



# Article Assessment of Environmental Pollution in Cement Plant Areas in Romania by Co-Processing Waste in Clinker Kilns

Cristian Ciobanu <sup>1,2</sup>, Paula Tudor <sup>2,\*</sup>, Irina-Aura Istrate <sup>3,\*</sup> and Gheorghe Voicu <sup>3,\*</sup>

- <sup>1</sup> Ceprocim SA, Strada Preciziei 6, 062203 Bucharest, Romania; ciobanu\_77@yahoo.com
- <sup>2</sup> Department of Management, Faculty of Entrepreneurship Business Engineering and Management, University Politehnica of Bucharest, Splaiul Independentei 313, 060042 Bucharest, Romania
- <sup>3</sup> Department of Biotechnical Systems, Faculty of Biotechnical Systems Engineering, University Politehnica of Bucharest, Splaiul Independentei 313, 060042 Bucharest, Romania
- \* Correspondence: paulavoicu85@yahoo.com (P.T.); ia\_istrate@yahoo.com (I.-A.I.); ghvoicu\_2005@yahoo.com (G.V.); Tel.: +407-23-850-975 (P.T.); +407-23-542-609 (I.-A.I.); +407-24-715-585 (G.V.)

**Abstract:** Worldwide, in the rotary kilns of cement plants, various amounts of combustible waste are burned, which would otherwise end up in municipal landfills. The paper first analyzes the literature on the co-processing of waste in cement manufacture and its influence on the environment and human health. Then, it shows how the combustion components of co-processed waste can influence the final characteristics of clinker and cement. The main objective of the paper is to determine the level of emissions of the resulting pollutants (total dust and flue gases: NOx, SO<sub>2</sub>, and CO) at the outlet of the chimney of the clinker kiln and flour mill to meet the requirements of the Integrated Environmental Permit (EIA) from Romania and present an estimation of the level of atmospheric air pollution using the climatological model of pollutant dispersion. Following these assessments (data shown), the cement factories will establish measures to reduce the pollution, if necessary, to comply with the regulations in force for the cement industry.

Keywords: cement plant; clinker kiln; environmental pollution; co-processing waste

# 1. Introduction

Avoiding waste generation and reducing waste quantities are the current ways to deal with waste problems worldwide. In this context, recycling and reuse of waste have priority. Thus, co-processing should not conflict with waste management, as it can be classified as an energy and materials recovery technology.

In the cement industry, in the manufacture of Portland clinker, the co-processing of energy waste is a heat treatment process with the simultaneous recycling of mineral materials from the waste and energy recovery in the same industrial process [1].

The mineral part of the waste replaces some of the primary mineral materials (limestone, clay, gypsum), and the fuel part provides energy in clinker production. Thus, the waste introduced is 100% recycled or recovered without producing additional residues. Moreover, the current technology also ensures the proper destruction of toxic components, which could be a problem for the environment.

Thus, waste co-processing ensures superior environmental protection in the cement industry than landfilling or incineration [2]. Therefore, the UNEP Basel Convention recognizes the method as a practical, safe and preferable option from the ecological point of view.

When we refer to the combined treatment called co-processing of waste (pre-treatment and co-incineration) that can be applied in a cement plant, we must take into account the advantages involved [1]:

- The flame temperature is very high (about 2000  $^{\circ}$ C), and the material reaches 1450  $^{\circ}$ C;
- At a temperature higher than 1100 °C, the standing time in the oven is around 5 to 6 s;



Citation: Ciobanu, C.; Tudor, P.; Istrate, I.-A.; Voicu, G. Assessment of Environmental Pollution in Cement Plant Areas in Romania by Co-Processing Waste in Clinker Kilns. *Energies* 2022, *15*, 2656. https:// doi.org/10.3390/en15072656

Academic Editors: Mejdi Jeguirim and Giovanni Esposito

Received: 1 February 2022 Accepted: 28 March 2022 Published: 5 April 2022

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/).

- There is a corresponding excess of O<sub>2</sub> required for the process and the achievement of total combustion;
- Gaseous acids are neutralized by their capture by limestone from raw materials.

Waste incineration is usually applied to residual waste that can no longer be recovered in any way so that it becomes inert, with minimal emissions to air and water. In this process, the harmful organic materials are destroyed, while the inorganic materials are integrated into the composition of the clinker (cement) [3,4].

By selecting combustible waste, the mass of landfill waste is much smaller (the volume is also minimized), conveniently using the calorific value of the residual waste while protecting energy resources.

Suppose these advantages are added to the full recovery of the caloric energy of the waste, together with the absence of the generation of other secondary materials (slag, ash) that require subsequent storage. In that case, it can be considered that this method is the best solution to solve the waste problem, conditions of total safety both for the environment and for the quality of the cement [1,2].

When taking over waste, especially if there are any suspicions, it is advisable to perform tests in the laboratory for the content of heavy metals, pH, calcination stones, calorific value, flash point, chlorine, sulfur, and others.

For cement producers, an advantage that must not be forgotten is that the co-processing offers an alternative for the use of traditional fuels and that is the use of waste as a partial substitution. Moreover, the co-processing of waste has a positive consequence, the reduction/elimination of greenhouse gas emissions that could be generated in the case of their storage or incineration in incinerators without energy recovery.

On the other hand, for waste generators, co-processing guarantees the destruction of the waste in an environmentally safe way, with the closure of the product life cycle and the avoidance of possible environmental problems with specific penalties.

For the environment and society, the method of co-processing waste can lead to the conservation of natural resources (coal, fuel oil, gas, gypsum, limestone, clay), as well as to the indirect reduction in gas emissions, if the waste were deposited or incinerated in incinerators. It also reduces environmental risks (uncontrolled storage, soil and water pollution, etc.) and avoids overcrowding of controlled landfills (dumps) [5].

Global research shows that co-processing can be a very effective technique for disposing of industrial waste in many developing countries, compared to other waste disposal methodologies. This is because it does not generate ash or other emissions, requires simpler auxiliary technology, and has lower installation costs. The justification for the co-processing of industrial waste was based on three case studies from India [6], where non-hazardous industrial waste is about 100 million tons/year and coal ash is about 70 million tons/year.

The analysis of co-processing in cement plants using Municipal Solid Waste (MSW) as a secondary fuel and some advantages of their incineration was also performed by Meystre and da Silva [7]. They show that the manufacture of Portland cement is a process that requires high consumption of thermal and electrical energy, and the cost of power in the final product is about 40%. This justifies efforts to reduce the costs associated with cement production by using high-efficiency equipment coupled with replacing fossil fuels and conventional raw materials with alternative products. However, there are still issues related to gaseous and liquid effluent emissions that increase costs through their control and treatment systems. MSW, when recovered and separated, can become products [7,8].

At the same time, the authors show that the main problem in using MSW is related to their initial sorting due to the direct influences on the final product. The calorific value of MSW can be obtained by analyzing their composition, the values reported in the literature being between 8.4–13.59 MJ/kg. However, municipal solid waste should only be incinerated if there is no better financial and environmentally sound way to recycle and reuse waste. Furthermore, the ash composition and the percentage of heavy metals generated by MSW incineration may alter the final quality of the cement.

The result is that the ash content of the fuel may give specific characteristics to the clinker used in the manufacture of cement, but these do not affect the performance of Portland cement. For example, the paper [9] shows that replacing up to 10% of sawdust ash cement does not affect the performance of Portland cement in terms of workability and compressive strength.

In the cement industry, not every material can be considered fuel. Each producer can establish the criteria depending on his own needs. For example, the Lafarge Cement Polska group set as criteria for alternative fuels: energy value >14 MJ/kg, chlorine <0.2%, sulfur <2.5%, polychlorinated biphenyls (PCB) <50 ppm, heavy metal <2500 ppm. In addition, the combustion of fuels must be uniform to constantly heat the raw materials, which implies a uniform distribution of particle size, a high and constant calorific value, without harmful contents (metals, glass, minerals), and a low moisture content [10–12].

