 doi:10.20944/preprints202108.0300.v1

Article

Used tires as fuel in clinker production: economic and environmental implications

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Abstract: The objective of this work is to compare how the gases emitted during the manufacture of the clinker vary in a cement plant, using two types of fuel: petroleum coke and unusable tires (UTs). The study is based on a case study using real time data on more than 40 process variables. Gases are analysed from two points of the production process: Sintering Kiln, main focus of emission to the atmosphere by chimney, and Preheater. The variation of CO and NO_x depending on the oxygen and fuel type is studied. The SO_2 levels are also analyzed, observing a decrease when using the UTs. The quality of the Clinker has been compared depending on the fuel type. The results are compared, on the one hand, with the quality of the clinker, determined by the content of the majority (C_3S, Alite) and minority (Free CaO) phases, and, on the other hand, with the Kiln sintering temperature, the most influential parameter in the productive process. It is verified that Clinker quality is maintained, regardless of the type of fuel used. Concluding that the use of UTs as fuel can generate an important economic and environmental benefit for cement companies and their environment.

Keywords: Clinker; used tires; pollutant gases; energy savings; environment impact.

1. Introduction

The scientific community has been reporting, over the last thirthy years, that the main sources of greenhouse gases and global warming are caused by massive use of fossil fuels such as coal, oil and natural gas [1,2]. Various proposals have been put forward to mitigate their effects [3], prominent among which is the use of alternative fuels to reduce emissions [4].

In the case of cement factories, substituting traditional fossil fuels not only reduces emissions, particularly CO_2, but also provides a use for wastes such as sludge, municipal solid waste and tires, yielding energy savings and environmental benefits [5-8], with some particular case studies analysed in this regard [9].

The cement companies emit into the atmosphere pollutants coming from scattered and point sources. Emissions from nonpoint sources are neither discharged through specific structures nor are they associated with combustion, grinding or drying processes. Instead, they arise from simple operations such as intermittent loading of lorries by diggers, stored piles of limestone and the circulation of vehicles on unpaved tracks. The only pollutants such nonpoint sources basically emit into the atmosphere are solid particles. Hence, the overall emissions have to be strictly controled to avoid adverse conditions for the environment and the inhabitants close to the emission sources [10].

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On the other hand, emissions from point sources are produced during the production process by the kiln, homogenization system, grinding, silos and thermal processing of materials, being discharged through ducts and chimney [11]. The most important source of emission into the atmosphere by chimney is the clinker kiln. The main pollutant compounds generated are solid particles, nitrogen oxides (NO_x) and sulphur dioxide (SO_2). Depending on the characteristics of the process, other compounds may also be emitted from the same sources, including carbon monoxide (CO), carbon dioxide (CO_2), hydrofluoric acid (HF), volatile organic compounds, etc. [12]. The emission of these pollutants is normally very low, but their control ensures the correct operation of the kiln in waste treatment activities [13,14].

The cement industry is very vulnerable to fuel price fluctuations. Consequently, an important effort has been made to improve energy efficiency over time, with reduction around 30% of the energy consumed to produce clinker since the 1970s [15]. In addition, the use of alternative fuels yields economic savings for companies in this sector [16] and they are an interesting approach to tackle the environmental impact generated [17].

The goals of this study are: a) to compare how the gases emitted during the manufacture of the clinker vary in a cement plant using two types of fuel: petroleum coke and unusable tires (UTs) and b) evaluate the introduction of UTs into the system from an economic and environmental point of view. In the first part of this research, several pollutants generated in a cement company are described (CO_2, CO, NO_x and SO_2), and how the fuel variation used to manufacture the clinker affects them, depending on using only fossil fuels (petroleum coke) or using a combination of petroleum coke and unusable tires. Other posible contaminants are beyond the scope of the study. The second part of this research analyses possible variations in the quality of the product, taking into account the parameters of the production process. Finally, an economic comparison is made with both types of fuel.

1.1 Clinker

The four major oxides that make up the chemical composition of the typical Portland clinker are 67% CaO, 22% SiO_2, 5% Al_2O_3, 3% Fe_2O_3; It also contains 3% minority elements such as Na^+, K^+, Mg^{2+}, Ti^{4+} and S^{2-}. While the production of Portland cement clinker is the result of a process of heating minerals such as clay and limestone ($CaCO_3$) at 1450 ºC. As warming progresses, a series of transformations occur:

- From 70 ºC to 110 ºC the free water of the raw materials evaporates.
- From 400 ºC to 600 ºC, the clay is broken down into its oxide-like components, mainly SiO_2 and Al_2O_3.
- In the next step, from 600 ºC to 1000 ºC, the limestone reacts with silicon dioxide to form dicalcium or belite silicate (Ca_2SiO_4), while excess $CaCO_3$ decomposes into calcium oxide (CaO) and carbon dioxide (CO_2).
- Finally, from 1100 ºC to 1450 ºC, partial fusion occurs, and Belite reacts with calcium oxide to form tricalcium silicate or Alite (Ca_3SiO_5).

These reactions, together with the burning of fuel to heat the mixture, are primarily responsible for the emission of carbon dioxide (CO_2) during cement manufacturing [18].

The typical final composition of a Portland cement clinker is characterized by being a majority of the most abundant oxides: CaO and SiO_2, which are the main components of the predominant phases, Alite and Belite. Other oxides are present in small amounts, but not insignificant, and correspond to the mineral phases such as tricalcium aluminate (C_3A), and ferrite (C_2AxF_{1-x} with $0 < x < 0.7$).

