprinosa većoj učinkovitosti proizvodnje cementa i smanjenju štetnih učinaka na okoliš su istaknuti.

Ključne riječi: BAT, cementni proces, smanjenje NO_x emisije, smanjenje SO_x emisije, smanjenje emisije prašine, smanjenje potrošnje energije, optimizacija

TABLE OF CONTENTS

1. INTRODUCTION.....	1
2. THEORY.....	3
2.1 Cement manufacturing process	3
2.2 NO _x emissions	4
2.3 Primary combustion control techniques for NO _x emissions reduction.....	6
2.3.1 Staged combustion in kiln	6
2.3.2 Staged combustion in the calciner (SCC) mechanism.....	6
2.3.2.1 Staged-air combustion.....	7
2.3.2.2 Sequenced fuel and air combustion.....	8
2.3.3 Low NO _x burners.....	9
2.3.4 Flame cooling	10
2.3.5 Process optimization for NO _x reduction	11
2.4 Secondary techniques for post-combustion NO _x control.....	13
2.4.1 Selective Catalytic Reduction (SCR).....	13
2.4.2 Selective Non-Catalytic Reduction (SNCR)	14
2.5 Emission of dust	15
2.5.1 Electrostatic precipitators (ESPs)	16
2.5.2 Fabric filters	17
2.5.3 Hybrid filters	18
2.6 SO _x emission	18
2.6.1 Wet scrubber.....	19
2.6.2 Activated carbon.....	20
2.7 Use of wastes as fuels and raw materials	20
2.7.1 Waste materials processing	23
2.7.1.1 Direct combustion	24
2.7.1.2 Gasification.....	24
2.7.2 Alternative fuels usage.....	24
2.7.2.1 Petroleum-based wastes.....	26
2.7.2.1.1 Used tires.....	27
2.7.2.2 Municipal solid waste.....	28
2.7.2.3 Meat bone meal.....	28
2.7.2.4 Biomass	29

2.7.2.5 Hazardous waste	29
2.7.2.6 Sewage sludge.....	30
2.8 Reduction of energy consumption.....	31
3. CONCLUSION.....	32
4. LITERATURE	33

1. INTRODUCTION

As a binding agent, cement is an essential component of concrete, the most frequently produced material by humans. The production of cement involves the depletion of natural resources, energy consumption, and results in undesirable side-effects for the environment. The manufacturing process requires a significant quantity of materials, pyroprocessing techniques, and fuel sources, including coal, petroleum, coke, natural gas, fuel oil, biomass, or different types of waste. The rate of economic growth and cement consumption are closely related. The practice of implementing the best available technology (BAT) has evolved over the years as a result of the necessity to introduce resource-saving and waste-minimization measures in industries. The cement industry is one of the first branches of industry for which a BAT document has been prepared. [1] BAT is known as the technology endorsed by lawmakers or regulators for satisfying output standards for a certain process, such as pollution abatement. BAT in the cement industry is used as the most effective and advanced group of methods in the development of activities that include energy consumption, emissions to air, consumption of water, consumption of raw materials, process waste, and emissions to water. The primary focus of research for implementing the BAT concept in all industries, including the cement industry, is related to emissions into the air. Main emissions of cement industries are atmospheric emissions from the kiln system. They derive from the physico-chemical reactions involving the raw material calcination (decarbonisation of limestone) and fuel combustion. [2] Emissions from cement plants include pollutants such as oxides of nitrogen (NO_x) and other nitrogen compounds, sulphur dioxide (SO_2) and other sulphur compounds, carbon dioxide (CO_2), dust and to a lesser extent; total organic compounds (TOC), metals and their compounds, hydrogen fluoride, hydrogen chloride (HCl) and carbon monoxide (CO). The need for an oxidizing environment and high temperatures during cement production favors NO_x emissions. The fundamental BAT methods for NO_x emission decrease include flame cooling, low NO_x burners, and staged combustion. Selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) are techniques for post-combustion NO_x emissions control. There are various primary point sources of dust emissions from cement plants. They consist of secondary operations, clinker coolers, kiln systems, and coal mills. Several strategies that can be used singly or in combination include completely covering dusty operations as well as

implementation of automatic devices and control systems. Devices for minimizing dust emissions are fabric filters, electrostatic precipitators (ESPs), or a combination of both, known as hybrid filters. Sulphur is released from various kiln system outputs. It is released as SO_2 in the exhaust gases, CaSO_4 and other mixed compounds in the clinker and the dust. Implementation of wet scrubber and addition of activated carbon to the process are responsible for minimization of SO_x emissions. Apart from the stated techniques, energy savings measures in cement industries are opportunities to indirectly reduce emissions released to the atmosphere. Implementing BAT process control optimization, which includes computer-based automatic control systems and the use of contemporary, gravimetric solid fuel feed systems, results in a smooth and stable kiln process, advantageous for all kiln emissions as well as the energy use.

All of the approaches previously noted where BAT technology assists in lowering emissions from the cement industry and reducing energy use are further discussed in this thesis.

2. THEORY

2.1 Cement manufacturing process

BAT for cement production today, with the lowest energy consumption, is the use of a rotary kiln in combination with a multi-stage cyclone preheater system and a calciner. The steps of the cement manufacturing process are presented in Figure 1. Raw material preheating, calcination, clinker burning, and clinker cooling are the main sub-processes. The raw material is collected, crushed, mixed with additives, and transported to the cyclone preheating system prior to preheating. [3]

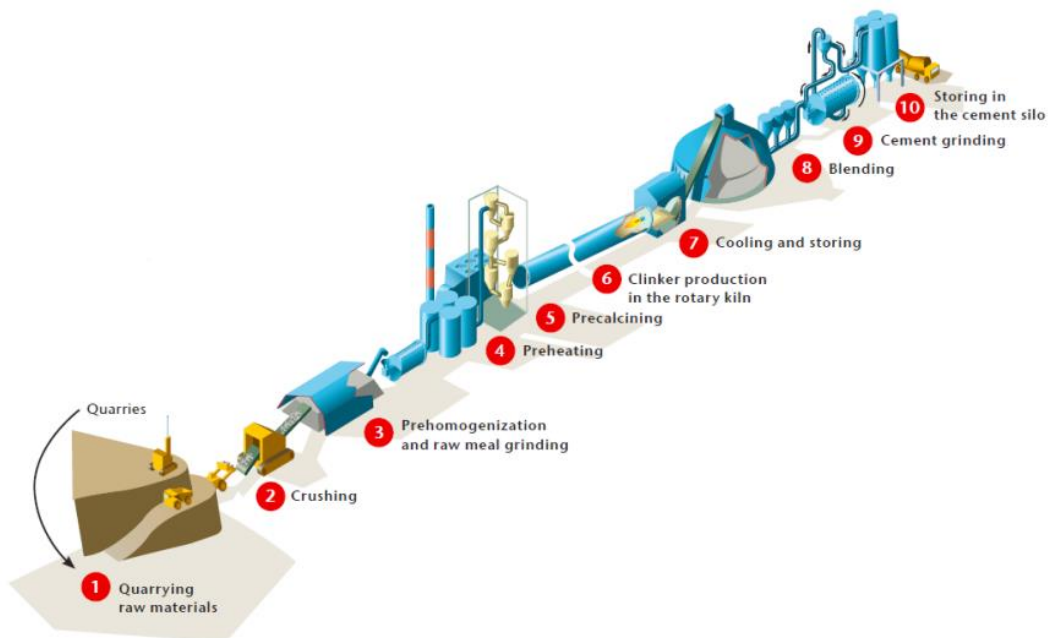


Figure 1. Cement manufacturing processes [3]

The raw material is heated by expanding of the hot flue gases from the rotary kiln in the opposite direction. This opposite direction movement effect is caused by particle separation within the gas cyclones. The highly tangential flow entering the cyclone separates the solid particles from the gas. The calciner is a combustion unit positioned just before the rotary kiln, and it is where the raw material, primarily limestone, is calcined. The calcination process is a strongly endothermic reaction that requires combustion heat from the fuel, implying that endothermic limestone calcination and exothermic fuel combustion occur concurrently. [3]

Clinker combustion is the most energy-intensive process in cement production. The clinker is produced in a rotary kiln. Rotary kiln slowly rotates on its axis and is exposed to high temperatures. Kilns are responsible for the majority of the NO_x emissions associated with cement production. After the rotary kiln clinkering process is completed, the cement clinker is rapidly cooled, preventing undesirable chemical reactions. Following the clinker cooling process, clinker is blended with various additives. The composition of cement is procured at this point. Following that, the cement is milled, deposited in a cement silo, and delivered to customers. [3]

2.2 NO_x emissions

Nitrogen oxides (NO_x) formation-friendly conditions are regularly attained in the cement production industry as a result of the high process temperatures. Most of the NO_x emissions come from cement kilns. Cement kilns produce NO_x emissions primarily as a result of two processes: thermal NO_x formation, which is the oxidation of nitrogen molecules in the combustion air, and fuel NO_x formation, which is the oxidation of nitrogen compounds in the fuel. [5]

Fuel combustion in the high-temperature kiln burning zone is the main contributor to thermal NO_x formation in cement kilns. In preheater and precalciner kiln systems, the secondary firing zone is where fuel and feed NO_x mostly form. The process points in cement manufacture where different NO_x formations occur are displayed in the Figure 2. [5]

