CO₂ REDUCTION OPTIONS IN CEMENT INDUSTRY – THE NOVI POPOVAC CASE

by

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The cement industry contributes about 5% to global anthropogenic CO_2 emissions, and is thus an important sector in CO_2 -emission mitigation strategies. Carbon dioxide is emitted from the calcination process of limestone, from combustion of fuels in the kiln, and from the coal combustion during power generation. Strategies to reduce these CO_2 emissions include energy efficiency improvement, new processes, shift to low carbon fuels or waste fuels in cement production, increased use of additives in cement production, alternative cements, and CO_2 removal from flue gases in clinker kilns.

Increased use of fly ash as an additive to cement and concrete has a number of advantages, the primary being reduction of costs of fly ash disposal, resource conservation, and cost reduction of the product. Since the production of cement requires a large amount of energy (about 2.9-3.2 GJ/t), the substitution of cement by fly ash saves not only energy but also reduces the associated greenhouse gas emissions. The paper evaluates the reduction of CO_2 emissions that can be achieved by these mitigation strategies, as well as by partial substitution of cement by fly ash. The latter is important because the quality of the produced concrete depends on the physical-chemical properties of the fly ash and thus partial substitution as well as the type of fly ash (e. g., the content of CaO) has an effect not only on energy consumption and emissions, but also on the produced concrete quality.

Key words: green house gases emission, cement industry, CO₂ decreasing

Introduction

Carbon dioxide emission and its reduction is the subject each sector of the society, especially economy, needs to deal with. Responsibilities and directives established with the aim to reduce the global warming are on one hand, and on the other is the responsibility of the companies and individuals in the attempt to find the way to reduce the emission of the green house gases (GHG) effect maintaining the satisfactory productivity.

The main emitters of GHG emissions are the following sectors: power generation, transport, buildings, and industry and manufacturing.

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The global cement industry itself is a major emitter and contributes around 5% towards anthropogenic CO_2 emissions through the chemical process of producing clinker and the extensive use of energy. Global cement production grew from 594 Mt in 1970 to 2284 Mt in 2005, with the vast majority of the growth occurring in developing countries, especially China. In 2005, China produced 1064 Mt (47% of world cement production), while India, Thailand, Brazil, Turkey, Indonesia, Iran, Egypt, Vietnam, and Saudi Arabia accounted for another 394 Mt (17%) [1].

Portland cement (the most common type of cement used in many parts of the world) is an important ingredient in concrete production and is one of the most intensive energy materials produced, after aluminum and steel (2.9 3.2 GJ/t) [2].

Carbon dioxide is emitted from the calcination process of limestone, from combustion of fuels in the kiln, and from the coal combustion during power generation.

In the search for a reduction of GHG effect several procedures are emphasized:

- improvements of the manufacturing processes (e. g. enhancing the energy efficiency of cement kilns),
- use of certain "waste" in the production processes (*e. g.* as alternative fuels in the cement kiln),
- optimizing the composition of cement (*e. g.* using blast furnace slag, power station fly ash, *etc.*), and
- substituting fossil fuel with biomass and/or fossil fuel waste.

Also, one of the possible ways to regulate the GHG emission is participation in the emission trading system (ETS).

As a new method alternative cements and CO_2 removal from flue gases in clinker kilns are stressed. Processes that are especially successful are alkali activated cements, magnesia cements, and sulfoaluminate cements. In many cases alternative cements have considerable potential in terms of environmental, engineering, and economic properties [3].

As one of the more effective ways for CO_2 emission reduction is the increased use of additives in cement production, especially fly ash [4, 5].

This paper presents a CO_2 emissions calculation methodology from the process of cement production based on the perceived places of its occurrence. Also, ways of its reduction are presented as well as the effects that might be accomplished.