The mineralogical composition of the clinker studied presented different phases. Alite (C_3S) or tricalcium silicate (Ca_3SiO_5) formed the principle compound in Portland clinker above 70%, accounting for the highest percentage by weight, while belite (C_2S) or dicalcium silicate (Ca_2SiO_4) presented a mean value of 7% by weight of the clinker ana-

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lysed. In commercial clinker. Aluminate (C_3A) or tricalcium aluminate ($Ca_3Al_2O_6$) presented a mean percentage of 8.5% by weight of the clinker studied. Tetracalcium aluminoferrite (C_4AF) [$Ca_2(AlFe)_2O_5$] presented a mean percentage of 8.85% by weight of the clinker analysed. We also detected other minor phases, such as free CaO.

1.2 Emissions

Table 1 gives emission data for kilns operating in the European Union, including the lowest and highest values allowed according to the current legislation and analysed in the study.

Table 1. Range of emissions from European cement kilns.

	mg/Nm3	kg/t clinker	t/year
NO_x	<200-3,000	<0.4-6	400-600
SO_2	<10-3,500	<0.02-7	<20-7,000
CO	500-2,000	1-4	1,000-4,000
CO_2	400-520	800-1040	0.8-1.04 million

Data are based on emissions from 2,000 m^3/t of clinker and the production of one million tons of clinker/year. Emissions intervals are annual averages and represent indicative values based on various measurement techniques. O_2 content is typically around 10%. The volume of gases emitted by clinker kilns usually ranges between 1,700 and 2,500 m^3 per ton of clinker (dry gas, 101.3 kPa, 273 K). Kiln systems with a preheater and precalciner normally produce gas volumes of around 2,000 m^3/t of clinker (dry gas, 101.3 kPa, 273 K) [19].

CO_2 emissions in dry cement manufacturing have a double origin: around 60% are generated by the decarbonation of the main raw material (limestone), which is chemically broken down into calcium oxide and CO_2. These emissions are called process and, currently, they cannot be reduced. The other 40% of the emissions comes from the fuels necessary to carry out the clinkerization process, which is the part that can be improved. In the last two decades, measures have been taken to reduce emissions, improving manufacturing techniques and the use of alternative fuels [20]. CO_2 emissions have been reduced from 540 t of CO_2/t of clinker in 1990 to 525 t of CO_2/t of clinker in 2014 [19].

The emission of CO is related to the content of organic matter in the raw materials and to the conditions of the manufacturing process, although it can also be caused by incomplete combustion when the control of the feed of solid fuels is not optimal. Depending on the characteristics of the quarries, between 1.5 g and 6 g of organic carbon per kg of clinker from raw materials are contributed to the process [21].

Assays performed with raw materials from various sources have shown that between 85% and 95% of the organic compounds present in the raw materials are completely oxidised to CO_2 in the presence of 3% excess oxygen, while between 5% and 15% is partially oxidised to CO, which in some particular raw materials, may exceed 2,000 mg/Nm^3 [22].

Nitrogen oxide and nitrogen dioxide (usually presented as NOx) are the predominant nitrogen oxides in the gases emitted by the cement kiln (NO> 90% of the nitrogen oxides). There are two main sources for the production of NOx: the first (so-called thermal) is produced by the reaction of the combustion air nitrogen with oxygen to form nitrogen oxides, and the second is due to the fuel, where the nitrogen compounds present in the fuel react with oxygen to form nitrogen oxides. Thermal NOx is mainly produced in the kiln's clinkerization zone, which is related to the temperature and oxygen content. The higher the excess oxygen is, the greater the thermal NOx formation. In addition, NOx formation may be influenced by the shape of the flame and its temperature, the combustion chamber geometry, the reactivity and nitrogen content of the fuel, the presence of moisture, the reaction time and the design of the fuel burner. The range of nitrogen oxides

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emissions in European kilns is between 200 mg and 3,000 mg NOx/m^3. On average, European cement kilns emit about 1,300 mg NOx/m^3, while the range of nitrogen oxides emissions in Spanish kilns is between 400 mg and 2,800 mg NOx/m^3 [23].

Sulfur dioxide (SO_2) emissions from cement factories are directly related to the content of volatile sulfur compounds in raw materials. Kilns that use raw materials with low volatile sulfur compounds have very low SO_2 emissions, in some cases below the detection limits. If organic compounds of sulfur (FeS) are used, the emissions of SO_2 content will be high. Hydrogen sulphide (H_2S) can also be generated. Sulphides and organic sulfur that exists in raw materials evaporate when the oil temperature begins to rise. 30% is emitted into the atmosphere or takes the raw mill, from the first stage of the cyclone exchanger. The sulphur present in fuels used to heat kilns with a preheater does not generate significant SO_2 emissions because of the strongly alkaline environment in the sintering zone, the calcining zone and in the lowest preheater stage, and remains trapped in the clinker. Excess oxygen (from 1% to 3% of O_2 maintained in the kiln to obtain good quality cement) oxidises the sulphur compounds released, converting them into SO_2. Emissions from European and Spanish kilns range from below the detection limit to values up to 3,500 mg/Nm^3 [24].

1.3 Usage of tires as fuel

The number of cars in Spain has grown exponentially since the 1960s, and this has generated an equivalent increase in used tires, reaching almost 300.000 t/year nowadays. Being one of the most promising alternatives for the future [25]. All the Spanish companies that use alternative fuels to manufacture clinker and cement have an environmental authorization by the competent body, in the case study the Ministry of Development and Environment from the Community of Castilla y León, where they have adapted to the Best Available Tecniques (BATs) and the State Plan for Waste Management Framework (PEMAR) 2016-2022, in accordance with Directive 2010/75/EU on industrial emissions. Therefore, the data obtained and used in this research is based on the current regulations and conditions established by law.

