



# Synthesis of belite cements at low temperature from silica fume and natural commercial zeolite

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## ABSTRACT

The paper herein proposes a new simple method for the synthesis of two reactive belite cements at low temperature (1000 °C). Silica fume, as subproduct of metallurgical industry and commercial natural zeolite were utilized as raw materials. The implemented raw materials were utilized with no additional purification process. Belite cements properties were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and gas sorption by BET (Brunauer, Emmett, and Teller) techniques. Hydration capacity of belite cements was calculated while the mechanical strength was determined in ordinary Portland cement pastes (PC) and gypsum pastes, respectively, using in each case a 10% partial replacement of the belite cements obtained. Results showed belite cements presented relatively high surface areas, at early ages mechanical strengths similar to those of alite cement and comparable to strengths of belite cements obtained by different synthesis methods. Cements obtained in this work showed good hydraulic reactivity properties.

## 1. Introduction

Calcination is the conventional method for the obtainment of Portland cement clinker. This method consists of grinding and mixing of raw materials (limestone, clay, etc.) in an adequate dosage. Resulting mix has a clinkerization temperature of 1450 °C so that the formation of the main component occur: alite ( $\text{Ca}_3\text{SiO}_5$ , C3S). Considering that the energy required to produce C3S is  $1810 \text{ kJ kg}^{-1}$ , calcination method for the obtainment of clinker represents two major disadvantages: long thermal treatment and elevated temperatures of synthesis, both of which cause high emissions of carbon dioxide ( $\text{CO}_2$ ) to the atmosphere. Belite Portland clinker is characterized by having a low content of calcium oxide (CaO), causing the presence of alite to diminish and favoring the formation of belite ( $\beta\text{-Ca}_2\text{SiO}_4$ , C2S) so production of clinker requires a reduced energy consumption ( $1350 \text{ kJ kg}^{-1}$ ), releasing less  $\text{CO}_2$  to the atmosphere. Nowadays the structural durability is an important basis of construction design rather than the traditional concept of strength in this way cement belite has better durability properties than conventional cement. Nevertheless, belite cement slowly hydrates, thus presenting low early-age compressive strength which will

significantly delay construction Schedule. This leads to do efforts to hydraulically stabilize active forms of belite and develop new cementitious materials of belite with good properties of hydraulic reactivity without problems in strength at short age and a reduction the  $\text{CO}_2$  emissions to the atmosphere due to its low obtaining temperature compared to cement of alite (PC). [1,2] Belite's low reactivity is due to its high thermodynamic stability, which is caused by its dense, compact crystalline structure [3,4].

Belite has five polymorphs ( $\gamma$ ,  $\beta$ ,  $\alpha'_L$ ,  $\alpha'_H$  and  $\alpha$ ) at different obtainment temperatures. All phases are metastable, except phase  $\gamma$ . Structures  $\alpha'_H$ ,  $\alpha'_L$  and  $\beta$  are derived from phase  $\alpha$  because of a progressive reduction in symmetry, which is caused in turn by the orientation of the tetrahedra of silicate groups ( $\text{SiO}_4^{-4}$ ), as well as position changes of calcium atoms (Ca) in the structure. Polymorph  $\gamma$  is a non-hydraulic phase of belite, stable at room temperature and crystallizes into an orthorhombic form, olivine-type. Phase  $\beta$  is a monoclinic structure at room temperature. Phase  $\alpha$  structure is still discussed. Polymorphs  $\alpha'$  are more hydraulic phases, phase  $\beta$ -C2S is also hydraulic but to a lesser extent [4–9]. The use of belite cements implies the stabilization the most reactive phases. This can be obtained by fast cooling

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and/or by the inclusion of ionic spaces as dopants ( $B^{3+}$ ,  $Ba^{2+}$ ,  $Na^+$  y  $K^+$ , etc.), capable of replacing atoms of calcium (Ca) and/or silicon (Si) in the structure, reducing the Ca/Si of  $\beta$ -C2S [8,10,11]. Introducing boron in the crystalline lattice of phases  $\beta$  and  $\alpha'$ -C2S increases its hydraulic properties [7,12]. Reactivity and hydraulic properties of the stabilized phase  $\beta$ -C<sub>2</sub>S depend on the type and quantity of stabilizing ions [13,14]. These treatments cause a greater reactivity in the belite cement, so that greater mechanical strengths appear even at early ages.

Conventionally,  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub> is synthesized by the calcination of calcium carbonate (CaCO<sub>3</sub>) and silicon dioxide (SiO<sub>2</sub>) through the reaction in solid state at temperatures greater than 1300 °C. Resulting belite shows low hydraulic reactivity. Different methods of synthesis of  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub> have been lately reported, showing good properties of hydraulic reactivity: sol-gel method, spray drying method, hydrothermal method or simply methods of synthesis which include the use of SiO<sub>2</sub> nanoparticles [15–19]. However, even though hydraulically reactive C2S is obtained through synthesis methods, the latter imply the use of costly starting materials, synthesis routes can be very complex, as well as high temperatures and very long synthesis periods of time. According to the above mentioned, those procedure are complicated and costly, which could affect both reproducibility and resulting powders. In recent years, combustion method has been used for the obtainment of advanced ceramics at low cost. This method produces ceramic oxides in very fine powder. This exothermic reaction has been observed to be very rapid and self-sufficient. The key element of this method is that the heat required for the chemical reaction to occur is produced within the very same reaction and not by an external source. This process is performed in an aqueous solution which contains stoichiometric quantities of one oxidant and one organic fuel, and carried out through redox reaction. [20,21] Studies have been reported on synthesis of aluminates and silicates through combustion reaction of a mix of water-soluble salts were ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) is assumed to work as an oxidizer and urea (CO(NH<sub>2</sub>)<sub>2</sub>) is the most frequently used fuel due to its low cost and produces less gases in comparison with other organic fuels. The use of ammonium nitrate in this work is because it is an oxidizing agent that promotes an increase in temperature in the reaction with urea, which will reduce the temperature of clinkerization up to 1000 °C. Furthermore, moderate use of this reagent is recommended, as it releases gases into the atmosphere, such as nitrous oxide, which impacts global warming more than CO<sub>2</sub> does. This represents a study area to propose the use of more eco-friendly oxidants. [22,23] So the synthesis in this work is based on some principles of the combustion reaction without reaching the incandescence for this reason is considered a new method. It is important to mention that in future work a commercial zeolite contaminated with urea will be used as a common subproduct in Mexico, that is why these reagents have been chosen to participate in the reaction, since this stage of the work involves pure materials to know the ideal system.

