ENVIRONMENTAL IMPACTS OF CEMENT PRODUCTION

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Будівельна промисловість є одним з лідерів щодо забруднення довкілля внаслідок вичерпування ресурсів і затрат енергії або утворення відходів. Крім того, спостерігається значна емісія від парників, кислотних газів від будівельної промисловості. Цемент належить до одного із найвикористовуваніших будівельних матеріалів у світі, а його виробництво невпинно зростає. А цементна індустрія є дуже енергомісткою. А також продукує велику кількість викидів, отруйних запахів і є дуже шумною. Пил, вуглекислота CO_2 , оксиди (NOx) азоту і двоокис (SO₂) є основними складовими викидів від цементних заводів, що створює великі проблеми. Представлено огляд стану екологічних проблем, пов'язаних з виробництвом цементу в Європі.

Ключові слова: цемент, цементна промисловість, екологія.

Building industry is one of the leaders in deterioration of environment by depleting resources and consuming energy or creation of waste. Also a considerable amount of emissions of greenhouse and acidifying gasses has the origin in building industry. Cement belongs to the most often used building materials and its production is increasing over the world. But the cement industry is an energy enormous intensive and products many emissions, odors and noise. The emissions from cement plants which cause greatest concern and which need to be dealt with are dust, carbon dioxide CO_2 , nitrogen oxides (NOx) and sulphur dioxide (SO₂). This paper deals with the review of the main environmental issues related to the cement production in Europe.

Key words: cement, cement industry, emissions.

Introduction. Concrete is the most common construction material used in building industry. Cement is a basic component of concrete used for building and civil engineering construction. On average approximately 1 ton of concrete is produced each year for every human being in the world. Therefore concrete (i.e. cement) is one of the World's most significant manufactured materials. Because of its abundance in the world market, understanding the environmental implications of concrete and cement manufacturing are becoming increasingly important [1].

In Europe the use of cement and concrete (a mixture of cement, aggregates, sand and water) in large civic works can be traced back to antiquity. In 2008 there were 268 installations producing cement clinker and finished cement in the European Union with a total of 377 kilns [4].

Output from the cement industry is directly related to the state of the construction business in general and therefore tracks the overall economic situation closely. The cement industry is an energy intensive industry with energy typically accounting for about 40 % of operational costs, i.e. excluding capital costs but including electricity costs. Traditionally, the primary solid fossil fuel used was coal. A wide range of other solid, liquid or gaseous fossil fuels are used, such as petroleum coke, lignite, natural gas and oil (heavy, medium or light fuel oil). In addition to these traditional types of fossil fuels, the cement industry has been using large quantities of waste fuels or biomass fuels, for more than 15 years.

The production of cement involves the consumption of large quantities of raw materials, energy, and heat. Cement production also results in the release of a significant amount of solid waste materials and gaseous emissions. The manufacturing process is very complex, involving a large number of materials (with varying material properties), pyroprocessing techniques (e.g., wet and dry kiln, preheating, recirculation), and fuel sources (e.g., coal, fuel oil, natural gas, tires, hazardous wastes, petroleum coke).

The cement manufacturing industry is under close scrutiny these days because of the large volumes of CO_2 emitted. Actually this industrial sector is thought to represent 5–7% of the total CO_2 anthropogenic

emissions [2]. Concern over the impact of anthropogenic carbon emissions on the global climate has increased in recent years due to growth in global warming awareness. In addition to the generation of CO_2 the cement manufacturing process produces millions of tons of the waste product cement kiln dust each year contributing to respiratory and pollution health risks [1]. The cement industry has made significant progress in reducing CO_2 emissions through improvements in process and efficiency, but further improvements are limited because CO_2 production is inherent to the basic process of calcinating limestone [3].

Life cycle assessment (LCA) is used to evaluate the impact of processes or products on the environment. The inclusion of every stage of the process or product's life cycle is fundamental to this analysis. In the case of products, every stage from the production of the raw materials to the end of their useful lives and their use and maintenance should be included. Thus, all significant environment impacts in their life cycle can be addressed [5]. For cement, a cradle to grave assessment is especially difficult because cement has so many end uses, and each use has a unique, often complex life-cycle [6]. Therefore inventory analyses and complete LCAs can be quite complicated [1].

This paper presents the review of the main environmental impacts related to the cement production based on the Reference Document on Best Available Techniques in the Cement, Lime and Magnesium Oxide Manufacturing industries [4].

Cement characterization. Cement can be defined as a finely ground, non-metallic, inorganic powder, and when mixed with water forms a paste that sets and hardens. This hydraulic hardening is primarily due to the formation of calcium silicate hydrates as a result of the reaction between mixing water and the constituents of the cement. In the case of aluminous cements, hydraulic hardening involves the formation of calcium aluminate hydrates. Traditional Portland cement is composed primarily of calcium silicate minerals (see Table 1).

