New Cements for Sustainable Development

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1 Introduction

Concrete, usually made with Portland cement is the most widely used material on Earth. It represents about 1.7 x 10^9 ton/year [1]. However, to produce 1 ton of concrete induces carbon dioxide emission of about 0.08 ton. In France, 2.6% of carbon dioxide is due to cement industry. At an international level, cement industry represents 5% of carbon dioxide emissions [1]. Research has been undertaken in order to reduce energy consumption and carbon dioxide emissions. Cement industry wants to be shown as an industry involved in sustainable development. After a presentation of the cement manufactory process versus energy consumption and carbon dioxide emissions, we present a general view of different solutions set up. The one we have chosen will then be detailed.

2 Portland cement manufactory process

2.1 Generalities

Portland clinker is made from a mix of 80% lime (from calcareous rocks) and 20% silica (from clay). This mix is put into a kiln at 1450°C, temperature which makes possible the clinkering (chemical transformation) of the Portland cement. From an environmental point of view this manufactoring process is not optimal. As a matter of fact, two factors need to be examined: energy consumption during the production and emission of carbon dioxide. The clinkering, or chemical transformation, induces carbon dioxide emissions only because limestone is part of the raw materials and so it decarbonates. A part of carbon dioxide emissions is also due to raw materials. In addition, the high temperature (1450°C) at which the manufacturing process takes place induces consumption of energy through fuels and so more carbon dioxide emissions. Another part of carbon dioxide emissions is also due to fuel consumption. These two ways of carbon dioxide production are linked.

We know that, nowadays, production of 1 ton of Portland clinker emits 815 kg of carbon dioxide and consumes, in North America, around 4.2GJ [1]. Energy consumption linked to the manufacturing process of clinkering varies a lot, because of the type of energy used (electric, hydraulic, …) and of the quality of kilns. In 1994, carbon dioxide emissions due to Portland cement manufacturing process come from raw materials (about 52%) and from fuels (about 48%) [1].

2.2 Carbon dioxide emissions due to energy consumption

In 1973, average kiln fuel consumption in United States was about 7GJ/t [1]. The oil crisis and then the sustainable development preoccupation have been an impulsion for the reduction of energy consumption. Two ways have been explored: amelioration of the manufacturing process and replacement of fossil fuel by substitution ones.

In order to improve the process itself, precalciners and new kilns have been developed and installed. Catalysts can also be used in order to decrease the clinkering temperature.

Use of industrial waste such as tires, animal flours or chemical industry wastes is nowadays usual. The use of nuclear energy or solar energy increases also. Experiments have also been made on microwave substituting a part of heating in a kiln [2]. With all these improvements we have won around 3GJ/t in thirty years.

2.3 Carbon dioxide emissions due to raw materials

Carbon dioxide emissions from raw materials are due to the "potential CO_2" contained within them through the limestone. Portland cement is composed of alite ($(CaO)_3SiO_2$ or C_3S), belite ($(CaO)_2SiO_2$ or C_2S), tetracalcium aluminoferrite ($(CaO)_4Al_2O_3Fe_2O_3$ or C_4AF) and tricalcium aluminate ($(CaO)_3Al_2O_3$ or C_3A). Alite and belite are the main components.

The reaction of fabrication of alite ($(CaO)_3SiO_2$ or C_3S) is the following one; it takes place at 1450°C.

$3CaCO_3 + SiO_2 \rightarrow Ca_2SiO_5+3CO_2$

For every ton of alite produced, 579 kg of carbon dioxide is emitted.

The reaction of fabrication of belite ($(CaO)_2SiO_2$ or C_2S) is the following one; it takes place at 1250°C.

$2CaCO_3 + SiO_2 \rightarrow Ca_2SiO_4+2CO_2$

For every ton of belite produced, 511 kg of carbon dioxide is emitted.

