



Optimal fluorite/gypsum mineralizer ratio in Portland cement clinkering

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ABSTRACT: This paper presents an analysis of the joint effect of fluorite and gypsum as mineralizers in the manufacture of Portland cement. A laboratory- scale Box-Behnken statistical design was used to quantify the effects of the explanatory variables fluorite content (0.00, 0.25, 0.50, and 0.75%), fluorite/gypsum ratio (2/15, 1/3 and 8/15), and clinkering temperature (1250, 1300, and 1350 °C) on the response variable free CaO content in the clinker produced. The clinker was characterized by the ethylene method, XRD, DSC and optical microscopy. Free CaO decreases of 81% and 56% were found in the mineralized clinker, compared to the same clinker without mineralizers, at 1300 °C and 1250 °C, respectively. Petrographic analysis showed that at lower temperatures, the amount of alite in the mineralized clinker was higher than the amount of alite in the clinker without mineralizers. The best condition was found for the fluorite/gypsum ratio of 2/15.

KEYWORDS: Mineralizers; Fluorite; Gypsum; Clinker; Clinkering

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RESUMEN: *Relación óptima de los mineralizadores fluorita/yeso en la clinkerización del cemento Portland.* Este artículo presenta el efecto combinado de la fluorita y el yeso como mineralizadores. Se usó el diseño experimental estadístico Box-Behnken, a escala de laboratorio, para cuantificar el efecto de la fluorita en porcentajes de 0.00, 0.25, 0.50 y 0.75%; relaciones fluorita/yeso de 2/15, 1/3 y 8/15; con temperaturas de clinkerización de 1250, 1300 y 1350 °C y la cal libre como variable de respuesta. El clinker producido fue caracterizado midiendo el contenido de cal libre por el método de etileno, DRX, DSC y microscopía óptica. Se encontró un descenso de la cal libre del 81 y 56% en el clinker mineralizado en comparación con el clinker sin mineralizadores a 1300 y 1250 °C respectivamente. El análisis petrográfico mostró que la cantidad de alita en el clinker mineralizado a bajas temperaturas es más alta que en el clinker sin mineralizadores. La mejor condición se encontró para la relación fluorita/yeso de 2/15.

PALABRAS CLAVE: Mineralizadores; Fluorita; Yeso; Clinker; Clinkerización

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1. INTRODUCTION

Portland cement is obtained by comminuting clinkers and adding one or more forms of calcium sulfate. The addition of other raw materials (pozzolans and

fillers) is allowed, provided that they do not negatively affect the properties of the resulting cement (1).

In the Portland cement manufacturing process, fuel costs during the clinkering stage account for approximately 30–50% of cement production costs (2).

This percentage is due to the high kiln operation temperature, which is around 1500 °C. This implies high fossil fuel-based energy consumption, greenhouse gas emissions, a short useful life of the refractory material, and high electricity usage, among other issues (3–6).

One of the most significant environmental problems of the cement industry is that 0.73–0.99 tons of CO₂ are emitted per ton of cement manufactured, depending on the clinker/cement ratio and other factors. From these data, some researchers have estimated that the cement industry is responsible for 5–7% of all global anthropogenic emissions (7, 8).

Many solutions have been proposed to address these drawbacks. These include: the use of energy alternatives (9), technological developments in the clinkering process (4), the use of by-products as raw materials (6, 9–11), the use of mineralizers and fluxes to reduce the clinkering temperature and accelerate the formation of the main mineral phases (10, 12, 13), the use of mineral additions to the cement (puzzolans and fillers) to lower the clinker/cement ratio (14), alternative cements (10, 15, 16), and the development of high-performance concrete (17), among others. The use of mineralizers has proven to be a very good option in this regard, but it is not yet fully understood.

Mineralization accelerates the formation process of the main constitutive phases of the clinker (C₃S and C₂S) by changing their thermodynamic stability. This allows them to appear at a lower temperature (12, 13). The inclusion of minor elements from mineralizers can lead to modifications in the hydraulic activity of silicates, due to the formation of solid solutions or changes in their structure (18).

Mineralizers can act as fluxes. A flux is a material with high heat transfer that melts at a lower temperature than the compound of interest, in this case the calcium silicates. Fluxes decrease the temperature at which aluminium and iron oxide melt. Furthermore, they decrease the viscosity and surface tension of the liquidus that facilitate the transport of reactants and allow silicates to form at lower temperatures (12, 13). This makes it possible to use less coal and thus emit lower levels of CO₂, NO_x, and SO_x into the atmosphere.

The mineralizers and fluxes studied in the clinkering process include Titanium, Manganese, Silver, Iron, Zinc, Chrome, Nickel, Copper (9, 19–22), phosphate gypsum (23), sulfate, fluorite (24–27), MgO (28, 29), and potassium fluoride (24).

In general, mineralizers are responsible for the following (26, 30, 31):

A decrease in:

- Clinkering temperature and liquid phase formation;
- Caloric consumption;

- Gas emissions (CO₂, SO_x, NO_x), due to decreased fuel usage;
- Residence time inside the kiln, due to the formation of phases at a lower temperature (with the same heating rate of a process without mineralization);
- Energy consumption in the milling process, because a more pulverized clinker is produced;
- Costs, due to decreased fuel usage.

