



## Evaluation of the Reactivity of Artificial Mixtures of Portland Cement Clinker Obtained by Flame Spray Pyrolysis

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### Abstract

The Portland cement clinker consists of 95% calcium oxide, silicon, aluminum and iron and 5% impurities of magnesium, sodium, potassium, titanium, sulfur, phosphorus and manganese. The constituents of the white clinker, formed from the combination of two or more of these main oxides, correspond to alite ( $3\text{CaO} \cdot \text{SiO}_2$  or  $\text{C}_3\text{S}$ ), belite ( $2\text{CaO} \cdot \text{SiO}_2$  or  $\text{C}_2\text{S}$ ) and celite ( $\text{Ca}_3\text{Al}_2\text{O}_6$  or  $\text{C}_3\text{A}$ ), giving to cement its characteristic properties. The fundamental properties of cement are its mechanical resistance, chemical resistance, hydraulic behavior and heat release during hydration. In this work, the reactivity of an artificial mixture of white clinker, formed from alite, belite and celite prepared by flame spray pyrolysis was evaluated. The phases were characterized by X-ray diffraction, scanning electron microscopy and microcalorimetry, to evaluate their formation and reactivity. The characterization showed that during the synthesis of belite, a greater amount of the polymorph alpha was produced, with some impurities. On the other hand, the synthesis of celite allowed the production of the polymorph CII. The reactivity was evaluated by microcalorimetry.



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### Introduction

Portland cement is a type of material obtained from the rotary kiln cooking of a mixture of limestone and clay in a rotary kiln, which is brought to sinter to form an intermediate product called clinker, which is mixed with gypsum, giving rise to Portland cement.<sup>1</sup>

The clinker consists of 95% of calcium oxides, silicon, aluminum and iron and 5% of impurities of magnesium, sodium, potassium, titanium, sulfur, phosphorus and manganese. The main constituents of the white clinker are correspond to alite( $3\text{CaO} \cdot \text{SiO}_2$  or  $\text{C}_3\text{S}$ ), belite ( $2\text{CaO} \cdot \text{SiO}_2$  or  $\text{C}_2\text{S}$ )

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and celite ( $\text{Ca}_3\text{Al}_2\text{O}_6$  or  $\text{C}_3\text{A}$ ), which give cement its characteristic properties.<sup>1</sup> A typical mineralogical composition of clinker is formed by 70% alite, 22% belite, 8% celite.<sup>2</sup>

Solid state reaction or partial melting process is the traditional process for the synthesis of the clinker phases<sup>3</sup> which has as advantage the simplicity of the process and the disadvantages as high power consumption, high emissions of  $\text{CO}_2$  and slow diffusion processes that lead to the formation of inhomogeneous phase.<sup>4</sup> Taking into account the above, according to N. Betancur-Granados,<sup>5</sup> In recent years, non-conventional methods have been sought for the production of nanometric cementitious materials, with a high production ratio, which can provide greater reactivity in each of the clinker phases. Therefore, considering the high volumes required in the production of cement, it is necessary to look for alternative methods of synthesis of the Portland cement clinker phases, towards processes that can be scaled. In this sense, spray technologies have a great potential for use since they are continuous processes, which can be easily taken to industrial production, allowing to go from a production of g/h to kg/h without changes in the characteristics of the particles.<sup>6-7</sup>

In this work, the reactivity of artificial clinker mixtures, formed from alite, belite and celite prepared by flame spray pyrolysis with liquid feed (FSP for its acronym in English) was evaluated. The formulation of the artificial mixture was chosen with respect to the mineralogical composition of a commercial white cement, in order to evaluate the reactivity. The products were characterized by X-ray diffraction, to determine the formation of the phases and the reactivity of the mixture was evaluated by microcalorimetry.

## Experimentation

### Materials

In this work, calcium nitrate tetrahydrate ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , 98%) from Baker, aluminum nitrate nonahydrate [ $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , 98.5%] from Merk, tetraethyl orthosilicate [ $\text{SiC}_8\text{H}_{20}\text{O}_4$ , 99%] of Sigma Aldrich and ethanol [ $\text{CH}_3\text{CH}_2\text{OH}$ , 96%] of ProtoKimica was used.