One of the advantages of recycling UTs in clinker kilns is that it is not necessary to remove the metal reinforcements in tires as this serves to partially replace the ferric corrector, which is used to form the tetracalcium aluminoferrite (C_4AF), in the mineralogical phases of clinker. Thus, one of the obvious benefits of using UTs in clinker kilns is the cost of preparing this alternative fuel, which is lower due to the metal reinforcements within the raw material.

When introducing alternative fuels, in addition to the emissions shown in Table 1, many other compounds can be found, such as polychlorinated dibenzodioxins (PCDDs), dibenzofurans (PCDFs), metals and their non-volatile and semi-volatile and volatile compounds. In combustion processes, the presence of chlorine and organic compounds can lead to the formation of dioxins and furans (PCDDs and PCDFs) if certain retention time and temperature conditions are met. Several studies performed in Europe show that cement production is not a major source of furans and dioxins, because the gases are placed a long time in a high temperature sintering kiln [26], despite the fuel used in the production process.

The measurements done indicate that cement kilns emit less than 0.1 mg of toxicity equivalents (TE/Nm^3), which it is the limit value in European legislation for waste incineration and co-incineration plants [27]. Since 2000, cement companies in Spain have contributed to compile the Spanish Ministry of the Environment's Inventory of Dioxins and Furans. By late 2001, around 40 measurements in 29 clinker kilns had been obtained, which all must be below the limit value of 0.1 mg TE/Nm^3.

Environmental legislation and the operation of factories usually focus on three emissions: nitrogen oxides (NOx), sulfur dioxide (SO_2) and particles, with an emission limit

 doi:10.20944/preprints202108.0300.v1

value of 500 mg/m^3, 400 mg/m^3 and 20 mg/m^3 respectively whne residues are co-incinerated. The concentrations are considered under normal conditions of pressure and temperature (101.3 kPa, 273º K) on a dry basis and for combustion gases standardized at 10% O_2.

2. Materials and Methods

This study is carried out in a cement factory from the North of Spain. All the data, materials and specific equipment are from the factory where this study is carried out. It is included a description of: its manufacturing process of Clinker, raw material for cement manufacturing, the type of rotary kiln, characteristics of the UTs used as fuel and the most relevant parameters for the process.

2.1 Materials for clinker manufacturing

The main chemical components for clinker manufacturing are lime, silica, alumina and iron oxide. Rocks and minerals used are, among others, limestone, marls and clay. They provide mineral compounds, such as calcium carbonate ($CaCO_3$), which is a source of lime in the manufacture of clinker. Table 2 shows the percentage of materials milled that enter the kiln.

Table 2. Percentages of the kiln inlet material.

Material	Percentage (%)
Limestone + Clay	96
Mineral of Fe	1.2
Sand	2.3

2.2 Rotary kiln

The POLRO rotary kiln (dry process) is and important element of the process, together with the Dopol towers, preheaters, cyclones, combustion chambers and calciners. In the rotary kiln is where boiling takes place and the raw flour becomes clinker, which has been preheated, in the preheater, and decarbonized in the calciner. Material in the kiln moves against the flow of the hot combustion gases, reducing the emission of pollutants since it acts as a circulating fluid bed: many compounds produced by the combustion and transformation of raw materials into clinker remain in the gas stream until they are absorbed, retained or condensed by the counter-current flow of raw materials [28,29]. The capacity of the material absorption depends on the area of the kiln where this material is and varies with its chemical composition and physical parameters, such as the sinterintering temperature or the kiln rotation speed. The temperature increases as the material and gases progress through the kiln, rising to a maximum of 1450 ºC for the material and 2100 ºC for the gases. The material leaving the calcination (decarbonation) stage of a kiln has a high CaO content and, therefore, a high capacity to absorb (neutralization) acids such as HCl, HF and SO_2. Table 3 gives the characteristics of the rotary kiln used in the case study.

The sintering temperature is the highest temperature reached in the kiln during the clinkering process, and it is the most important parameter in production [30,31]. The temperature is related to the stabilization zones of tricalcium silicate or alite (C_3S), and the content of free Cal (CaO) [32]. Theoretically, the area with the highest amount of C_3S is between the minimum temperature of 1250 ºC and the maximum of 1450 ºC. Therefore, it is necessary to work at sintering temperatures within this range.

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Table 3. Specifications of the rotary kiln used to obtain samples.

Variable	Value
Diameter	4.2 m (4 m at the output)
Length	60 m
Slope	4%
Maximum speed	3.5 rpm
Number of supports	2

2.3 Tires used

Car tires consist of various materials, including steel, textile fibres and elastomers. Table 4 shows the percentage of materials relative to the total mass of tires. These average values are adjusted to those used in the factory studied.

Table 4. Composition of the tires.

Material	Percentage (%)
Natural and synthetic rubber	48
Carbon black	23
Steel wires	18
Textile cables	3
Other chemical products	8

Some 70% of the tire mass consists of hydrocarbon derivatives. These substrates are suitable for obtaining fuels and chemicals via thermochemical transformation. The minimum calorific value of UTs is around 7,100 kcal/kg.

Carbon and oxygen account for 88% of a tire. Complete destruction of a tire is ensured at temperatures above 800 ºC and with gas retention at high temperatures, such as occur in clinker kilns. This complete destruction prevents the formation of intermediate products resulting from incomplete combustion, such as black smoke and odors. Sulphur (average of 1.3% by weight of tires) is neutralised as sulphates, which is less than in traditional fuel. This transformation is due to the highly alkaline nature of the material being fused in clinker manufacture. Besides, the metal component of tires can partially replace the iron additions used as a flux in the composition of cement rawmix.