An increase in:

- C₃S content, due to increased ionic mobility;
- C₃S and C₂S reactivity, due to the crystalline structure formed by trace elements;
- Final product strength properties, due to the new crystalline structure;
- Cement mill production, because the higher porosity of the clinker produced makes it easier to mill;
- Service life of furnace firebrick, due to the lower working temperatures.

Most mineralizers employed contain fluorine, due to its electronegativity. The most common of these are fluorides and fluoro-silicates (12, 13).

CaF₂ is the material that is most used at a global level, because it acts as both a mineralizer and a flux. It lowers the alite formation temperature by improving solid-state diffusions (28). CaF₂ also reduces the formation temperature, viscosity and surface tension of the liquid phase (28). At bench/lab scale, fluorite causes the clinkering temperature to decrease by around 130 °C (26). When 0.4 wt.% CaF₂ is added to the clinker, the amount of alite increases and the mechanical properties improve by about 20% (32). According to Chatterjee (4), this improvement in cement strength occurs because the fluorine enables the alite to change from a monoclinic (M₃) to a rhombohedral polymorph.

The use of gypsum in some cement factories has had positive environmental and energetic results (25). However, a disadvantage of using sulfate as a mineralizer is that it causes belite stabilization, which inhibits alite formation (4, 10). This effect is counteracted if sulfate is combined with fluoride (33).

The use of CaF₂ and CaSO₄·2H₂O in clinkering can allow the maximum clinkering temperature decreases to 1350 °C (34) due to the formation of fluorellestadite (3C₂S·CaSO₄·CaF₂), which is an intermediate phase in the liquid phase formation (30). For this reason, these mineralizers are capable of partially substituting for C₃A and C₄AF (35, 36). This combination has been so successful that some researchers suggest that other mineralizers without F and SO₃ are not likely to be put into actual use (37).

Other researchers have shown that coal consumption in the production of white cement can be reduced by 9% by using a CaF₂-CaSO₄ mixture (30). It is known that when fluorite and gypsum are

combined as mineralizers, the fluorite accelerates alite formation, while the gypsum diminishes the liquid phase formation temperature. Additionally, fluorite and gypsum are natural minerals that are readily available for industrial use.

In the present research, we determined the optimal fluorite/gypsum ratio for reaching the maximum decrease in clinkering temperature for gray cement production.

2. EXPERIMENTAL

Clinkers with and without mineralizers were produced in the laboratory with reagent oxides, at different temperatures (1250, 1300, and 1350 °C).

Raw materials were characterized by X-Ray fluorescence (XRF) to determine their chemical composition.

Samples were formulated with CaO, SiO₂, Al₂O₃, Fe₂O₃ and with the mineralizers CaF₂ and CaSO₄·2H₂O. A reference clinker was produced in the laboratory for each temperature, taking into consideration the lime saturation factor (LSF=95.18), silica modulus (SM=2.51) and alumina modulus (AM=1.59). Fluorite and gypsum were added to raw meal in percentage in weight, with fluorite in 0.25, 0.50, and 0.75 wt.% and a fluorite/gypsum ratio of 2/15, 8/15, and 1/3 (Table 1).

Afterwards, the raw meal was homogenized and spheres with a diameter of 2.5 cm were formed using deionized water.

Clinker formation was studied mainly on the basis of free lime content in the burned samples.

TABLE 1. Matrix tests according to the Box-Behnken design

Test	CaF ₂ /CaSO ₄ ·2H ₂ O Ratio	Mineralizer (CaF ₂) %	Temperature °C
1	2/15	0.25	1300
2	2/15	0.75	1300
3	8/15	0.25	1300
4	8/15	0.75	1300
5	2/15	0.50	1250
6	2/15	0.50	1350
7	8/15	0.50	1250
8	8/15	0.50	1300
9	1/3	0.25	1250
10	1/3	0.25	1350
11	1/3	0.75	1250
12	1/3	0.75	1350
13	1/3	0.50	1300
14	1/3	0.50	1300
15	1/3	0.50	1300
Central 1	1/3	0.50	1300
Central 2	1/3	0.50	1300
Central 3	1/3	0.50	1300

This is the most widely used procedure because the calcium oxide, initially formed by CaCO₃ dissociation, is gradually consumed by the clinker phases (20). The free lime was measured with the ethylene method; optical microscopy; Differential Scanning Calorimetry (DSC); and X-Ray Diffraction (XRD).

2.1. Materials

Reagent grade CaO, SiO₂, Al₂O₃, and Fe₂O₃ were used. Aldrich, Carlo Erba and Sigma supplied these oxides.

Fluorite (CaF₂) with 80.99% purity was obtained from Minera Las Cuevas (Mexico) and Gypsum (CaSO₄·2H₂O) was obtained from Spain.

2.2. Methods

2.2.1. Chemical analysis

X-ray fluorescence (XRF) was performed on raw materials using beads fused with lithium boride (B₄Li₂O₇). The equipment used was a Thermo ARL 9800 XP spectrometer.