### Flame Spray Pyrolysis Method

The clinker phases, belite ( $2\text{Ca} \cdot \text{SiO}_2$  or  $\text{C}_2\text{S}$ ) and celite ( $\text{Ca}_3\text{Al}_2\text{O}_6$  or  $\text{C}_3\text{A}$ ) phases were synthesized through flame spray pyrolysis (FSP) using metallorganic precursors and inorganic salts in stoichiometric amounts. On the other hand, the triclinic alite phase was acquired commercially in the company CTL company.

The starting solution to obtain 7 g of belite ( $2\text{CaO} \cdot \text{SiO}_2$  or  $\text{C}_2\text{S}$ ) was prepared by dissolving 8.55 g (0.041 mole) of tetraethyl orthosilicate ( $\text{SiC}_8\text{H}_{20}\text{O}_4$ ) and 19.19 g (0.081 mole) of calcium nitrate tetrahydrate ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ) in 355 mL of ethanol, with a ceramic loading of 2.5%, the percentage of which corresponds to the mass ratio of the product (belite) and the solvent (ethanol). The solution was fed with a flow of 30 mL/min and a pressure of dispersion gas of 200 kPa, to form an spray, using a airblast nozzle directed towards acetylene / oxygen oxidant flame. The reaction took place in 12.5 minutes and the resulting powders were collected in an electrostatic precipitator with a voltage of 15 kV (DC).

Similarly, to obtain 5 g of celite ( $\text{Ca}_3\text{Al}_2\text{O}_6$  or  $\text{C}_3\text{A}$ ), a solution was prepared with 13.11 g (0.056 mol) of calcium nitrate tetrahydrate ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ) and 13.88 g (0.037 mol) of aluminum nitrate nonahydrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) in 127 mL of ethanol, with a ceramic loading of 5%; the solution was fed with a flow of 50 mL/min and pressure of dispersion gas of 200 kPa, with an approximate reaction time of 4 minutes.

### Reactivity of the Artificial Mixture

White cement clinker was prepared by mixing alite, belite and celite taking as reference a typical composition for white Portland cement, corresponding to 70% alite (0.7074 g), 21% belite (0.2100 g) and 9% celite (0.0906 g). The reactivity of the mixture was measured using a TAM Air microcalorimeter, introducing the sample in glass ampoules of 20 mL, using air as standard. The equipment was stabilized for 24 hours, followed by the injection of deionized water into the ampoules with a water/solid ratio of 0.87, using an admix device and stirring for two minutes. The heat released and the heat flow were measured for 8 days.

### Characterization

The mineralogical analysis was carried out by means of X-ray diffraction (XRD) in a XPert PANalytical Empyrean Series II-Alpha 1 diffractometer, 2012 model using Cu- $k\alpha$  radiation. The scans were continuous from  $10^\circ$  to  $70^\circ$  ( $2\theta$ ) with increments of  $0.02$  and  $50$  s per step. The mineralogical phases were identified using the Xpert Highscore software.

The morphologies were evaluated by scanning electron microscopy (SEM) in an EVO Model MA10, Carl Zeiss. The powders were dispersed in acetone for 10 minutes using an ultrasonic bath and deposited on a polished silicone support. The samples were coated with gold using a QT150R sputter, Quorum Technologies.

To measure the heat release and the reactivity of the sample, a TAM Air microcalorimeter from TA Instruments of an isothermal principle with an air thermostat at  $25^\circ\text{C}$  was used.