As with primary fuels, alternative fuels also influence clinker production, both the process itself and the quality of the finished product. In addition, depending on the physical properties or chemical composition, alternative fuels influence the production process of the clinker in various forms. Thus, the dimensions of the fuel particles, which affect the combustion rate and the furnace's sintering area, must be considered.

Regarding the chemical composition of the fuel, the influences related to the volatility of the compounds on the operation of the furnace (e.g., alkali salts) should be mentioned first. The non-volatile elements resulting from the combustion of fuels will be related to the chemical composition of the clinker and will be part of its composition, altering its properties, with phosphorus being one of these elements [10,11].

Factors that can influence the quality of the clinker when burning alternative fuels are ash composition, fuel moisture, calorific value, and particle size [10,11].

Recycling materials or mixed and soiled residues in the cement industry can be considered a complementary option to existing recycling processes, as their ash passes into the clinker during the combustion process and thus finally into the cement [11].

Generally, the ash of solid recovered fuel (SRF) consists of oxides of elements, which are essential for clinker manufacturers. SRF is a sorted fuel derived from non-hazardous solid waste, including municipal or commercial waste. Clavier et al. [13] show that the ash of this waste has the elemental composition needed to produce clinker and is a potential substitute for traditional raw materials for cement manufacture. Moreover, the incineration of waste in a suitable separate plant and the subsequent introduction of ash (pre-treated) into the cement composition is more expensive than the direct burning of this waste in clinker kilns (then used in the production of cement).

Also, Linda Monroy Sarmiento et al. [3,14] point out that the use of MSW as an alternative fuel in clinker kilns should only be carried out based on their mineralogy and limited share of chloride and alkali content which decreases the permitted replacement quantities.

Viczek et al. [15,16] also show that approximately 77% of the ash of mixed commercial waste consists of four main chemical components required for cement clinker production:  $SiO_2$ , CaO, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> (in order of their weight). In addition, SRF ash also contains small amounts of other elements that can be introduced as part of the raw materials, namely  $SO_3$ , MgO, TiO<sub>2</sub>, K<sub>2</sub>O, Na<sub>2</sub>O, and P<sub>2</sub>O<sub>5</sub> (also in the order of their weight).

Gotze et al. (2016) made a detailed study of the chemical composition of the ash of the main household waste, using several specialized works in the field, and showed their share, origin, and importance for the cement industry [17].

In the EU, the cement industry has already replaced about 43% of fossil fuels with alternative fuels derived from waste and biomass to provide thermal energy in making gray clinker, with a technical replacement potential of 60%. This percentage is expected to increase to 95% in the future, with increasing amounts of waste being an opportunity for waste management [18]. However, there are considerable differences in co-processing rates across the EU Member States, ranging from 7% to 95%. If the co-processing rate of waste in the cement industry were to increase to 60%, CO<sub>2</sub> emissions could be reduced by

26 million tons, and the cost of investing in waste incineration plants dedicated to energy transformation will decrease by about 12 billion euros.

However, implementing waste co-processing technologies in the cement industry encounters some barriers related to unclear legislation, lack of financial support, public acceptance, etc. [19]. Another problem is the sorting and processing of waste is not performed systematically. Nevertheless, the use of waste co-processing in the Ukrainian cement industry has reduced coal consumption in clinker production by up to 262 kt/y, reducing CO<sub>2</sub> emissions of up to 284 kt<sub>eq</sub>/year from coal replacement. Furthermore, for the waste management sector, the potential for co-processing has been identified, i.e., the elimination of MSW up to 1213 ktMSW/year, respectively, the reduction in greenhouse gas emissions by up to 111 ktCO<sub>2eq</sub>/year in landfills.

Two important factors that can affect life are identified: the increase in greenhouse gases and of the environmental temperature [20,21]. According to the literature, in 2015,  $CO_2$  emissions from clinker in the manufacturing process contributed about 4% of total global emissions. In addition, the emissions from fuel combustion in the cement production process accounted for about 8% of global  $CO_2$  emissions [22].

The share of waste in the fuel mixture is also expected to be approximately 10%. In such cases, co-incineration represents burning the fuel mixture containing waste to divert the combustion plant from its regular use. Therefore, a redesign of clinker kilns and related fuel supply systems is needed for higher percentages.

The most widely used fuel in the cement industry is coal, but many other fuels (gas, oil, liquid waste, solid waste, petroleum coke) have been used successfully to burn cement kilns, either alone or in various combinations [23]. Due to harmful emissions, the cement industry is constantly looking for solutions to reduce them, as large amounts of carbon dioxide (CO<sub>2</sub>), nitrogen oxide (NOx), sulfur dioxide (SO<sub>2</sub>) are released into the atmosphere, and it is estimated that 5% of global carbon dioxide emissions come from cement production.

To reduce these emissions, other depollution systems requiring electricity are needed, only the use of SCR (Selective Catalytic Reduction) technology to reduce NOx, increasing electricity demand of 5 kWh/t.clinker [24].

Improving energy efficiency can reduce carbon dioxide emissions from fuel while reducing the cost of a unit of cement production [25].

At the European level, there are two important regulations that refer to the emissions similar to the ones resulting (around 50 pollutants are covered for the threshold values both for air and water) from the cement industry: the European Waste Incineration Directive (2000/76/EC) and the European Polluting Emissions Register (EPER, 96/61/EC) [26]. It was noted that the emissions resulting from the cement furnace do not exceed the thresholds mentioned in the regulations.

Unfortunately, at the national level, the alternative resources provide only 25 to 30% of the thermal energy for the clinker process (even though in the last years large investments, of over 130 million euros, were made).

Due to the fact that in the period between 2004 and 2020, a large quantity of industrial and municipal waste (around 4 million tons) was co-processed in the national cement plant; it can be said that more than 1.2 million tons of fossil fuel on one side and as many tons of  $CO_2$ , on the other side, were saved.

Some studies have also shown adverse effects on respiratory health in people exposed to cement dust, exemplified by the increased frequency of respiratory problems [27,28]. It was also specified that people in the areas adjacent to the cement factories are severely affected by respiratory problems, gastrointestinal diseases, etc. [29]. Several studies have also shown links between exposure to cement dust and chronic lung function impairment and respiratory symptoms in humans. In addition, cement dust irritates the skin [30].

In our paper, we want to present data on total dust and flue gas emissions, such as NOx, SO<sub>2</sub>, and CO, which are released into the atmosphere at some cement plants in Romania. The values are determined by a specialized laboratory. These analyses are performed periodically, according to standardized procedures, and the values of the parameters must

fall within limits specified by the EIA of each plant, correlated with European standards. Otherwise, cement plants will establish measures to reduce pollution. Furthermore, we must specify that in the rotary kilns of cement factories, different amounts of combustible waste (mentioned in the paper) are burned together with conventional fuel (coal/coke, oil, or natural gas). The ash resulting from combustion is integrated into the contents of the clinker, which is then used in the manufacture of cement. It also estimates atmospheric air pollution levels using the climatological pollutant dispersion model.

#### 2. Materials and Methods

## 2.1. The Process of Obtaining the Clinker and the Flue Gas Discharge to the Stack

Obtaining the clinker in the rotary kiln is a crucial phase for the quality of the final cement, and for this purpose, a material temperature of 1400–1500 °C must be maintained in the kiln, with the maximum gas temperature reaching about 2000 °C required for heat exchange in the kiln. Furthermore, clinker combustion is carried out in an oxidizing atmosphere to have the certainty of complete combustion, which requires a continuous excess of oxygen.

In 2015, Romania recorded the highest waste disposal rate of precisely 72%, well above the European Union average of 25.6%. However, in 2017, the recycling rate was less than 5% nationally. In 2018, the situation was: 5.8 million tons of waste, with a collection rate of 82.3% and a recycling rate of 3%, the second-lowest level in the European Union (before Bulgaria). Of the total waste collected in Romania, 56% is organic matter, 9.9% paper and cardboard, 9.9% is plastic waste, then 4.1% glass, 2.3% metal, and 17.8% other types of waste.