2.2.2. High temperature furnace

A BLF 17/3 Carbolite furnace was used to produce the clinker, with a maximum temperature of 1700 °C and 220 V. The heating rate for all tests was the same (10 °C/min); only the maximum clinkering temperature changed. The residence time for each sample at higher temperatures was always 40 minutes. Clinkering processes were carried out in an artisanal crucible made from refractory brick, reference ALMAG AF of Refratechnik. When the heating process for each test was completed, the crucible with the red hot sample was removed from the furnace. All clinkers were cooled with air from a compressor at 5 psi for 10 minutes to reach a final temperature of approximately 40 °C.

2.2.3. X-ray diffraction (XRD)

The XRD patterns were collected in a PANalytical X'Pert PRO MPD, with a Cu source, Bragg-Brentano configuration, a range from 15° to 70° of 2theta, an X Celerator detector step of 0.016° and an accumulation time of more than 10000 counts in the main peak. The mineralogical analysis was performed by Rietveld methodology using High Score Plus software and the Inorganic Crystal Structure Database (ICSD).

2.2.4. Differential Scanning Calorimetry (DSC)

This was performed using SDT Q600 equipment with an inert atmosphere of N₂, an alumina melting pot of 90 mL, a scan rate of 20 °/min and a temperature ramp from 25 °C to 1500 °C.

2.2.5. Optical Microscopy

An OLYMPUS MMQC-005 petrographic microscope, model BX41, was used to qualitatively analyze the clinker obtained, in order to identify the phases formed. The petrographic analysis was performed with reflected light on polished specimens etched with nital (nitric acid at 1% in isopropyl alcohol).

2.2.6. Measurement of free lime with the ethylene method

This test was performed to provide an indicator of the degree of clinkering in the material. Free lime was measured by dissolving CaO in a methanol:ethylene glycol (1:2) mixture at a temperature of 80 °C with constant agitation. After the solution was filtered, it was titrated with 0.1 N hydrochloric acid using bromocresol green - Methyl red as a mixed indicator.

2.2.7. Experimental design

A Box-Behnken statistical design was used in this study. The factors considered were fluorite content, fluorite/gypsum ratio and clinkering temperature. The response variable was free lime. The levels of each factor were taken from previous studies on mineralization (26, 35). This study explored the effects of fluorite and gypsum at low and high levels. Table 1 shows the matrix design for randomized trials. The central points are additional experimental runs located at a midpoint between the lower and higher level of all factors. This is done to estimate experimental error and adjust the model.

3. RESULTS AND DISCUSSION

3.1. Characterization of raw materials

The X-Ray Fluorescence (XRF) results showed that the oxides and mineralizers used had high purity (Table 2). This enables a better understanding of the effect of fluorite and gypsum on clinkering temperature and prevents that mineralizers interact with other compounds as contaminants.

3.2. Characterization of clinkers

3.2.1. Measurement of free CaO in the clinker: Free CaO determined by titration is shown in Table 3

The results obtained were grouped by clinkering temperature, as follows (Figures 1, 2, and 3):

At 1300 °C and 1250 °C (Figures 2 and 3) all the formulations with mineralization had less free CaO than the reference sample, as a result of more efficient

TABLE 2. Chemical analysis of raw materials by XRF

Oxide (%)	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	CaO	CaF ₂	CaSO ₄ ·2H ₂ O
SiO ₂	–	–	98.65	–	4.75	1.58
Al ₂ O ₃	–	93.80	0.03	–	0.42	0.57
Fe ₂ O ₃	93.37	–	0.05	–	0.10	0.18
CaO	–	0.21	0.39	85.81	43.50	33.50
MgO	–	–	–	–	–	0.20
SO ₃	–	0.32	–	0.82	0.05	42.10
F	–	–	–	–	47.80	–
Na ₂ O	–	0.02	–	–	–	–
K ₂ O	–	–	0.08	–	0.14	0.08
MnO	–	0.01	0.01	–	–	0.01
P ₂ O ₅	–	–	–	0.05	0.18	0.05
Sr	–	–	–	–	–	0.09
TiO ₂	–	0.01	0.04	–	0.14	0.01
Cr ₂ O ₃	–	–	–	–	0.01	–
L.O.I	0.25	5.81	0.76	12.33	3.91	22.30

TABLE 3. Matrix tests according to the Box-Behnken design, and free lime obtained

Test	CaF ₂ /CaSO ₄ ·2H ₂ O Ratio	Mineralizer (CaF ₂) %	Temperature °C	Free CaO in clinker
1	2/15	0.25	1300	6.95
2	2/15	0.75	1300	1.93
3	8/15	0.25	1300	8.15
4	8/15	0.75	1300	4.29
5	2/15	0.50	1250	5.42
6	2/15	0.50	1350	2.24
7	8/15	0.50	1250	8.28
8	8/15	0.50	1300	2.54
9	1/3	0.25	1250	10.39
10	1/3	0.25	1350	4.04
11	1/3	0.75	1250	5.49
12	1/3	0.75	1350	3.14
13	1/3	0.50	1300	6.24
14	1/3	0.50	1300	5.32
15	1/3	0.50	1300	5.20
Central 1	1/3	0.50	1300	4.70
Central 2	1/3	0.50	1300	5.22
Central 3	1/3	0.50	1300	5.20

clinkering (the reaction of the raw materials with the mineralizers increased alite production). The reference sample at 1350 °C (Figure 1) had lower free CaO than the mixtures with fluorite and gypsum at the same temperature. One hypothesis to explain this behavior is that when the samples reached 1350 °C, fluorine volatilization occurred and this became a

