Synthesis of Hydraulically Active Calcium Silicates Produced by Combustion Methods

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ABSTRACT:

Portland cement is synthesized from a mixture of limestone and clay at high temperature (1450 °C) via a conventional process (solid-phase synthesis), in which partial fusion of raw materials and the formation of clinker nodules are produced. The clinker is mixed with a small percentage of gypsum and ground together to make the cement. This synthesis process holds the cement industry accountable for 5–8% of global anthropogenic CO₂ emissions. The production of a ton of cement emits between 0.62 and 0.97 tons of CO₂ into the atmosphere, depending on the processing plant. Furthermore, the use of fossil fuels in cement production is another important factor in the environmental impact of this industry. The production of 1 ton of clinker consumes approximately 5.86 GJ per tons of clinker produced in wet processes and 3.35 GJ per tons of clinker produced by dry process. Some researches have reported the possibility to obtain silicate and aluminat cement by alternative synthesis methods, which optimize both time and temperature, such as Pechini method, sol-gel method and microwave assisted method. The combustion methods, another alternative, are chemical redox processes in which the use of chemical precursors and organic fuels at high temperature generate a self-sustaining fastwave. The said wave is characterized by the fact that once the initial exothermic reaction starts, it generates a reaction wave (0.1–10 cm/s) at high temperature (1000–3000 °C) that propagates, in a self-sustaining way, through the heterogeneous mixture which leads to the formation of the solid material. For this reason, and the irreplaceable role of cement in the construction industry, this paper shows the advances in the production of silicates, similar to those found in the Portland cement, by combustion synthesis method.

INTRODUCTION

Cement is the most successful and important construction material nowadays. The evolution of its production is linked to the economic activity, level of industrialization and infrastructure development of countries, hence its rise in per capita consumption. Cement consumption has become one of the most significant indicators of economic growth analysis [1]. No material has yet been identified as a viable cement replacement [2]. In 2008, global consumption per capita was 510 kg/year [3], in 2012 the global cement production was 3859 million tons/year, equivalent to a per capita consumption of 548 kg/year [4], and by 2050 this is expected to multiply by a factor of 2.5, equivalent to a per capita consumption of 1005 kg/year and a production close to 9650 million tons per year [5].

Portland cement can be described as a system of four major oxides, namely CaO, SiO₂, Al₂O₃, and Fe₂O₃. It is produced from calcining to partial fusion of an homogeneous mixture of limestone and clay by a solid-phase synthesis process at high temperature (1450° C). This
promotes the formations of clinker nodules, which are then interground with a small percentage of gypsum to obtain cement [6].

Clinker is essentially a synthetic rock containing four major crystals: alite, belite, celite, and ferrite. Alite (Ca$_3$SiO$_5$ or C$_3$S) and belite (Ca$_2$SiO$_4$ or C$_2$S), are two solutions of calcium silicates with small percentages of impurities. These silicates provide the main mechanical properties to the cement. Celite (3CaO.Al$_2$O$_3$ or C$_3$A) and ferrite (4CaO.Al$_2$O$_3$.Fe$_2$O$_3$ or C$_4$AF) are two phases of calcium aluminates, which form the interstitial phase between the long crystals of the two main calcium silicates [7].

Of all Portland cement components, alite (C$_3$S) is the most important and accounts for 50 – 70% in volume. Its composition and crystal structure can be modified by substitution of external ions, especially Mg$^{2+}$, Al$^{3+}$ and Fe$^{3+}$. The C$_3$S is usually triclinic, but may become monoclinic or trigonal (rhombohedral) by modifying its external ions and temperature, as shown in Figure 1 [6].

![Figure 1. Polymorphs and crystal structure of alite [6].](https://doi.org/10.1557/opl.2015.321)

Belite (C$_2$S) constitutes 15 – 30% of ordinary Portland cement volume. It can be modified by incorporation of external ions present in the β polymorph. The C$_2$S can occur in four polymorphic modifications: α (trigonal), α' (rhombic), β (monoclinic) and γ (rhombohedral), as shown in Figure 2. The α modification is not hydraulic, α' has low mechanical resistance, γ is almost inert, and β has good hydraulic performance, and is most common [6].

