

# **Slag Cement Production in Terms of Emission Reducing**

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## Abstract

Today in cement world many companies started to use alternative materials for cement production. Some of these alternative material have direct and indirect impact on emissions, energy consumption etc. In order to reduce  $CO_2$  and other emissions some cement plants intend to introduce granulated blast furnace slag (GBFS) as partial substitution of cement clinker in final product (cement). Increasing of granulated blast furnace slag content lead to decreasing clinker content in slag cement. This will have the effect in the way that we will have to produce/use less clinker for production 1 ton of cement. This information is important because according to the current clinker/cement technology production, most of the  $CO_2$  emission is result of decarbonatization of calcium carbonate during the burning process<sup>2</sup>. Some estimates put the cement industry total as high as 5% of total global anthropogenic  $CO_2$  emissions. In this paper will be presented comparison of  $CO_2$ ,  $NO_x$ ,  $SO_x$  and CO emission in ordinary Portland cement and cement produced by granulated blast furnace slag.

Keywords: CO2 emission, granulated blast furnace slag, cement, clinker

# **1.Introduction**

The specific CO<sub>2</sub> emission depends from the type of cement and it vary from cement plant to cement plant. Generally the production of 1,0 t of Portland cement causes about 0,815 t CO<sub>2</sub> emission. On the other hand the production of 1,0 t of slag cement containing 75% of granulated blast furnace slag causes emission of only 0.300 t CO<sub>2</sub>. These data include the calcination process, emissions from fossil fuel burning, and the use of electricity. Only the decarbonization of the raw materials during the clinker production causes about 0.5 t CO<sub>2</sub> for each ton of clinker. Building the precalcinator into the cyclone heat exchanger could have a positive impact on decreasing CO<sub>2</sub>, NO<sub>x</sub> and CO emissions [3]. World-wide it can be assumed that 68 Mt blast furnace slag are not granulated. If this tonnage would be granulated and used as a cement constituent, every year about 11 Mt coal equivalent (321 PJ) primary energy would be saved and 64.5 Mt CO2 would be avoided.

Most emissions especially  $CO_2$  emission is associated with kiln for cement clinker burning and ancillary equipment used for pyro processing process. These emissions are generated by two mechanisms [1].

- a. Reaction-based  $CO_2$  generation the thermochemical decomposition reaction or calcining of limestone (CaCO<sub>3</sub>  $\rightarrow$  CaO + CO<sub>2</sub>) and other minor raw materials produce  $CO_2$
- b. Fuel-based  $CO_2$  generation the combustion of fuels, used to obtain the high temperature needed for the calcining reactions, produce  $CO_2$ .

Technological scheme of cement production process is presented in figure 1.



Figure 1. Cement production process

Sulphur dioxide  $(SO_2)$  emissions from a cement manufacturing process are dependent upon the sulphur content of the raw materials and fuels used. If a raw material or fuel with little or no sulphur content is used within a kiln, then there will be little or no SO<sub>2</sub> emissions. If there is a high sulphur content within the raw meal then the sulphide and organically combined sulphur will combust in the preheating stage, the majority of SO<sub>2</sub> formed is scrubbed out by the raw meal and only a small portion may be emitted to the atmosphere[3].

Other emissions include nitrogen oxides  $(NO_x)$  and carbon monoxide (CO).  $NO_x$  is produced during combustion due to the elevated temperatures in the kiln and to the presence of nitrogen in the air/fuel mixture. The temperatures at the firing end of the kiln approach 1,870°C.  $NO_x$  is produced in this environment due to the reaction of nitrogen in air with excess oxygen. The amount of  $NO_x$  produced is dependent upon the temperature and the amount of oxygen present. The higher the temperature or higher excess oxygen used in the kiln, the higher the resultant  $NO_x$  emissions will be.

CO can result from poor solid-fuel feed systems in which sub-stoichiometric combustion will produce CO. However, the high temperature and long residence time associated with kiln operations provide little opportunity for CO emissions to occur [2].

Figure 2 shows the effect of the substitution of clinker by granulated slag for cement with 35% granulated slag. The calculations are based on an average fuel energy consumption of 3500 MJ/t clinker, the use of hard coal as fuel and a CO<sub>2</sub> emission factor for electricity generation of 0.67 t CO<sub>2</sub>/MWh. Under these conditions, the production of one ton of Portland cement, which was produced using 5% sulphates and 5% minor additional constituents is associated with a total CO<sub>2</sub> emission (including that for the electricity) of 0.842 t CO<sub>2</sub>/t cement. As a result of clinker substitution with 35% granulated slag, a reduction in the specific fuel-derived CO<sub>2</sub> emissions of approx. 0.09 t CO<sub>2</sub>/t would be attained. Additional thermal energy is, however, necessary for the drying of the granulated slag (ca. 0.02 t CO<sub>2</sub>/t cement) and if necessary for the transport from the steel works to the cement works (not taken into account here). By far the greatest saving effect is produced by the reduction of the raw material-related CO<sub>2</sub> emissions from the limestone, with just 0.15 t CO<sub>2</sub>/t cement. In total, a reduction of approx. 0.22 t CO<sub>2</sub>/t cement [4].