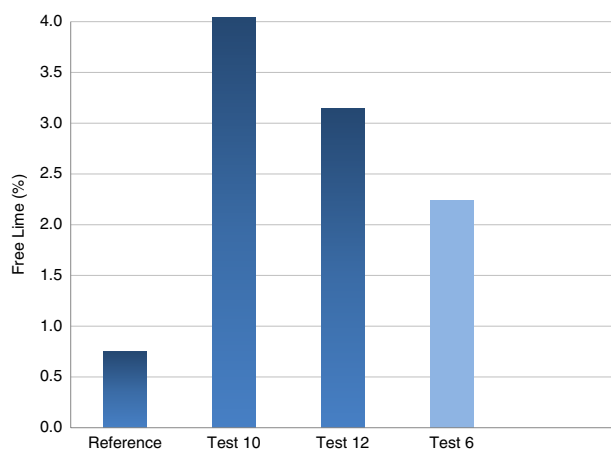


FIGURE 1. Free CaO at 1350 °C.

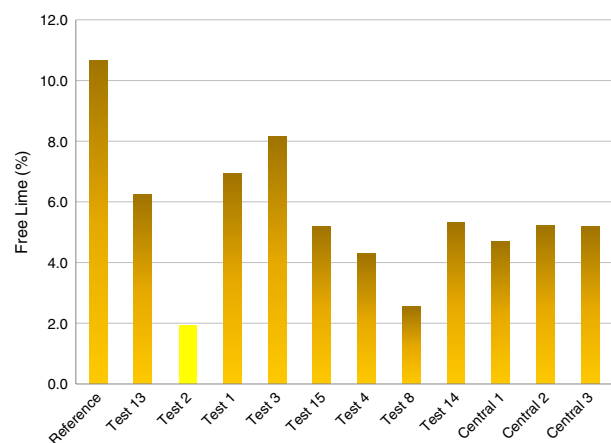


FIGURE 2. Free CaO at 1300 °C.

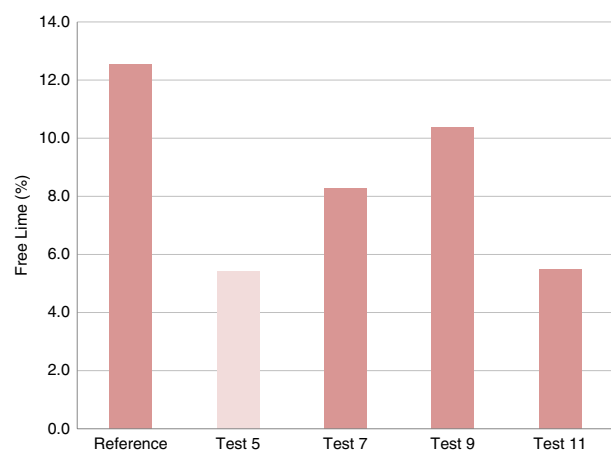


FIGURE 3. Free CaO at 1250 °C.

limiting factor for mineralization. It is well known that fluorine evaporates easily at high temperatures, like alkalis and sulfates (28).

The tests that showed the lowest free CaO (tests 6, 2, and 5) are highlighted in Figures 1, 2, and 3. These formulations had a $\text{CaF}_2/\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ratio of 2/15. The high fluorite content (0.75 and 0.5%) facilitated the reaction of C_2S with CaO to form C_3S .

In Figure 2 and Table 3, when comparing the reference at 1300 °C (without mineralization) with test 2 ($\text{CaF}_2/\text{CaSO}_4 \cdot 2\text{H}_2\text{O}=2/15$, temperature=1300 °C, and fluorite=0.75) an 81% decrease in free CaO can be observed in the mineralized clinker. Moreover, in Figure 3 and Table 3, when comparing the reference at 1250 °C with test 5 ($\text{CaF}_2/\text{CaSO}_4 \cdot 2\text{H}_2\text{O}=2/15$, temperature=1250 °C, and fluorite=0.50) a 56% decrease in free CaO can be observed. Thus, the $\text{CaF}_2/\text{CaSO}_4 \cdot 2\text{H}_2\text{O}=2/15$ ratio plays an important role in reducing clinkering temperature, i.e., in the formation of calcium silicates (C_2S and C_3S). The effect of the 2/15 fluorite/gypsum ratio on the clinker was more noticeable at 1300 °C.

3.2.2. X-ray diffraction (XRD)

Table 4 and Figures 4, 5, and 6 show the identification and quantification of clinker phases with and without mineralizers. In order to ensure a good fit of the calculated pattern to the observed data, we looked for a weighted-profile R-value (Rwp) below 10% for all samples.

Figure 4 (1350 °C) and Table 4 show that alite content decreased and belite content increased when mineralizers were present. This is consistent with the higher free lime content found in these samples by titration, which means that the clinkering process for the mineralized clinker was incomplete at this temperature.

Figures 5 and 6 (1300 °C and 1250 °C) and Table 4 show that alite content increased and belite content decreased when mineralizers were present. This is consistent with the lower free lime content found in these samples by titration, which means that the mineralized clinker was more sintered at these temperatures. This result is consistent with those of researchers including Akin (21), who found that C_3S formation increased with the addition of fluorine.