![Figure 2. Polymorphs and crystal structure of belite [6].](https://doi.org/10.1557/opl.2015.321)

The aluminate phase is 5 – 10% of ordinary Portland cement volume. Celite (C$_3$A) can be modified in composition and sometimes also in structure. The substitution of external ions, especially Si$^{4+}$, Fe$^{3+}$, Na$^+$ and K$^+$ features four polymorphs: cubic I, cubic II, orthorhombic and monoclinic [6].

Ferrite (C$_4$AF) accounts for 5 – 15% of Portland cement volume. This aluminate is modifiable in composition by variations of the Al/Fe ratio, or by the incorporation of external ions. It is rarely crystalline, except when the cooling is very slow [6].

It has been established that producing one ton of cement, depending on the type of the plant, generates an emission of CO$_2$ into the atmosphere between 0.62 and 0.97 tons [1, 3, 19, 20]. The collection and processing of the raw materials, the decarbonization of limestone during synthesis, the fuel burnt, and the final grinding of the clinker turning into cement generate this CO$_2$. Moreover, the use of fossil fuels in cement production constitutes another important factor of the environmental impact of this industry. The production of one ton of
clinker requires approximately 5.86 GJ of energy during the wet process. The same production via the dry process requires 3.35 GJ of energy [1, 5, 21, 22].

For these reasons, among others, researches on cement, especially those focused on how to improve its properties, behavior and particular characteristics, have been of great interest. The common goal amongst researchers is to reduce negative environmental impacts of the cement industry.

Studies have reported the possibility of making the cement silicates and/or the aluminates by alternative synthesis methods, which optimize time and temperature during the process. Some of these methods are: Pechini [8, 9] and sol-gel method [2, 10-12]. Another method is microwave assisted synthesis [13-15], which is a solid-phase synthesis process different from the conventional method. This process yields interesting results given its efficiency in the heating of raw materials compared with the traditional synthesis method. Zapata and Bosh [16] show how the solution combustion synthesis (SCS) can be a way to produce belitic clinker using calcite and zeolites as sources of silica and calcium; and ammonium nitrate and urea as fuels. Similarly, Huang and Chang [17] synthesized nanocrystals of β-dicalcium silicate at low temperature and Fumo et al. [18] reported the production of calcium aluminate (CA, CA₂ and C₁₂A₇) using the SCS method.

**SOLID STATE SYNTHESIS - CONVENTIONAL METHOD OF SYNTHESIS**

To achieve the required high temperatures in solid-phase cement synthesis at industrial level, the use of fossil fuels is necessary because of its high-energy output. Most of the raw materials, and large percentages of the total energy required for the production of cement, are consumed during calcination process (clinkerization)[16]. When burnt, fossil fuel emits CO₂ into the air, thus becoming a highly polluting process, considering the quantity of annual global production of cement. The conventional synthesis preparation requires high temperatures and long waiting time, because of the low diffusion of solid-phase reactions. When the heating rate is increased, the mixtures of raw materials decompose in a thermal activation process, in which high ion diffusion facilitates solid-phase reactions [23].

The main reactions of the clinkering process can be divided into three groups:

1. Reactions below 1300 °C: The series of reactions include the decomposition of limestone (decarbonation), the decomposition of clay minerals, the reaction of CaO with silica, and decomposition products from the clay, to form belite, celite and ferrite.
2. Reactions between 1300 – 1450 °C (sinterization): The melt is formed, particularly from the celite and ferrite phases. At 1450 °C, about 20 – 30 % of the mixture is liquid. Most of the belite and nearly all the lime react in the presence of melt to form alite, leading to formation of clinker nodules in the mass.
3. Reactions during cooling: The liquid phase turns into a vitreous phase composed by celite and ferrite. The polymorphic transitions of alite and belite take place [6].