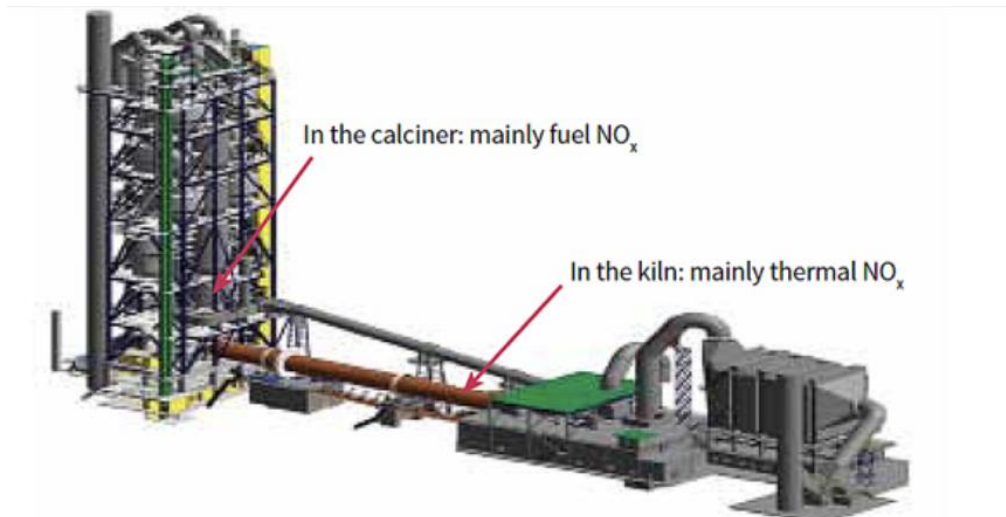


Figure 2. Process points of NO_x formation in cement units [4]

Despite of thermodynamically advantageous circumstances at lower temperatures, once created, NO can only decompose to a certain extent. In order to reduce NO_x generation, strategies for reducing NO_x emissions are being focused on lowering combustion temperature, oxygen concentration in the high temperature combustion zone, and gas residence time at high temperatures. [5]

Two types of NO_x control strategies that apply to the cement industry are: techniques for controlling combustion that have a focus on lowering NO_x generation, known as primary techniques, and secondary techniques for post-combustion NO_x control. Primary techniques imply flame cooling, low NO_x burners, mid kiln firing, addition of mineralizers to improve the burnability of the raw meal, staged combustion in combination with a precalciner, and process optimisation. Secondary techniques refer to SNCR technique and SCR technique. Both process control strategies are centered on establishing optimal kiln operating parameters that increase cement production and energy efficiency while lowering NO_x emissions. [5]

The type of fuel burned has a significant impact on the flame temperature. When compared to coal burners, gas burners often produce higher temperatures and intensities. The oxygen concentration in the combustion zone is affected by the amount of surplus air used, the source and ratio of primary and secondary combustion air, and the temperature. Modification of these parameters enables the possibility of a reduction of NO_x emission. [5]

2.3 Primary combustion control techniques for NO_x emissions reduction

2.3.1 Staged combustion in kiln

The staging of fuel combustion takes place within two different zones. In the first zone, beginning combustion occurs in a primary fuel-rich zone. This zone enhances the high temperatures required to complete the clinkering reactions. The formation of thermal and fuel NO_x is minimized due to the fuel-rich environments and the lack of available oxygen. In the second zone, fuel combustion is finished with the addition of secondary combustion air to complete the combustion process. The gas temperature in the second zone is much lower than in the first because the gas is combined with cooler secondary air, minimizing NO_x formation despite the excess available oxygen in this zone. For effective combustion air staging, indirect-fired kilns are required. [5]

2.3.2 Staged combustion in the calciner (SCC)

Staged combustion in the calciner performs in several steps, as presented in Figure 3. By introducing fuel, combustion air, and raw meal in stages NO_x formation is minimized and NO_x is converted to nitrogen. NO_x formed in the kiln's combustion zone is chemically reduced by firing fuel in this region while retaining a reducing environment at the kiln feed end. The calciner region retains a reducing atmosphere by controlling combustion air so that the calcining fuel is first burned under reducing conditions to reduce NO_x , and then burned under oxidizing conditions to complete the combustion reaction. Controlling the introduction of raw meal allows temperature regulation in the calciner. Both fuel NO_x and thermal NO_x are controlled by these mechanisms. [5]

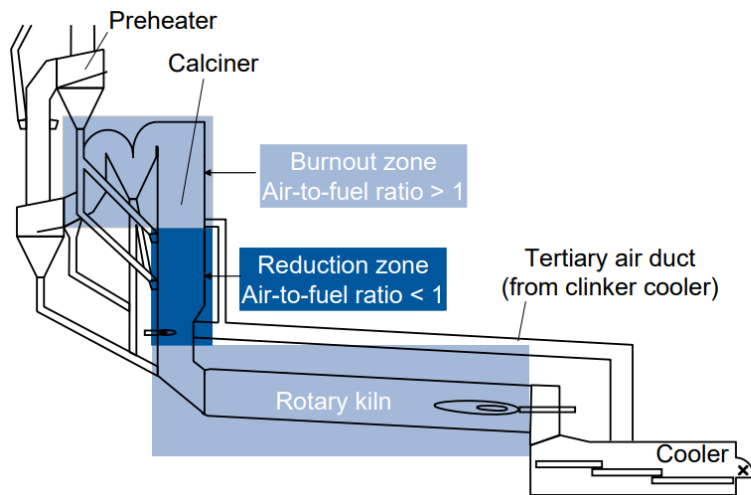


Figure 3. Principle of NO_x reduction by SCC [5]

SCC has four stages of combustion. The rotary kiln is the first stage, where clinker burning can be optimized. The kiln feed inlet is the second stage, which provides reducing conditions for NO_x produced during the sintering process. The raw meal is calcined in the third stage after fuel is introduced into the calciner. To create a reducing atmosphere, calcining fuel is mixed with tertiary air. The remaining tertiary air is introduced as top-up air in the final stage to complete the residual combustion process. [5]

2.3.2.1 Staged-air combustion

One kind of SCC system is a staged-air combustion system in the Figure 4. The calciner burner is vertically positioned in a distinct combustion chamber with staged-air combustion. [5]

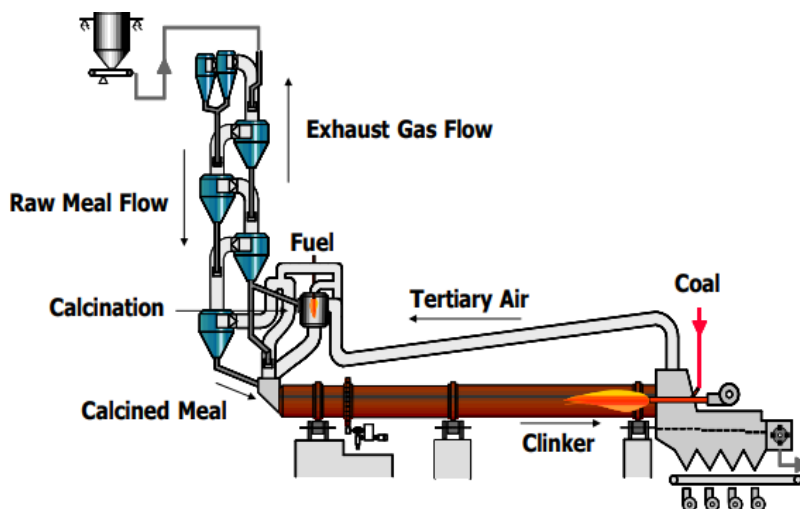


Figure 4. Staged-air SCC [5]

This form of combustion chamber is often applied for difficult-to-burn materials like petroleum coke. In this instance, NO_x in the kiln exhaust is eliminated by burning fuel (coal) in a reducing environment. [5]

2.3.2.2 Sequenced fuel and air combustion

A sequenced fuel and air introduction system (Figure 5) is another type of SCC system. All fuel is burned in a reducing atmosphere near the kiln inlet, and tertiary air is provided in the calciner's lower section. Raw meal is divided and introduced at various stages of the calciner. [5]

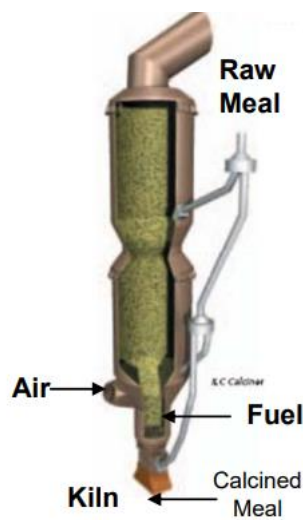


Figure 5. Sequenced fuel and air [5]

For sequenced fuel and air system all calciner fuel is injected at the bottom of the calciner, prior to the kiln inlet, as opposed to other calciner types that stage air or fuel. Tertiary air is added right above the fuel. A high-temperature reduction zone is made in the kiln riser duct, and the calciner is partially integrated into the riser. Following the reducing zone, the temperature is rapidly lowered by the tertiary air, and SO_2 volatilization is constrained. Due to the decreased probability of sulphur compounds coating surfaces, coating and clogging are not issues. [5]

2.3.3 Low NO_x burners

Low NO_x burners are used to split two different combustion zones. Although low NO_x burner design (Figure 6) come in a wide variety, the fundamental concept is the same. [7]