The facilities for the reception and storage of used tires consist of two bunkers of 335 m^3 each. Two hoppers are fed by a crane bridge with a grapple of 1.5 m^3 capacity. Under each of these hoppers there is a band dosing machine, for the control of the material. Regarding the dosing system, the material is transported by conveyor belt to the secondary burner in the precalciner zone. The storage of unusable tires follows the regulations established in Royal Decree 1619/2005, of December 30, on the management of unusable tires.

2.4 Emission control

An emission control is carried out at the cement plant. The results are stored in the company's database and the Air Pollution Emission Registration Book, required by the current legislation. In these books, the results of the emission measures of pollutants into the atmosphere are recorded; as well as any incident that could occur in the installation referring to the atmospheric environment. The values registered in the different focuses must be below the emission limits established by the current environmental authorization (ORDER FYM/787/2017).

 doi:10.20944/preprints202108.0300.v1

More than 40 values are registered and stored in the company database. For this study the following have been considered in the rotary kiln: O_2 output from the kiln, CO output from the kiln, NOx output from the kiln, Secondary air temperature, sintering temperature, O_2 analysis to the preheater, CO analysis to the preheater and SO_2 output in the chimney; the following quality parameters have also taken into acocut: Alite and Free Lime. These last parameters are fundamental for the production process of Portland clinker. Alite is a major compound of clinker, having the largest percentage of weight, while free lime is the fraction that has not reacted during the sintering procees and does not mix in the crystallographic phases of the clinker. Ideally, the percentage should be as close to zero as possible, however this would mean that the clinkering temperature would have been very high, as well as the residence time in the kiln. Under these conditions the energy consumption would be very high. The values of free lime range from the lower limit of 0% to the upper limit of 3%.

The parameters of the rotary kiln and clinker quality are identified and recorded in the database in different periods of time. The quality parameters are analyzed every two hours, and those from the kiln every 5 minutes, making averages of the hours and comparisons between them. Values analyzed are those recorded in the cement factory database for thirty days, studying 160 values for each type of fuel, having 320 values in total. These data are analyzed to determine the variations that exist when 100% fossil fuel (petroleum coke) is used and when 40% of alternative fuels are used, in this case unusable tires [18].

Hence, the parameters analyzed are: the gases emitted by the kiln and the preheater (CO, O_2 and NOx) and SO_2 in the chimney. Initially, only petroleum coke is used; and subsequently, a percentage of alternative fuels UTs (40%) and petroleum coke (60%), are used. [33]. Most of the alternative fuels are introduced into the preheater, where the consumption of 40% UTs is around 80% of all the fuel that is introduced, compared to 20% that is used in the kiln. The entire production process is regulated through a control centre, Figue 1. Data obtained is stored with the quality parameters [34]. Table 5 gather the kiln parameters ilustrated in Figure 1.

Table 5. Kiln parameters recorded in the database.

Parameter number	Kiln parameter
1	O_2 emissions
2	CO emissions
3	NOx emissions
4	Secondary air temperature
5	Sintering temperature
6	Analysis of O_2 in the preheater
7	Analysis of CO in the preheater

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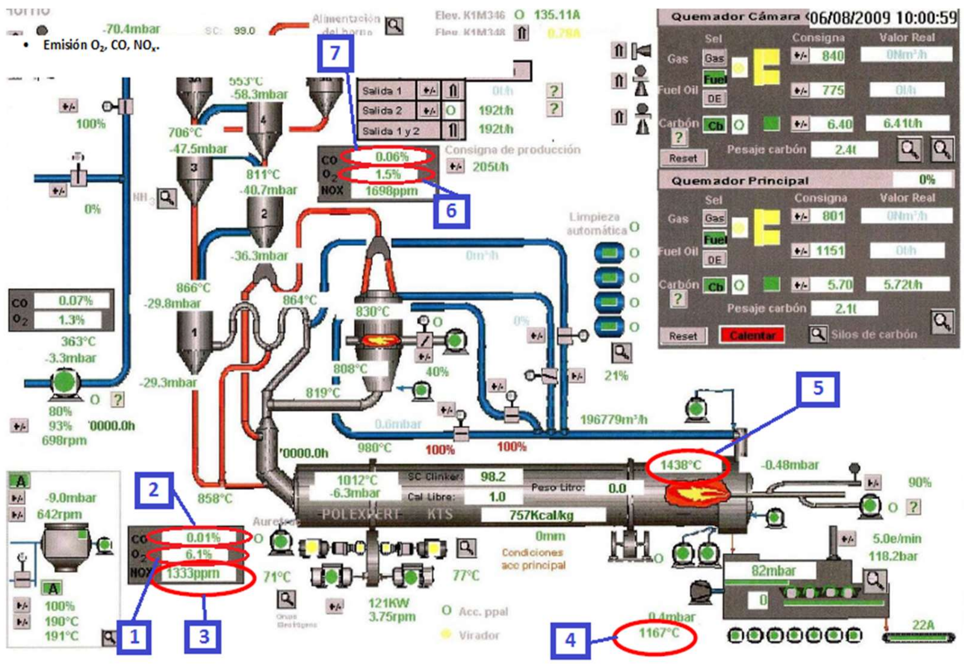

Figure 1. View of the kiln in the control centre.

The sintering temperature is the highest temperature reached in the kiln during the clinkering process, and is measured by a pyrometer sited close to the fuel outlet nozzle between 1-2 meters from the end and directed towards the clinker [35]. This value is recorded every five minutes, and hourly averages were calculated for comparison with quality values obtained from diffraction diagrams and X-ray fluorescence [36].

The hot air in the clinker cooler, heated by the cooling material and the external temperature, is distributed in three lines: temperature of the clinker going to the silos; temperature of the dust collected by the filter, which is taken to the cooler; and temperature of the secondary and tertiary air going to the kiln. The secondary air temperature cooler input parameter is the secondary air temperature from the cooler as it enters the kiln, which is recorded by a temperature probe.