CO₂ emission in the cement industry

Process overview

This paper presents one of the most common processes in the modern cement production, the dry method cement production with a four-stage cyclone pre-heater which is situated in the Cement Factory in Novi Popovac in Serbia. The process which is presented in fig. 1 incorporates a rotary kiln, a pre-heater, a cooler, and a combustor (burner). The characteristic parameters of the process such as raw material and fuel consumption, clinker production and volumes of flue gas components production are presented in tab. 1. The high temperatures in the cyclone pre-heater and the rotary kiln cause the continuous transformation of the raw mixture into sintered clinker.

672





Figure 1. Clinker production cycle

Table 1. Characteristic parameter	s of	the
process in the rotary kiln		

Material							
Clinker production	[t per day]	2000					
Raw material (limestone)	[kgkg ⁻¹ cl]	16.211					
Specific fuel consumption							
Anthracite	[kgkg ⁻¹ cl]	0.1151					
Scrap tires	[kgkg ⁻¹ cl]	0.0157					
Flue gases							
Carbon dioxide emission	[m ³ h ⁻¹]	38200					
Carbon dioxide emission	[t per year]	14390					

The production cycle of cement typically consists of four stages. The first stage is transport and preparation of raw materials. The second stage, where the most energy is consumed, is related to the clinker production. The third stage is production of Portland cement, and the last (fourth) stage consists of transport of the finished goods, quality assurance, and other minor processes.

The raw materials used for cement production are limestone and small quantities of other materials. The raw materials are crushed and ground in special mills. The exit product is called raw

meal. After homogenization, the raw meal is fed into the top of the pre-heater moving from the top (first stage pre-heater) to the bottom (fourth stage pre-heater) (fig. 1). Hot gases coming from the rotary kiln are moving in the opposite direction. Raw material coming out the pre-heater and entering the rotary kilns comes to the process of calcination and sintering, and clinker production. The chemical composition of the clinker is presented in tab. 2.

673

Oxide composition				
Silicon dioxide (SiO ₂), [%]	20.62			
Aluminum oxide (Al ₂ O ₃), [%]	5.57			
Ferro (III) oxide (Fe ₂ O ₃), [%]	2.28			
Calcium oxide (CaO), [%]	67.23			
Magnesium oxide (MgO), [%]	2.31			
Sulfur three oxide (SO ₃), [%]	0.43			
Potassium oxide (K ₂ O), [%]	0.82			
Sodium oxide (Na ₂ O), [%]	0.31			
Rest (O), [%]	0.43			
Free calcium oxide (CaO), [%]	1.28			

Table 2. Clinker composition

In general, calcination can be presented by following reversible reaction:

$$CaCO_3$$
 CaO CO_2 (1)

It should be noted that the formation of a certain amount of CaO starts at a temperature of about 550 °C. Further increase in temperature, in the zone of calcination, has as a result acceleration of calcination and releasing of large amounts of CaO (and CO₂). In the transitional zone, the temperature increases and the calcination goes to the end.

Produced clinker goes into the cooler in which comes to its intensive cooling and warming at the same time the outside coming air which goes in the rotary furnace (such as the so-called secondary air). Clinker goes out of the cooler and on the transportation system that still leads it to cement mill. During the movement of raw materials and flue gases, the temperature of gases in the direction of movement decreases (from res of new materials in grassing (70, 1420, 80)

1900 °C to 350 °C), while the temperature of raw materials increases (70-1420 °C).

Figure 1 presents the scheme of the rotary kiln with a four-stage pre-heater and cooler, including the materials flow directions and temperatures of the materials in the individual parts.

Fuel that is used for providing energy necessary for the process may be different. The most widely used fuel is high quality coal, anthracite, and natural gas. In addition to these conventional fuels, many other alternative fuels such as old tires, municipal waste, *etc.* can be used, in an attempt to reduce energy consumption and GHG emission.

Composition	Dry sample mass fraction, [%]		Fly ash mass fraction, [%]	
	Anthracite	Scrap tires	HFA	LFA
С	72.0	64.20	40.40	44.7
Н	1.5	5.00	16.50	18.2
0	5.5	4.40	5.69	17.80
N	1.0	0.10	27.70	11.7
S	0.49	0.91	1.93	1.52
Ash	15.2	25.2	1.17	0.42
Higher heating value, [kJkg ⁻¹]	31400	36340	1.84	2.16

Table 3. Composition of the used fuel (coal and scrap tires) and fly ash

674

To supply the necessary energy, the fuel can be delivered to the combustor present at the upstream of the rotary kiln (primary delivery) or by direct insertion in the transition from the pre-heater and the rotary kiln (secondary delivery of fuel).