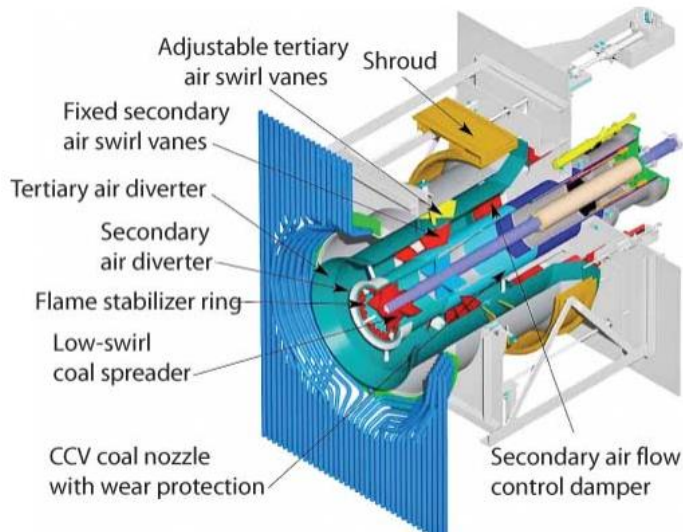


Figure 6. Controlled combustion venturi, low- NO_x burner, with two air zones [6]

During the first phase of combustion, flame turbulence and air/fuel mixing are reduced. To begin, a fuel-rich, oxygen-lean, high-temperature combustion zone is created by decreasing the quantity of primary air in the primary combustion zone and postponing the combustion of all of the fuel. A portion of the flue gas can be reprocessed into the primary combustion zone to decrease the oxygen levels of the primary air and generate a fuel-rich atmosphere. The recycled flue gas can be mixed with the primary combustion air or injected directly into the flame zone. Although temperatures are high, as required to complete clinkering reactions, thermal NO_x formation is inhibited in the primary combustion zone due to a lack of oxygen. The fuel combustion is completed in a secondary, oxygen-rich combustion zone. The secondary combustion zone is cooled by mixing in cooler secondary combustion air. Despite the availability of excess oxygen, NO_x formation is inhibited in the secondary combustion zone due to reduced temperature. [7]

Rotary kilns, including the precalciner and the main kiln, can use low NO_x burners. However, a decrease in NO_x emissions is not always achieved after the use of low NO_x burners. The burner's configuration is needed to be optimized. [7]

2.3.4 Flame cooling

Flame cooling technology implies temperature lowering and the concentration of hydroxyl radicals is increasing, when water is added to the fuel or the flame directly, using various injection techniques, (Figure 7), such as the injection of one fluid (liquid), two fluids (liquid and compressed air or solids), or liquid/solid wastes with a high-water content. [7]

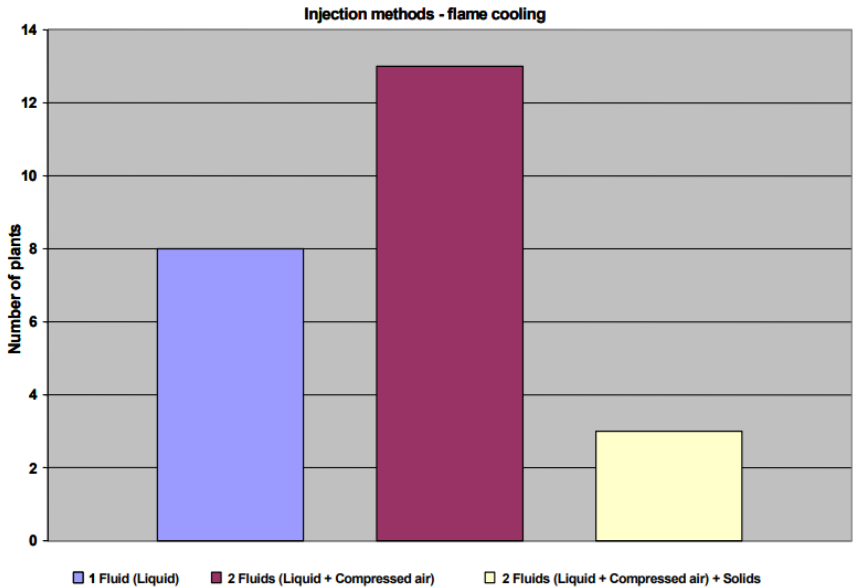


Figure 7. Injection methods used for flame cooling in cement manufacture [7]

NO_x reduction is accomplished through the use of flame cooling. Reduction efficiencies ranging from 10% to 35% have been noted. Emission ranges achieved are illustrated (Figure 8) through the use of flame cooling. Two plants achieved levels of less than 500 mg/Nm³, seven plants achieved levels of 500-800 mg/Nm³, and eleven plants achieved levels of 800-1000 mg/Nm³ (yearly average values). [7]

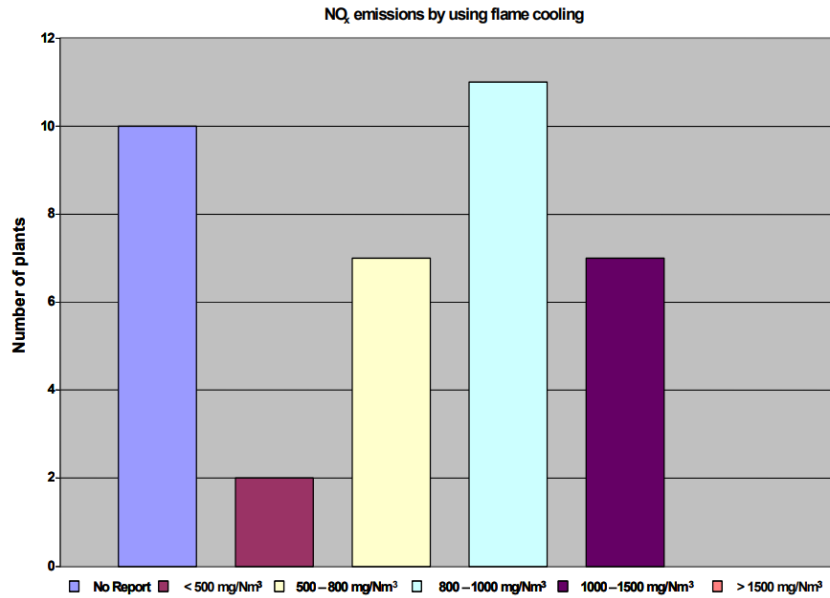


Figure 8. Achieved NO_x emissions ranges by using flame cooling in several cement plants in the EU-23+ [7]

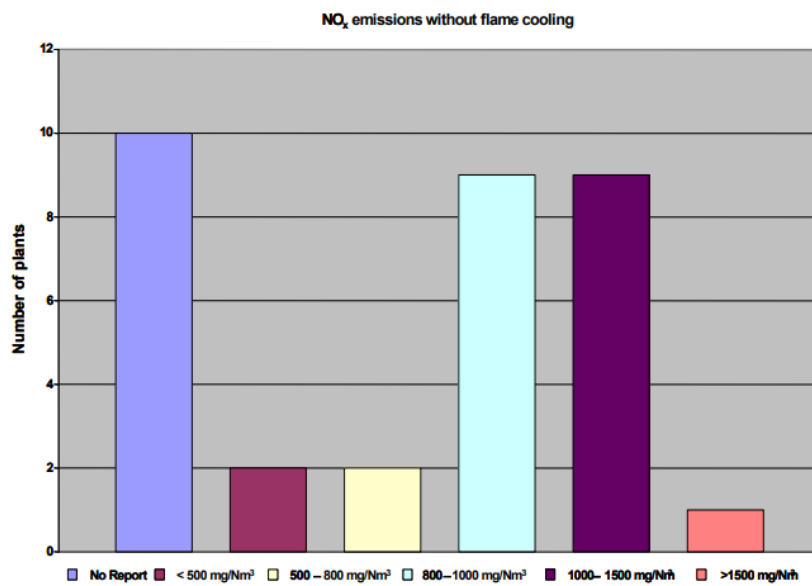


Figure 9. Achieved NO_x emissions ranges from several cement plants in the EU-23+ not using flame cooling [7]

NO_x emissions ranges, achieved by several cement plants without using flame cooling comparing to these emission ranges attained by several plants, are demonstrated in Figure 9. [7]

2.3.5 Process optimization for NO_x reduction

Process optimization can be used to reduce NO_x emissions by smoothing and optimizing the kiln operation and firing conditions, optimizing the kiln operation control, and homogenizing

the fuel feedings. Process control techniques, an enhanced indirect firing technique, optimized cooler connections and fuel selection, and optimized oxygen levels are used as general primary optimisation techniques. Automatic monitoring technology is represented in Figure 10. [11]