The conventional synthesis of pure phases is formed from oxides of CaO, Al₂O₃, SiO₂ and Fe₂O₃. The materials are homogenized and dried at temperatures between 80 °C and 105 °C [24]. The initial calcinations aims to remove CO₂ from CaCO₃ and is performed at a rate of 16 °C/min up to 1000 °C, in order to avoid the violent evolution of CO₂. The resulting material is then ground to a particle size close to 63 microns.
The process is repeated by heating the furnace at a specific temperature and for a certain
period of time; followed by cooling of the material and milling [2]. The waiting time at
maximum temperature is ten minutes [23]. In the laboratory, the synthesis protocol for C₃S is
two hours of heating at 1600 °C, and leaving it in this state for two more hours. For C₂S and
C₃A the time is 1.45 hours heating at 1450 °C and left in this condition for four hours. For
C₄AF this is 1.30 hours at 1300 °C and leaving it at this temperature for two hours [2].

In view of all the above, and given the importance of this material for the development of
countries’ economy, research on cement must account for the environmental demands of
society and government to this industry. Until now, the strategies for mitigation of
environmental impact of the cement industry have focused on: (1) Modifying the clinker
burning process, (2) developing or adapting new fuels, (3) capturing and/or reducing
emissions of CO₂ in the clinker synthesis process, (4) implementing more efficient
technologies, (5) improving the cement properties with the addition of supplementary
cementitious materials, nanotechnological developments, etc, and (6) developing new
cementitious materials that could replace the process partially or completely.

ALTERNATIVE SYNTHESIS METHODS

The alternative synthesis methods have become feasible for the clinker synthesis, because
they use paths different to those of solid-state processes, looking for a high-performance
material which requires strict control of its chemical composition, microstructure and
particle-size distribution [25]. In the literature, one of the most important attributes, due to the
gases generated in these synthesis methods, is the possibility to obtain products with a
particle-size distribution within the submicrometer range [2]. This implies that cement
produced by these routes may be more reactive in comparison to traditional Portland cement,
since its hydration heat, setting time, mechanical strength and durability are modified.

Sol-Gel Method

This is a process in which a Sol — colloidal suspension of solid particles in a liquid
medium— forms an intermediate step. The subsequent transformation of the suspension into
gel, forms an extending three-dimensional network through liquid [26]. The method has
many variations, but can be grouped into two main paths: polymeric sol-gel from alkoxides
and colloidal sol-gel. The first path is based on the hydrolysis and subsequent condensation
of metal alkoxides, whereas the second is based on the destabilization of a colloidal
dispersion in a liquid medium. In both cases, the process for obtaining the gel involves the
development of the following steps: (1) Hydrolysis, (2) polymerization, (3) nucleation, (4)
growth, and (5) agglomeration [27].

Chrysafi et al. [2], synthesized belite using metallic calcium nitrates (Ca(NO₃)₂·H₂O) as
source for Ca, and two different sources for silica: (1) 30% silica sol in water and (2)
onaqueous tetraethylorthosilicate (TEOS). This research concluded that the β polymorph of
C₂S is not stable at room temperature. However, it showed that both paths were successful in
the formation of β polymorph without any chemical stabilizers. Once the final product was
synthesized at 1000 °C for three hours, it consisted of very fine spherical crystals of the order
of 1–3 microns.

Meanwhile, Stephan et al. [11] synthesized pure phases of silicates and calcium
aluminates from silica sol and calcium nitrates at different temperatures: 1140, 1230 and
1500 °C. Samples were heated for 18 hours. The results from this study showed that it is possible to produce a pure phase of β-Ca2(SiO4) by the sol-gel process at a temperature of 1200 °C. Above this temperature, the main phase found was γ-Ca2(SiO4) and was the only phase present at 1400 °C. They found significant differences between sol-gel and conventional samples. These researchers also synthesized alite. The average particle-size of C3S through sol-gel after two minutes of grinding was 6.5 microns, whereas for the conventional method it was 8.4 microns after 12 min of grinding. Additionally, C3A was synthesized through sol-gel process for 14 h, at 1260 °C.

**Pechini method**

The Pechini method involves the polyesterification of a polycarboxylic acid with a polyhydric alcohol. The most popular variant of the method uses citric acid and ethylene glycol, since they form very stable complexes with most metals [28].