The reaction of fabrication of C_3A ($(CaO)_3Al_2O_3$) is the following one:

$3CaCO_3 + Al_2O_3 \rightarrow (CaO)_3Al_2O_3 +3CO_2$

For every ton of C_3A produced, 489 kg of carbon dioxide is emitted.

The reaction of fabrication of C_4AF ($(CaO)_4Al_2O_3Fe_2O_3$) is the following one:

$4CaCO_3 + Fe_2O_3 + Al_2O_3 \rightarrow (CaO)_4Al_2O_3Fe_2O_3 +4CO_2$

For every ton of C_4AF produced, 362 kg of carbon dioxide is emitted.

While considering a Portland clinker composed of 20% of C_2S, 60% of C_3S, 10% of C_3A and 10% of C_4AF, we obtain that producing 1 ton of clinker emits 535 kg of carbon dioxide.

In order to reduce carbon dioxide due to raw materials, different ways have been explored. Some researchers are working on sulfoaluminate belite cement [3]. Indeed, belite is produced at a lower temperature than a lite and the reaction of belite fabrication emits less carbon dioxide than the alite one. Interesting work is done using industrial waste such as phosphogypsum and low calcium fly ash [4] as raw materials for the fabrication of sulfoaluminate belite cement. Concrete made with pozzolans-based cements, such as silica fume, which is a waste of industry or metakaolin - [5], [6] - are also developed. Some cement used for particular applications can show an interest from an environmental point of view. It's the case, for example, of blast furnace slag cement which was used in foundations due to its resistance to sulphatic reactions [7]. A lot of work is also done on recycling industrial wastes. We can cite for example the work of Cyr and al [8].

In a concern of sustainable development, we are working on a sulfoaluminate clinker [9] which we are going to present in the following. This clinker is an experimental one, for the moment it is not marketed in Europe. According to Gartner [1] it is one of the most promising low-CO_2 alternatives to Portland cement.

3 Sulfoaluminate clinker

3.1 Generalities

Sulfoaluminate clinker is made from a mix of limestone, bauxite and sulphate calcium. The clinkering of that mix takes place at a lower temperature than Portland clinker, around 1250°C – 1300°C. Its composition is: 60-70% of yeelimite or kleinite ($(CaO)_4(Al_2O_3)_3SO_3$ or $C_4A_3\overline{S}$), 10-20% of belite (C_2S), 0-14% of tetracalcium aluminoferrite (C_4AF), 0-7% of calcium aluminate ($(CaO)_{12}(Al_2O_3)_7Fe_2O_3$ or $C_{12}A_7$), [9].

3.2 Clinkering reactions

The clinkering reactions of the various components of sulfoaluminate clinker are given in the following, [10].

Yeelimite: $3CaCO_3+3Al_2O_3+CaSO_4 \rightarrow (CaO)_4(Al_2O_3)_3SO_3+3CO_2$ reaction (a)

Fabrication of 1 ton of $C_4A_3\overline{S}$ ($(CaO)_4(Al_2O_3)_3SO_3$), using process (a), produces 216 kg of carbon dioxide.

Belite: $2CaCO_3 + SiO_2 \rightarrow Ca_2SiO_4+2CO_2$

Fabrication of 1 ton of C_2S produces 511 kg of carbon dioxide.

Tetracalcium aluminoferrite:

$4CaCO_3+Fe_2O_3+Al_2O_3 \rightarrow (CaO)_4Al_2O_3Fe_2O_3 +4CO_2$

Fabrication of 1 ton of C_4AF produces 362 kg of carbon dioxide.

Calcium aluminate: $12CaCO_3 + 7Al_2O_3 \rightarrow (CaO)_{12}(Al_2O_3)_7 +12CO_2$

Fabrication of 1 ton of $C_{12}A_7$ ($(CaO)_{12}(Al_2O_3)_7Fe_2O_3$) produces 381 kg of carbon dioxide.