Continuous monitoring is used, at selected points established by the current regulations, to obtain the emissions. Among other, the variables used in this study: SO_2, NOx and CO. The percentage of NOx that contains the material at the entrance of the kiln is analyzed by means of an extractive probe. Subsequently, a sample is taken, cooled, dusted and then analyzed.

3. Results and discussion

Table 6 allows to compare the results obtained using Petroleum coke and 40% UTs as fuels. It shows: a) the sintering temperature, b) the clinker composition (%Alite and Free CaO) and the concentration of O_2, CO, NOx and SO_2 emitted in the furnace, preheater and stack. Oxygen is kept the minimum necessary for combustion to be complete.

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Table 6. Summary of the variables used and the results obtained for the manufacture of clinker with the fuels used.

			Fuel			
			100% Petroleum coke		60% Petroleum coke 40% UTs	
Gases	O_2 (ppm) (*σ*)	kiln	7.39	*(1.01)*	7.19	*(1.64)*
		preheater	2.23	*(0.64)*	6.15	*(2,32)*
	CO (ppm) (*σ*)	kiln	3.92 10^{-2}	*(2.38 10^{-2})*	5.16 10^{-2}	*(4.05 10^{-2})*
		preheater	0.15	*(0.19)*	5.93 10^{-2}	*(4.74 10^{-2})*
	NO_x (ppm) (*σ*)	kiln	905.69	*(236.29)*	753.74	*(164.98)*
	SO_2 (ppm) (*σ*)	chimney	407.16	*(185.08)*	294.46	*(123.60)*
Mean sintering temperature (ºC) (*)			1,361.27		1,292.28	
Clínker quality parameters		Alite (%) (**)	> 70		> 70	
		CaO (%) (***)	< 2.0		< 2.5	

(σ): standard deviation; (*): statistical study given in Table 7; (**): data distribution given in Figure 2; (***): data distribution given in Figure 3.

3.1 Emissions from the kiln

The mean CO emission calculated with fossil fuel is 3.92 10−2 ppm, while with the addition of tires as fuel is 5.16 10−2 ppm (Table 6). There is a decrease in O_2 and an increase in CO. This increase in CO is due to carbon monoxide is generated by the incomplete combustion of the fuel produced by a lack of oxygen. This fact can happen by an unacurate regulation of the oxygen by the staff of the control room.

Regarding NOx emissions, a decrease of 17% is observed using 40% UTs. Data ranges from an average of 905.69 ppm with fossil fuels to 753.74 ppm in the case with tires. Experimentally, it has been found that nitrogen oxide produced in the sintering kiln is released as a result of: flame temperature and shape, excess oxygen, gas retention time in the combustion zone, loading temperature and load retention time in the combustion zone. The amount of NOx produced by the secondary burner depends on the nitrogen content of the fuel, excess oxygen and flame temperature. This parameter increases with temperature, and more nitrogen in the combustion air leads to an increase in nitrogen oxide and alite content.

Surprisingly, emissions of the nitrogen oxides decreased when 40% used tires were added as fuel. This effect was related to a reduction in sintering temperature and a lower oxygen content at the extreme end of the kiln, with the result that less NOx was generated. However, O_2 content must be balanced against the increases in CO and SO_2 that occur when the percentage of oxygen drops; the formation of a reducing atmosphere in parts of the kiln can also exert a substantial influence.

In the cement manufacturing process, NO may be oxidised to NO_2 at lower temperatures, but normally, NO accounts for more than 90% of NOx emissions.

3.2 O_2 and CO in the preheater

When UTs were used as fuel, the preheater required more oxygen than when fossil fuels were used (Table 6). Using only fossil fuel, the mean oxygen input into the preheater was 2.23 ppm, whereas when using UTs it was 6.15 ppm. As can be seen in this table, a smaller amount of carbon monoxide was detected at the preheater. With fossil fuel, the mean CO into the preheater was 0.15 ppm, whereas when it was 5.93 10−2 ppm for UTs,

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which means 60% lower CO using 40% UTs. Hence, the O_2 inlet is increased for the correct combustion of the UTs, which means less CO formation at the preheater outlet.

3.3 SO_2 output from the chimney

The basic raw material, limestone, has already a high sulfur content. As can be seen in Table 6, there was a reduction in SO_2 when UTs were added as a percentage of the fuel. The usage of only fossil fuel gave a mean value of 407.16 ppm, whereas it was reduced to 294.46 ppm using UTs. The following points, in order of importance, are the main reason of this difference:

1. Unlike fossil fuels, with around 6% sulfur, tires contain 1.3% of sulphur, which implies a decrease in the raw material input.
2. The reduced volatility of SO_2 at lower flame and combustion temperatures.
3. The oxidising atmosphere in the kiln, together with stable kiln operation.

3.4 Sintering temperature

The sintering temperature varied during the process. When petroleum coke was used as fuel, the mean operational temperature was 1360 ºC, whereas when a percentage of UTs were used a fuel, the mean temperature was 1292 ºC. This temperature difference means a reduction in CO_2 and energy savings, Table 7. It was estimated that the decreasing sintering temperature of 50 ºC means a reduction in CO_2 emissions of more than four thousand tons a year [35,37].

Table 7. Statistical parameters of the sintering temperature.

Sintering Temperature	Petroleum coke	Tires
Arithmetic means	1,361.27	1,292.28
Standard deviation	67.17	42.79
Standard error	5.33	3.39
Interval errors considering 95% confidence	10.52	6.70
Upper limit of the interval with 95% confidence.	1,371.80	1,298.98
Lower limit of the interval with 95% confidence	1,350.75	1,285.57
p-value	$8.81631\ 10^{-24}$	

3.5 Clínher quality parameters

Regarding the quality parameters, some changes occur in alite and free lime when adding a part of tires as fuel, but maintaining the same quality of the clinker.