Hong and Young [8] synthesized the phases α', β and γ of C2S using the Pechini method. The α'-C2S phase was obtained at 700 °C and during 1 h of synthesis. By increasing the temperature gradually, the α'–phase is transformed into β-C2S which stabilizes between 800–1200 °C. At 1300 °C the γ-phase of C2S begins to appear, becoming the only present phase at 1400 °C. Gaki *et al.* [9] synthesized C3A and C4AF using this method and found that this technique successfully synthesized these phases, obtaining fine, well-formed grains. The final synthesis process took three hours at 1000 °C.

**Conventional Microwave Synthesis Method**

This is a method of solid-phase synthesis. Li *et al.* [13], who synthesized C3S, and Long *et al.* [15], who synthesized C3S, β-C2S and C4AF, showed that this method improves the synthesis and requires lower temperatures (compared to the conventional synthesis process for C3S) (by about 100 °C). However, very few researchers have further investigated the clinkerization process with microwave, due to the fact that the heating process of these kilns is very slow and inefficient, making its industrial implementation complicated [15].

Consequently, Long *et al.* [15] proposed a new burning method, which involves heating the material in an electric furnace and then transferring it to a microwave for very short periods of time (1-2 minutes), depending on the desired phase. The generation of heat inside the microwave is simultaneously generated in the whole sample, making it less dependent on the heat transfer than the conventional method. As a result, the sample is synthesized more uniformly [13]. Long *et al.* [15], for the Portland cement calcination, heated different samples at 1000, 1100, 1200, and 1300 °C in an electric furnace, and transferred them to the microwave oven for heating during 135, 95, 60, and 40 seconds respectively. The displayed findings showed how the combination of electric and microwave heating is more efficient, and that mineral rate formation is also faster than with the conventional method.

**Combustion Synthesis Methods**

Combustion methods are effective energy-saving techniques for the synthesis of a great variety of advanced materials that surpass conventional oven technologies. They have become important methods for synthesis and processing of advanced ceramics, catalysts, composite materials, alloys, intermetallic compounds and nanomaterials [29-32]. Methods for combustion can be distinguished as follows: Self-propagating High-temperature Synthesis
(SHS), Low temperature Combustion Synthesis (LCS), Solution Combustion Synthesis (SCS), and Volume Combustion Synthesis (VCS), also known as thermal explosion.

The basis of combustion synthesis comes from thermochemical concepts used in chemical propulsion. The formation of a fuel-oxidant mixture is important in the field of propulsion and explosives. The main parameters are closely linked to the stoichiometry of the mixture. The stoichiometric composition of the redox mixture for combustion is calculated based on the total oxidizing and reducing valencies of the oxidizer and the fuel, in pursuit of releasing the greatest amount of energy during the reaction [18]. Autocombustion method is characterized by the fact that once the initial exothermic reaction starts, by means of an external heat source, a reaction wave is generated (typically 0.1 – 10 cm/s), of high-temperature (between 1000 – 3000 °C). The wave propagates through the mixture in a self-sustaining manner and leads to the formation of solid material, without involving any additional energy [30].

In the Solution Combustion Synthesis (SCS) method, the whole sample is heated uniformly until the automatic reaction starts in the entire volume. This synthesis method is less controllable and is used for weak exothermic reactions that require preheating before ignition [30]. Typically, SCS involves a self-sustaining reaction in metal nitrate solutions and different fuels, which can be classified depending on the type of reactive groups (amino, hydroxyl and carboxyl) attached to the hydrocarbon chain [33]. Combustion methods have a number of features that give unique properties to the synthesized products, such as enabling reactants to mix at a molecular level, thus allowing uniform and precise formulation of the desired composition at a nano scale. The elevated reaction temperatures ensure product purity and high crystallinity. The process is very short, and a wide variety of gases are formed during the synthesis that inhibit the particle size growth [30].