Yeelimite: $3(CaO)_{12}(Al_2O_3)_7+7CaOSO_3 \rightarrow 7(CaO)_4(Al_2O_3)_3SO_3+15CaO$ reaction (b)

Fabrication of 1 ton of $C_4A_3\overline{S}$, using process (b), produces 371 kg of carbon dioxide.

As it is shown, two ways of producing yeelimite coexist and it is a combination of these two processes which conduct to yeelimite formation. In the following, we will consider that the combination of reactions (a) and (b) is with equal share.

3.3 Environmental assessment

Following the mineralogical analysis given in [9], the clinker we used consisted of the following majority hydraulic phases:

- $C_4A_3\overline{S}$: 53 %
- C_2S : 18 %
- $C\overline{S}$: 12 %
- C_4AF : 15%
- residual: around 2%

The calcium sulphate ($CaOSO_3$, $C\overline{S}$) is obtained from gypsum by the following reaction:

$CaOSO_3(H_2O)_2 \rightarrow CaOSO_3 + 2\,H_2O$

This reaction takes place between 105°C and 300°C and emits no carbon dioxide.

Considering the previous percentage of the different components of the sulfoaluminate clinker on which we work and being given that yeelimite is obtained by a combination of reactions (a) and (b), we obtain 305 kg of carbon dioxide emitted for 1 ton of clinker produced.
So from the point of view of carbon dioxide emitted, sulfoaluminate clinker is interesting.
Clinkering temperature of sulfoaluminate clinker is lower than Portland clinker's one, it induces a clinkering cost less important.

Sulfoaluminate clinker is also more friable than Portland clinker, so it induces a less important energetic cost due to crushing.

The following table is given as a summary in order to compare sulfoaluminate clinker and Portland clinker:

	Portland clinker	**Sulfoaluminate clinker**
CO_2 emitted per ton of clinker	535 kg/t	305 kg/t
Specific heat consumption during clinkering [11]	3.845 GJ/t	3.305 GJ/t *
Energetic cost of crushing [12]	45 to 50 kWh	20 to 30 kWh

* This data has not been given exactly for our type of sulfoaluminate clinker. The clinker used by [11] contained less $C_4A_3\overline{S}$ and more C_2S. So we can suppose that the specific heat consumption during clinkering associated to our clinker is less important. But because we don't have the specific heat consumption of the clinker we used, we are going to support our example on the data given by [11].

4 Application example

In order to improve this clinker, we have made an experimental program, in which tests are performed on concrete cylinder specimens. The cement used for this concrete is a mix of the sulfoaluminate clinker presented previously and gypsum. Gypsum is essential. Indeed, hydration of yeelimite occurs while gypsum is present. The detailed reactions of hydration of the mix used are presented in [9]. The gypsum used is blue sulykal DH which chemical composition is:

Chemical composition	%
P_2O_5	0.06%
SO_3	46.87%
CaO	32.25%
K_2O	0.01%
Na_2O	0.15%
Fe_2O_3	0.01%
Al_2O_3	0.02%
SiO_2	0.36%
F	0.01%

The siliceous aggregates Palvadeau are used to avoid undesired reactions. Three types of sand (0/0.315mm, 0.315/1mm, 1/4mm) and two types of gravel (4/8mm, 8/12mm) are used.
The detailed experimental program and results are given in [9]. In this paragraph, we just want to compare two concretes made with a binder composed of sulfoaluminate clinker and gypsum on the one hand, and a Portland cement on the other hand, from an environmental point of view. For the two concretes composed of sulfoaluminate clinker and gypsum, we will vary quantity of gypsum added in the binder.
The granular skeleton for the three concretes will be the same (values of $1m^3$):

- Aggregate 0/0.315: 80 kg/m^3
- Aggregate 0.315/1: 130 kg/m^3
- Aggregate 1/4: 330 kg/m^3
- Aggregate 4/8: 300 kg/m^3
- Aggregate 8/12: 805 kg/m^3

The three concretes have the same binder mass: 400 kg/m^3.