Most Portland cement is made in a rotary kiln. According to the diagram in Figure 1, the rotary kiln for the clinker (4) is arranged in the central part, with a length of 97 m and a diameter of 5.7 m, fed with conventional fuel at one end where there is a burner of the corresponding fuel (8) at the opposite end being fed with the mixture prepared and finely chopped, and preheated with the gases discharged from the furnace. To this end, the furnace may also be fed with different quantities of used tires (5), oil sludge (6), or other categories of properly processed combustible waste. The diagram shown in Figure 1 (dry method) has a two-branch supply scheme (1 and 2) through which the raw material is brought in to be appropriately processed before burning. The coal used for combustion is finely ground in a Pfeiffer mill (19) and brought to the kiln burner.

The axis of the oven is slightly inclined, and the burner is placed at the lower end. The rotation causes the clinker to gradually pass along the furnace into which it enters at the cold end until the hot end, where it eventually falls and cools.

The hot gases leaving the furnace (Figure 1) enter the heat exchanger, then, a part is transmitted to the conditioning tower (wetting) (21) of the raw material (raw meal) and is evacuated through a fan to the bag filter/electrofilter (26), one part goes to the raw meal mill (22) to dry the grinding material, being then evacuated using the dust removal cyclone (25) to the same filter (26), and another part goes from the heat exchanger (3) to the coal mill (19) for the preparation of coal. Finally, the gases from the filter (26) are discharged into the atmosphere using the central chimney positioned behind the filter.



**Figure 1.** Simplified clinker diagram using raw materials and alternative fuels. 1. fan branch A; 2. fan branch B; 3. heat exchanger (preheater) for raw materials in the form of flour; 4. rotary kiln for clinker production; 5. supply used tires; 6. oil sludge (or sludge) feed system; 7. NOx reduction system; 8.burner; 9. grill cooler; 10.clincher crusher; 11.clincher carrier (conveyers); 12. prefiring; 13. charcoal dust bag filter; 14. milled coal silo; 15. dosing system; 16. grill cooling electrofilter; 17. primary air fan; 18. coal bunker; 19. Pfeiffer coal mill; 20. filter 2 cooler dust removal; 21. conditioning (wetting); 22.raw meal mill; 23. raw material drying tower; 24. dry tower dust removal cyclones; 25. cyclone dust removal mill; 26. Oven filter-mill.

## 2.2. Isokinetic Sampling of Emissions (Total Dust)

It is necessary to know the processes that originate in the gas flow from the stack and the methods for dust collection and flow determination. If the suspended dust is composed of particles with a diameter greater than 5  $\mu$ m or a concentration greater than 5 mg/m<sup>3</sup>, it cannot be considered homogeneous, and sampling must be performed with nozzles for speed regulation and defined as isokinetic.

Isokinetics means that the sampling rate must be set so that the velocity of the gas entering through the sampling nozzle is equal to or as close as possible to the velocity of the gas in the basket. Therefore, compliance with the isokinetic conditions is mandatory in the case of particle size determinations.

Particular attention must be given to the position and distribution of sampling points because the gas flow is not always laminar, and the particle size distribution is not uniform. Therefore, it is recommended that the pipe sampling section is in a straight section, at a distance of at least five hydraulic diameters from the top of the sampling plane (from the top of the basket) and two hydraulic diameters from the bottom and the sampling locations must be selected accordingly (ISO 9096/2017).

The ISOSTACK BASIC TCR Tecora equipment (TCR Tecora, Cogliate, Italy), used in sampling, consists of a gas analyzer with a display and infrared printer, gas sampling probe with a length of 2500 mm,  $\phi$  80 mm, max. 1000 °C, transducer for measuring the differential pressure and/or gas velocity, with the possibility to connect a Pitot tube to calculate the flue gas flow, with a length of 2500 mm, max. 1200 °C, dew point calculation, and software for analysis and operation.

The Isostack Basic TCR Tecora automatic sampling system is made in accordance with US EPA, Unichim, and the recent ISO 9096/2017 standards.

The stack gases are automatically sampled through the sampling sensor nozzles at the same speed as the stack (isokinetic conditions). These adjustments are made automatically without operator intervention in resolving the complex relationships that control the conditions of the fluid dynamics at the stack and the sampling parameters. Figure 2 presents an example of dust sampling with "in-stack" and "out-stack" filtration devices.



**Figure 2.** Example of dust sampling with "in-stack" and "out-stack" filtration devices. 1. sampling nozzle; 2. filter holder; 3. Pitot tube; 4. temperature sensor; 5. temperature indicator; 6. static pressure measurement; 7. dynamic pressure measurement; 8. support tube (depending on the type); 9. cooling and drying system.

The simplified scheme of the sampling system is shown in Figure 3.



**Figure 3.** Simplified scheme and the components of the sampling system for the clinker furnace emission stack.

If these conditions are met, it is possible to collect the particulate sample in a filter attachment placed along with the sensor. The hot flue gases are then driven by a cooling accessory to retain the water and condensate content before entering the sampler and control unit. Finally, a representative, complete sample is extracted from the gas flow and entrained solid particles and the amount of dust retained on the filter the volume of extracted gas (according to ISO 9096/2017) is determined gravimetrically.

A partial volume flow is isokinetically extracted from the main source of extracted volume. The particles contained in this flow are collected in the measuring filter. Quantitative analysis of these particles is performed gravimetrically. The concentration of particles in the main flow is calculated using the partially extracted volume and the amount of particles contained in the partial volume.

The standardized reference method for dust measurement is based on the gravimetric determination of the mass concentration of dust harvested under isokinetic conditions using the automatic isokinetic dust sampling system [31].

The isokinetic sampling probe is connected to the sampler using the umbilical cord, which is connected to the temperature sensor and the Pitot tube. Next, attach the sampling probe to the metal box in which the glass filter container is inserted, and to this filter a sampling hose is attached. It is connected to the condensing/cooling device and then to the silica gel hatch, and from the hatch to the sampler. Next, connect the thermosetting cables, both for the probe and for the metal box of the filter. To prevent condensation, these will keep the probe's temperature and box at around 20 °C to prevent condensation. Finally, the sampling probe is fixed at the sampling points using the supplied flange.

Before sampling, the filters are dried in the oven for one hour at 105  $^{\circ}$ C, left to cool in the desiccator for at least 4 h, and then weighed. The cooling and weighing operation is repeated until it reaches a constant mass. The same operations will be carried out after sampling, and subsequent calculations must be made to determine the concentration of dust.

The determination of the total dust concentration in the gases was carried out according to standardized procedures SR EN 13284-1: 2018 and ISO 9096: 2017, and the flue gas concentration (directed emissions/emissions from fixed sources) according to the procedures SR ISO 10396: 2008 and SR EN 15267-3: 2008.

The measurement of the physical parameters (pressure, temperature, speed/flow, humidity) was completed according to the standardized procedures (directed emissions/ emissions from fixed sources): SR EN 15259: 2008, SR ISO 14164: 2008, SR EN 14790: 2017, SR ISO 10396: 2008, SR EN ISO 16911-1: 2013.

#### 2.3. Flue Gases Extraction (NOx, CO, SO<sub>2</sub>) from the Stack

The extraction of flue gases (NOX, CO, SO<sub>2</sub>) from the stack was performed with the gas analyzer TESTO 350 XL (Testo SE & Co.-Germany, Keison products, Kirchzarten, Germany), which is a portable device, consisting of a central unit for analysis, a unit of control and three types of probes with which the following parameters can be measured in the pipe:

- Temperature and composition (O<sub>2</sub>, CO, NO, NO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>S, CxHy / HC and a module for CO<sub>2</sub> measured in IR);
- Temperature, relative humidity, and dew point temperature;
- Gas velocity.

The sampling probe for determining the gas temperature and composition is equipped with a ceramic filter to retain impurities in the gases. In addition, the analysis unit has a built-in sampling probe that ensures a flow rate of 1.3 L/min. The gas analysis is performed by the unit of analysis using electrochemical cells (Figure 4).



Figure 4. Gas analyzer TESTO 350 XL.