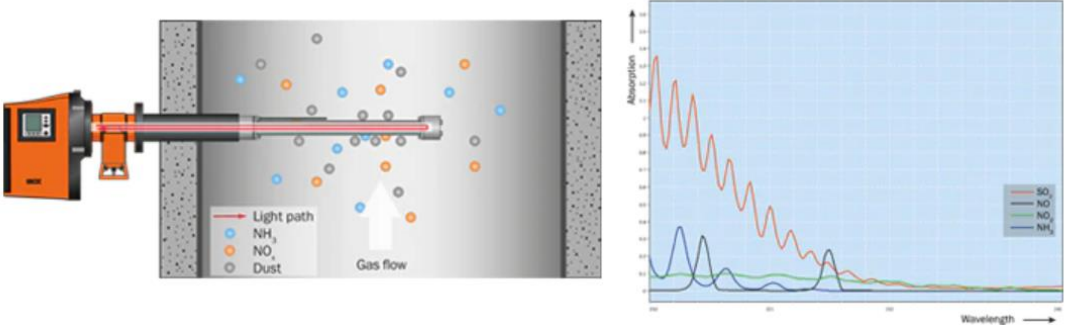


Figure 10. Automatic monitoring technology (optical path and UV absorption spectra) [8]

By stabilizing process parameters, the clinker burning process is typically optimized to reduce heat consumption, improve clinker quality, and increase the lifetime of the equipment. Secondary effects of this optimization include reduced NO_x , SO_2 , and dust emissions. All kiln emissions benefit from smooth and stable kiln operation, close to design values for process parameters. Optimisation techniques include homogenizing raw material, ensuring uniform coal dosing, and improving cooler operation. It is crucial to have good designs of transport conveyors, and feeders, such as a modern, gravimetric solid fuel feed system, to ensure that the feed rate of solid fuel is steady with minimal peaks. [7]

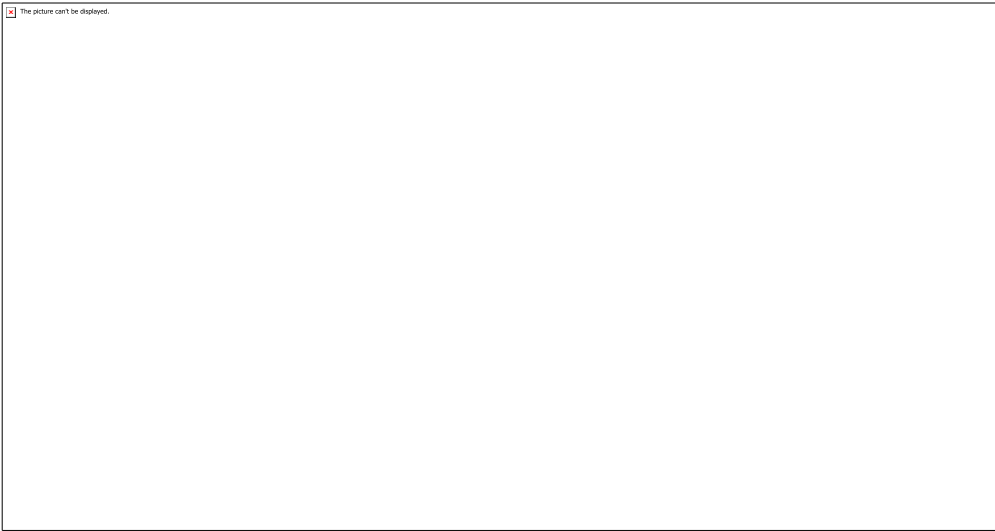


Figure 11. Control and optimization techniques in cement manufacturing [9]

The control and optimization of the cement manufacturing contributing to NO_x emission reduction, is illustrated on Figure 11.

2.4 Secondary techniques for post-combustion NO_x control

2.4.1 Selective Catalytic Reduction (SCR)

Selective Catalytic Reduction implies hot flue gases injection with anhydrous ammonia through a grid system before being routed over a catalyst bed to perform NO_x reduction processes. Frequently, air or steam is used to dilute the ammonia. About 95% of the NO_x emissions in the flue gas are in the form of NO. The most often used catalysts are blends of SO_x -resistant vanadium pentoxide and titanium dioxide. As an alternative to traditional metal-based catalysts, zeolite-based catalyst materials have also been created that can function at greater temperatures. Usually, the catalyst is mounted as a monolithic honeycomb on ceramic materials like alumina. The active base metal and zeolite catalysts frequently make up the majority of the substrate material. [5]

Depending on the specific catalyst used, the optimal temperature for catalytic reactions varies. Due to issues with clogging, the SCR system is fitted after the particle collection. The implementation of an SCR unit also requires flue gas reheating to raise the flue gas temperatures to an adequate level because the normal SCR working temperatures are higher than the usual kiln exhaust flue gas temperatures. [5]

The mechanism of catalytic performance and NO_x decomposition is demonstrated in the Figure 12.

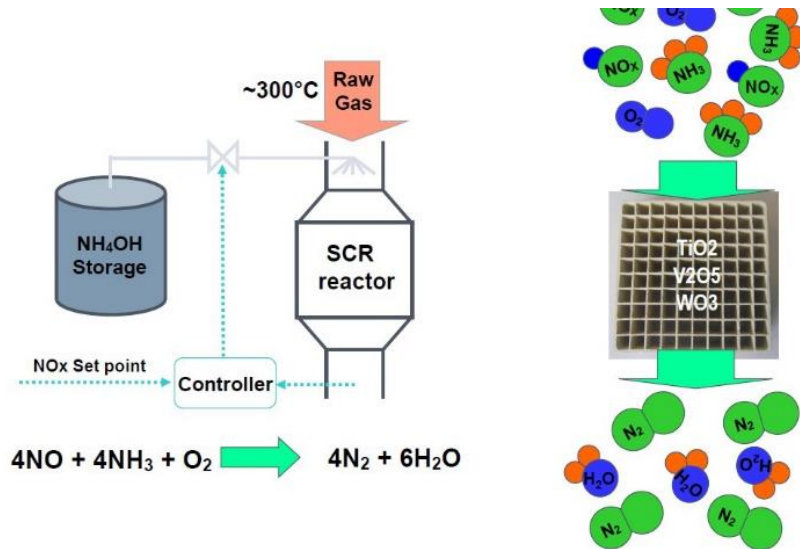


Figure 12. The mechanism of SCR performance for NO_x abatement [10]

Using the right reagent ratio, catalyst bed volume, and operating parameters, the SCR reactor system is able to achieve the desired NO_x reduction. [5]

SCR is a promising method for reducing the NO_x emissions from cement kilns. To establish the precise NO_x reduction in the operating settings and flue gas atmosphere of the cement kiln, additional research is required. [5]

2.4.2 Selective Non-Catalytic Reduction (SNCR)

Selective non-catalytic reduction (SNCR) involves injecting ammonia water, ammonia precursor compounds, or urea solution into the combustion gas to reduce NO to N_2 . To maximize the use of the injected reduction reagent and to sustain higher NO_x reduction efficiency it is vital to inject the agent within the proper temperature range. The reaction has an optimum effect in a temperature range of about 830°C to 1050°C . Urea up to 32%, followed with ammonia water up to 27%, is the most prevalent agent. Ammonia carriers can also be made from waste products from other manufacturing operations. In order to limit the ammonia, slip and obtain the best efficiency of NO_x removal, a favorable ammonia stoichiometric distribution is crucial. [7]

The residence time is an important factor in SNCR performance. The time needed for the process includes mixing injected ammonia solutions/urea with flue gas, evaporation of water,

decomposition of NH_3 to NH_2 and free radicals, decomposition of urea to NH_3 if urea is used, and NO_x reduction reaction chemistry. Increasing the residence time available for mass transfer and chemical reactions improves NO_x removal in general. [7]

The SNCR technique used in cement factories is illustrated on Figure 13.

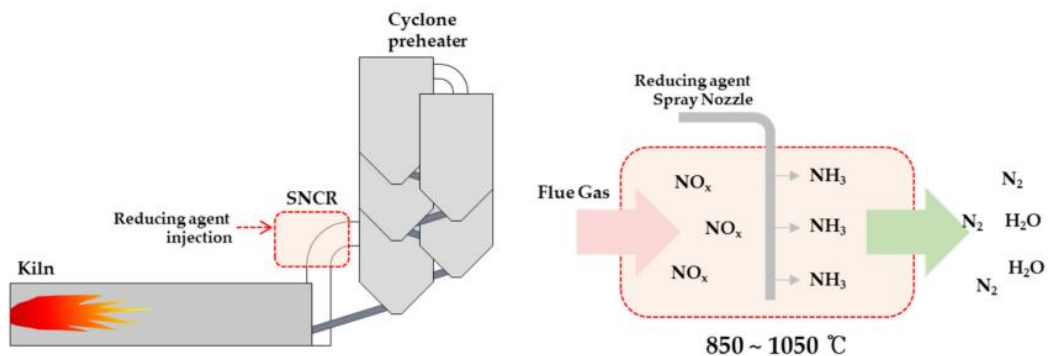


Figure 13. SNCR mechanism in the cement production [11]

Multiple stages have been organized by the reducing agent spray nozzles to regulate the process. At the point of application, the reducing agent is needed to be continually measured, allowing it to be automatically modified to each comfortable temperature. By preventing NH_3 from passing through the lowest injection of the reducing agent and greatly increasing NO_x reduction efficiency, thereby lowering economic costs. [7]

2.5 Emission of dust

The main sources of diffuse dust emissions are the handling, storage, and transportation of clinker, fuels, and raw materials at the manufacturing site. Proper installation maintenance has the indirect effect of lowering dispersed dust. Several strategies that can be used singly or in combination include completely covering dusty operations, such as grinding and mixing, covering conveyors and elevators, usage of automatic devices and control systems and performing of vacuum cleaning for proper maintenance of the installation. Vacuum systems are used to stop diffuse dust formation, during removal operations. [7]

