ИЗПОЛЗВАНЕ НА ЕКОЛОГОСЪОБРАЗНИ ЦИМЕНТИ И БЕТОНИ ЗА НАПРАВАТА НА УСТОЙЧИВИ КОНСТРУКЦИИ

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GREEN CEMENT AND CONCRETE FOR SUSTAINABLE STRUCTURES

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Abstract:
Due to the increasing global needs of the construction sector, building materials' consumption grows very fast and opens the door for new alternative materials. Meanwhile, industries generate millions of tons of residual by-products, which are mainly deposited. Concrete as the most widely used material worldwide could become greener as a result of the application of recycled aggregates on one hand and green cement on the other hand. This article discusses the possibilities for utilization of industrial residuals in green building materials. The focus is on cements with zero or low quantity of Portland cement. This transforms industrial residuals into secondary raw materials with a particular environmental effect - a sufficient decrease in CO2 emissions. Details of the cement manufacturing process are reported.

Keywords:
Green Cement, Alkali-Activated Binders, Industrial Residuals, Alternative Materials, Advanced Technology.

1. INTRODUCTION

Construction materials play an important role in building integrity. The proper structural design and the required physical and mechanical properties of the materials are responsible for the strength and durability of the structures. Sustainable structures can be constructed using green alternative materials with similar or better properties than traditional building materials, or by reusing traditional ones in a better way. Green materials are mostly based on recycled products or wastes, which could partially or entirely replace natural materials extracted from non-renewable resources. The utilization of waste materials in construction turns them into a secondary source for materials production. This strategy will reduce landfill deposition, protect the nature, reduce costs and lead to lower energy consumption compared to the production of traditional building materials and save energy for production of non-renewable ordinary building materials.

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A special tool called European Technical Approval (ETA) is used for alternative materials, which are not included in the harmonized European Standards for construction sites. ETA is a European certificate which supports the introduction of non-conventional building materials, by guaranteeing the performance and characteristics of the alternative materials even without CE marking. ETA is valid in all EEA countries. Industrial wastes can be utilized by ETA.
The construction of sustainable structures encompasses several areas of sustainability throughout the process of utilization of the structures. It starts from sustainable urban planning, design and construction, then sustainable exploitation and maintenance and finishes with sustainable recycling at the end of its life cycle [1]. During the time of structural design appropriate building materials in respect of the 3R concept (reduce, reuse and recycle) should be considered. Concretes and also cements as their component are the two most widely used materials in the world. The application of green cements and green concretes reduces the use of standard natural aggregates and ordinary binders. This article aims to give an overview of the novel aspects of structural materials' design in line with the concept of sustainability, which becomes more practical than theoretical. Different types of green cements composed mainly of by-products – solid, liquid and gases will be discussed, as well as green concretes developed on recycled aggregates, cured or surface treated with alternative materials for better performance.

2. CURRENT CEMENT AND CONCRETE PRODUCTION

Ordinary Portland Cement (OPC) is the dominant type of binder used for contemporary construction. According to the European Standard 197-1, cements are classified into 5 types in respect to their composition (table.1). Each type is divided into subtypes, which define the exact percentage of Supplementary Cementitious Material, which could be blended with OPC. OPC requires only 5% of additional material out of clay and limestone, which should adjust its mineral composition. In comparison, American Standard for Testing and Materials (ASTM C150/C150 M) gives a similar classification (Type I÷V) [2], but cements groups are divided according to mineral composition, heat of hydration and rate of gained strength.