In the presented process anthracite and scrape tires are consumed. Its specific consumption and characteristics are presented in tab. 1 and tab. 3.

In tab. 3 the composition of the two types of fly ashes, which are most often used in the production process, is presented: fly ash with high content of CaO (HFA) and fly ash with low content of CaO (LFA).

Carbon dioxide emission

In order to estimate GHG emission from the process of cement production it is important to identify the potential recourses of GHG emissions. A facility involved in cement production may have various stationary and mobile fuel combustion processes occurring on-site that lead to GHG emissions. Several primary process sources directly linked with the clinker production (*e. g.* limestone calcination) or with other facility system may also result in GHG emissions, depending on the configuration of the specific facility. The main sources in Novi Popovac facility, where CO_2 is emitted, are the clinker production process in rotary kiln and stationary combustion.

Clinker production process

The clinker (cl) production process occurring in the kiln results in CO_2 emissions from the calcination of limestone to produce lime, eq. (1). The emissions are essentially directly proportional to the CaO and MgO content of clinker (chemical composition of the clinker is presented in tab. 2) and should be based on the quantity of produced clinker (daily clinker production is presented in tab. 1).

For CO_2 emissions calculation from the calcination process based on clinker production data, it is used the following eq. (2) [6]:

$$Emissions (clinker production)_{CO_2} EF_{cl} Q_{cl}$$
(2)

where EF_{cl} is the emission factor for the clinker produced (tonnes CO₂/tonne clinker), and Q_{cl} the quantity of clinker produced (tonnes).

The eq. (2) assumes that all of the CaO and MgO in the clinker is from a carbonate source (*e. g.* $CaCO_3$, MgCO₃ in limestone).

The *EF* for clinker is based on the CaO and MgO content of the clinker and the stoichiometry of the calcination reaction, as follows:

$$EF_{cl} = \frac{44.0}{56.1} CaO = \frac{44.0}{40.3} MgO$$
 (3)

where 44.0/56.1 is the stoichiometric ratio of CO_2/CaO ; according to Annex VII of 2007/589/EC (tab. 2) stoichiometric ration is 0.785.

 CaO_{cl} is the calcium oxide content of clinker produced, corrected for other CaO sources, if applicable.

44.0/40.3 is the stoichiometric ratio of CO_2/MgO .

 MgO_{cl} is the magnesium oxide content of clinker produced, corrected for other MgO sources, if applicable.

According to eq. (3), and data from tab. 2 the *EF* is calculated as:

$$EF_{cl} = \frac{44.0}{56.1} 0.6723 = \frac{44.0}{40.3} 2.31 = 52.73 = 2.57 = 0.553 \text{ t} \text{CO}_2 \text{ per t clinker}$$
 (4)

According to the IPCC methodology Default Values for CO_2 Emission Factor for clinker is 0.525 [7].

Carbon dioxide emission from clinker production according to eq. (2) and date for quantity of clinker production (2000 t per day, tab. 1) and calculated EF (0.553 t CO₂/t clinker) are:

 $Emission (clinker production)_{CO_2} \quad 0.553 \text{ t } CO_2 \text{ per t clincer } 2000 \text{ t clinker per day}$ $365 \text{ days per year} = 403690 \text{ t } CO_2 \text{ per year}$ (5)

Stationary combustion emissions

Estimation of the quantity of CO_2 emissions from stationary combustion processes according to the detailed fuels-based approach is available using the general eq. (6):

$$Emission (stacionary \ combustion)_{CO_{2}} \quad EF_{ab} \quad EF_{ab} \tag{6}$$

where a is the fuel type, and b the sector or source activity.