### Results and Discussion

In Fig. 1, the X-ray diffraction patterns of all the synthesized phases are shown. The alite sample shows the presence of two polymorphs, corresponding to triclinic as main phases in the sample (code ICSD 98-016-2744) and monoclinic

polymorphs (code ICSD 98-008-1100). The presence of the monoclinic phase could be the result of temperature variations during the reaction, since the alite can present different polymorphisms as the temperature increases, first a triclinic crystalline structure, then monoclinic and finally rhombohedra.<sup>8</sup>

The  $\text{C}_2\text{S}$  sample shows mainly the formation of  $\alpha$ - $\text{C}_2\text{S}$  (code ICSD 98-008-2996) as main phase. This sample obtained by FSP, was then calcined at  $800^\circ\text{C}$  for 2 hours at a heating rate of  $10^\circ\text{C}/\text{min}$ , in order to achieve the complete formation of the crystalline phase. The peak located at  $27.28^\circ$  ( $2\theta$ ) belongs to a low quartz (code 98-007-1393), which could be given as an impurity, during the calcination process, by a slight calcium deficiency in the formulation.

The celite sample shows the formation of cubic  $\text{C}_3\text{A}$  II (code ICSD 98-015-1369), without the need for a subsequent thermal process, due to the high energy provided to the reaction, the volume of solution used, the feed flow of the solution and the similarity in the starting precursors, allow the reaction to develop in a short time. The peaks located at  $34.1^\circ$  and  $53.8^\circ$  ( $2\theta$ ) belong to  $\text{Al}_2\text{O}_3$  (code ICSD 98-016-1061), which could be formed as a secondary product, by reacting with the oxygen excess of the oxidant flame used in the process.

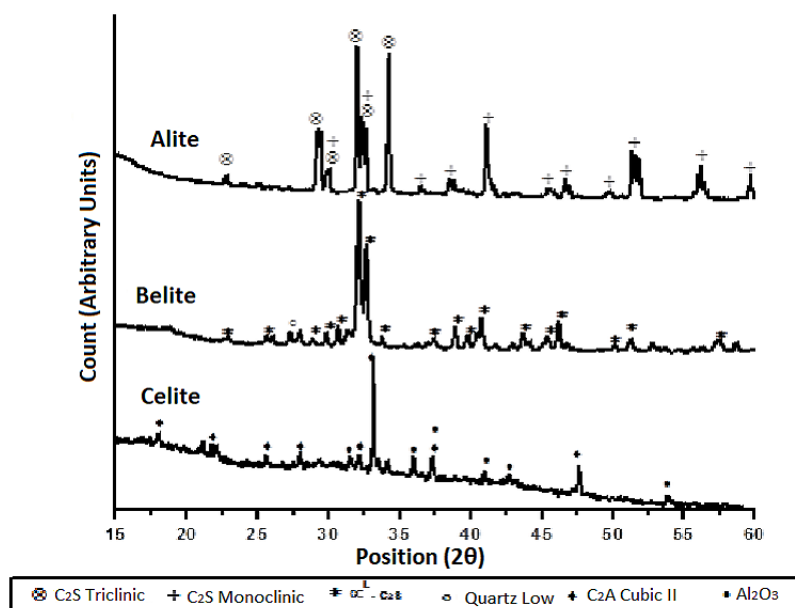


Fig. 1: X-ray diffraction patterns of the samples

In Fig. 2, the SEM microscopy of the  $C_2S$  phase synthesized by FSP is shown, where it is possible to observe an agglomerate of nanoparticles with spherical morphology and sizes around 100 nm, while a conventional belite is also rounded but has diameters around from 10 to 20  $\mu m$ , so it is expected that the reactivity will increase appreciably. It is possible to identify a homogeneity in the distribution of the particle size, attributed to a moderate feed flow of the starting solution promoting an adequate contact between the precursor and the flame. Otherwise, high feed flows, allow high collision

between the particles affecting the structure of the flame and increasing in the agglomeration degree.<sup>9</sup>

The reactivity of the clinker mixture and the individual phases were evaluated by isothermal calorimetry, which continuously measures the heat flow associated with physical processes and chemical reactions that occur during a phenomenon that requires exchanging heat with the external environment, as seen in Fig. 3. The calorimetric studies have revealed that the behavior of the heat flow in the activation of these materials is