Primary point sources of cement plant dust emissions vary. They include coal mills, kiln systems, clinker coolers, as well as secondary operations. By lowering the overall dust load and

utilizing high efficiency dedusting devices, a significant portion of the fine dust can be decreased. Fabric filters, electrostatic precipitators (ESPs), or a mix of both, known as hybrid filters, are the principal dry flue-gas filter technologies used for dust reduction. Both ESPs and fabric filters have benefits and drawbacks. During optimal operation, they have a very high dedusting efficiency. To ensure adequate efficiency, both types of filter technologies need to be properly maintained. [7]

2.5.1 Electrostatic precipitators (ESPs)

Electrostatic precipitators (ESPs) produce an electrostatic field that travels across the path of the air stream's particulate particles. The particles become negatively charged and move in the direction of positively charged collection plates. Periodically, the material is knocked loose by rapping or vibrating the collection plates, then it drops into the collection hoppers below. It is crucial that ESP rapping cycles are optimized to minimize particulate re-entrainment and hence minimize the potential to influence plume visibility. [7]

Since the particulate's specified collection efficiency is better than 99.99 percent, it is possible to obtain emissions of dust of just a few mg/Nm^3 . If the ultrafine particles can aggregate, ESPs are incredibly effective instruments for collecting them. ESPs have a robust design that makes them highly applicable and also generally insensitive to process disruptions. It is frequently possible to update existing ESP installations instead of completely replacing them, which lowers expenses. Along with dust, the ESP also eliminates contaminants such as metals and dioxins that may be present and adsorb to the dust particles. Schematic representation of electrostatic precipitator is shown in the Figure 14. [7]

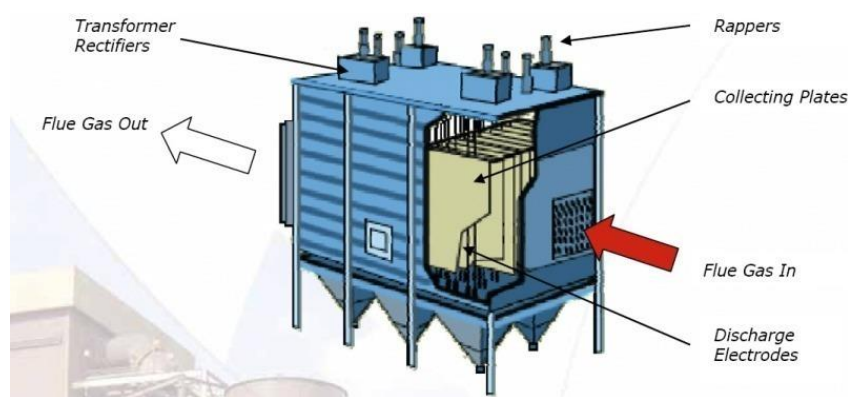


Figure 14. Schematic representation of electrostatic precipitator [12]

Electrostatic precipitators have been effectively constructed for dust collection from rotary kiln exhaust gas and clinker cooler exhaust gas due to their high efficiency, low pressure loss, high availability, and energy efficiency. Almost all cement kiln applications for dust collection from kiln exhaust gas, or the exit air from grate coolers can apply the ESP. [7]

2.5.2 Fabric filters

The use of fabric-based dust collectors is highly efficient. Well-designed and well-maintained fabric filters can achieve separation efficiency higher than 99.9%. [7]

The fundamental idea behind fabric filtering is to utilize a fabric barrier that allows for gas permeation but captures dust. The filter medium is mainly arranged geometrically. However, there is a distinction between filter pockets, which are typically installed horizontally, and fabric filter with cylindrical filter bags (Figure 15), which are hung vertically. [7]

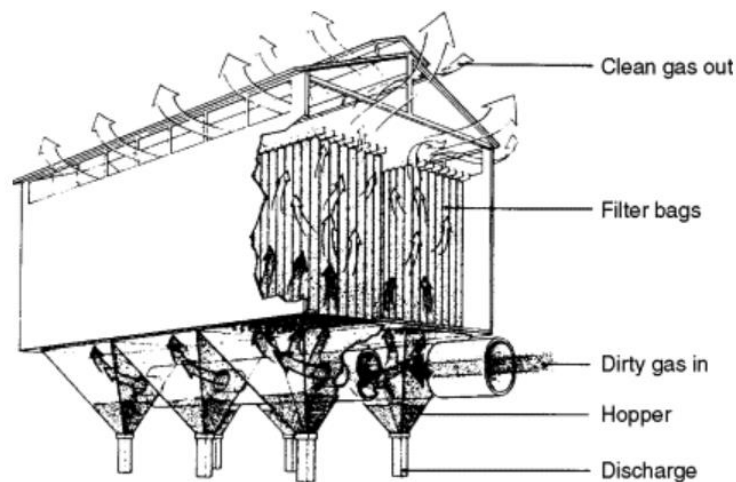


Figure 15. Industrial fabric filter device [13]

Fabric filter operation implies initially dust deposition on the fabric's surface fibers as well as deeper within the fabric, but when the surface layer thickens, the dust itself takes over as the main filter medium. Off-gas may vent from the bag's interior outward or inversely. The resistance to gas flow rises as the dust layer becomes thicker. Therefore, to manage the gas pressure drop through the filter, periodic cleaning of the filter media is required. The fabric

filter not only filters out dust but also other contaminants like metals and dioxins that may be present and adhere to the dust particles. [7]

2.5.3 Hybrid filters

Hybrid filters combine ESPs and fabric filters in a single device. They typically originate as a result of ESP conversions. The larger particles are collected using the electrostatic precipitation on the equipment's inlet end, and the subsequent fabric filter section serves as a polishing unit to remove the finer particles. Hybrid filter's operating principle is displayed (Figure 16). [14]

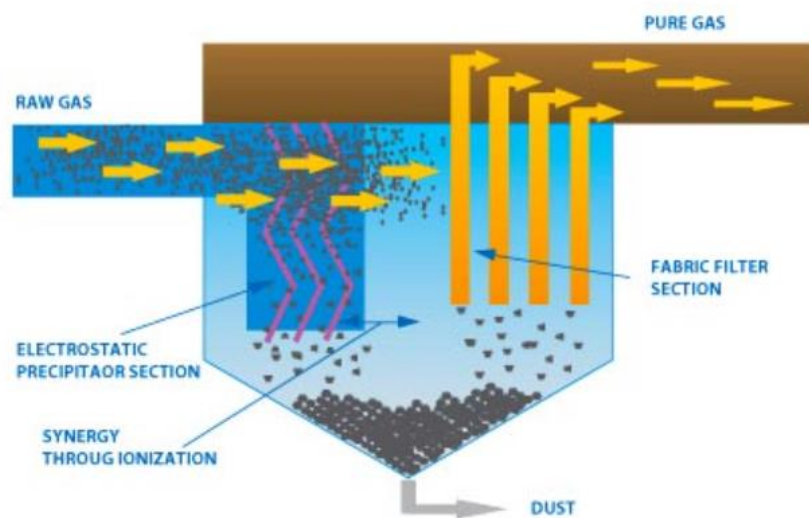


Figure 16. Hybrid filter's operating principle [14]

Larger particles from the atmosphere can be easily collected using electrostatic precipitators without high energy input. This makes it possible to use the electric field's ionization and agglomeration effects to decrease the pressure drop across the filter bags. Bag filters are independent of power supply variations and achieve lower emission values. [14]

2.6 SO_x emission

The amount of volatile sulphur in the raw materials and in the fuels, dictate how much SO₂ is released from cement plants, which is dependent on the overall intake of sulphur compounds and the process type used. The circulation of sulphur that takes place in the kiln system has an

impact on both the production and possible emissions of SO_x . The sulphur is released from several kiln system outputs, including CaSO_4 , SO_2 in exhaust gases, and other mixed compounds in clinker and dust. However, the majority of the sulphur is either released from the process or integrated into the clinker. [7]

Considering SO_2 control, the first step implies basic process optimization techniques, such as optimizing the clinker burning process, which includes kiln operation smoothing, hot meal distribution uniformity, and avoiding reducing conditions in the burning process, as well as the choice of raw materials and fuels. Additionally, SO_2 collection in the kiln charge depends on the oxygen content in the kiln inlet area. Long kilns' SO_x and NO_x levels are decreased and increased, respectively, by increasing the oxygen content. However, the clinker burning process needs too much oxygen to provide the desired product value. As a result, there is always an enough supply of oxygen to ensure the production of sulphates, which are released from the kiln system through the clinker, in the hot gas chamber of the grate preheater or the bottom section of the cyclone preheater. By modifying the back-end oxygen content, it is possible to optimize SO_x while still preserving the environment. Additional end-of-pipe strategies can be used in situations where existing solutions are insufficient. Further analyzed technologies that contribute to SO_2 emission reduction, are: activated carbon addition to the process and wet scrubber implementation. [7]

2.6.1 Wet scrubber

The most common method for flue-gas desulphurization in coal-fired power plants is the wet scrubber. The wet process is a proven method for cutting SO_2 emissions from cement production processes. A liquid or slurry that is injected in a spray tower absorbs the SO_x . Of all flue-gas desulphurization (FGD) techniques, wet scrubbing systems have the highest removal efficiency for soluble acid gases and the lowest solid waste production rates. Wet scrubbers, however, also drastically cut down on HCl, residual dust, and, to a lesser extent, metal and NH_3 emissions. [7]

Fundamental operating principles of a wet scrubber are shown (Figure 17).