N

The following formulas are used to convert the values of the ppm flue gas results given by the appliance to  $mg/m^3$ :

$$NO_{x}[ppm] = NO[ppm] + NO_{2}[ppm]$$

$$NO\left[\frac{mg}{Nm^{3}}\right] = 1.34NO[ppm]$$

$$NO_{2}\left[\frac{mg}{Nm^{3}}\right] = 2.05 \text{ NO}[ppm]SO_{2}\left[\frac{mg}{Nm^{3}}\right] = 2.92 \text{ NO}[ppm]$$

$$NO_{x}\left[\frac{mg}{Nm^{3}}\right] \text{ uscat} = NO_{x}[ppm] \text{ actual} \times 2.05 \times \frac{100}{100 - \text{H2O}(\%)}$$

$$IO_{x} \text{ recalc. la } O_{2} = 10\% \left[\frac{mg}{Nm^{3}}\right] \text{ uscat} = NO_{x}\left[\frac{mg}{Nm^{3}}\right] \text{ uscat} \times \frac{(21 - 10)}{(21 - O_{2} \text{ mas.})}$$

$$\begin{split} &SO_2\Big[\frac{mg}{Nm^3}\Big] uscat = SO_2[ppm] \text{ actual } \times 2.92 \times \frac{100}{100 - H2O(\%)} \\ &SO_2 \text{ recalc. la } O_2 = 10\% \Big[\frac{mg}{Nm^3}\Big] uscat = SO_2\Big[\frac{mg}{Nm^3}\Big] \text{ uscat } \times \frac{(21-10)}{(21-O_2 \text{ mas.})} \end{split}$$

#### 3. Results

#### 3.1. General Sampling Results

The results obtained from the measurements are presented in Table 1. Although, the working conditions were different in each experimental case, the table shows both the results obtained under real working conditions and data calculated at  $10\% O_2$ .

In all cases shown in Table 1, the clinker kiln worked with the raw material mill.

The data analysis in the table shows that the values of the environmental parameters analyzed in the paper were within the norms provided by AIM.

For example, the emissions of dust and gases in the chimney (pos.16, Figure 1, height 70 m), on 24 March 2021, were below the permitted limit values contained in the AIM, revised in 2018 (20 mg/Nm<sup>3</sup>—for dust; 500 mg/Nm<sup>3</sup>—for NOx; 400 mg/Nm<sup>3</sup>—for SOx; 2000 mg/Nm<sup>3</sup>—for CO), both for branch A and branch B, under the conditions wherein the temperature of the measuring point was 138.8 °C and 139.8 °C, respectively, at the two supply branches. The measurements were performed with TESTO 350 analyzer unit for flue gas analysis, in the gas flow conditions: 195,508.0 Nm<sup>3</sup>/h—at branch A; 129,334.0 Nm<sup>3</sup>/h—at branch B, using SR ISO 10396/2008 and SR EN 15267/2009 as working procedures.

Thus, the average of the six measurements performed for branch A presented the following values of pollutant emissions:  $1.02 (\pm 0.27) \text{ mg/Nm}^3$ —for dust, 293.43 ( $\pm 6.62$ ) mg/Nm<sup>3</sup>—for NOx, 279.97 ( $\pm 3.97$ ) mg/Nm<sup>3</sup>—for CO, values calculated for a reference concentration of 10% O<sub>2</sub>, because the oxygen concentration at the measuring point had an average value of 8.85%. Therefore, SOx emissions were below the detection limit of the device.

At the beginning of the measurements, the outside environment's temperature was  $11.7 \,^{\circ}$ C, the atmospheric humidity was 50.3%, and the relative air pressure was 98.84 kPa.

Six measurements were also performed for branch B, and their mean values were: 0.89 ( $\pm$ 0.17) mg/Nm<sup>3</sup>—for dust, 406.65 ( $\pm$ 14.04) mg/Nm<sup>3</sup>—for NOx, 241.09 ( $\pm$ 3.38) mg/Nm<sup>3</sup>—for CO, values calculated for the reference concentration of 10% O<sub>2</sub> because the concentration of O<sub>2</sub> at the measuring point had an average value of 7.99% ( $\pm$ 0.14%). Therefore, SOx emissions were also below the detection limit of the device.

For this case, the outside environment's temperature was 21.7  $^{\circ}$ C, the atmospheric humidity was 63.5%, and the relative air pressure was 98.83 kPa.

We must remember that the rotary kiln operated continuously with traditional and alternative fuels, with a production capacity of 128.4 t/h, the proportions of fuel types being: coal/coke oil—8.62 t/h (53.97%), with power caloric 28,436 GJ/t; used tires and rubber—3.7 t/h (23.17%), with a calorific value of 25 GJ/t; fluff/mixed solid waste—3.65 t/h (22.86%), with calorific value 4.67 GJ/t.

For the same consortium, but in a different area of the country, the pollutant emissions (dust, NOx, SOx, CO) in the stack (35 m) of the rotary clinker kiln in operation (because the kiln has two branches A and B), during the period 25–27 May 2021, were also below the permitted limit values, included in the Integrated Environmental Authorization AIM, (30 mg/Nm<sup>3</sup>—dust, for the other emissions the values being the same as before), provided that the temperature of the measuring point was 123 °C. These emissions showed values (average of six determinations):  $3.74 (\pm 0.67) \text{ mg/Nm}^3$ —for dust, 406.64 ( $\pm 56.29$ ) mg/Nm<sup>3</sup>—for NOx, 895.06 ( $\pm 240.5$ ) mg/Nm<sup>3</sup>—for CO, calculated values for the reference concentration of 10% O<sub>2</sub>, as the oxygen concentration at the measuring point had an average value of 10.68% ( $\pm 0.1\%$ ). The SOx emissions were, here too, below the detection limit of the ISOSTAC BASIC + TESTO 350XL device, according to the measurement procedure SR ISO 14164: 2008, SR EN 14790: 2017, and SR EN 16911-1: 2013.

Maggungent			Co	ombustible, %	Duet	NOv	<b>SO</b> -	CO
Date	Emission Source		Coal/Cocs (%)	Combustible Waste (%)	(mg/Nm <sup>3</sup> )	(mg/Nm <sup>3</sup> )	(mg/Nm <sup>3</sup> )	(mg/Nm <sup>3</sup> )
	Branch A: C.R. 1 +	(1)			12.06	342.00	b.d.l.	436.04
10 November 2020	Raw mill	(2)	_ 89.9	Fluff—5.05 Cellulose—0.65	9.26	263.15	b.d.l.	333.66
Cement plant A	Branch B: C.R. 1 +	(1)		Used tires—4.4	8.88	482.10	b.d.l.	523.75
	Raw mill	(2)			7.17	390.67	b.d.l.	421.58
	Branch A: C.R. 1 +	(1)			17.18	499.85	b.d.l.	457.91
	Raw mill	(2)	_ 77	Fluff—6.49 Lower coal—0.7	14.62	425.19	b.d.l.	388.28
5 April 2021 Cement plant A	Branch B: C.R. 1 +	(1)		Used tires—12.68	11.53	445.53	b.d.l.	695.41
Centern plain A	Raw mill	(2)			12.34	476.63	b.d.l.	743.2
	C P 2 + Payr mill	(1)	<b>91 07</b>	Fluff—7.68	3.35	342.35	b.d.l.	111.66
	C.R. 2 + Raw mill	(2)	01.97	Used tires-10.35	2.96	302.85	b.d.l.	98.85
15 October 2019 Cement plant B	C.R. + Raw mill	(1)	82.35	Fluff—8.75	4.83	183.13	b.d.l.	1196.88
		(2)		Oil waste—3.05	6.11	232.56	b.d.l.	1514.02
8 October 2020	C.R. + Raw mill	(1)	90 1E	El	3.22	314.47	b.d.l.	127.09
Cement plant B		(2)	80.15	Flum—19.85	3.68	351.63	b.d.l.	138.38
19 April 2021	C.R. + Raw mill	(1)	70 (0	Fluff—3.87	0.49	343.50	b.d.l.	928.81
Cement plant B		(2)	79.09	Used tires—13.9	0.61	430.65	b.d.l.	1152.76
	Branch A: C.R. + Raw mill	(1)	87 65		6.07	433.23	b.d.l.	478.54
14 November 2019		(2)		Used tires—12.35	4.98	356.09	b.d.l.	393.09
Cement plant C	Branch B: C.R. +	(1)			6.28	441.10	b.d.l.	544.59
	Raw mill	(2)			5.48	385.18	b.d.l.	475.45
	Branch A: C.R. +	(1)			8.65	448.91	b.d.l.	654.16
10 March 2020	Raw mill	(2)	81.4	Used tires_18.6	7.29	381.90	b.d.l.	551.97
Cement plant C	Branch B: C.R. +	(1)	0	0300 1103 10.0	12.36	292.13	b.d.l.	669.38
	Raw mill	(2)			6.47	235.23	b.d.l.	540.67
	Branch A: C.R. +	(1)			1.13	324.15	b.d.l.	309.38
24 March 2021	Raw mill	(2)	59.6	Fluff/Mixed solid	1.02	293.43	b.d.l.	297.97
Cement plant C	Branch B: C.R. +	(1)	_ 07.0	Used tires—20.3	1.05	480.97	b.d.l.	285.21
	Raw mill	(2)			0.89	406.65	b.d.l.	241.09
	Limits according to IEP						400	2000