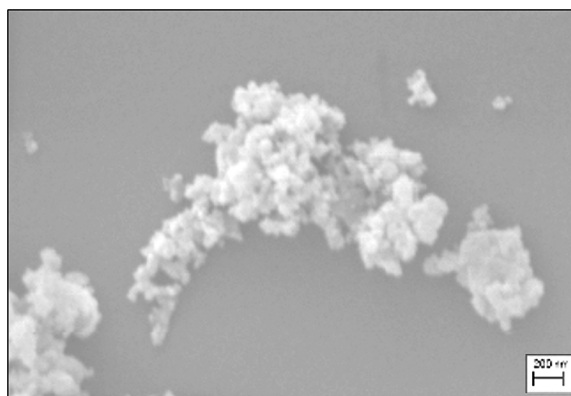


Fig. 2: SEM microscopy of the  $C_2S$

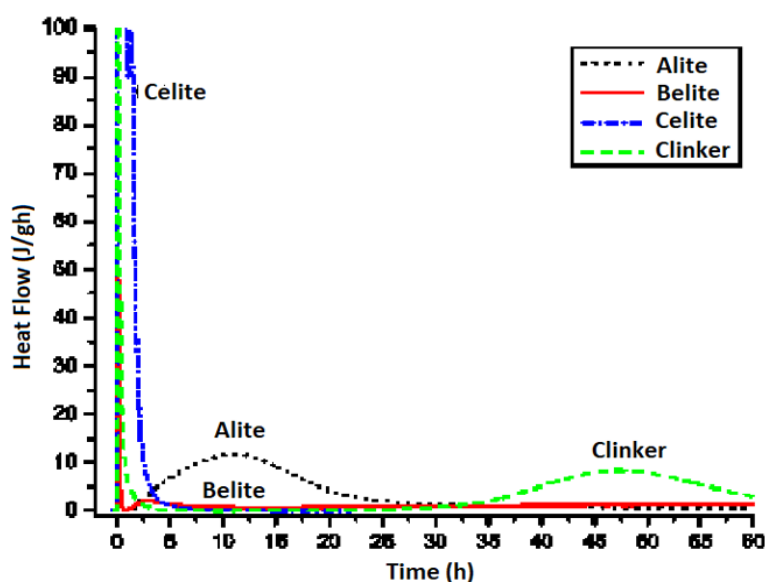


Fig. 3: Comparison of the changes in the hydration of Clinker,  $C_3S$ ,  $C_2S$  and  $C_3A$  during isothermal calorimetry..

represented by a curve of two peaks associating each of them with different reaction stages.<sup>10</sup>

Fig. 4 shows the first dissolution peak obtained by calorimetry for all the phases, alite ( $C_3S$ ), belite ( $C_2S$ ), celite ( $C_3A$ ) and Clinker mixture respectively. This peak comprises two stages, one in which a rapid exothermic reaction occurs due to the initial hydrolysis and the release of calcium, silicon and aluminum ions, follow by the period of deceleration of the heat evolution due to the formation of calcium silicate hydrate (C-S-H) and hydrated tricalcium aluminate ( $C_3AH_6$ ).<sup>11</sup>

The heat flow curves for the four samples shows that celite ( $C_3A$ ) presents a greater release of heat and reaches its maximum peak in a shorter time of hydration. This phase is the constituent with higher impact in the hydration kinetics of the clinker at early ages, after alite ( $C_3S$ ).<sup>12</sup> Once in contact with water, during the first stage, the celite tends to undergo a dissolution releasing calcium and aluminum ions to the surface of the particle of ( $C_3A$ ), reacting with water molecules to form hydrated tricalcium aluminate ( $C_3AH_6$ ) and releasing a high amount of heat with respect to the other phases.

The peaks that follow the celite phase ( $C_3A$ ), in heat release are the mixture of clinker, belite ( $C_2S$ ) and finally the alite ( $C_3S$ ) respectively, reaching its maximum in the same hydration

time at (approximately 9 minutes), but presenting different heat flow values, due to it is controlled by the rate of dissolution. Thus, belite ( $C_2S$ ) and celite ( $C_3A$ ) phases synthesized by flame spray pyrolysis method (FSP), having a nanometric particle size show a higher dissolution speed compared to the alite phase ( $C_3S$ ) which has a larger particle size due to the production method (solid state reaction), implying a slower dissolution rate and therefore a lower release of heat. In addition, the first peak of the clinker mixture shows a high heat release, due to the dissolution speed of the belite ( $C_2S$ ) and celite ( $C_3A$ ) phases.