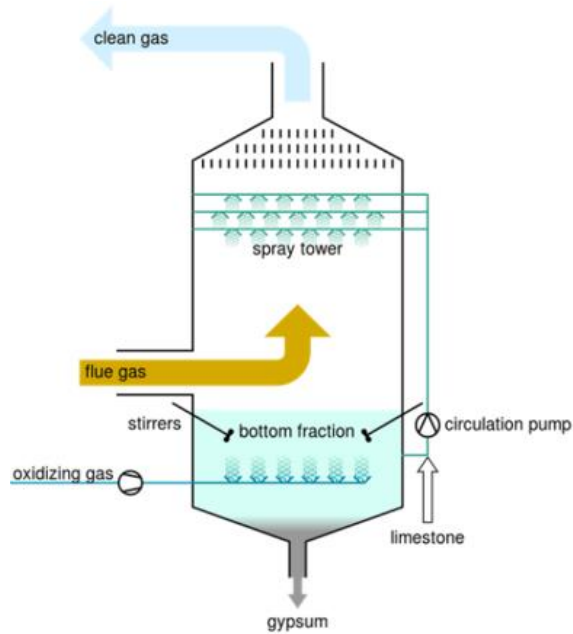


Figure 17. Wet scrubber operation principles [15]

The slurry is sprayed in the opposite direction of the exhaust gas flow and caught in a recycle container at the bottom of the scrubber, where the sulphite that has produced is oxidized to sulphate by air, creating calcium sulphate dihydrate. Depending on the physico-chemical characteristics of gypsum, the dihydrate is separated, and the water is then returned to the scrubber for use in cement manufacturing. [7]

2.6.2 Activated carbon

Activated carbon can be used to adsorb pollutants from exhaust gases, including SO_2 . The activated carbon filter is either built as a packed bed with modular partition walls or is utilized for the injection approach. Periodically, used activated carbon is relocated to a different silo and changed with new adsorbent. The trapped materials are released into the system and mostly fixed in the cement clinker by using the saturated coke as fuel in the kiln. [7]

2.7 Use of wastes as fuels and raw materials

Since they are completely binded in the clinker and for purpose of minimization of adverse impacts on air emissions, waste materials used as raw materials or fuels in cement kilns must satisfy certain quality standards. As a general rule for quality standards, waste allowed as fuels or raw materials need to provide the cement kiln with calorific value and material value from

waste material. In order to satisfy requirements for alternative fuels introductions in cement plant, certain principles (Table 1) need to be provided. [16]

Table 1. Guiding principles for co-processing alternative fuels in cement kilns [16]

Principle	Description
co-processing respects the waste hierarchy	<ul style="list-style-type: none"> -waste should only be utilized in cement kilns if there are no other, more environmentally and economically sound options. -co-processing should be seen as an integral component of waste management. -co-processing is consistent with international environmental agreements.
additional emissions and negative impacts on human health must be avoided	<ul style="list-style-type: none"> -negative effects of pollution on the environment and human health must be prevented or kept at a minimum -air emissions from cement kilns burning alternative fuels cannot be statistically higher than those of cement kilns burning traditional fuels
the quality of the cement must remain unchanged	<ul style="list-style-type: none"> -the product (clinker, cement, concrete) must not be used as a sink for heavy metals -the product must not have any negative impacts on the environment (e.g., leaching) -the quality of the product must allow for end-of-life recovery
companies that co-process must be qualified	<ul style="list-style-type: none"> -country specific requirements must be reflected in regulations -stepwise implementation allows for build-up of necessary management and handling capacity -co-processing should be accompanied with other changes in waste management processes in the country

If certain requirements are satisfied, certain wastes with sufficient calorific values can be utilized as fuels in cement kilns in place of traditional fossil fuels like coal. They frequently only operate after a specific pre-treatment to deliver chemically treated fuels for the burning of clinker. Different factors, such as physical criteria, chemical requirements, as well as reactivity, play a significant part in the decision to use waste as fuel since they might affect kiln operation and emissions. The points at which fuels are added to the kiln must be taken into consideration depending on the types of waste used and their properties since how the fuels are fed into the kiln might affect the emissions. [16]

Fuels fed through the main burner typically experience the highest combustion temperatures. Temperatures and residence times for each feed point are influenced by kiln operation and design. To uphold environmental, safety, and quality standards, special control and process procedures are required. Safety management must be considered when managing hazardous wastes, such as when storing and feeding. When utilizing waste fuels made from pre-treated and sorted waste fractions, safety management for possibly self-igniting materials should be considered. [17]

The range of fuels is extremely wide. Traditional kiln fuels are gas, oil or coal. Materials like waste oils, plastics, auto shredded residues, waste tires and sewage sludge are often proposed as alternative fuels for the cement industry. Also, all kinds of slaughterhouse residues are offered as fuel nowadays. To be able to use any of these fuels in a cement factory, it is necessary to know the composition of the fuel. The choice is normally based on price and availability. The energy and ash contents are also important, as are the moisture and volatiles contents. All kinds of varieties from liquid to solids, powdered or as big lumps can be encountered when dealing with alternative fuels, requiring a flexible fuel feeding system. It can be fed directly into the burning zone in the kiln itself or into the pre-heating system for dissociating part of the carbonates from the meal before it enters the kiln for clinker formation. [17]

Alternative fuels differ from regular fuels in their qualities. Alternative fuels typically have higher material densities and transport properties, and these aspects have a significant impact on the burning process. High replacement ratios cause significant changes in the burning process. The key aspects of the burning process that are affected are those connected to the kiln's temperature profile, such as the sintering temperature, the length of the burning zone, and

the cooling conditions. As a result, the clinker's properties, including as the burning grade, granulometry, and degree of crystallization, can be substantially adjusted. [17]

In the cement industry, a variety of alternative fuels can be used. Different materials can be safely co-incinerated in cement rotary kilns. This indicates that the full mass of fuel, including the ash residue, is absorbed into clinker, a byproduct of the cement manufacturing process. It is achieved that no additional ash disposal is required. Organic portions are destroyed in the kiln due to the extremely high temperature, and hazardous elements such as heavy metals are securely lodged in the clinker minerals. They become inert, or immobilized, in this manner, and it is impossible to reactivate them in any way by mechanical action, thus it cannot be washed away with water. [18]

2.7.1 Waste materials processing

Multiple technical solutions for using waste materials in cement factories are accessible in terms of the best possible routes to use waste materials in the cement industry. Waste materials can be used as alternative fuels and raw materials in the kiln. Waste, on the other hand, can be processed beforehand using gasification or incineration methods. In these circumstances, byproducts from these steps, such as gas from gasification or ashes from incineration, can be used as fuel or raw materials in the cement production. Schematic representation of technical approaches of waste materials processing is displayed in the Figure 18. [18]

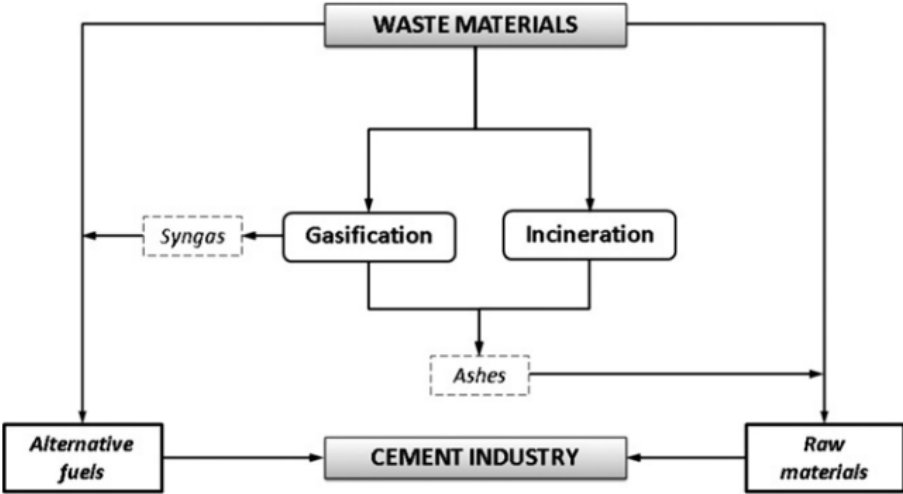


Figure 18. Summary of available technical options to use alternative fuels [18]

2.7.1.1 Direct combustion

Direct combustion is a well-known technology that has been used in recent years. The pyro-processing system provides the opportunity to reduce energy consumption and emissions associated with the direct combustion of alternative fuels in the pre-heater and pre-calciner systems. Furthermore, lower temperatures lessen NO_x emissions. [18]

The quality of the fuel is less limited in systems with precalciners, and the kiln performance and clinker quality are less affected by the fuel quality. Direct combustion, on the other hand, demands pre-conditioning operations in cleaning, drying, and homogenizing, prior to the use of alternative fuels in order to produce consistent heating values, and the preprocessing equipment must be incorporated into the plant. [18]

2.7.1.2 Gasification

The gasification of alternative fuels is based on the production of a rich energy producer gas composed of a mixture of hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), water vapour, and methane (CH_4), often known as synthesis gas. Synthesis gas is then co-fired in the kilns, pre-heaters, and pre-calciners with a gas burner. The technique used to produce synthesis gas from alternative fuels comprises of circulating fluidized bed gasifiers in traditional gasification systems or plasma gasifiers in high-temperature gasification systems. The fluidized bed gasifier is the most extensively utilized gasification technique for industrial-scale applications. The advantages of fluidized bed gasifiers are the extremely good temperature control, high reaction speeds, high carbon conversion ratio, and high gas quality. The main downside is that fluidized bed gasifiers often increase the drag of fine particles produced by ash and fuel elutriation. [18]

2.7.2 Alternative fuels usage

The introduction of alternative waste is dependent on the composition and type of these materials, as well as the final mixture with traditional fuels and original raw meals, which may necessitate modifications to manufacturing equipment or intermediary processes in some cases if there is complete or very high fuel substitution with alternative wastes. Knowledge of these attributes is critical because the alternative fuel's chemical purity must adhere to environmental

protection rules, and its calorific value must be stable enough to allow control of feeding in the rotary kiln. The physical shape must be simple to transfer to a cement plant. [19]

When operating with alternative fuels, all types of variations, from liquid to solid or powdered form, might be encountered. [20]

Variety of alternative fuels according to their aggregate state are presented in the Table 2.