This approach requires a good knowledge of the quantity and the quality of fuel types consumed in the source combustion processes identified and the use of $CO_2 EF$ that are fuel-specific. To calculate CO_2 emissions under this approach, the first step is to determine the quantity of fuel combusted for each fuel type used in the stationary combustion process(es). The next step is the choice of an appropriate *EF* for each fuel type consumed. It is good practice to use a facility-specific or locally available *EF* as this should be more representative of local or facility conditions with regards to fuel types and/or operating conditions.

Carbon dioxide emission factor

Carbon dioxide *EF* for fuel combustion are primarily dependant on the properties of the fuel and, to a lesser extent, the combustion technology. The following general equation (adapted from Joint EMEP/CORINAIR, 2001, [8]) can be used to determine a $CO_2 EF$, by fuel type, for the detailed fuels based approach:

$$EF_{\rm CO_2} = \frac{44}{12} C_{\rm C \ fuel} \quad \infty \tag{7}$$

where EF_{CO_2} is the facility *EF*, by fuel type (in mass of CO₂ permass of fuel [*e. g.* kgkg⁻¹, tt⁻¹]), 44/12 the stoichiometric ratio of CO_2/C (according to Annex VII of 2007/589/EC, tab. 2, stoichiometric ratio) is 3.664, C_{C fuel} the carbon content of fuel (in mass of C per mass of fuel [*e. g.* kgkg⁻¹, tt⁻¹]), and ∞ the fraction of carbon oxidized.

The fuel composition data for the fuel combusted at the facility can be used to determine the carbon content of the fuel. In tab. 3 the chemical composition of anthracite and scrape tire is presented. It is assumed that the only product of the oxidation process is CO_2 . Products of incomplete oxidation, such as carbon monoxide (CO), are assumed to undergo complete oxidation to CO_2 in the atmosphere after being emitted [9]. Thus, all carbon from these emissions is accounted for in the total for CO_2 emissions ($\infty = 10$).

The EF are:

$$EF(anthracite)_{CO_2} = \frac{44}{12} 0.72 \ 1 \ 2.64 \ t \ CO_2 \ per \ t \ fuel$$
 (8)

$$EF(scrape \ tires)_{CO_2} = \frac{44}{12} 0.642 \ 1 \ 2.35 \ t \ CO_2 \ per \ t \ fuel$$
 (9)

For fuels where the carbon content varies significantly from year to year (such as coal), a new *EF* should be developed for each inventory period.

Carbon dioxide emission from combustion process can be calculated as a sum of CO_2 emission from anthracite and scrap tires combustion. Having in mind the consumption of anthracite of 0.1151 t/t clinker and scrape tire of 0.0157 t/t clinker (tab. 1), and clinker production of 2000 t per day, tab. 1, the CO_2 emission on the year basis is then:

$$Emission (stacionary combustion)_{CO_2} Emission(anthracite) CO_2$$

$$Emission (scrapetires)_{CO_2} 365 day per year 2000 t clinker per day (Q_a EF_a Q_{st} EF_{st})$$

$$730000 (0.1151 2.64 0.0157 2.35) 248853t CO_2 per year$$
(10)

Carbon dioxide emission from whole process of clinker production is:

 $Emission_{CO_2} Emission (clinker production)_{CO_2} Emission (stacionary combustion)_{CO_2}$ $403690 t CO_2 \text{ per year } 248853 t CO_2 \text{ per year } = 652542 t CO_2 \text{ per year } (11)$

It is clear that CO_2 emission from the clinker production is almost twice higher than the emissions from combustion process.

The specific emission (SE) from facility per t produced clinker is:

$$SE_{CO_2} = \frac{(652542 \text{ t CO}_2 \text{ per year}) / (2000 \text{ t clinker per day})}{365 \text{ days per year}} = 0.902 \text{ t CO}_2 \text{ per t clinker}$$
(12)

Carbon dioxide reduction

A general approach of CO_2 reduction starts with the identification of the main sources of emissions and after that through good knowledge of processes and energy consumption try to reduce emissions. In that way two main principles are possible:

Carbon dioxide emission reducing from clinker production:

- decreasing the clinker factor in blended cement,
- use of non carbonated calcium sources in the raw mixture, and
- use of alternative raw material that contains carbonates (fly ash, slag, gypsum, anhydrite, fluorite).