The free CaO of the mineralized clinker was lower than that of the clinker without fluorite and gypsum (Figures 5 and 6). This indicates that the mineralizers improved the clinkering process.

3.2.3. Differential Scanning Calorimetry (DSC)

Figures 7, 8, and 9 show that the raw material with mineralizers presented clinkering (C_3S and C_2S formation) at lower temperatures than the raw material without mineralizers.

The DSC technique also showed that the mineralizers had the greatest effect at temperatures between 1250 °C and 1300 °C.

TABLE 4. Mineralogical analysis of the clinker with and without mineralization (XRD)

	Quantitative analysis of clinkers (wt.%)					
	1350 °C without Mineralizer	1350 °C with Mineralizer Test 6	1300 °C without Mineralizer	1300 °C with Mineralizer Test 2	1250 °C without Mineralizer	1250 °C with Mineralizer Test 5
	C ₃ S	55.0	44.7	37.6	48.2	29.2
β-C ₂ S	24.1	36.5	41.8	32.1	49.4	36.1
C ₃ A cubic	5.1	3.3	–	2.4	–	1.8
C ₃ A orthorhombic	0.4	–	3.0	–	3.9	–
C ₄ AF	14.2	13.9	9.2	15.3	5.7	16.8
CaO	0.4	0.4	2.4	–	6.2	0.4
MgO	0.4	0.5	0.6	0.4	0.6	0.5
K ₂ SO ₄	–	–	0.6	–	1.1	–
CaSO ₄ ·2H ₂ O	–	–	–	0.4	–	0.6
CaSO ₄ ·1/2H ₂ O	0.4	–	1.2	–	1.3	–
CaSO ₄	–	–	–	0.5	–	–
Ca(OH) ₂	–	0.7	3.7	0.6	2.6	2.4
11CaO·7Al ₂ O ₃ ·CaF ₂	–	–	–	–	–	1.5

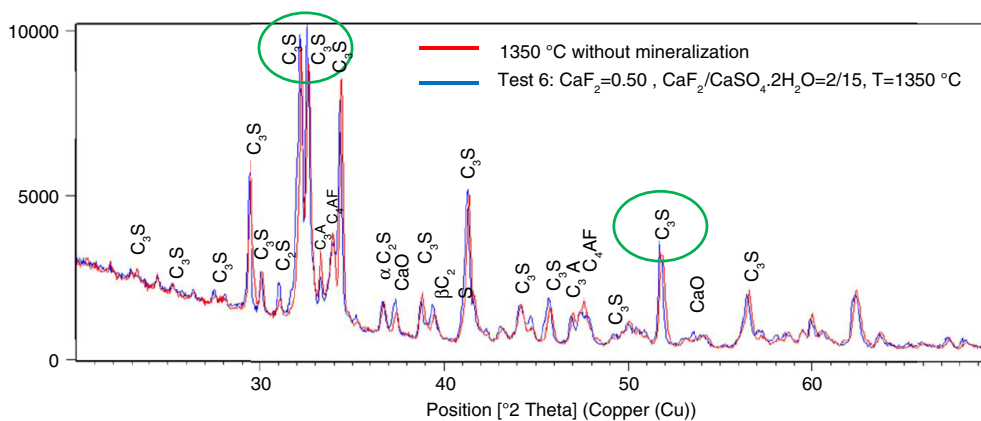


FIGURE 4. Diffraction patterns of raw mixture without mineralizer and test 6 mixture at 1350 °C.

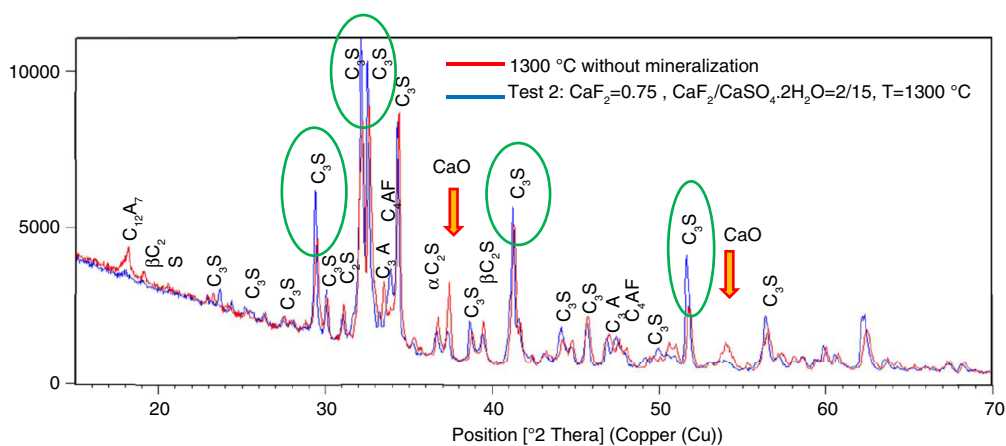


FIGURE 5. DRX of raw mixture without mineralizer and test 2 mixture at 1300 °C.