Table. 1. Classification of cement types, according to EN 197-1 [3]

CEM I	Portland Cement (PC)	PC and up to 5% of minor additional constituents (the original OPC)
CEM II	Portland Composite Cement	PC with up to 35% of other SCM such as ground limestone, fly ash (FA), ground granulated blast furnace slag (GGBS)
CEM III	Blast Furnace Cement	PC with a high percentage of blast furnace slag (60-75%)
CEM IV	Pozzolanic Cement	PC with up to 55% of selected pozzolanic constituents
CEM V	Composite Cement	PC blended with GGBS, FA and pozzolanic material

Cement production has a severe negative impact on nature because of the extraction of natural raw materials and the massive release of CO_2 emissions. The environmental impact of clinker production is significant, the less clinker is produced, the more sustainable the cement is. CEM II is the most common type of cement produced with almost 57%, followed by OPC with 27% [4]. Unfortunately, the application of CEM V is rather limited compared to other types of cement. Indeed, CEM V can be considered the first sustainable cement due to the high volume of SCMs used. The main sources of emission in the OPC manufacturing process are two: the calcination process and the combustion fuel used to heat the raw materials. The amount of CO_2 released also depends on type of fuel. The less emissions released, the more sustainable the cement is.

The hydration process of cement minerals with water produces a stable, amorphous solid hydrate, which continues to grow and expand in the presence of water. The main function of cement in concrete is to bind together the aggregates (fine and coarse), but the coarse aggregate is the one which gives the strength of ordinary concrete.

Green concrete is a type of concrete that uses waste materialc, its production process does not lead to environmental destruction, or it has high performance and life cycle sustainability. Green concrete could partially or fully replace cement or fine or coarse aggregates with wastes from different origin. The production of green concretes follows the 3R concept. It has a positive impact on decreasing of the global warming and waste deposition thanks to the utilization of different types of wastes. The novel CO_2 concept for treatment of concrete could utilize sufficient quantities of waste gasses, mainly those generated by OPC production.

3. NOVEL ALTERNATIVE GREEN CEMENT TYPES

There are several approaches, which can be used for the reduction of carbon emissions and improving the energy efficiency of concrete production in general. Updating the manufacturing process by optimizing the technology leads to energy efficiency improvements up to a certain limit. Then there are several alternatives: replacing the fuels used; utilization of industrial by-products on a small or large scale and application of alternative liquids and gasses for activation.

3.1. Cements produced with alternative fuels

Coal and petroleum coke are the two traditional fuels used for burning cement clinker. Natural gas and fuel oil are also used, but to a lesser extent. Approximately 40% of the total CO_2 emissions of a cement plant are generated from the burning [5]. Nowadays, alternative fuels like biomass are used quite often in developed countries These can be agricultural and animal waste; wood, textiles and plastics from demolition activities; rubber tires; industrial and municipal sewage sludge; solid waste; solvent and oil, etc. The effect of each type of alternative fuel in the cement kiln is different, but in general most of them lead to the production of less CO_2 emissions compared to coal and contribute to the clinker production. However, if the correct blend of fuels is used, the quality of the clinker will not be affected and no hazardous materials will be formed during production. On the other hand, alternative fuels can change the characteristics of the clinker like the porosity of the granules, the burning grade, the crystal size of the clinker phases or the reactivity and the performance characteristics of the cement. During the last decades the application of alternative fuels has moved from the laboratories to practice [6]. The European countries substitute up to 70% of ordinary fuels with alternatives [5]. The substitution rates are limited by legal and political barriers, regulated by national environmental regulations.

3.2. Cements with high quantity of Secondary Cementitious Materials

The utilization of industrial wastes in blended cement is a very good example of recycling residuals, which has been successfully implemented for several decades and included in building standards. Due to this transformation, industrial residuals are now considered ‘Supplementary Cementitious Materials’ (SCMs), which are divided into two groups: cementitious and pozzolanic materials. The first ones have binding properties by themselves and the second ones exhibit cementitious properties combined with calcium hydroxide (lime). Standardized SCMs in blended cements with industrial origin are: limestone, ashes, slags and fumes. There are also other SCMs with natural origin like pozzolans (natural and natural calcined) and burnt shale. Each SCM affects different properties of the cement and lead to improvement of some of the characteristic of the blended cement such as strength (early or later) setting time (initial or final), workability, durability, etc.

But there are many other industrial residuals, which are still waiting to be developed and included in standards (fig.1). Changing the status of wastes to SCMs can open the door for a wide range of new applications of these materials.