Fig. 5 (a) and (b) show the second peak of the calorimetric curve for alite ( $C_3S$ ) and belite ( $C_2S$ ), respectively, after the induction period has elapsed. During the first peak the dissolution of the phases occurred and the C-S-H was formed on the surface of the particles from reaction between the calcium and silicate ions released on the surface. Reached the saturation point, a first layer of C-S-H precipitates on the surface, resulting in the deceleration stage of the heat evolution. A slow dissolution of the particles continues during the induction stage, increasing the concentration of dissolved units, which means that the liquid has diffused through all the material, generating pre-cores and possible cores for their subsequent growth and formation of the reaction products.<sup>10</sup>

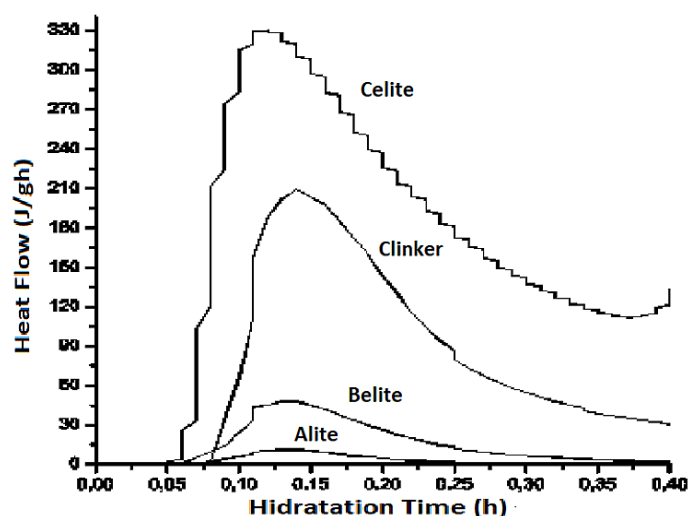


Fig. 4: Comparison of changes in the hydration of Clinker,  $C_3S$ ,  $C_2S$  and  $C_3A$  during the first peak of the isothermal calorimetry curve

As seen in Fig. 5 (a) and (b), the time required to reach the maximum point of the second peak in alite ( $C_3S$ ) is greater than for the belite ( $C_2S$ ), since the particle size has a direct relationship with its reaction speed. Considering that the  $C_2S$  has smaller size than  $C_3S$ , the time of diffusion of the liquid throughout the particle is faster, causing that almost all of the  $Ca^{2+}$  and  $Si^{4+}$  ions have been released once the induction period has ended, therefore, the nucleation and growth of the C-S-H gel occurs more quickly.

The calorimetric curve of the  $C_3A$  celite Fig.5 (c) shows a shorter hydration time to reach its maximum peaks compared to the alite ( $C_3S$ ) and belite ( $C_2S$ ) phases. The heat released by the celite is higher, having an important effect on the initial hydration kinetics of the clinker.<sup>12</sup> Once the phase comes in contact with the water, it starts a dissolution of the structure, releasing calcium and aluminum ions from the surface of the particles, which react with the

water to form hydrated tricalcium aluminate ( $C_3AH_6$ ), in a highly exothermic process.

In Fig.5 (d) it is observed that the second peak of the heat release curve for the clinker mixture requires a long period of induction to be formed in comparison with the individual phases, because the reaction rates of each component change with respect to those shown by the pure phases in the mixture, giving place to a greater number of reactions and interaction of ions, which begin to compete with each other to reorganize and finally promote the formation of the C-S-H gel and hydrated tricalcium aluminate ( $C_3AH_6$ ). Additionally, one of the reasons why this second peak requires a longer formation time, may be the precipitation of calcium aluminate hydrates on the surface of calcium silicates, inhibiting the formation of C-S-H, since there is no presence of gypsum, which help to control the quick setting time of celite.<sup>12,14</sup>