Table 2. Alternative fuel options for the cement industry [20]

Category	Fuels
Gaseous fuels	Refinery waste gas, landfill gas, pyrolysis gas, natural gas
Liquid fuels	Tar, chemical wastes, distillation residues, waste solvents, used oils, wax suspensions, petrochemical waste, asphalt slurry, paint waste, oil sludge
Solid fuels	Petroleum coke (petcoke), paper waste, rubber residues, pulp sludge, sewage sludge, used tires, battery cases, plastics residues, wood waste, domestic refuse, rice husks, refuse derived fuel, nut shells, oil-bearing soils, diapers, etc.

In recent years, waste materials have been routinely used in European cement plants. The extent to which alternative fuels are used varies by country. The replacement ratios of fossil fuels by alternative fuels for a number of European countries (Table 3) is shown between 2010 and 2011. As demonstrated, the Netherlands had the greatest ratio (83%), but numerous countries obtained considerable replacement ratios, such as Austria, Germany, and Norway around 60-63% or Switzerland and Belgium between 47 and 49%. However, despite having low replacement ratios of 8.6 and 22.4%, respectively, Italy and Spain have expanded their amount of alternative fuel substitution in recent years. In Spain, the usage of alternative fuels grew by nearly 22% compared to 2004, when around 175.000 t of waste materials were recovered materially or

energetically. These findings highlight the significant untapped potential of alternative fuels in the cement industry. [18]

Table 3. Replacement ratios of fossil fuels with waste materials in selected European countries [18]

Country	Replacement ratio (%)	Country	Replacement ratio (%)
Italy	8.6	Austria	63.1
Spain	22.4	Switzerland	49.0
Denmark	25.0	Belgium	47.3
France	29.4	Germany	62.0
Sweden	29.0	Netherlands	83.0
Norway	60.0	United Kingdom	39.5

The most widely used materials, especially because of waste management considerations such as petroleum products, municipal solid waste, meat bone meal, biomass, hazardous waste and sewage sludge are further described. [18]

2.7.2.1 Petroleum-based wastes

Petroleum products, such as tires, waste oils, rubber, plastics, petroleum coke (petcoke), and asphalt, account for approximately 30% of waste-based fuels globally. Tires and waste oils are the most frequent of these fuels. Waste fuels derived from petroleum have significant calorific values. [16]

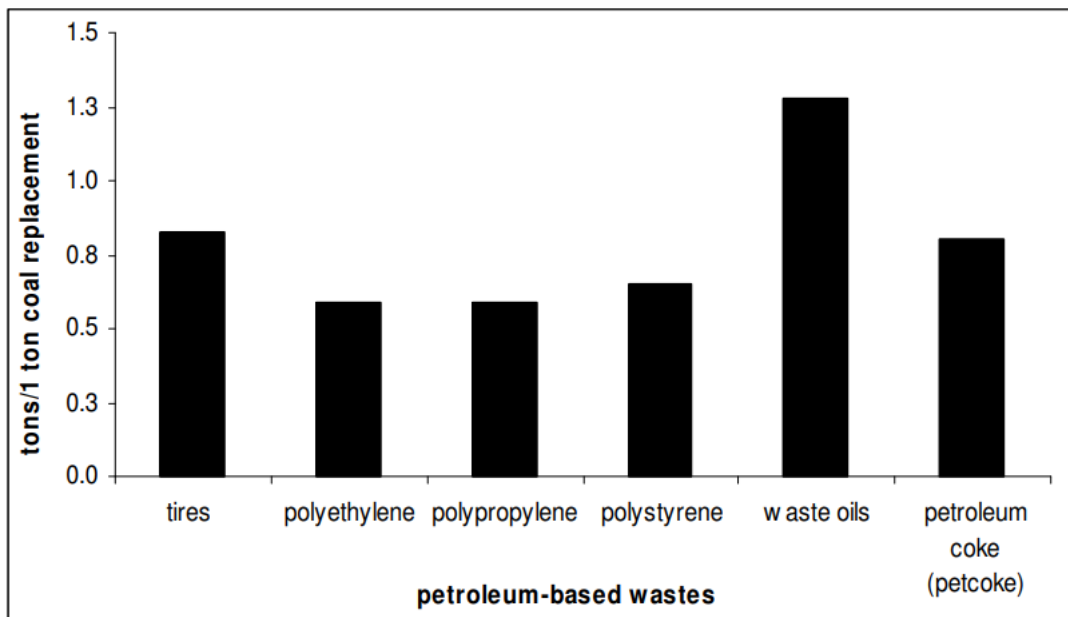


Figure 19. Tons of petroleum-based wastes necessary to replace one ton of coal in a cement kiln [16]

The amount of petroleum-based waste required to replace one ton of coal (Figure 19) is determined by the material's energy value and water content. [16]

2.7.2.1.1 Used tires

Tires are a byproduct of the automotive industry. Rubber fuel is one of the most commonly utilized alternative fuels in the cement industry due to its high carbon content, high calorific value, and low moisture content. Utilized rubber can be used as an alternative fuel in cement plant furnaces in any shape, from whole to shredded to a fine-grained form. When finely chopped rubber is put directly into the furnace, it can be blended with pulverized coal; however, the process of removing iron from rubber to manufacture fine-grained rubber incurs additional expenses, whereas using complete tires does not. [16]

One further advantage is that tires contain iron. When tires are used to make clinker, the residence period in the furnace is long enough to completely burn the rubber, converting the iron carcasses into iron components that are integrated into the clinker mineral. [16]

Worn tires are good sources of energy, particularly when used as secondary fuels. Due to the properties of these machines, which integrate very high temperatures with an oxidizing

environment and a relatively long material residence time, tires can be entirely destroyed in the rotating kiln. The absence of smoke or odors is prevented by full combustion. [16]

2.7.2.2 Municipal solid waste

Municipal solid waste (MSW) production is increasing notably, and MSW has become a common alternative fuel in the cement industry. However, most cement plants do not directly burn unsorted MSW due to the heterogeneous nature of the waste and the presence of components that could pose quality and environmental concerns. [20]

Refuse Derived Fuels (RDF) or waste fuel is a type of solid alternative fuel derived from municipal or industrial solid waste, such as plastic or from materials that are difficult to recycle after decomposition. RDF is often composed of municipal garbage that has been removed of non-combustible components such as stone, iron, gravel, and other non-combustible materials. RDF is the material that remains and is used as a secondary fuel in the manufacturing of clinker. [20]

Solid Recovered Fuel (SRF) is a diverse set of fuels generated from municipal solid waste, industrial, commercial or construction waste. SRF is categorized according to the limit values of three important fuel qualities. The most essential attribute of SRF is its net calorific value, which is a measure of its market value and reflects the value of SRF as a fuel. [21]

2.7.2.3 Meat bone meal

Meat bone meal (MBM) is made in bone meal processing factories, which combine, chop, and boil animal guts and bones. Co-incineration in cement kilns is the best method for destroying MBM and utilizing its calorific value. MBM has a lower carbon content and a higher ash and chlorine concentration than coal. The majority of the chlorine in MBM exists as common salt (NaCl), and the sulphur level is slightly lower than in coal. While a high calcium concentration is beneficial in cement, a high phosphate content can have a negative impact on the manufacturing process and cement quality. [20]

2.7.2.4 Biomass

The primary role of biomass is to reduce greenhouse gas emissions. The quantity of CO₂ emitted during burning is equal to the amount of CO₂ absorbed during plant development, therefore the amount of CO₂ emitted during combustion is minimal. Furthermore, biomass is an energy source that can be used in place of fossil fuels. Biomass and its byproducts, such as liquid biofuels and biogas, are not only potentially renewable, but also similar enough to fossil fuels to allow for direct replacement. [20]

Biomass can be used in cement plants through two major modes, namely direct combustion and transformation into producer gas. This can happen in two ways: first, by mixing crushed and pulverized biomass with coal or petcoke for use in the kiln, and secondly, by direct feeding of biomass in solid lump form, such as pellets, into the rotary kiln, pre-heater or pre-calciner combustion chamber. The biomass can also be transformed into producer gas and co-firing it in the kilns using a gas burner. [20]