In this cement factory, values of more than 70% are considered optimal for the alite majority phase. All the results obtained from the factory exceed this value, regardless of the type of fuel. In Figure 2, an interval study of the C_3S results is carried out depending on the type of fuel. It is observed that 87% of the values using petroleum coke are between 74% and 79% of C_3S. For the same interval, the alite using alternative fuels reaches 84% of the values. It is, therefore, noted that the quality values are adequate for both fuels.

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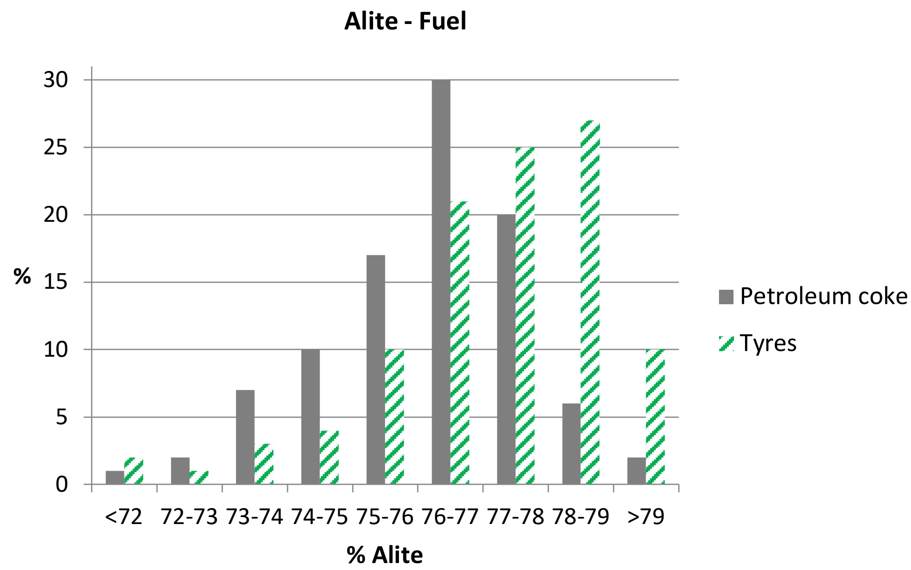

Figure. 2. Variation in alite depending on type of fuel used.

When using petroleum coke to make the clinker, 70% of the samples have values lower of than 0.5% of the CaO phase. While using tires as fuel, the results of free lime are more distributed, although always with values lower than 2.5% of CaO, Figure 3. Therefore, the higher the kiln sintering temperature, the lower the amount of free lime the clinker will have. Sintering temperature is higher when only petroleum coke is used as fuel, instead of using the mix (60% petroleum coke + 40% UTs).

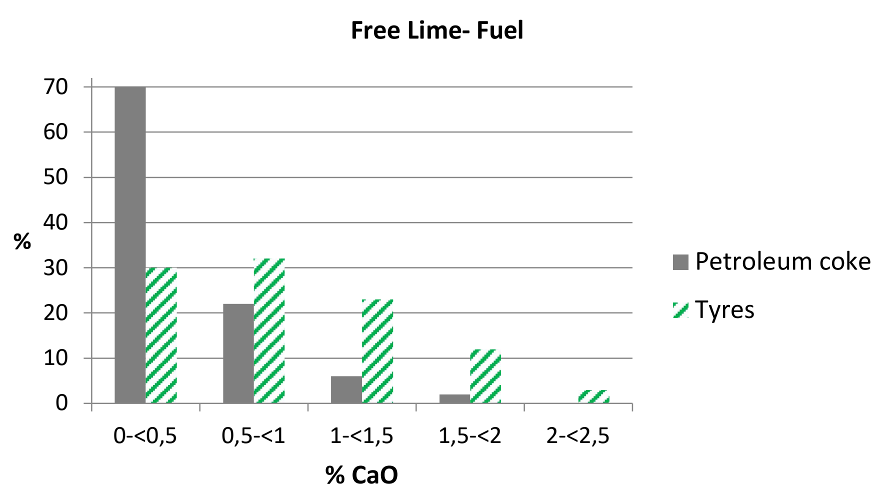

Figure 3. Variation in free lime (CaO) depending on the type of fuel used.

3.6 Economic assessment

Based on real economic and consumption data obtained from the case study, the price of petroleum coke is about 80 €/t whereas the average cost of used tires is 25 €/t. Assuming an annual consumption of 100,000 t with a calorific value of 8,200 kcal/tcoke, the exclusive use of petroleum coke as fuel to manufacture clinker would cost 8,000,000 €/year. In a second case, using 40% alternative fuel (UTs, with a calorific value of 7,200

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kcal/tUTs) combined with 60% fossil fuel would cost 5,938,000 €/year, see Table 8. Thus, using a percentage of alternative fuel for clinker production would yield an economic saving of around 25%. As the average cost of fuel in a cement factory represents 30% of the total cost, the economic savings using UTs represents 8% of the whole process studied.

Table 8. Economic comparison between two types of fuel.

Economic assessment						
Fuel		**Calorific value (kcal/t)**	**Measurement (t)**	**Price (€/t)**	**Cost (€/year)**	**Total cost (€/year)**
Petroleum coke		8,200	100,000	80	8,000,000	8,000,000
Alternative fuel	60% petroleum coke	8,200	60,000	80	4,800,000	5,938,000
	40% UTs	7,200	45,556	25	1,138,900	

Besides, a decrease of 50 ºC in the sintering temperature supposes an energy saving of 175 kg/hour in petroleum coke and, therefore, a cost saving of 126,000 €/year.