Auto-combustion method consists of preparing an equimolar solution of metal salt nitrates, to which glycerine or other ignition-promoting agent is added. This forms a solution similar to the unit with a ratio of NO₃⁻/NH₂; whereby water is slowly evaporated until the formation of a gel or resin [34]. The formation mechanism of this gel is not totally clear, but it is known to depend on the type of metal used in the synthesis. The organic compound complexes with different metals in different manners and channels, leading to different characteristics for the gel [34]. The gel is then heated to a temperature at which the combustion process occurs (approximately 300 °C). In this process, the organic compound acts as fuel for the reaction, and the nitrate and amino groups react to form nitrogen gas. This reaction is very exothermic and is responsible for the combustion of the carbonaceous material. Besides the formation of nitrogen, CO₂ is formed because this reaction takes place in an air atmosphere [35].

The application of combustion methods for manufacturing clinker, or any of its phases, have been reported by Fumo et al. [18], who synthesized calcium aluminates; Huang and Chang [17], who synthesized nanocrystals of β- Ca₂SiO₄ at low temperature; and Zapata and Bosch [16], who synthesized belite cement clinkers at low temperature.

Fumo et al., [18] reported the synthesis of three calcium aluminates at 500 °C: the CA, CA₂ and C₁₂A₇, using hydrated crystalline salts (nitrates) as precursors and urea as fuel. Huang and Chang [17], synthesized β-Ca₂SiO₄ with SCS, using colloidal silica and calcium nitrate as precursors and citric acid as fuel. Findings showed that increasing the calcination temperature from 650 to 1100 °C, results in higher crystallization and lower specific surface area, making the belite more reactive, and increases its hydration release heat. After the
combustion process, the resulting powder is brought to an electric furnace and calcined in air at 650 °C for four hours [17]. These authors concluded that the synthesis of β-Ca$_2$SiO$_4$ occurred successfully, at a synthesis temperature of 650 °C.

Meanwhile, Zapata and Bosch [16], studied the synthesis of belite cement at low temperatures, using calcites as calcium source, and zeolites as source for silica and alumina, by a modified method of combustion inspired by Cruz [36] and Burgos-Montes et al. [37]. The process reported by Zapata and Bosch [16] start by the grinding of the raw materials (calcite and zeolite), followed by the addition of ammonium nitrate and urea, as fuel. Subsequently, the mixture is heated for three minutes at 70 ºC and then for two minutes at 250 ºC. Once the gel is obtained, it is brought to a furnace at 1200 ºC, where the combustion process takes place for 15 minutes. The samples synthesized by modified combustion methods were analyzed with XRD method, and showed the formation of belite, alite, calcium aluminate and gehlenite. The authors reported that they managed to lower the synthesis temperature by 250 ºC compared to the conventional synthesis method, and established that the urea is most appropriate fuel, since it produced the lowest volume of gases.

CONCLUSIONS

Advances in the Manufacture of Calcium Silicate by Combustion Methods

Considering the issues reported in the previous section, this paper presents some preliminary experimental results. The current study suggests the use of chemical combustion methods to obtain hydraulically active calcium silicates. Since the technique does not use fossil fuels, it benefits from the energy efficiency and mitigation of CO$_2$ emissions compared to the conventional synthesis process.

This research presents an alternative method to identify the hydraulic activity from the synthesis material: the standard issue Moisture Analyzer (MA), reported by Mendoza et al. [38]. This MA requires lower temperature and reduced time compared to other mass-loss techniques, e.g. Thermogravimetric Analysis (TG), due to dehydration of silicate hydrates during its reaction with water. Additionally, an XRD analysis was performed on one of the synthesis materials, in this specific case of alite made using citric acid as a fuel.

This aims to identify formed phases similar to the calcium silicate of Portland cement (alite and belite). Synthesized samples were mixed with water and tested within five days. Hydraulic performance results are presented below.

Conclusions of the State of the Art

1. It reviewed the state of the art, it can be concluded that it is possible to produce calcium silicates using aluminates and alternative methods of synthesis [2].
2. The proposed sol-gel method could be applied successfully to prepare C$_3$S; very fine spherical crystals, from 1 to 3 microns, were obtained. Three hours of synthesis were required at 1000 ºC. The β-C$_2$S synthesized does not need chemical stabilizers, maybe due to the small particle-size generated during the synthesis process [2].
3. Microwave synthesis C$_3$S containing Al$_2$O$_3$ as an additive to obtain allowed temperatures below 1300 ºC, in comparison with 1450 ºC of the conventional method [23].
4. Researchers report from the synthesis of calcium silico-aluminates and calcium aluminates using the Pechini method, that some metastable phases, and good homogenization at low temperatures, were obtained with particle sizes of about 50 nm [24].