Figure 2. Reduction of CO<sub>2</sub> emissions in t CO<sub>2</sub>/t cement

# 2. Experimental

The results presented in experimental part of this paper are obtained on the basis of laboratory and industrial tests. Samples for examination were prepared in laboratory mill by mixing different component in order to get slag cement with different content of slag and clinker. Sample preparation procedure was carried out in the following steps:

- Collecting of samples for slag cement preparation,
- Analyses of all collected samples
- Mixing of samples (slag, clinker and gypsum) in different proportions,
- Grinding of prepared samples (specific surface or Blain ~ 4300 cm<sup>2</sup>/g) in laboratory mill

The composition of laboratory prepared cement samples is listed in table 1.

Table 1. Composition of laboratory prepared samples						
	Content of clinker	Content of fly	Content of	Content of gypsum		
	(%)	ash (%)	granulated blast	(%)		
			furnace slag (%)			
CEM II	67.00	25,00	4,00	4,00		
Slag cement I	57,00	-	39.00	4,00		
Slag cement II	28,00	-	68,00	4,00		
Slag cement III	14,00	-	82,00	4,00		





Figure 3. Composition of CEM II (without slag)

Figure 4. Composition of slag cement I





Figure 5. Composition of slag cement II

The cement production process is intensive in energy as well as in raw material demand. Limits of technical improvements to lower the environmental impact of the cement production have been reached in the European cement industry. Remaining potential to reduce environmental impacts is provided by the reduction of the clinker content in cement by producing blended cements. Other main constituents for cement like granulated blast furnace slag (gbfs), fly ashes from power plants, natural and industrial pozzolanas or limestone can be used.

The production of blended cements including slag cements results in lower emission and lower energy consumption since less clinker from the energy intensive process is needed to produce such blended cements. According to results of emission for CEM II production in industrial conditions was made a calculation of CO<sub>2</sub>, NO<sub>x</sub>, SO<sub>x</sub> and CO emission as we can see from the table 2 and accompanying diagrams.

Table 2. Emissions during the cement production process						
Sample name	CO <sub>2</sub> emission	NOx emission	SOx emission	CO emission		
-	(t)	$(mg/m^3)$	$(mg/m^3)$	$(mg/m^3)$		
CEM II	0,829	0,00107	0,0000062	0,00111		
Slag cement I	0,705	0,00091	0,0000053	0,00094		
Slag cement II	0,346	0,00045	0,0000026	0,00046		
Slag cement III	0,173	0,00022	0,0000013	0,00023		





NOx emission during the cement production process



### 3. Results and discussion

According to EU standard (EN 197-1) it is possible to produce three types of slag cements (CEM III/A, CEM III/B and CEM III/C) with different content of slag. For production of CEM III/cement allowed content of slag is between 36 - 65%, for CEM III/B content of slag is 20 - 34% and for CEM III/C allowed content of slag is 5 - 19% [5].

In this paper were made examination of each type of CEM III cement and compared with ordinary Portland cement (CEM II). As we can see from the table and diagrams utilisation of slag as alternative material in cement production has a big impact on emissions. Regarding  $CO_2$ ,  $NO_x$ ,  $SO_x$  and CO emission it is obviously that production of cement with granulated blast furnace slag has lower emissions than ordinary cement CEM II.

Comparison of CO<sub>2</sub> emission we can see that CO<sub>2</sub> emission during the CEM II production is 0,829 t CO<sub>2</sub>/t cement while for slag cement production the emission of CO<sub>2</sub> vary from 0,173 to 0,705 t CO<sub>2</sub>/t slag cement. The similar situation is with NO<sub>x</sub> emission where CEM II production results in greater emission than slag cement. NO<sub>x</sub> emission for CEM II is 0,00107 t NO<sub>x</sub>/t cement while for cement with granulated blast furnace slag is between 0,00022 and 0,00091 t NO<sub>x</sub>/t cement. Emissions of SO<sub>x</sub> and CO during the slag cement production is also significantly lower compared with ordinary cement CEM II.

#### 4. Conclusions

The requirement for reducing  $CO_2$  and other emissions in cement industry has led to the development and production of cements with low clinker content and thus high content of alternative components. One of such type of cement is slag or blast furnace slag cement. Carbon dioxide ( $CO_2$ ) which is part of cement production process is classified as a greenhouse gas. In cement manufacturing, almost one ton of  $CO_2$  is released for every ton of cement produced.

The cement industry has reduced  $CO_2$  emissions significantly since the early 1980's and continues to develop methods that minimize the release of greenhouse gasses. Good approach for solving problems with emissions is utilization some materials which are waste from technological process eg. waste from thermo power plant process (fly ash as by product), hot metal production in blast furnace (slag) etc.

The advantages for application of these materials are numerously. One of the advantages is that by using these waste materials as slag we are doing good thing for environment in a way of reducing the disposal of waste material on landfill. The second maybe important thing is that by application of these waste materials as cement constituent we reduce emissions of harmful gases as  $CO_2$ ,  $NO_x$ ,  $SO_x$ , CO during the cement production process. On the other hand quality of the slag cements is very similar to ordinary cement.

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