4. Conclusions

The results obtained provides an interesting insight of the usage and comparison between petroleum coke and alternative fuels, used tires, from a real case study. Analysing the emissions generated, the technical operability and economic implications of both fuel options. Despite the usage of alternative fuels is common, the study displays real values and its benefits, which is not easy to have real continuous data of the two types of fuel in the same cement plant.

In this regard, it has been proved that energy recovery from used tires yields economic and environmental benefits. The use of 40% UTs as fuel reduced the amount of NO_x, CO and SO_2 generated in the production process with respect to the use of 100% petroleum coke. At the exit of the kiln, using the UTs as a fuel by 40%, the amount of NO_x decreases, by 17% with respect to the use of fossil fuel and SO_2 also decreases from 407.16 ppm to 294.46 ppm. The sintering temperature of the kiln is 5% higher when using only petroleum coke as fuel than when using 40% UTs. The usage of UTs also requires a greater amount of oxygen, so that the combustion can be complete and it created lower quantities of CO, 60% lower in the preheater than using petroleum coke.

On the other hand, the quality parameters and the clinker remain the same. The main clinker compound, alite, is maintained, 84% of the UTs data show values above 74% of C_3S, while it is 87% for petroleum coke. The behavior of free lime is within the established limits, not reaching 2.5% of free CaO in both cases, observing a slightly better result with petroleum coke. Regarding the economic perspective, the UTs fuel is 25% cheaper than fossil fuel, being another important reason for its usage instead of traditional fuels.

Author Contributions: Conceptualization, A.M.C., Ll.S., A.V., and M.B.; methodology, A.M.C., Ll.S., and F.G.-F.; validation, A.M.C., M.B. and F.G.-F.; formal analysis, A.M.C., A.V., V.C. and M.B.; investigation, A.M.C., F.G.-F., V.C., and M.B.; writing (original draft preparation), A.M.C., A.V., F.G.-F., and M.B.; writing (review and editing), A.M.C., Ll.S., F.G.-F-. and M.B. All authors have read and agreed to the publishedversion of the manuscript.

Funding: This research was funded by project ULE 2015-T-98.

Acknowledgments: The authors thank the cement factory for providing the facilities and funding to carry out this study, particularly the director, Pedro de Lama.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Ambikesh Kumar M., Manish Kumar J. and Suvendu Kumar D. Ambient air quality and indexing with reference to suspended particulate matter and gaseous pollutants around a cement plant in OCL India Limited, Rajgangpur, Odisha, India. *Current Science* **2019**, 116 (11):1905-1909.
2. Samad, S., Shah, A., Lambachiya, M. C., and Desai, S. B. Strength development of binary cement concrete, using Pulverized Fly Ash (PFA) under various curing conditions. *Scientia Iranica* **2019**, 26 (2): 615-624. DOI: 10.24200/sci.2017.4537.
3. International Energy Agency, 2015. "Energy Climate and Change". [https://www.iea.org/publications/freepublications/publication/WEO2015SpecialReportonEnergyandClimateChange.pdf]
4. Ilickovic, Z., Zilic, F., Sadadinovic, J., Andrejas, F., and Begic, S. Impact of the use of alternative fuels in cement production on emission of harmful pollutants. *Glasnik Hemicara I Tehnologa Bosne I Hercegovine* **2017**, 49, 19-24.
5. Castañón, A.M. Energy Saving and Environmental Impact Reduction in a Cement Factory by a Statistical Control System. 4th International Congress on Energy and Environment engineering and management, Merida, 2011
6. Liu G., Yang L., Zhan J., Zheng M., Li L., Jin R., Zhao Y., and Wang M. Concentrations and patterns of polychlorinated biphenyls at different process stages of cement kilns co-processing waste incinerator fly ash. *Waste Management* **2016**, 58, 280–286.
7. Moretti, L., and Caro S. Critical analysis of the Life Cycle Assessment of the Italian cement industry. *Journal of Cleaner Production* **2017**, 152, 198-210.
8. Ortiz-Rodriguez, O., Ocampo-Duque, W., Duque-Salazar, L. Environmental Impact of End-of-Life Tires: Life Cycle Assessment Comparison of Three Scenarios from a Case Study in Valle Del Cauca, Colombia. *Energies* **2017**, 10 (12) 2117. DOI: 10.3390/en10122117.
9. Hemidat, S.; Saidan, M.; Al-Zu'bi, S.; Irshidat, M.; Nassour, A.; Nelles, M. Potential Utilization of RDF as an Alternative Fuel to be Used in Cement Industry in Jordan. *Sustainability* **2019**, 11, 5819. https://doi.org/10.3390/su11205819
10. Xu, X.; Wang, Q.; Hu, H.; Wang, X. Air Pollution Control: An Analysis of China's Industrial Off-Peak Production Policy through the Quasi-Natural Experiment Method. *Sustainability* **2021**, 13, 4808. https://doi.org/10.3390/su13094808
11. Benhelal, E., Zahedi, G., and Shamsaei, E. Global strategies and potentials to curb CO2 emissions in cement industry. *Journal of Cleaner Production* **2013**, 51, 142-161.
12. Rahman A., Rasul M.G., Khan M.M. K. and Sharma S.C. Assessment of Energy Performance and Emission Control Using Alternative Fuels in Cement Industry through a Process Model. *Energies* **2017**, 10 (12), 1996; https://doi.org/10.3390/en10121996
13. Conesa J.A., Ortuño N., Abad E., and Rivera-Austrui J. Emissions of PCDD/Fs, PBDD/Fs, dioxin like-PCBs and PAHs from a cement plant using a long-term monitoring system. *Science of the Total Environment* **2016**, 571, 435–443. http://dx.doi.org/10.1016/j.scitotenv.2016.07.009.
14. Richards G, and Agranovski I. E. Dioxin-like pcb emissions from cement kilns during the use ofalternative fuels. *Journal of Hazardous Materials* **2017**, 323, 698–709. http://dx.doi.org/10.1016/j.jhazmat.2016.10.040
15. Cantini, A.; Leoni, L.; De Carlo, F.; Salvio, M.; Martini, C.; Martini, F. Technological Energy Efficiency Improvements in Cement Industries. *Sustainability* **2021**, 13, 3810. https://doi.org/10.3390/su13073810
16. Benhelal, E., Zahedi, G., and Hashim, H. A novel design for green and economical cement manufacturing. *Journal of Cleaner Production* **2012,** 22, 60–66.
17. An, J.; Middleton, R.S.; Li, Y. Environmental Performance Analysis of Cement Production with CO2 Capture and Storage Technology in a Life-Cycle Perspective. *Sustainability* **2019**, 11, 2626. https://doi.org/10.3390/su11092626
18. Castañón, A.M. *Optimization of the Clinker Production Process. Application to the Tudela-Veguín Factory*. The University of León, Spain, 2011.
19. OFICEMEN, 2017. Cement Manufacturers Association of Spain. (Oficemen). "Roadmap of the Spanish cement industry for the reduction of carbon emissions to 2050".
20. Krishna R., Reddy, F., Archana Gopakumar, S.M., Jyoti K., Chetri S.M., Girish Kumar, S.M., Dennis G. and Grubb, M. Sequestration of Landfill Gas Emissions Using Basic Oxygen Kiln Slag: Effects of Moisture Content and Humid Gas Flow Conditions. *Journal of Environmental Engineering* **2019**, 145 (7): 04019033.
21. OFICEMEN, 2009. Study of measurement, calculation and estimation methods for emissions of PRTR substances suitable for the cement sector in Spain." PRTR Guide, Cement Sector.
22. Ruiz, M. L. Determination and evaluation of dioxin and furan emissions in cement production in Spain. Universidad Complutense de Madrid, 2007. ISBN: 978-84-669-3150-2
23. Canales C. *Guide to Best Available Techniques in Spain for Cement Manufacturing. Ministry of the Environment* 2002, [http://www.concretonline.com/index.php?option=com_content&task=view&id=735&Itemid=35#resumen
24. Gutiérrez Cañón, P. *Study of the variation of polluting gases in the manufacture of clinker*. Project. University of Leon, 2012.
25. Chatziaras, N., Psomopoulos, C.S., Themelis N.J. Use of waste derived fuels in cement industry: a review. *Management of Environmental Quality: An International Journal* **2016**, 27(2), 178 – 193. doi.org/10.1108/MEQ-01-2015-0012.
26. Kajaste, R., Hurme, M. Cement industry greenhouse gas emissions – management options and abatement cost. *Journal of Cleaner Production* **2016**, 112(5), pp. 4041-4052, doi.org/10.1016/j.jclepro.2015.07.055.
27. Directive 2000/76 / EC of the European Parliament and of the Council of 4 December 2000 about the incineration of waste.