Table 1. Results on the composition of NOx, SO<sub>2</sub>, CO and dust in the stack of the clinker kiln.

Notes: The values in this table represent the average of two measurements at each working point. (1) measured values in working conditions; (2) calculated values at 10% O<sub>2</sub>; b.d.l.—below the detection limit O<sub>2</sub> = 8.07%—Branch A; O<sub>2</sub> = 10.72%—Branch B; O<sub>2</sub> = 8.56%—CR 2, at plant A in 2021; O<sub>2</sub> = 6.68%—Branch A; O<sub>2</sub> = 7.38%—Branch B, at C.R. plant A in 2020; O<sub>2</sub> = 12.26%-C.R.—2021; O<sub>2</sub> = 11.15%-C.R.-2020; O<sub>2</sub> = 12.31%—C.R., at plant B in 2019; O<sub>2</sub> = 8.85%—Branch A; O<sub>2</sub> = 7.99%—Branch B-2021; O<sub>2</sub> = 7.95%—Branch A; O<sub>2</sub> = 7.38%—Branch B, at plant C-in 2020; O<sub>2</sub> = 7.60%—Branch A; O<sub>2</sub> = 8.40%—Branch B, at plant C in 2019. All plants are equipped with bag filters, except for the C cement plant which in 2019 and 2020 was provided with an electrofilter before leaving the main basket.

At the beginning of the measurements, the outside environment's temperature was 14.8 °C, the atmospheric humidity was 70.4%, and the relative air pressure was 95.4 kPa. The flow of dry flue gas at the exhaust was 275862.0  $\text{Nm}^3/\text{h}$ .

As fuels in the clinker kiln were used: coal/coke—7.38 t/h, used tires—3.3 t/h, wood waste—0.35 t/h, fluff—2.09 t/h, cellulose—0.89 t/h, lower coal—1.35 t/h.

A representative average sample was taken from the clinker obtained at a cement plant, and the chemical composition and mineralogical composition was determined by optical microscopy. The Bogue calculation established the following calculation relations for the mineralogical constituents  $C_2S$  and  $C_3S$  [18], their result is given in Tables 2 and 3 and the images obtained are presented in Figures 5 and 6:

% 
$$C_3S = 4.07\% \text{ CaO} - 7.60\% \text{ SiO}_2 - 6.72\% \text{ Al}_2\text{O}_3 - 1.42\% \text{ Fe}_2\text{O}_3$$
  
%  $C_2S = 8.60\% \text{ SiO}_2 + 5.06\% \text{ Al}_2\text{O}_3 + 1.07\% \text{ Fe}_2\text{O}_3 - 3.05\% \text{ CaO}$ 

Table 2. Chemical analysis of clinker after preparation (according to [19] and [20]).

Characteristic	U.M.	Value
LSF (lime saturation factor)	%	96.3
M <sub>SI</sub> (silica moduli)	-	2.15
M <sub>AI</sub> (alumina moduli)	-	1.62
CaO liber	%	0.81
C <sub>3</sub> S (Bogue calculation)	%	60.5
C <sub>2</sub> S (Bogue calculation)	%	15.17

Table 3. Mineralogical composition of the clinker \* resulting from preparation by light microscopy.

Clinker Mineralogical Components	Sample 1	Sample 2
Alit, %	~70	~70
Belit%	~10	~10
Interstitial mass, %	~20	~20
Alite crystal dimensions, µm	3–80	3–80
Belite crystal dimensions, μm	10–25	10–25

\* in accord with [18,19]; Note [20,21]: large crystals result from an extended stay in the clinker area, which has a negative impact on the grindability of the clinkers, idiomorphic belit crystals indicate an efficient cooling at low temperature.



**Figure 5.** Microphotographs representing the morphology of alite crystals present in the clinker. Enlarge images: (**a**,**b**) M200X; (**c**,**d**) M1000X.



**Figure 6.** Microphotographs representing the morphology of the belit crystals present in the clinker nodules. Enlarge images: (**a**,**d**) M200X; (**b**,**c**) M1000X; (**d**) secondary belit for alite crystals.

## 3.2. The Characteristics of the Fuels Used in the Combustion Process of the Clincker

The average samples of primary fuel and combustible waste were analyzed from a compositional point of view in an accredited laboratory (elemental analysis and oxide analysis in ash). The results are summarized in Tables 4 and 5.

Characteristic	Fuel Type					
	Coal + Coke Oil Mixture	Fluff				
	Elementary analysis					
Humidity, %	1.19	3.77				
Ash content, %	14.90	14.83				
Volatile matter content, %	19.33	65.24				
Sulfur content, %	1.63	0.10				
Chlorine content	<0.01	0.07				
Lower calorific value, kcal/kg	6805	4905				
Oxidic analysis of ash						
SiO <sub>2</sub>	23.35	33.98				
$Al_2O_3$	9.83	13.83				
Fe <sub>2</sub> O <sub>3</sub>	1.22	8.32				
CaO	14.02	22.18				
K <sub>2</sub> O	1.39	1.12				
Na <sub>2</sub> O	0.37	2.46				

Table 4. The characteristics of the fuels used in the combustion process of the clinker.

All alternative fuels (Figure 7) allowed for co-incineration at cement plants are part of the list of wastes accepted for co-incineration without significant impact on the environment, mentioned in the "Guide for incineration of waste in cement plants". The kiln areas through which the waste is incinerated and the maximum feed capacity are determined according to the type of used waste so that the temperatures required for complete combustion and emission control are ensured. Refueling is continuous, except for start/stop periods when only conventional fuels are used.

Characteristic	U.M.	Value
Fine grinding		
R <sub>90µm</sub>	%	5.88
R <sub>200µm</sub>	%	1.76
Granulometry		
Cumulative past < 1 $\mu$ m	%	1.6
Cumulative past < 4 $\mu$ m	%	7.8
D <sub>50%</sub>	μm	22.1

Table 5. The main characteristics of the ground coke oil + coal mixture.

Notes: the value of the fineness of grinding expressed on the 90  $\mu$ m sieve is appropriate (recommendation R<sub>90µm</sub>  $\leq$  8%) considering that the coal-oil coke mixture with different grinding skills and implicitly for combustion was used for combustion; the value of R<sub>200µm</sub> is higher than the recommendation of R<sub>200µm</sub>  $\leq$  1%, with negative consequences on the atmosphere in the furnace and the volatility of sulfur [32–34].



Figure 7. The diagram for establishing fuel waste supply points.

Coal, coke oil, and their substitutes are brought to the solid fuel depot, from where they are picked up and transported to the grinding plant, where they are brought to the established fineness. From the storage silo, the material is extracted, dosed, and transported pneumatically to the main burner of the furnace.

Energy-efficient alternative fuels are transported to the feed bins and, after dosing, are transported to the co-incineration plant.

Due to the high temperatures in the clinker kiln, the organic content of the waste used as alternative fuels is completely destroyed.