Carbon dioxide emission reducing from combustion process:

- energy efficiency improvement,
- substituting fossil fuel with biomass and waste,
- fuel switching from coal or petroleum fuel to natural gas, and

substituting fossil fuel with alternative fuels.

Decreasing the clinker factor in blended cement by substituting clinker by fly ash, provides savings both in the production process as well as in the fuel consumption. Energy transport costs of alternative raw material, which is used, is minor compared to the main energy consumption [10]. Substituting clinker by alternative materials, such as fly ash, of about 10% would lead to an annual reduction of the emission CO_2 of 65258.2 t $(0.1.652582 \text{ t } CO_2/t_{cl})$, eq. (11). Converted to the produced amount of clinker, CO_2 emission reduction would be about 90.2 kg CO_2/t_{cl} .

Using fly ash in cement makes possible to obtain cement and concrete of a very good quality. Standards of a large number of countries allow the usage of fly ash in the amount of 15-30%. Depending on the quality of cement wanted to obtain, this percentage can be raised. Results have shown that the fly ash affects positively to the operating characteristics of the cement paste as the improvement of the sulfate resistance and the reduction of 'bleeding' in cement pastes [10]; corrosion resistance growth [11], better behavior upon higher and high temperature actions [12], and other. By micronising fly ash it is possible to achieve its consumption up to 50% while achieving the wanted cement quality [13, 14].

Installing system for variable air volume on ventilators for air inlet in the combustion process, the combustion in the rotary kiln would be improved, which would cause reduced consumption both the prime energy sourse and the electrical power for ventilator operations [15]. By application of such measures a minimum saving can be expected, *i. e.* increase of the process energy efficiency at 10% [16]. Increasing of the energy efficiency of the process of about 10% would lead to consumption reduction of 10% which would be seen in the CO₂ emission reduced of about 24885.3 t CO₂ per year, eq. (10), (*i. e.* CO₂ emission reduction per a unit of clinker produced would be 34.1 kg/t_{cl}).

Having in mind that consumption of anthracite for kilogram clinker production is 0.1151 kg, by substituting anthracite with natural gas for the same clinker production, annual emission of CO₂ can be reduced for 76588.7 t CO₂. Natural gas has greater value of lower heating value in relation to anthracite ($H_{\rm L}^{\rm NG}$ = 48970 kJ/kg, $H_{\rm L}^{\rm ant}$ =21600 kJ/kg); at the same time it has significantly smaller emission factor ($\varepsilon_{\rm CO_2}^{\rm NG}$ 56100 kg / TJ, $\varepsilon_{\rm CO_2}^{\rm ant}$ 98300 kg / TJ), implicating that for the production of energy from anthracite annual emitted amount of CO₂ will be 178404.6 t, while in case of usage of natural gas 101815 t will be emitted, which represents decrease of 57% of CO₂ emission.

It is obvious that much better results are achieved with the increased fly ash participation in the clinker, so attention should be focused on finding ways to use more fly ash in clinker.

Conclusions

As shown by this approach, CO_2 emission from the clinker production is almost twice higher than the emissions from combustion process.

Because of that, special attention is focused on the clinker production, understanding that reduction of CO_2 emissions from the clinker production very often leads to decreasing of energy consumption.

Comparing the effects achieved, on one hand by increasing energy efficiency of the process and on the other by substituting one part of blended cement with fly ash, it can be concluded that the most effective way to reduce CO_2 emissions is by reducing the clinker factor. The big potential for CO_2 reduction also lies in substituting anthracite with natural gas.

This paper presents the calculated EF wich amounts to 0.553 t CO₂ per t clinker. According to the IPCC methodology Default Values for CO₂ Emission Factor for Clinker is 0.525. The calculated EF is 5.3% larger than the Default Values, which shows that the observed plant is working below the current world norms of CO₂ emission.

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