 doi:10.20944/preprints202108.0300.v1

28. Chen Y. L., Chang J. E., Shih P.H., Ko M.S., Chang Y. K., and Chiang L.C. Reusing pretreated desulfurization slag to improve clinkerization and clinker grindability for energy conservation in cement manufacture. *Journal of Environmental Management* **2010**, 91(9), 1892-1897.
29. Cortada M. M., Kaare L., Jappe L., Glarborg P., and Dam-Johansen K. Review: Circulation of Inorganic Elements in Combustion of Alternative Fuels in Cement Plants. *Energy Fuels* **2015**, 29 (7), pp 4076–4099. DOI: 10.1021/ef502633u.
30. Richards, G., and Agranovskim, I. E. Air emission from the co-combustion of alternative derived fuels within cement plants: Gaseous pollutants. *Journal of the Air & Waste Management Association* **2015**, 65(2):186–196. DOI: 10.1080/10962247.2014.984084.
31. Richards, G., and Agranovskim, I. E. Influence of Co-Combustion of Alternative Derived Fuels on Air Emission from Cement Plants: Particulates and Trace Species. *Clean Soil Air Water* **2016**, 44: 47–54.
32. Taylor, H. F. W. Cement Chemistry. Thomas Telford Services Ltd, 1997.
33. Aktar Ishak S., Hashim H., and Sie Ting T. Eco innovation strategies for promoting cleaner cement manufacturing. *Journal of Cleaner Production* **2016**, 136, 133-149.
34. Castañón, A.M., García-Granda, S., Guerrero, A.M., and Gómez-Fernández, F. A research of the mineralogy phases of clinker in a Spanish cement using the method of Rietveld. *Dyna* **2012**, 79 (173), 41-47.
35. Castañón, A.M., S. García-Granda, A. Guerrero, M.P. Lorenzo, and S. Angulo. Energy and environmental savings via optimisation of the production process at a Spanish cement factory. *Journal of Cleaner Production* **2015**, 98 (2015) 47-52.
36. Tobón J, Restrepo O, and Restrepo O. I. Effects of some Colombian mineral additions in the manufacture of Portland cement clinker I. *Dyna* **2007**, 152, 263-276
37. Cao Z., Shen L., Zhao J., Zhong S. and Yang Y. Modeling the dynamic mechanism between cement emissions and clinker quality to realize low-carbon cement. *Resources Conservation and Recycling* **2016**, 113, 116-126. DOI: 10.1016/j.resconrec.2016.06.011