Table1

Raw materials	Sources	(% mass)
Lime	Limestone, shells, chalk	60 - 67
Silica	Sand, fly ash	17 – 25
Alumina	Clay, shale, fly ash	2-8
Iron oxide	Iron ore	0 - 6

Raw material composition of clinker, the primary component of Portland cement [4]

The chemical composition of Portland cements of type CEM I produced in Slovak republic by the most important producers measured by XRF analysis using SPECTRO iQ II (Ametek, Germany) in our laboratories is in Table 2.

Table2

Chemical composition of cements CEM I in Slovak republic

Components	Producer L	Producer H	Producer T
(% mass)	CEM I 42,5N	CEM I 42,5R	CEM I 42,5N
Na ₂ O	0.11	0.11	0.11
MgO	1.60	2.10	3.82
Al ₂ O ₃	4.19	4.31	4.29
SiO ₂	18.59	19.84	19.31
P ₂ O ₅	0.58	0.09	0.09
SO ₃	3.31	2.96	3.26
Cl	0.04	0.05	0.02
K ₂ O	1.16	0.59	0.53
CaO	55.62	62.05	56.62
TiO ₂	0.21	0.26	0.21
MnO	0.03	0.17	0.38
Fe ₂ O ₃	2.66	3.01	3.30

The chemical composition of Slovak cements measured is similarly to the chemical composition of the ordinary Portland cementsTechnical data. The office building in the centre of Kosice city (see Fig. 1) as large as 4000 m2 has been step by step reconstructed since 1996. The heat consumption of the building in 1996 was about 3200 GJ per year.

Cement Manufacturing Process. The cement manufacturing process is diagramed in the flowchart in Figure 1. Processes required energy inputs and heat. Coal fly ash slag or pozzolans may be blended with the raw material. The addition of these optional materials will result in lower emissions [6]. A typical kiln size has come to be around 3000 tonnes clinker/day. The clinker burning process is the most important part of the process in terms of the key environmental issues for cement manufacture: energy use and emissions to air.

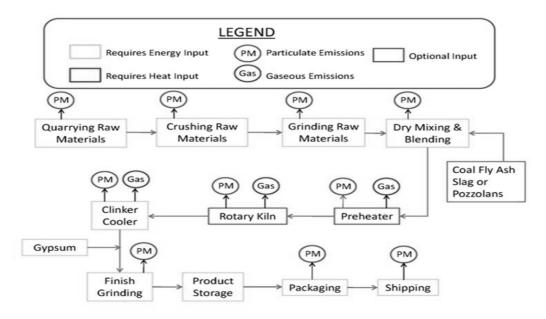


Figure 1. Process flow diagram for the manufacture of cement [6].

To produce 1 tone of clinker, the typical average consumption of raw materials in the EU is 1.52 tones. Most of the balance is lost from the process as carbon dioxide emissions to air in the calcination reaction (CaCO3 \rightarrow CaO + CO2) [1]. The amount of clinker needed to produce a given amount of cement can be reduced by the use of supplementary cementitious materials such as coal fly ash, slag, and natural pozzolans (e.g., rice husk ash and volcanic ashes). The addition of these materials into concrete not only reduces the amount of material landfilled (in case of industrials byproducts), but also reduces the amount of clinker required per ton of cement produced. Therefore cement substitutes may offer reduction in environmental impacts and material costs of construction [4].

The purpose of a mass balance is to evaluate the mass components entering and exiting the system taking into account the law of mass conservation. The evaluation of all mass balance items requires a previous knowledge of process data like raw materials and fuel compositions, gas streams, atmospheric data, etc. In a cement plant, with a system consisting of raw mill, preheater, kiln and cooler, the following input and output flows are important:

- input flows:
 - o raw materials (conventional and/or waste);
 - o energy (fuels (fossil and/or waste and/or biomass), electrical energy);
 - water (including fuel moisture, raw material moisture, air moisture and water injection in raw mill);
 - o air (primary air, transport air, cooling air and leak air);
 - o auxiliary agents (mineral additions, packaging material).
- output flows:
 - o clinker;

- o process losses/waste (filter dusts);
- o emissions to air (e.g. dust, NO_x, SO_x; see also mass balance);
- o emissions to water (in rare cases) [4].

Environmental impacts. The main environmental issues associated with cement production are consumption of raw materials and energy use as well as emissions to air. Waste water discharge is usually limited to surface run off and cooling water only and causes no substantial contribution to water pollution. The storage and handling of fuels is a potential source of contamination of soil and groundwater. Additionally, the environment can be affected by noise and odors.

The key polluting substances emitted to air are dust, carbon oxides nitrogen oxides (NOx) and sulphur dioxide (SO2). Carbon oxides, polychlorinated dibenzo-p-dioxins and dibenzofurans, total organic carbon, metals, hydrogen chloride and hydrogen fluoride are emitted as well. The type and quantity of air pollution depend on different parameters, e.g. inputs (the raw materials and fuels used) and the type of process applied.