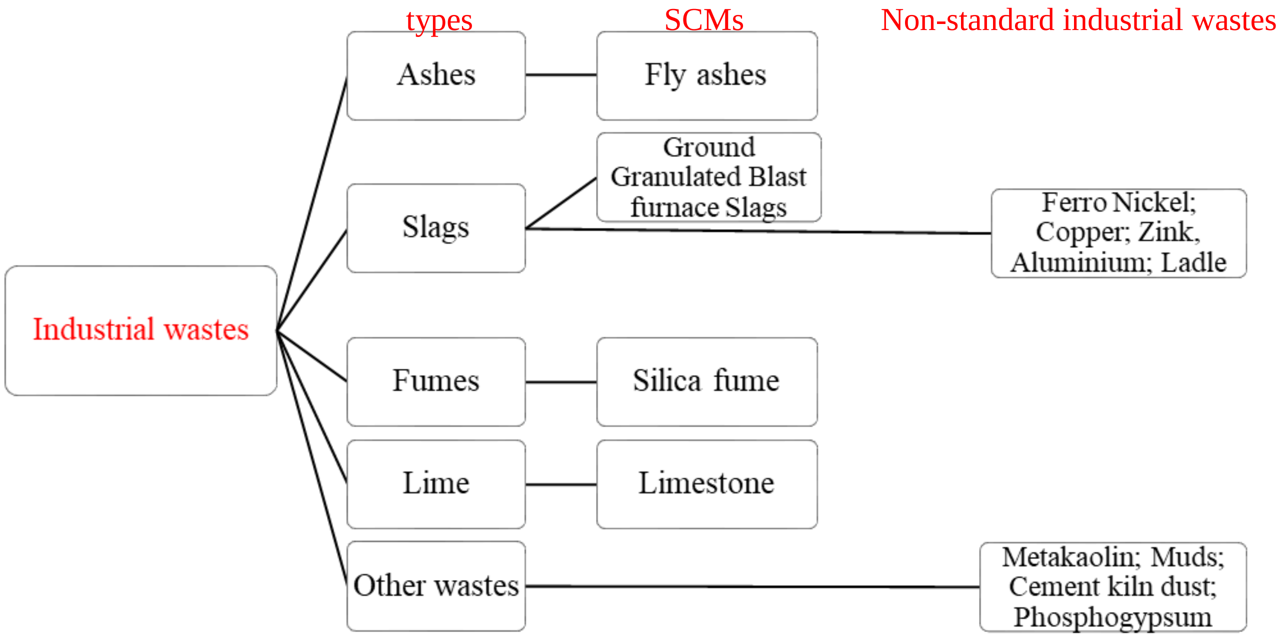

Figure. 1. Industrial wastes, partially classified as Secondary Cementitious Materials and non-classified wastes

Natural SCMs, which have also been researched for the last few decades, can be divided into two groups according to the origin: vegetal and animal. For example, SCMs of vegetal origin are: rice, hemp, bamboo, wood cellulose, flax, banana, sunn, jute, etc. and of animal origin: hair of different animals such as horse, sheep, goat, alpaca, etc. They can also be used as fibers in concrete.

3.3. Alkali-activated cements

Alkali-activated cements (AACs) contain up to 95% industrial wastes (in the solid part) and the rest is the activator - usually NaOH, Na_2SiO_3, KOH, K_2SiO_3, RbOH or C_3OH and some water. The utilization of such high percentage of waste leads to decrease in the comparably high percentage of emitted CO_2, which is released during the clinker production. As a result of the chemical reaction of the waste with the activator a binder is formed, which has better durability and longer lifetime and its mechanical properties correspond to those of OPC. The difference in the new hydration products in AACs is that they contain mostly calcium-aluminate-silicate-hydrates (CASH), unlike ordinary calcium-aluminate-hydrates (CSH) in OPC.