The composition of the first concrete, which we call C1, made with sulfoaluminate clinker and gypsum is:

- CSA mass: 310 kg/m^3
- Gypsum mass: 89 kg/m^3
- Water mass: 246 kg/m^3

The water to binder ratio is 0.6. The percentage of gypsum added to the mass of the binder is 22%.

The composition of the second concrete, which we call C2, made with sulfoaluminate clinker and gypsum is:

- CSA mass: 254 kg/m^3
- Gypsum mass: 146 kg/m^3
- Water mass: 246 kg/m^3

The water to binder ratio is also 0.6. The percentage of gypsum added to the mass of the binder is 36%.

Durability of these concretes is studied in detail in [9] through expansion tests and water porosimetry tests in particular.
Taking into account carbon dioxide emitted through raw materials, fabrication of 1 m^3 of concrete C1 leads to 94.6 kg of carbon dioixide emitted while concrete C2 leads to 77.5 kg of carbon dioxide emitted. The more important quantity of carbon dioxide emitted by concrete C1 is due to the less quantity of gypsum added, since fabrication of gypsum does not emit carbon dioxide.

Let's compare these concretes with a concrete made with a Portland clinker. The composition of such a concrete is the following, also considering the same granular skeleton:

- Portland cement mass: 400 kg/m^3
- Water mass: 200 kg/m^3

The water to binder ratio is 0.5.

Taking into account carbon dioxide emitted through raw materials, fabrication of 1 m^3 of this concrete leads to 214 kg of carbon dioxide emitted.

Let's compare the resistances obtained for each concrete at various times of maturation (1day, 3, 7 28 days).

Concrete	Rc 1 day	Rc 3 days	Rc 7 days	Rc 28 days
C1	19 MPa	26 MPa	40 MPa	40 MPa
C2	19 MPa	29 MPa	35 MPa	44 MPa
"standard"	9 MPa	23 MPa	31 MPa	

Tests are actually in progress but we can suppose that the resistance obtained at 28 days will be at least 40 MPa for the Portland concrete.
From the point of view of resistance, we can consider that resistances of three concretes obtained at 28 days are equivalent (about 40MPa). It is however interesting to note that different applications can be considered between concrete C1 and C2. Indeed the resistance obtained at 7 days for concrete C1 is the same as its resistance obtained at 28 days. It will be an interesting concrete when early age resistances are required.

The following table, based on the values of the previous table, is given as a summary in order to compare sulfoaluminate concrete and Portland concrete, or "standard" concrete:

	Portland concrete	**Sulfoaluminate concrete C1**	**Sulfoaluminate concrete C2**

CO_2 emitted for clinker producing	214 kg/m^3	94.6 kg/m^3	77.5 kg/m^3
Specific heat consumption during clinkering	1.54 GJ/ m^3	1.02 GJ/ m^3	0.84 GJ/ m^3

From an environmental point of view, sulfoaluminate concrete proves its interest. Its durability has to be explored, but in terms of resistance it shows comparable results with "standard" concrete, with higher early age strenghts.
Concerning the energetic cost of crushing, we are not able for the moment to evaluate it in bond with the quantity of cement needed in the formulation of concrete. The companies concerned did not give us this cost. We have to consider the energetic cost of crushing of each clinker and also the crushing cost of the gypsum used in the sulfoaluminate concrete.

5 Conclusion and perspectives

As it has been shown previously, the properties of a concrete made with this particular clinker added with gypsum are interesting from a point of view of carbon dioxide emissions and energy consumption, but also from a point of view of durability and resistance. These aspects are more detailed in [9].
In order to be able to build a tool able to evaluate environmental effect of various types of concrete, we have now to take into account the availability of the raw materials used in the fabrication of sulfoaluminate clinker and the one used as aggregates.

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