#### 3.3. Estimation of Air Pollution Level with Total Dust and Polluting Gases

This estimation was made using the pollutant dispersion climatological model—Breeze AERMOD 9.1, which is software based on AERMOD (a mathematical dispersion model). This program was developed by the US EPA (the United States Environmental Protection Agency). This program is up-to-date because the last modification was made in 2019. The program uses a Gaussian-type dispersion model, which can predict the concentrations of pollutants such as NOx, NOx, SOx, CO, and others from several types of pollutant emitting sources [31].

Dispersion modeling involves several intermediate steps, such as preparing meteorological and topographic data. Thus, this model considers the topographical and climatic characteristics for each location (source of pollution) and can predict concentrations of pollutants from point sources, surface, or volume. Two types of climatic data are used: surface, hourly and radiosonde [31]. These two types of data were entered into AERMOD through the AERMET module, going through verification stages, QA (Quality Assurance), and merging. After processing, two types of information relevant to the area and the study period resulted, horizontally and vertically [31].

The wind rose was also generated, containing details on the periods of calm, the general directions of the wind, and the percentage for each of them during the reference period. Finally, the topographic data were processed in the QGIS software and entered in AERMOD through the AERMAP module, integrated into the program, with the help of which the topographic data were correlated with those related to the emission sources and their receivers.

Modeling the dispersion of air pollutants at the level of the area of interest was performed for 2020, using the measurements of pollutant concentrations in the basket of emission sources (stacks) within the cement production line as input data for sources.

The analysis took into account the irregularities of the terrain, the use, and the albedo of the land surface around the station for correct extrapolation of the data set. The wind rose is shown in Figures 8 and 9. The atmospheric calm was 4.6%, and the main wind direction was W-E. (Figure 8 shows the wind rose with the wind direction "Blowing From").



Figure 8. The wind rose made with the AerMet module for the area of interest.

WindrosePlot	WindroseTa	able Data	Table I	Data	TimePlot	Data Rose P	lot	DataRose	Table
Dir \ Spd	<= 1.54	<= 3.09	<= 5.1	4	<= 8.23	<= 10.80	)	> 10.80	Total
0.0	2.17	2.90	3	.77	0.2	6 0.0	1	0.00	9.12
45.0	1.56	1.22	0	.41	0.0	0.0	0	0.00	3.19
90.0	2.03	2.33	1	.88	0.0	5 0.0	0	0.00	6.28
135.0	2.83	4.47	7	.08	0.2	8 0.0	0	0.00	14.67
180.0	1.08	0.50	0	.19	0.0	0.0	0	0.00	1.78
225.0	0.84	0.85	0	.54	0.0	5 0.0	0	0.00	2.28
270.0	5.95	11.30	19	.64	1.7	9 0.3	5	0.01	39.05
315.0	5.61	4.54	7	.41	0.6	3 0.0	0	0.00	18.19
Total	22.09	28.13	40	.92	3.0	5 0.3	6	0.01	94.56
Calms									4.57
Missing									0.88
Total									100.00

Figure 9. Speed frequency wind data.

# 3.4. Digital Terrain Model and Analyzed Area (Area of Interest)

The digital terrain model (DTM), also known as the digital height model, creates a digital representation of topography and terrain [31]. Topographic data were obtained from Copernicus Land Monitoring (Copernicus European Digital Elevation Model), processed via QGIS software, and integrated into AERMOD software with the AERMAP module. Topographic data were correlated with those related to the emission sources and the Cartesian network of receivers [31].

The area of interest was created in Google Earth Pro and was set at a square area of approx.  $50 \text{ km}^2$  (7 × 7 km) with a cement plant in the center. Its surface in relation to the Cement Factory can be seen in Figures 10–13.



Figure 10. Area of interest for the Cement Plant (Google Earth Pro).



Figure 11. Digital terrain model for Romania (QGIS).



Figure 12. Area of interest (analyzed area) (QGIS).



Figure 13. Digital terrain model in the module: left) AERMAP; right) 3D Analyst.

The software calculates the concentration values for all the hours throughout the year and all the receivers, resulting in the maximum pollutant concentration for the chosen period (Figure 14). Dispersion modeling was performed by an accredited laboratory based on the emissions and gas/air flows measured during 2020. For the mathematical modeling, surface meteorological data from a local station were used, and meteorological data with vertical profile from the station Bucharest Băneasa. The obtained results were compared with the limit value of the concentration for each pollutant, according to the Romanian Law 104/2011.



Figure 14. Representation of emission sources (stacks) in Google Earth Pro.

The results obtained, according to the calculations, for the concentrations of NOx,  $SO_2$  and CO are presented in Tables 6–8, in which:

- Elevation—represents the elevation (altitude) of the terrain for the analyzed objective in relation to the sea level; in this situation, an average elevation value of 494 m was considered.
- Emission—represents the average of the values taken into account; for NOx, SO<sub>2,</sub> and CO the values from the measurement campaigns carried out by the accredited laboratory were used.
- Stack height—represents the height of each source in relation to the ground level.
- Temperature—represents the average of the values measured by the accredited laboratory for the basket of each machine.
- Speed—represents the speed of the gas in the pipeline and the average of the values measured by the accredited laboratory for each machine was taken into account.
- Diameter—represents the diameter of each stack.

Air Speed Elevation Emission Stack Height Temperature, Diameter Nr Description (m) (g/s) (m) (°C) (m/s) (m) 1 Kiln stack line 2 494 36.222 67 125.43 16.67 3.6 Stack 1 (branch 2 494 21.178 67 124.47 16.55 2.3 A) CR + RM Stack 2 (branch 3 494 10.722 67 127.57 16.77 2.3 B) CR + RM

**Table 6.** Input data in Breeze AERMOD software—NOx.

Table 7. Input data	in Breeze AERMOD	software—SO <sub>2</sub> .
---------------------	------------------	----------------------------

Nr.	Description	Elevation (m)	Emission (g/s)	Stack Height (m)	Temperature, (°C)	Air Speed (m/s)	Diameter (m)
1	Kiln stack line 2	494	5.242	67	125.43	16.67	3.6
2	Stack 1 (branch A) CR + RM	494	7.270 *	67	124.47	16.55	2.3
3	Stack 2 (Branch B) CR + RM	494	7.270 *	67	127.57	16.77	2.3

\* measurement performed only on branch A of the clinker rotary kiln line no. 1.

Table 8. Breeze AERMOD—CO software input data.

Nr.	Description	Elevation (m)	Emission (g/s)	Stack Height (m)	Temperature, (°C)	Air Speed (m/s)	Diameter (m)
1	Kiln stack line 2	494	86.916	67	125.43	16.67	3.6
2	Stack 1 (branch A) CR + RM	494	13.029	67	124.47	16.55	2.3
3	Stack 2 (branch B) CR + RM	494	11.087	67	127.57	16.77	2.3

Notes: For each branch of the kiln, the afferent stack was taken into account;  $NO_2$  was considered NOx.

# 3.5. Estimating the Level of Environmental Pollution with Polluting Gases

For NOx, from the analysis and processing of data obtained by determinations at the chimney flues, the maximum modeled concentrations (hourly and annual concentration) are shown in Table 9 and Figures 15 and 16, respectively.

Table 9. Maximum NOx concentrations extracted from modeling (hourly and annual).

Source	Maximum Hourly Concentration, (µg/m³/h)	Maximum Annual Concentration, (µg/m <sup>3</sup> /year)
Clinker kiln-modeled values	120.74	3.87
Limit value—Law 104/2011 for the protection of human health	200	40
Limit value—Law 104/2011 for the protection of vegetation and natural ecosystems	-	30



Figure 15. Hourly NOx concentration in the area of interest—Google Earth Pro.



Figure 16. Annual NOx concentration in the area of interest—Google Earth Pro.

The modeled NOx concentrations indicate that the maximum hourly and annual values comply with the limit values provided in Law 104/2011, according to the data presented in Table 8.

It is observed that the maximum value of the hourly concentration is found at the boundary of the analyzed area, in the NW corner of the factory for which the data are presented, and the maximum value of the annual concentration is at the eastern limit of the same factory.