5. Combustion method shows CO₂ reduction using a fuel different from coal, and once the synthesis process is complete, the resulting particle-size indicates that it is possible to reduce the total emissions generated by conventional synthesis in a percentage that would range between 40 and 50% [16].

**Conclusions of the initial experimental phase**

1. Once the initial experimental phase, it can be concluded that it is possible to produce hydraulic active calcium silicates using combustion methods such as Solution Combustion Synthesis (SCS) and Self-propagating High-temperature Synthesis (SHS).

2. Initially, the Solution Combustion Synthesis (SCS) was identified as the best method for the combustion synthesis. This process is much more controlled that Self-propagating High-temperature Synthesis (SHS), because is helpful when getting the synthesis material.

3. SCS with the method there is not observed any difference in the final product of synthesis when solid silica or colloidal silica as SiO₂ source used.

4. Given the synthesis temperature defined at the experimental process, it was established that the initial pH should be acidic and between 1 and 2, when citric acid and glycine are used as fuel. The natural pH of citric acid is less than 1 (between 0.45 and 0.67), while the natural pH of glycine is between 5.65 and 6.83.

5. Decreasing the pH of the glycine from its natural state to the pH established between 1 and 2 is decreased with nitric acid (about 5 ml). The solution pH is controlled by using a solids digital pH meter.

6. After running the established design of experiments, it was concluded that combustion could not be obtained by using urea as fuel, with any of the two methods (SCS and SHS) and any of the established pH.

7. With glycine as a fuel, combustion was obtained by both methods, there was not a clear identification of process variation by changing the pH. It shows speed variations related to changes the pH of the solution.

8. The solution method of combustion synthesis (SCS) is highly exothermic, this energy is not allowed to obtain the synthesis material. By contrast, let us pick up the SCS material synthesis. The material obtained by both methods (SHS and SCS) is a white fine powder.

9. For the synthesis of alite with citric acid as fuel, combustion could be obtained at pH values below 2. The material obtained in the synthesis process is a fine gray powder.

**Conclusions from the Hydraylicity Curves**

As shown in Figure 3, we employed an alternative method to identify the hydraulic activity of the material of the synthesis using a standard issue Moisture Analyzer (MA). It can be observed that the curves still show a loss of mass above 110 °C and the increase in temperature is associated, as reported by Mendoza et al. [38], to dehydration of the synthesis products. 1 g of synthesizing material from each of the selected samples is weighed and water is added in a W/C ratio = 2.00.

First, samples were allowed to rest for four days for curing; then, samples were heated in an oven for 24 hours, at 50 °C, intended for drying of the free water in the mix. Finally, the
material is removed from the sample and then macerated to a size less than 75 microns particle, and taken to the MA. The maximum temperature in the MA is 240 °C.

**Figure 3.** Hydraulicity Curve [Temperature (°C) / Mass loss (%)]

**Conclusions of the XRD – Hydraulically Calcium Silicates with Citric Acid as Fuel**

In the diffraction pattern, Figure 4, the major peaks are observed between 32.412 and 33.027 (2θ) that might be associated with the formation of calcium silicates; because of the coincidence of the peaks from the belite and alite, we assume that they correspond to this type of silicates. Also, we observe peaks of 80%, 75% and 70% of belite and 45% of alite.

In the diffraction pattern of Figure 5, one can see the main peaks of the hydration products of CSH and Ca(OH)₂. The 100% between 29.258 and 29.515 (2θ), the 80% in 47.22, 31.475 60% and 40% at 57.22 (2θ). Is also the major peaks of portlandite at 34.101 100% and 74% at 18.066 (2θ). Which could be associated with the formation of products of hydration of calcium silicates.

**Figure 4.** XRD – Belite Synthesis Product  
**Figure 5.** XRD – Products alite hydration
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