Biomass has a low calorific value when compared to other fuel replacements such as petroleum-based wastes and other chemical and hazardous wastes. The carbon neutrality of biomass is one reason to use it; nevertheless, significant conventional fuel offsets require massive amounts of biomass. [20]

The relatively low calorific value of biomass can create flame instability; however, this can be handled by using lower replacement rates and adjusting air flow and flame form. Because biomass changes with time, care must be made to use the material before it begins to degrade. The oldest biomass should be fed into the kiln first, so that new biomass is rotated into the bottom of storage facilities. Because the flow behavior of different materials is extremely diverse in relation to biomass conveyance, cement kiln operators must select the method for injecting fuel into the kiln that will facilitate a steady and adequate heat value. [16]

2.7.2.5 Hazardous waste

Certain permitted hazardous wastes have been used as alternative fuel in cement factories. Chemical and hazardous wastes account for approximately 12% of global fuel replacement in cement kilns today, and comprise items such as wasted solvent, outmoded insecticides, paint

residues, and anode wastes. Because chemical and hazardous wastes have the potential to contribute to undesirable emissions, cement kiln operators must follow correct storage and handling guidelines. Chemical and hazardous wastes have substantially higher calorific values than biomass. Because most chemical and hazardous wastes are liquids, the grinding and shredding stage is omitted, resulting in capital and operational cost savings for the receiving cement plant. According to calculations based on average values, tons of chemical and hazardous wastes necessary to replace one ton of coal in a cement kiln are presented in the Figure 20. Values are dependent on the material's energy value and water content. [16]

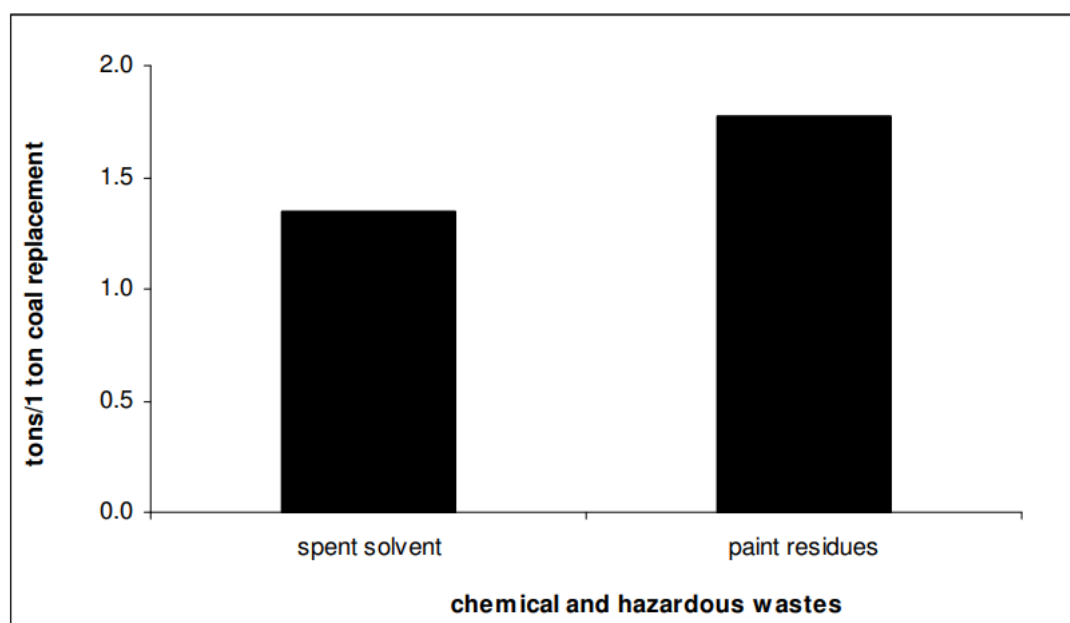


Figure 20. Tons of chemical and hazardous wastes necessary to replace one ton of coal in a cement kiln [16]

Electricity savings enhance the net reduction in carbon emissions associated with coal substitution. Co-firing of chemical and hazardous wastes has potentially harmful environmental and human health repercussions if not handled properly. In accordance with the guiding principles for good practice in fuel substitution, cement factories that accept hazardous wastes must have appropriate technical capacity and infrastructure to ensure worker and environmental safety. [16]

2.7.2.6 Sewage sludge

Conventional disposal options include landfill disposal, discharge into the sea, and use in agriculture as organic fertilizer. Traditional disposal methods, however, have environmental

and economic constraints. Increased landfill disposal prices, combined with increasingly strict environmental rules, make conventional garbage disposal a less appealing alternative. The most suitable way of alternative disposal of waste sludge is its incineration and disposal of ashes in controlled landfills. Sludge ash contains a high concentration of SiO_2 , Al_2O_3 , and Fe_2O_3 , which can influence cement quality if excessive amounts of sludge are used. The spectrum of different elements in waste sludge and its thermal value are determined by the sludge's origin and the waste sludge processing method itself. [21]

The disposal of sewage sludge generated by sewage treatment plants is a major waste management issue. As an alternative fuel source, cement industries can utilize sewage sludge with calorific energy potential. As a result, dried sludge is also utilized as an alternative fuel in rotary kilns. Sewage sludge contains a lot of water. This is a crucial consideration when using sewage sludge in gasification and, especially, combustion operations. The cost of drying it before usage, as an alternative fuel or raw material is significant. Sewage sludge is often dried using waste heat from the cement kiln. It is either used as fuel in the cement kiln's main furnace or gasified beforehand and used as an alternative fuel in cement kilns, heaters, or pre-calciners. The leftover non-combustible components of the sludge are utilized as raw materials in cement manufacturing in both circumstances. When used appropriately, sewage sludge has minimal environmental impact. The calorific value of sewage sludge varies greatly depending on the properties of the wastewater from which it is derived and the treatment the sludge receives. Raw sludge contains less energy than treated sludge, such as anaerobically digested sludge. [21]

2.8 Reduction of energy consumption

Energy optimization techniques are needed to be applied at different plant units in order to reduce energy consumption. For new facilities and significant upgrades, kiln systems with multistage cyclone preheaters with an incorporated calciner and tertiary air duct are regarded as standard procedure. Raw materials with a high moisture content are required to be processed through three-stage cyclone plants. [7]

Improvements to the cooler include the installation of a contemporary clinker cooler, the use of cooler grate plates with higher flow resistance to generate a more consistent cooling air distribution, and controlled cooling air delivery to the various grate sections. Some of kiln improvements include high capacity utilization, optimized diameter ratio, optimized kiln firing

systems, uniform and stable operating conditions, process control optimization, use of mineralizers and reducing air-in leakage. Intensive precalcination of the raw meal, low pressure drops, homogenous hot meal distribution in the kiln riser and low-pressure drop are a few instances of calciner improvements. High cyclone collection efficiency, homogenized meal distribution over the gas duct cross-sections, and uniform distribution of solid and gas flows in a two different preheater cyclone stages are examples of preheater advancements. They also include low pressure drop and a high level of heat recovery in the cyclones. Low moisture content of fuels and raw materials, easily flammable fuels with high calorific values, homogenizing and even feeding of fuels and of kiln feed material are characteristics of improved material handling. The key potentials of these technologies in terms of environmental advantages include decreased energy use, decreased emissions to water, air, and land, reduced costs for raw materials, increased manufacturing yields, and decreased waste. [7]

3. CONCLUSION

The principles of the BAT technology implementation in the cement industry are described through the presentation of the basic problems during cement production, along with the possibility of elimination of the same adverse effects that represent a threat to the environment and affect the efficiency of the process.

Analysis of the impact on the reduction of NO_x gases showed that the amount of oxygen in the fuel combustion zone has a significant effect on the formation of NO_x gases. The working principle boils down to the fact that thermal NO_x formation is inhibited in the primary combustion zone due to a lack of oxygen and in the secondary combustion zone it is inhibited due to reduced temperature. The SCR approach of NO_x reduction to N_2 with the application of NH_3 and a catalyst at adequate temperature range is described. SNCR effectiveness is represented. It has been identified that usage of SNCR in order to sustain higher NO_x reduction efficiency requires injection of the agent within the proper temperature range. To a lesser extent, flame cooling also promotes the NO_x reduction. Based on the provided analysis, it has been concluded that optimizing oxygen levels and process conditions generally reduces the formation of NO_x gases.

For dust collection from rotary kiln and clinker cooler exhaust gas, electrostatic precipitators have been recognized as effectively constructions, due to their high efficiency, low pressure

loss, high availability, and energy efficiency. The removal of dust through gas permeation and dust capture using a fabric filter is proven to be also highly effective.

For cement manufacturing processes, wet scrubbing systems are considered to provide the highest removal efficiencies for soluble acid gases of all flue-gas desulphurization including SO_x. Addition of activated carbon adsorption assists in capturing SO₂ from flue gas.

Replacement of traditional with alternative fuels is described as favorable option in cement manufactories according to its calorific value and its environmental impact after application. Overall cement production efficiency is improved by stabilizing process parameters.

Considering BAT as a dynamic concept, its evaluation is an evolving process. New procedures and measurements are being established, science and technology are constantly improving, and innovative technologies are being effectively applied in the cement industry and variety of other industries.

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