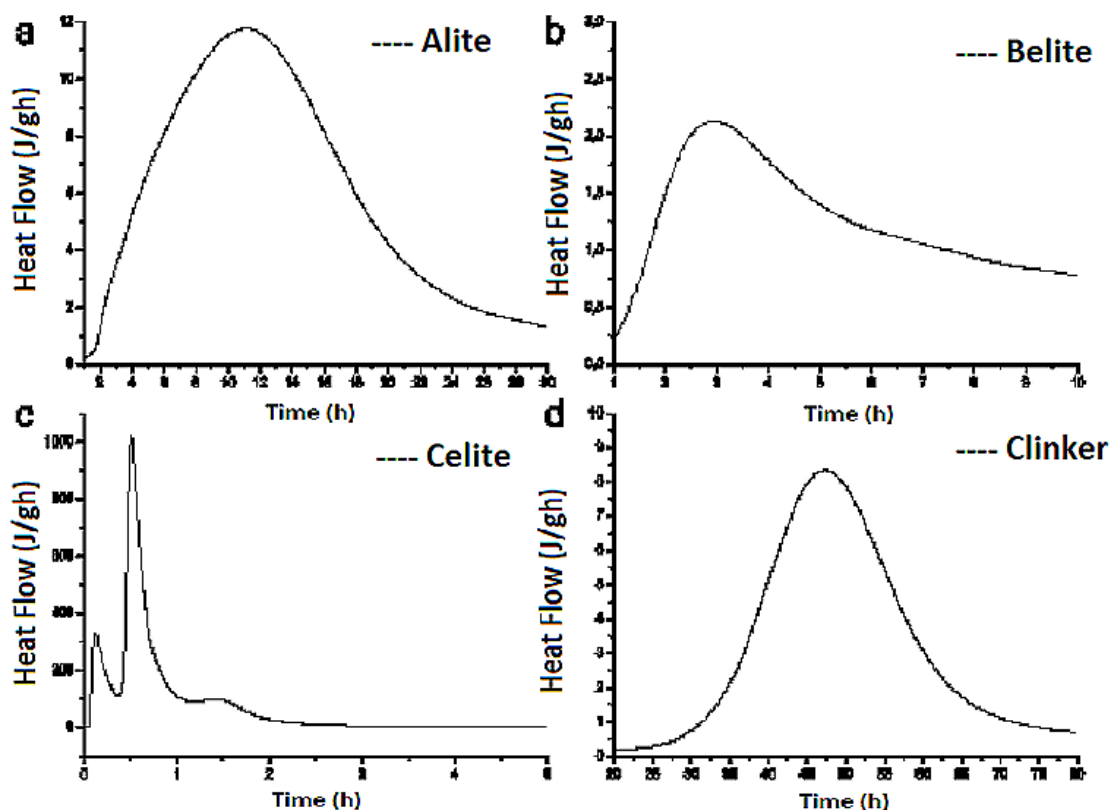


Fig. 5: Second hydration peak (a) alite, (b) belite, (c) celite and (d) clinker mixture obtained by isothermal calorimetry

### Conclusions

The X-ray diffraction results of the belite ( $C_2S$ ) and celite ( $C_3A$ ) phases show that the formation of the cementing phases is possible by flame spray pyrolysis method (FSP).

The hydration measurements of the clinker mixture and its individual phases by isothermal microcalorimetry show that the main factor that intervenes in the hydration process is the dissolution speed of the particles, which depends on the particle size. Smaller sizes, in the order of nanometers, favor a deep contact of water with the surface of the components, increasing the dissolution speed. Thus, a comparison between the micrometric phase of alite ( $C_3S$ ) synthesized by the conventional solid state reaction method and the nanite phase of belite ( $C_2S$ ) synthesized by flame spray pyrolysis method (FSP), belite showed a greater reactivity, since it was hydrated in less time with respect to the alite.

In relation to the clinker mixture, it was observed that its hydration requires a longer period of time

compared to the phases that compose it, because there is a competition between the intrinsic chemical reactions of the process, due to a greater availability of ions of calcium in the medium and the formation of hydrated tricalcium aluminate ( $C_3AH_6$ ).

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### Conflicts of interest

The authors have no conflicts of interest to disclose.

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