The durability of OPC, which is mostly responsible for the lifetime of the concrete, depends on its chemical composition, reaction with water during the time of hydration and later on different environmental effects on new hydration products and soluble products ($Ca(OH)_2$). Decreasing the level of OPC usually leads to an improvement in cement durability [4] when reactive wastes such as slags or pozzolans are added. AACs can contain cement up to 5% to intensify the reaction and form additional secondary chemical formations.

AACs are a real competitor to OPC from mechanical and durability standpoint, but from an economic perspective, the price of the activators is still high. However, the price is not what hampers the commercialization of these new binders, but legislation. The standards for cement and concrete require a narrow range of variation of the quantity of clinker. Meanwhile BSI wrote the “Principles of the equivalent durability procedure (EDP)” [7], which is based on the traditional method of ensuring durable concrete, without traditional methods for concrete mix design using the so called “candidate concrete”, and gives a chance to all kinds of alternative materials to prove their characteristics in practice.

3.4. CO_2 cements

Calcium silicate-based cements (CSC) are a new type of cements, produced by Solida Technologies®, which use the waste CO_2, generated by ordinary cement production, for the carbonation of CSC. CSC is a non-hydraulic calcium silicate cement with reduced lime content, which efficiently stores CO_2 during concrete curing [8]. Using CO_2 curing, the lime content in CSC clinker is reduced by about 45%, which is 30% less than the content in OPC. This reflects to 200°C lower temperature for burning OPC and a 30% reduction of the fuel and CO_2 emissions. Moreover, the low-lime chemistry of CSC allows the reaction between lime and silica to occur at the clinker temperature of 1250°C. This also reflects in a reduction of CO_2 emissions – a comparable table is given in table 2.

Table 2. CO_2 emission during production of OPC and CSC [8]

CO_2 emission from:	Per ton of OPC clinker	Per ton of CSC clinker
Limestone decomposition	540kg	375kg
Fossil fuel combustion	270kg	190kg
Total CO_2 emissions	810kg	565kg

The first industrial CSC clinker was produced in North America by LafargeHolcim. The effect of this technology was proven and even some savings in the specific heat consumption were achieved due to the different behavior of CSC in the kiln compared to OPC clinker.

The manufacturing of concrete based on CSC does not require a special mixing and forming process. But the chemical process of setting and hardening differs. The low-lime, calcium silicate and C_3S_2 components of CSC do not hydrate when water is added during concrete mixing and forming. In the presence of water CSC based concrete reacts with CO_2 as in the following equation:

$$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2$$

This reaction requires CO_2 gas pressure and a moderate temperature of about 60°C. These parameters turn CSC concrete into precast concrete. The hydration of CSC concrete occurs very fast and it is limited only by the ability of CO_2 to diffuse throughout that stage of the process. Thin elements of up to 1 cm are cured for 6 hours and 25 cm elements for 24 hours, which makes this technology very highly productive for precast elements.

3.5. Mg-oxide based cements

Water-activated-magnesium-oxide based cement is a very old type of cement, similar to those used by the Chinese to build the Great Wall [5]. This type of cement requires about 30% less energy for its production and it has some advantages compared to OPC. There are several companies, which have patented various types of cement based on magnesia and caustic magnesia – Tec-Cements, Eco-Cements, Enviro-Cements, Ceramicrete, Novacem etc. The reactive magnesia hydrates to brucite, $Mg(OH)_2$, and when it is exposed to CO_2 it reacts and forms magnesite [5]. One of the novel researches in magnesium-based cements proved that they can absorb more CO_2 than is released during their production [9], which gave the name of the new type of cement ‘carbon-negative cement’. One of the patented technologies for production of Mg-oxide based cements includes a standard autoclaving process (180°C and 150bar pressure), followed by air heating (700°) for production of MgO and then blending with hydrated magnesium carbonates. One of the benefits of this process is the recycling of CO_2 produced during the manufacturing process (of 1,0t released CO_2, 1,1t CO_2 are recycled).

4. DEVELOPMENTS IN GREEN CONCRETE PRODUCTION

Green concrete technology becomes more and more popular thanks to scientific research due to its significant contribution to the sustainable development in construction. Application of different techniques, mostly related to waste valorization in all states, are noted below.