For CO, the modeled maximum daily concentration (8 h average concentration) is shown in Table 10 and Figure 17.

Table 10. Maximum CO concentrations extracted from modeling (daily).

Source	Daily Concentration (Average for 8 h), mg/m <sup>3</sup>
Clinker kiln-modeled values	0.050
Limit value—Law 104/2011 for the protection of human health	10



Figure 17. Annual CO concentration in the area of interest—Google Earth Pro.

It is observed that the maximum value of the modeled CO concentration complies with the limit value provided in Law 104/2011, according to Table 10.

For SO<sub>2</sub>, the maximum modeled concentrations (hourly and daily) are shown in Table 11 and Figures 18 and 19.

	<b>Table 11.</b> Maximum SO <sub>2</sub>	concentrations	extracted fi	rom modeling	g (hourl	ly and o	daily	).
--	--	----------------	--------------	--------------	----------	----------	-------	----

Source	Maximum Hourly Concentration, μg/m <sup>3</sup>	Maximum Daily Concentration, μg/m <sup>3</sup>
Clinker kiln—modeled values	23.71	6.69
Limit value—Law 104/2011 for the protection of human health	350	125



Figure 18. Hourly  $SO_2$  concentration in the area of interest—Google Earth Pro.



Figure 19. Daily SO<sub>2</sub> concentration in the area of interest—Google Earth Pro.

It is observed that the maximum hourly and daily values of the modeled  $SO_2$  concentrations comply with the limit values provided in Law 104/2011, according to Table 11.

In the case of the hourly concentration, the formation of two zones of agglomeration of SO<sub>2</sub> emission is observed, both at the limit of the analyzed area and in the corners of V and NV.

## 4. Discussion

From the data presented in the paper and the results obtained by on-site measurements at three cement factories in Romania, the following can be deduced:

- Dust emissions, measured at the stacks of the equipment belonging to the cement production line in the period January–November 2020, fall within the emission limit imposed by the integrated environmental permit, of 30 mg /Nm<sup>3</sup> at 10% O<sub>2</sub>, with values in the range 3.78–24.57 mg/Nm<sup>3</sup>;
- Pollutants emissions (dust, NOX, CO, SO<sub>2</sub>) measured in 2020 (May, June, August, September, and November) at clinker kiln line no. 1 and line no. 2 were within the limit values provided in the integrated environmental permit;
- Emissions of pollutants (dust, NOX, CO, SOx) monitored at clinker kiln line no. 1 and line no. 2 in the conditions of use in the combustion of a thermal energy proportion between 4.98–50.64% combustible waste (used tires, lower coal, railroad sleepers–impregnated wood, fluff, plastic waste, waste paper, and cardboard, used oil, sunflower seed husks, corn biomass, vegetable waste, blast furnace sludge were as follows:
  - Dust emissions have been within the limits of the Integrated Environmental Permit (IEP)—30 mg/Nm<sup>3</sup> 10% O<sub>2</sub>; the variation range was relatively constant, between 0.48–19.88 mg/Nm<sup>3</sup> at 10% O<sub>2</sub>;
  - NOx emissions were within the limit set in the IEP —500 mg/Nm<sup>3</sup> at 10% O<sub>2</sub>; the variation range was between 273.56–484.07 mg/Nm<sup>3</sup> at 10% O<sub>2</sub>;
  - SOx emissions were within the limit set in the IEP —400 mg/Nm<sup>3</sup> at 10% O<sub>2</sub>; the variation range was between 4.81–225.79 mg/Nm<sup>3</sup> at 10% O<sub>2</sub>;
  - CO emissions were within the limit provided in the integrated environmental permit—2000 mg/Nm<sup>3</sup> at 10% O<sub>2</sub>; the variation range was between 253.08–1523.29 mg/Nm<sup>3</sup> at 10% O<sub>2</sub>.

The concentrations of pollutants in the air, calculated with the climatological model of dispersion of pollutants—Breeze AERMOD 9.1, based on the emissions of dust and measured pollutant gases, are within the limit values provided in law 104/2011.

We must specify that the reduction in pollution can be made by:

- Replacement of filters (electrofilter or bag filter) and existing equipment with more efficient and less consuming (different types of separators, respectively adding a Precalciner on the heat exchanger to increase the productivity of the oven);
- Cleaning and maintenance works (water spraying on the factory platform, sweeping, etc.), according to some factory procedures;
- Incineration of waste in the furnace (their type, depending on the incineration, also depends on the resulting pollution).

# 5. Conclusions

In this paper, the following activities were performed:

- Carrying out measurements and/or taking over the monitoring data of the pollutant emissions (dust, CO, NO<sub>X</sub>, and SO<sub>2</sub>) for the equipment from the production line;
- Interpretation of the results obtained from measurements/monitoring and comparison with the maximum permitted limits contained in the Integrated Environmental Authorization of the cement plant;
- Assessment of environmental pollution by dispersion analysis, based on measurements;
- Establishing pollution reduction measures, if necessary, for compliance with the regulations in place for the cement industry.

Analyzing the results of the performed measurements regarding the emissions of dust polluting gases, it is recommended for emissions at point sources the followings:

- Monitoring the emissions of dust and polluting gases with the frequency provided in the EIA;
- Thorough control of the chemical composition of combustible waste to comply with the required emission limits;
- Maintenance of depollution and monitoring equipment for pollutant emissions to comply with the limit values set out in the EIA.

Burning (co-incineration) of waste in clinker kilns from Romanian cement plants is a recovery operation because it has the following advantages:

- ✓ For waste generators
  - The certitude that they have a total elimination with no impact on the environment;
  - The life cycle of the products is closed;
  - The issues related to negative environmental impact, and also related to penalties, can be resolved.
- ✓ For cement producers
  - The partial use of alternative materials (which will ensure a reduction in the use of traditional fuels and raw materials) is ensured;
  - There is active involvement in environmental protection which will lead to the transformation of this industry from the polluter to a person who remediate the problem.
- ✓ For the community
  - Conservation of natural resources is achieved: coal, crude oil (fuel oil), natural gas, limestone, gypsum, marl, etc.;
  - CO<sub>2</sub>, greenhouse gas emissions are reduced;
  - The energy efficiency of cement kilns increases;
  - The environmental impact is low:
    - Air emissions (strictly regulated) through the oven-heat exchanger system that neutralizes acid gases;
    - A high temperature ensures complete combustion;
  - There is no waste (ash or slag) that requires storage (avoid overcrowding of controlled landfills-dumps);

Environmental risks are reduced (uncontrolled storage, soil and water pollution, etc.).

Implementing the BAT (best available techniques) in the cement industry in Romanian cement plants ensures permanent emission control. This way the impact on the environment is considerably reduced. The activities that helped were: continuous monitoring systems for clinker furnaces, process automation, periodic installation and replacement of modern dust filters, investment in reduction installations [35]. Selective non-catalytic NOx emissions and in low NOx burners, conservation of natural resources by partial substitution of traditional fuels and raw materials with some waste alternatives (co-processing of waste into cement manufacturing process) [35]. New composite cement developed and marketed in recent years have a higher percentage of mineral additives. They help reduce greenhouse gas emissions and energy consumption, thus conserving natural resources [35].

Finally, the air quality around cement plants must be closely monitored regularly to ensure compliance with the recommended regulations in force.