Consumption of raw materials. Cement manufacture is a high volume process. Typical averages in Table 3 indicate consumptions of raw materials for the production of cement in the European Union. The figures in the final column are for a plant with a clinker production of 3000 tones/day or 1 million tones/year, corresponding to 1,23 million tones cement per year based on the average clinker content in European cement [4].

Table 3

Materials (dry basis)	Per tonne clinker	Per tonne cement	Per year per Mt clinker
Limestone, clay, shale, marl, other	1.57	1.27	1 568 000
Gypsum, anhydrite	-	0.05	61 000
Mineral additions	-	0.14	172 000

Consumption of raw materials in cement production in tones [4]

The use of wastes as raw materials in the clinker burning process can replace a relatively large amount of raw materials. The quantities of wastes used as raw materials in clinker production have more than doubled since 2001. In 2004, waste raw materials used in clinker production allowed the cement industry to make a direct saving of almost 14 million tonnes of conventional raw materials, which is equivalent to about 6,5 % of the natural raw materials needed. However, these waste raw materials have to show and meet characteristics, chemical element sand components which are necessary for the clinker burning process. These waste materials may have an impact on the emissions behaviour of the process and an effect on the emissions.

In Table 4 there are listed the consumption of wastes used as raw materials characterized by chemical elements used by the EU-27 in 2003 and 2004 for clinker production [4].

Consumption of energy. The cement production needs the very high amount of energy. Energy cost represents 40% of total production costs involved in producing of 1 tone of cement. Thermal energy demand (fuel) and electrical energy demand are the most important. Specific energy consumption depends on size and plant design, raw materials properties and its moisture, specific caloric values of fuel, throughput of kiln, type of clinker and many other factors.

Thermal energy demand is in range of 3000 - 6500 MJ per 1 tone of clinker, the electricity demand range from 90 to 150 kWh per 1 tone of cement [4].

Consumption of water. Water is used at a number of stages during the production process. In only some cases, water is used for the preparation of raw material, in clinker burning and cooling processes, such as the cooling of gases, as well as in the technological process for slurry production. In the semi-dry process, water is used for pelletising the dry raw meal. Plants using the wet process use more water (per tonne of cement produced) in preparing the kiln feed slurry and a typical water consumption of 100 - 600

litres water per tonne clinker is reported. Furthermore, for special applications, water is used for clinker cooling and a water usage of around 5 m3/hour has been reported. In most cases, the water consumed is not potable water [4].

Table 4

Wastes used as raw materials				
Desired (primary) chemical elements	Examples of waste streams Quantities 200 (million tonne)		-	
Si	Spent foundry sand	1.52	1.5	
Ca	Industrial lime Lime slurries Carbide sludge Sludge from drinking water treatment	2.2	2.44	
Fe	Pyrite cinder Synthetic hematite Red mud	3.29	3.37	
Al		0.71	0.69	
Si-Al-Ca-Fe	Fly ash Slags Crusher fines	3.37	3.78	
Soil		0.45	0.5	
Others		1.56	1.71	
Total		13.1	13.89	

Wastes used as raw materials characterized by chemical elements used in cement manufacturing in the EU-27 in 2003 and 2004 [4]

Emissions to air. Emissions to air and noise emissions arise during the manufacture of cement. Furthermore with regard to the use of waste, odors can arise, e.g. from the storage and handling of waste. In this section, ranges of air pollutant emissions are presented for the process of cement production, including other process steps, such as the storage and handling of, e.g. raw materials, additives and fuels including waste fuels.

The IPPC Directive [7] includes a general indicative list of the main air-polluting substances to be taken into account, if they are relevant for fixing emission limit values. Relevant to cement manufacture including the use of waste are:

- oxides of nitrogen (NOx) and other nitrogen compounds,
- sulphur dioxide (SO2) and other sulphur compounds dust,
- total organic compounds (TOC) including volatile organic compounds (VOC),
- polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs and PCDFs),
- metals and their compounds,
- hydrogen fluoride (HF),
- hydrogen chloride (HCl),
- carbon monoxide (CO).

Not mentioned on the list, but considered to be relevant for cement production is carbon dioxide (CO2). Furthermore, emissions of NH3 may be considered to be relevant, especially when using secondary measures/techniques for NOx reduction. The main emissions from the production of cement are emissions to air from the kiln system. The main constituents of the exit gases from a cement kiln are nitrogen from the combustion air; CO2 from calcination of CaCO3 and combustion of fuel; water vapour from the combustion process and from the raw materials; and excess oxygen. Emission data from kilns in operation is given in Table 5.