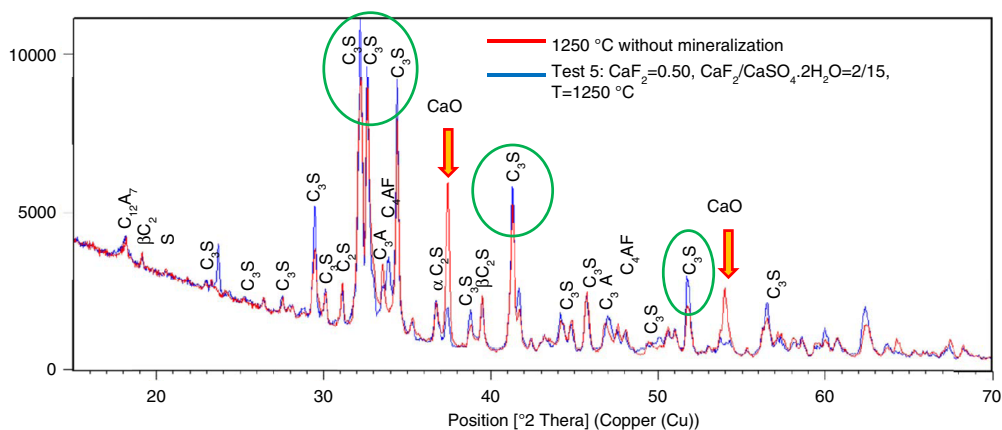


FIGURE 6. DRX of raw mixture without mineralizer and test 5 mixture at 1250 °C.

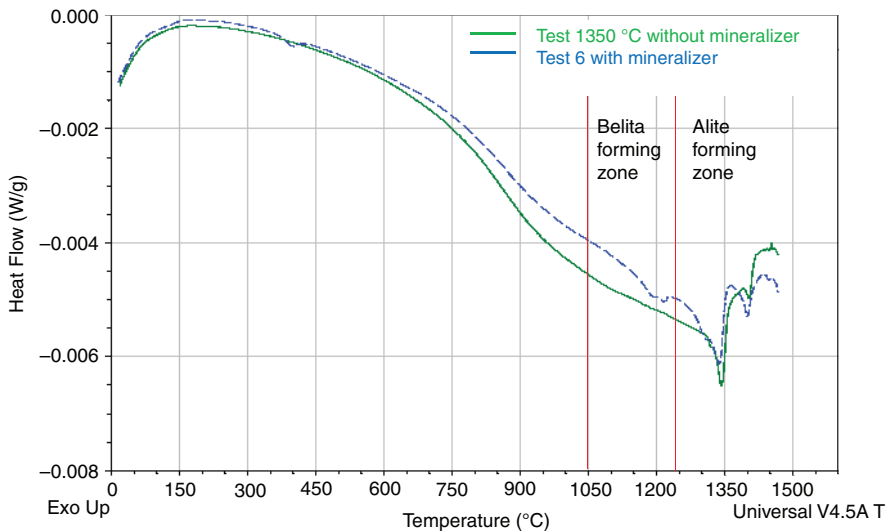


FIGURE 7. DSC of raw mixture without mineralizer and test 6 mixture at 1350 °C.

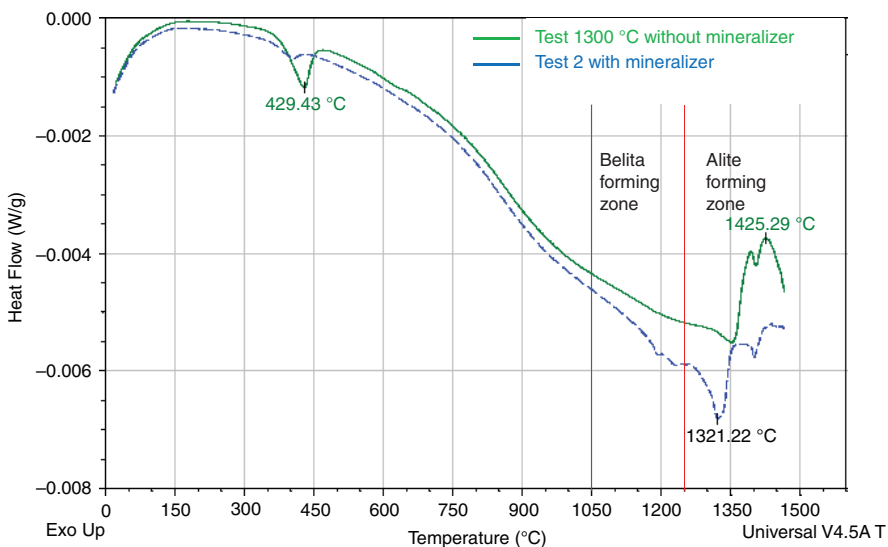


FIGURE 8. DSC of raw mixture without mineralizer and test 2 mixture at 1300 °C.