**Author Contributions:** G.V., C.C. conceptualization, methodology, validation and supervision, I.-A.I., P.T. translation, validation, and visualization. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

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

#### References

- Ciobanu, C.; Voicu, G.; Istrate, I.A.; Tudor, P. Pollution reduction through waste co-processing in Romanian cement plants. In Proceedings of the International Symposium ISB-INMA '2021—Agricultural and Mechanical Engineering, Bucharest, Romania, 29 October 2021; pp. 370–377.
- 2. Co-Processing. Available online: https://www.geocycle.com/co-processing (accessed on 10 December 2021).
- Georgiopoulou, M.; Lyberatos, G. Life cycle assessment of the use of alternative fuels in cement kilns: A case study. J. Environ. Manag. 2018, 216, 224–234. [CrossRef] [PubMed]
- Ghosh, S.K.; Parlikar, U.V.; Karstensen, K.H. Sustainable Management of Wastes through Co-Processing; Springer Science and Business Media LLC: Singapore, 2022.
- The Advantages of Co-Processing Waste (in Romanian). Available online: https://www.holcim.ro/ro/dezvoltare-durabila/ avantajele-co-procesarii-deseurilor (accessed on 18 November 2021).
- Baidya, R.; Ghosh, S.K.; Parlikar, U.V. Co-processing of industrial waste in cement kiln—A robust system for material and energy recovery. *Procedia Environ. Sci.* 2016, 31, 309–317. [CrossRef]
- Meystre, J.A.; Silva, R.J. The possibility of coprocessing municipal solid waste—MSW in clinker kilns to cement production. *Technol. Therm. Eng.* 2013, 12, 34–39. [CrossRef]
- Ragazzi, M.; Rada, E.C.; Antolini, D. Material recovery in integrated waste management systems: An innovative approach for the characterization of the gaseous emissions from residual MSW bio-drying. *Waste Manag.* 2011, *31*, 2085–2091. [CrossRef]
- 9. Elinwa, A.U.; Mahmood, Y.A. Ash from timber waste as a cement replacement material. *Cem. Concr. Compos.* **2002**, 24, 219–222. [CrossRef]
- Rahman, A.; Rasul, M.G.; Khan, M.M.K.; Sharma, S. Industrial Waste as Alternative Fuel in Cement Industry: Its Impact on Environment. In Proceedings of the 7th WSEAS International Conference on Energy & Environment: Recent Researches in Environmental and Geological Science, Kos Island, Greece, 14–17 July 2012; pp. 108–114. Available online: https://hdl.handle. net/10018/927953 (accessed on 20 December 2021).
- 11. Rahman, A.; Rasul, M.G.; Khan, M.M.K.; Sharma, S. Recent development on the uses of alternative fuels in cement manufacturing process. *Fuel* **2015**, *145*, 84–99. [CrossRef]
- 12. Strigac, J. Effect of selected alternative fuels and raw materials on the cement clinker quality. J. Civ. Eng. 2015, 10, 81–92. [CrossRef]
- 13. Clavier, A.; Paris, J.M.; Ferraro, C.C.; Townsend, T.G. Opportunities and challenges associated with using municipal waste incineration ash as a raw ingredient in cement production—A review. *Resour. Conserv. Recycl.* 2020, *160*, 104888. [CrossRef]

- Sarmiento, L.M.; Clavier, K.A.; Paris, J.M.; Ferraro, C.C.; Townsend, T.G. Critical examination of recycled municipal solid waste incineration ash as a mineral source for Portland cement manufacture—A case study. *Resour. Conserv. Recycl.* 2019, 148, 1–10. [CrossRef]
- Viczek, S.A.; Aldrian, A.; Pomberger, R.; Sarc, R. Origins of major and minor ash constituents of solid recovered fuel for co-processing in the cement industry. *Waste Manag.* 2021, 126, 423–432. [CrossRef]
- 16. Viczek, S.A.; Aldrian, A.; Pomberger, R.; Sarc, R. Determination of the material-recyclable share of SRF during co-processing in the cement industry. *Resour. Conserv. Recycl.* **2020**, *156*, 1046962020. [CrossRef]
- 17. Gotze, R.; Boldrin, A.; Scheutz, C.; Astrup, T.F. Physico-chemical characterisation of material fractions in household waste: Overview of data in literature. *Waste Manag.* **2016**, *49*, 3–14. [CrossRef] [PubMed]
- 18. Co-Processing of Waste in EU Cement Plants: Status and Prospects. Available online: https://circulareconomy.europa.eu/platform/en/good-practices/co-processing-waste-eu-cement-plants-status-and-prospects (accessed on 12 December 2021).
- 19. Kleshchov, A.; Hengevoss, D.; Terentiev, O.; Hugi, C.; Safiants, A.; Vorfolomeiev, A. Environmental potential analysis of co-processing waste in cement kilns. *East. -Eur. J. Enterp. Technol.* **2019**, *4*/10, 13–21. [CrossRef]
- Bhatty, J.I.; Miller, F.M.; Kosmatka, S.H.; Bohan, R.P. (Eds.) Innovations in Portland Cement Manufacturing; Portland Cement Association: Skokie, IL, USA, 2011.
- 21. Odagiu, A. Monitorizarea Calitatii Mediului 1; BIOFLUX Publishing House: Cluj-Napoca, Romania, 2016.
- 22. PBL Netherlands Environmental Assessment Agency. Trends in Global CO2 Emissions: 2016 Report. Available online: edgar.jrc. ec.europa.eu/.../jrc-2016-trends-in-global-co2-emissions-2016-report-103425 (accessed on 20 January 2022).
- Chinyama, M.P.M. Alternative Fuels in Cement Manufacturing. In *Alternative Fuel*; InTech Open: London, UK, 2011; Available online: <a href="http://www.intechopen.com/books/alternative-fuel/alternative-fuels-in-cement-manufacturing">http://www.intechopen.com/books/alternative-fuel/alternative-fuels-in-cement-manufacturing</a> (accessed on 26 January 2022).
- Powering the Cement Industry. Available online: https://cembureau.eu/media/ckkpgrg1/cembureau-view-cement-sectorelectricity-use-in-the-european-cement-industry.pdf (accessed on 10 November 2021).
- Verma, Y.; Mazumdar, B.; Ghosh, P. Dataset on the electrical energy consumption and its conservation in the cement manufacturing industry. *Data Brief* 2020, 28, 104967. [CrossRef] [PubMed]
- Cocarta, D.M.; Rada, E.C.; Ragazzi, M.; Badea, A.; Apostol, T. A contribution for a correct vision of health impact from municipal solid waste treatments. *Environ. Technol.* 2009, 30, 963–968. [CrossRef] [PubMed]
- 27. Kallenborn, R. Persistent organic pollutants (POPS) as environmental risk factors in remote high-altitude ecosystems. *Ecotoxicol. Environ. Saf.* **2006**, *63*, 100–107. [CrossRef]
- 28. Al-Neaimi, Y.I.; Gomes, J.; Lloyd, O.L. Respiratory illnesses and ventilatory function among workers at a cement factory in a rapidly developing country. *Occup. Med.* 2001, *51*, 367. [CrossRef]
- 29. Adak, M.D.; Adak, S.; Purohit, K.M. Ambient air quality and health hazards near min-cement plants. *Pollut. Res.* 2007, 26, 361–364.
- 30. Ikli, B.I.; Demir, T.A.; Urer, S.M.; Beker, A.; Akar, T.; Kalyoncu, C. Effects of chroniuum exposure from a cement factory. *Environ. Res.* **2003**, *9*, 113–118. [CrossRef]
- 31. Lisnic, R.; Jinga, S.I. Study regarding the efficiency of a wet FGD system on the dispersion of SO<sub>2</sub> emissions. *Rom. J. Mater.* **2021**, 51, 78–84.
- 32. Radu, D.; Ghizdavet, Z. Relationships between burnability indices of the raw mix for clinker production. *Rom. J. Mater.* **2016**, *46*, 303–312.
- Buzdugan, G. Calculation of the mineralogical composition of the Portland cement clinker (in Romanian: Calculul compozitiei mineralogice a clinckerului de ciment Portland). In *Mechanical Engineer's Manual*; (in Romanian: Manualul Inginerului Mecanic); Technical Publishing House: Bucharest, Romania, 1976; Volume 1, pp. 274–275.
- Fechet, R.; Zlagnean, M.; Moanta, A.; Mohanu, I. The effect of mineral sterile from tailing ponds used that the addition of the raw mix, on the properties of clinker and Portland cement. *Rom. J. Mater.* 2010, 40, 315–322. [CrossRef]
- 35. Holcim. Raport Anual de Mediu. 2019. Available online: https://www.holcim.ro/sites/romania (accessed on 22 January 2022).