Reported emissions from European cement kilns ¹⁾				
Pollutant	mg/Nm ³	kg/tone clinker	tones/year	
No _x (as NO ₂)	145 - 2040	0.33 - 4.67	334 - 4670	
SO ₂	up to 4837 ²⁾	up to 11.12	up to 11125	
Dust	0.27 - 2273)	0.00062 - 0,5221	0.62 - 522	
СО	200 - 2000 ⁴⁾	0.46 - 4,6	460 - 11500	
CO ₂		approx. 672 g/t _{cement}	1.5456 million	
TOC/VOC	1 - 60 ⁵⁾	0.0023 - 0.138	2,17 - 267	
HF	0.009 - 1,0	0.021 - 2.3 g/t	0,21 - 23.0	
HCL	0.02 - 20.0	0.046 - 46 g/t	0.046 - 46	
PCDD/F	0.000012 - 0,27 ng I - TEQ/Nm ³	0.0276 - 627 ng/t	0.0000276 - 0.627 g/year	
Reported emissions from European cement kilns ¹)				
Metals ⁷⁾	mg/Nm ³	kg/tone clinker	tones/year	
	·			
Hg	0 - 0.03 ⁶⁾	0 - 69 mg/t	0 - 1311 kg/year	
\sum (Cd, Tl)	0 - 0.68	0 - 1564 mg/t	0 - 1564 kg/year	
$\sum_{i=1}^{n} (As, Sb, Pb, Cr, Co, Cu, Mn, Ni, V)$	0 - 4.0	0 - 9200 mg/t	0 - 9200 kg/year	

Data of emissions ranges from European cement kilns [4]

¹⁾ Mass figures are based on 2300 m³/tone clinker and one million tones clinker per year. Emissions ranges are yearly averages and are indicative values based on various measurement techniques. The reference O_2 content is normally 10 %

- ²⁾ Values from SO₂ measurements in the clean gas of 253 rotary kilns. 11 measurements are above the scale. Of these, 7 are of '0' substitution rate, 3 are '0 – 10', and one is 'above 40'. High SO₂ emissions are to be expected when the raw materials contain volatile sulphur compounds (e.g. pyrite). Indeed, these oxidisable compounds may be converted to SO₂ as early as in the upper cyclone stages. This SO₂ can be captured in the raw mill by the finely ground raw material
- ³⁾ The figures are values from continuous dust measurements in the clean gas of 253 rotary kilns. 8 measurements are above the scale. The emission levels largely depend on the state of the abatement equipment
- $^{4)}$ In some cases, CO emissions can be higher than 2000 mg/Nm³ and up to 5000 mg/Nm³ (11.5 kg/tone clinker), e.g. due to NO_x reduction
- ⁵⁾ Yearly average values from 120 measurements; only a few values range above 60 mg/Nm³ (up to 122.6 mg/Nm³ or 0.28 kg/tone clinker)
- ⁶⁾ Collected from 306 spot measurements with an average value of 0.02 mg/Nm³ and an upper value of 0.57 mg/Nm³ (1311 mg/tone clinker)
- ⁷⁾ '0' implies LOD=level of detection

The emission ranges within which kilns operate depend largely on the nature of the raw materials; the fuels; the age and design of the plant; and also on the requirements laid down by the permitting authority. There are also channeled emissions of dust from other sources, such as grinding (milling) and handling operations, raw materials, solid fuel and product. There is a potential for the diffuse emissions of dust from any outside storage of raw materials and solid fuels as well as from any materials transport systems, including cement product loading. The magnitude of these emissions can be significant if these

aspects are not well engineered or maintained and being released at a low level can lead to local nuisance problems [4].

Emissions to water. In general, cement production does not generate effluent. In cement production by using the dry or the semi-dry process, water is only used in small quantities, e.g. for cleaning processes. In principle, no emissions to water occur because water is recycled back into the process [4].

Noise. Noise emissions occur throughout the whole cement manufacturing process from preparing and processing raw materials, from the clinker burning and cement production process, from material storage as well as from the dispatch and shipping of the final products. The heavy machinery and large fans used in various parts of the cement manufacturing process can give rise to noise and/or vibration emissions, particularly from:

- chutes and hoppers;
- any operations involving fracture, crushing, milling and screening of raw material, fuels, clinker and cement;
- exhaust fans;
- blowers;
- duct vibration.

Plants are required to comply with reduction standards in compliance with national legislation, and noise surveys are being conducted and evaluated. Natural noise barriers, such as office buildings, walls, trees or bushes are used in the cement industry to reduce noise emissions [4].

Conclusion. A current trend in the field of cement production is the focus on low-energy cements, utilization of waste in cement production and the associated reduction of CO2 emissions. Evaluation of cement impact to environment is a very important process. There are new ways of assessment in this field. Environmental assessment and eco-labeling of cements has been proceeded in Slovak republic for several years.

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