The production of 1 ton of Portland cement emits 0.6–0.8 tons of CO<sub>2</sub> [24,25]. Nevertheless, the environmental impact of Portland cement is caused by its great demand, since the production volume is very high. Cement global production is approximately 2.8 million tons and it is expected to increase to 4 million tons by 2050. Cement industry is facing cost increments in energy supply, requirements for reduction of CO<sub>2</sub>, and insufficient supply of raw materials of good quality [26]. According to all this environmental issues, cement industry must change its consumption patterns and reduce CO<sub>2</sub> emissions to the atmosphere. This can be achieved by generating environmental consciousness, which encourages the use of industrial by-products and/or recycling for the production of cement, as well as alternate, environment-friendly methods of synthesis which reduce CO<sub>2</sub>.

Silica fume is one of the most used waste materials in cement industry. Silica fume is also known as microsilica, which is a subproduct of the foundry process in the silica and ferrosilicon industry. Reduction of high purity quartz is carried out at temperatures up to 2000 °C, producing vapors of SiO<sub>2</sub>, which are in turn oxidized and condensed at

low temperature areas as tiny particles composed of non-crystalline silica. By-products of metallurgic silicon and ferrosilicon alloys have non-crystalline silica contents of about 85–95%, although this percentages may vary depending on the silicon content of the alloy produced. Silica fume has a high content of amorphous SiO<sub>2</sub> and is composed by small, spherical particles of less than 1 μm and with a surface area between 13,000 and 30,000 m<sup>2</sup>/kg. Its particles are approximately 100 times smaller than Portland cement particles. Moreover, silica fume contains small quantities of magnesium, iron and other oxides. It is a white or gray powder, depending on its origin. Silica fume is a highly pozzolanic material due to its extreme fineness and high content of SiO<sub>2</sub>, it is used as mineral additive in cement and concrete to improve properties such as compressive strength, abrasion strength, permeability reduction, protection of steel reinforcement against corrosion, sulfate strength, among others [27–30].

The use of new raw materials for the cement production is another alternative solution to the appreciation of conventional materials. Natural zeolites are crystalline aluminosilicates which contain great quantities of SiO<sub>2</sub> y Al<sub>2</sub>O<sub>3</sub> [31,32], so they present pozzolanic activity. According to the above, zeolites, as well as other pozzolanic materials are capable of improving compressive strength, reducing times of hydration, and reducing cement and concrete porosity, so improvements in durability are observed [32–36].

In the article herein, belite phase cements will be synthesized by means of simple, new method under low temperature. The main raw materials are silica fume, byproduct of metallurgic industry and commercial natural zeolite with great abundance in Mexico. Synthesis reaction of belite phase cement will be carried out in presence of ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) and urea (CO(NH<sub>2</sub>)<sub>2</sub>), oxidizing agent, and reducing agent (organic fuel), respectively, which do not participate in the direct formation of belite but in the formation of the precursor, which is later calcined at 1000 °C. It is worth mentioning that the synthesis method, together with the use of these raw materials, has not been previously reported in literature. This new synthesis method is proposed through the use of new raw materials considered wastes and low cost alternate fuels, in order to obtain eco-friendly cements with good hydraulic reactivity and properties comparable to those of Portland cement.

## 2. Materials and methods

### 2.1. Raw materials

Materials utilized include calcium carbonate (CaCO<sub>3</sub>); silica fume (SiO<sub>2</sub>), supplied by BASF; commercial natural zeolite distributed by Grupo Minero San Carlos, composed chiefly by heulandite; ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>); and urea (CO(NH<sub>2</sub>)<sub>2</sub>). All reagents were utilized without additional purification. Ammonium nitrate was employed as oxidizing agent while urea is the reducing agent which in turn acts as fuel and is oxidized by the nitrate ions. Ordinary Portland cement and gypsum were used as reference pattern in order to compare the properties of the belite cements obtained.

### 2.2. Preparation of belite cements

Synthesis of belite cement using silica fume (BCSF) was performed by dissolving the materials in 10 mL of distilled water, considering the following order of addition: 8.0069 g of CaCO<sub>3</sub>, 2.4032 g of silica fume, 3.6046 g of CO(NH<sub>2</sub>)<sub>2</sub> and 6.404 g of NH<sub>4</sub>NO<sub>3</sub>. Resulting aqueous solution was placed in a stainless steel melting pot, previously heated on a hotplate, where it was maintained during 15 min. This process was carried out under the fume hood due to gas release. In this step it should be emphasized that the raw materials never made red-hot ignition as it happens with the conventional combustion method, for this reason it is considered a new simple method of combustion. Subsequently, precursor obtained was emptied in a platinum melting pot for furnace

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