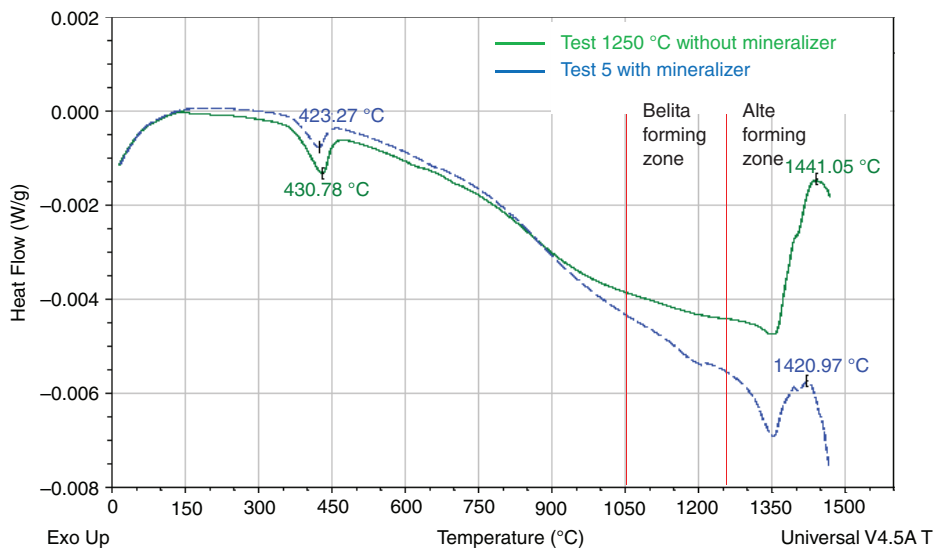


FIGURE 9. DSC of raw mixture without mineralizer and test 5 mixture at 1250 °C.

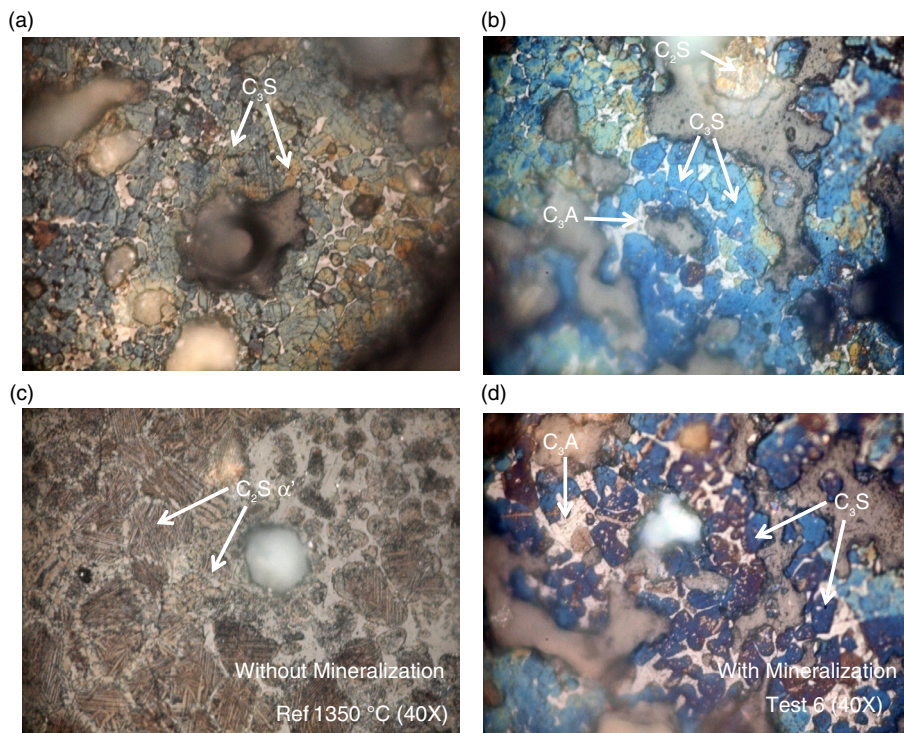


FIGURE 10. Petrographic comparison of mineralized clinker - test 6 (photographs b and d) and clinker without mineralizers (photographs a and c), at 1350 °C.

3.2.4. Optical Microscopy (Petrography)

Figures 10, 11, and 12 show better-defined particles of calcium silicates and calcium aluminates in the mineralized clinker than in the clinker without mineralizers at the same temperature.

This indicates that the mineralizers had a positive effect on the clinking process. The clinking process at 1250 °C (Figure 12) requires a longer time or higher sintering temperature in order to achieve the complete formation of the clinker's phases.