4.1. Application of different types of recycled materials

Recycled concrete aggregates (RCAs) made from construction and demolition wastes (C&D) are one of the most popular recycling materials used in building construction. However, every year in Europe more than 850 mil tons of C&D are generated [10]. Their application is still limited due to the worse performance of RCAs in respect to the mechanical and physical properties compared to ordinary aggregates. RCAs have high content of impurities, lower density and higher water absorption, but if they are adequately separated and combined with proper quantity of natural aggregates they could be used for many purposes.

According to the standard EN 12620 [11] there are 7 categories based on the constituents of recycled aggregates:

- Rc – concrete, concrete products, mortar, concrete masonry units;
- Ru – unbound aggregates, natural stone, hydraulically bound aggregates;
- Rb – clay masonry units (bricks and tiles), calcium silicate masonry units, aerated non-floating concrete;
- Ra – bituminous materials;
- Rg –glass;
- FL - floating material in volume;
- X – gypsum plaster, cohesive material (clay and soil);

The exact proportions of these materials applied in RCAs are determined in standard EN 933-11 [12] and should also fulfil the requirements of the category specified in EN 12620 and the recommendations of EN 206 [13] for concrete with recycled aggregates.

4.2. Novel concrete composition

There are several directions of development in novel concrete mix design:

- Application of higher percentages of SCM than specified in the standards;
- Minimal utilization of ordinary PC, together with intensification of hydration;
- Optimization of the mix design for making more self-compacting and self-flowing mixtures.
- Application of alternative fillers for optimization of the particle size distribution.

4.3. Curing of concrete using CO_2 technology

CO_2 capture, storage and activation makes this novel technology for curing concrete environmentally friendly. This gives a wide range of applications of CO_2 based on the chemical reaction between CO_2 and the cement particles in the presence of water or water vapor. This technology can replace steam curing with rapid curing and produce concretes with good mechanical properties, volume stability and low energy consumption [14].

4.3.1. Curing of elements

CO_2 curing gives almost the same strength of concrete elements as stream curing does for the same mix design. This technology is appropriate for ordinary concrete with unsaturated capillary pores. The concrete mix should be wet enough and with sufficient workability before CO_2 is applied [15]. Pre-conditioning of concrete elements is very important, as the higher the CO_2 curing degree is, the drier the pre-conditioning environment should be. Compared to stream curing, CO_2 curing gives better dimensional stability of the main hydration products.

4.3.2. Surface treatment

Surface treatment is one of the methods that effectively improves concrete durability and is mostly used for marine structures and bridge decks [16]. When CO_2 reacts with dry cement it forms calcium carbonate which compacts the microstructure by reducing the porosity and changing the pore size distribution. The improved microstructure gives higher strength, lower absorption and aggressive agent migration.

4.3.3. Enhancement of recycled concrete aggregates

Recycled concrete aggregates (RCAs), generated from construction and demolition wastes, need to be improved before being applied in concrete, due to the reduction of their mechanical properties compacted to ordinary aggregates. The application of CO_2 makes RCAs alternative materials with better performance thanks to their reaction with calcium hydroxide and CSH which increases the volume of new formations and reduces the porosity.

5. FINAL REMARKS

In the foreseeable future concrete will keep its key role in construction. In order to fulfil the perpetual changes of the environmental norms, cement and concrete should ensure sustainability. The construction industry is facing three key challenges – the need to reduce CO_2 emissions, to improve energy efficiency and to recycle higher percent of wastes in general.

Nowadays, the focus is on sustainability of cements by proper selection of constituents from waste materials. Constant chemical composition and physical properties of wastes will help their standardization, which are still deposited to a great extent. European legislation must approve the use of new binders for structural purposes as others have already done.

The requirements for concrete are mostly related to standard cement production. Once concrete mix design is released from these restrictions, alternative materials can be included efficiently. New standards should be developed which focus mainly on the final properties of concrete.

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