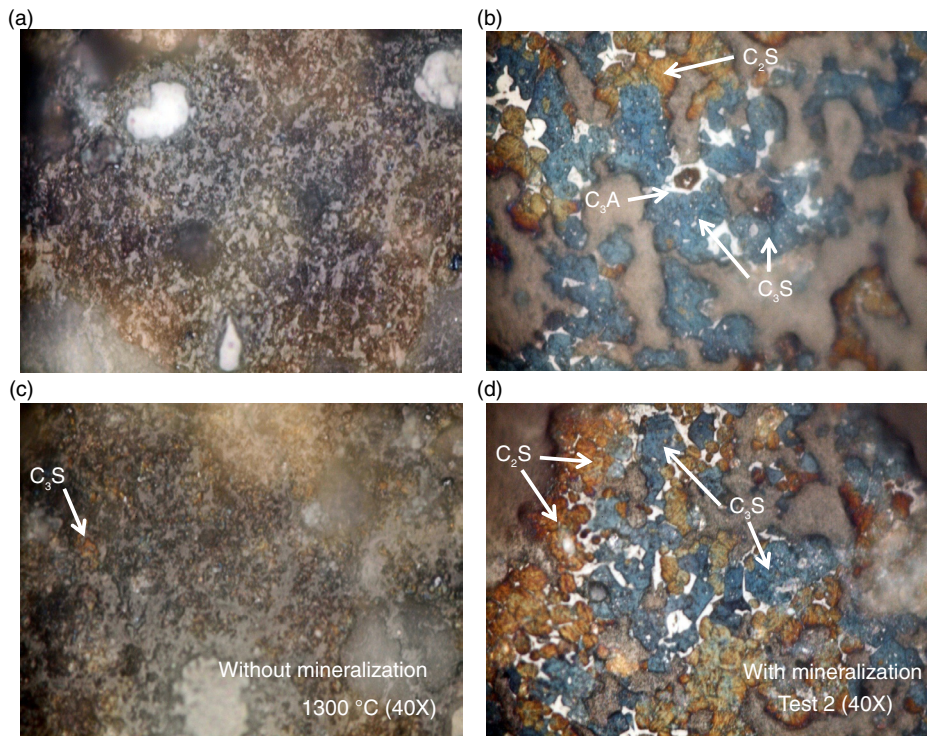


FIGURE 11. Petrographic comparison of mineralized clinker - test 2 (photographs b and d) and clinker without mineralizers (photographs a and c), at 1300 °C.

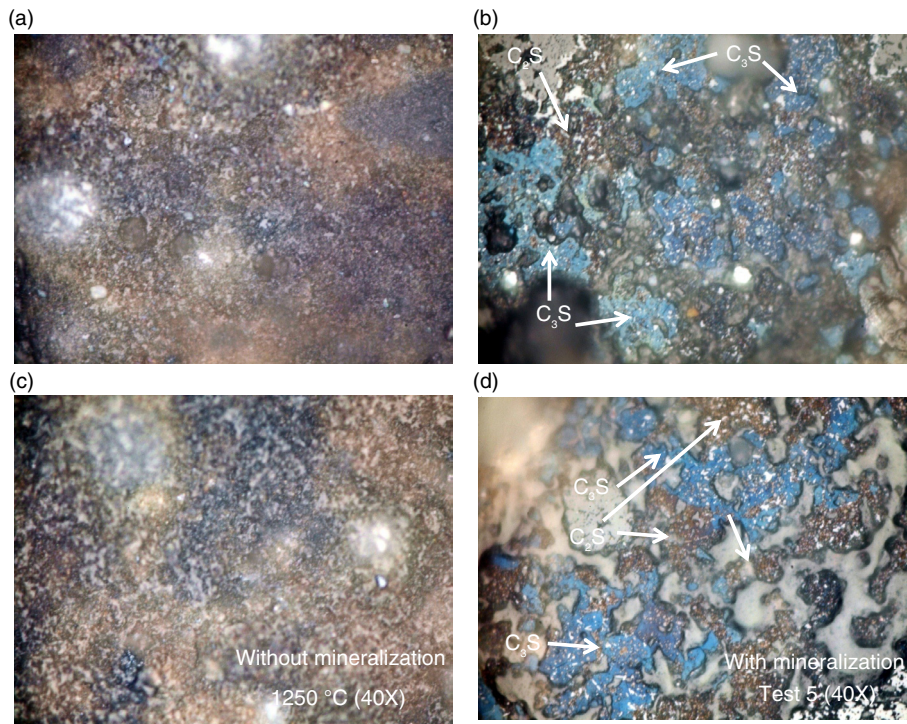


FIGURE 12. Petrographic comparison of mineralized clinker - test 5 (photographs b and d) and clinker without mineralizers (photographs a and c), at 1250 °C.

TABLE 5. Alite size

Sample	Alite size (μm)
Ref 1350 °C	7.82
Test 6	11.00
Ref 1300 °C	<7.00
Test 2	28.00
Ref 1250 °C	<7.00

An idiomorphic, equidimensional alite shape was obtained at a $\text{CaF}_2/\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ratio of 2/15 and a temperature greater than or equal to 1300 °C (tests 2 and 6). The clinker also had improved reactivity in these conditions because it obtained a reactive phase of belite as α' and α at lower temperatures. In contrast, xenomorphic crystals with irregular shapes were observed in the clinker without mineralization, indicating a lack of clinkering. This result is consistent with those of researchers including García-Díaz et al. (19), who found that CaF_2 affected clinker phase content and polymorphism.

In regard to the assessment of alite size, the samples with mineralizers always presented larger alite sizes (Table 5). Test 2 reached a regular size

(28 micrometers) with evidence of a complete reaction and crystallization. Based on this, it can be concluded that the fluorite/gypsum ratio of 2/15 works efficiently at 1300 °C, allowing crystalline phases to form at a lower temperature.

Free CaO measurement in the clinker, XRD, DSC and optical microscopy were used to show that fluorite and gypsum have a significant effect at temperatures of 1300 °C and 1250 °C. It can be concluded that the fluorite/gypsum ratio of 2/15 works efficiently at 1300 °C, since the best results corresponded to that sample (the greatest amount of alite, the least belite, the smallest amount of free lime and regularly sized alite).

3.2.5. Statistical model

The R-programming language was used in the analysis and modeling of the Box-Behnken experimental design, because it has statistical packages to optimize the process variables. For this boundary, curves were generated to identify the trend of the variables studied. The results obtained in the simulation showed the same behavior as the experimental results. The behavior obtained (Figure 13) showed that increases in fluorite and temperature led

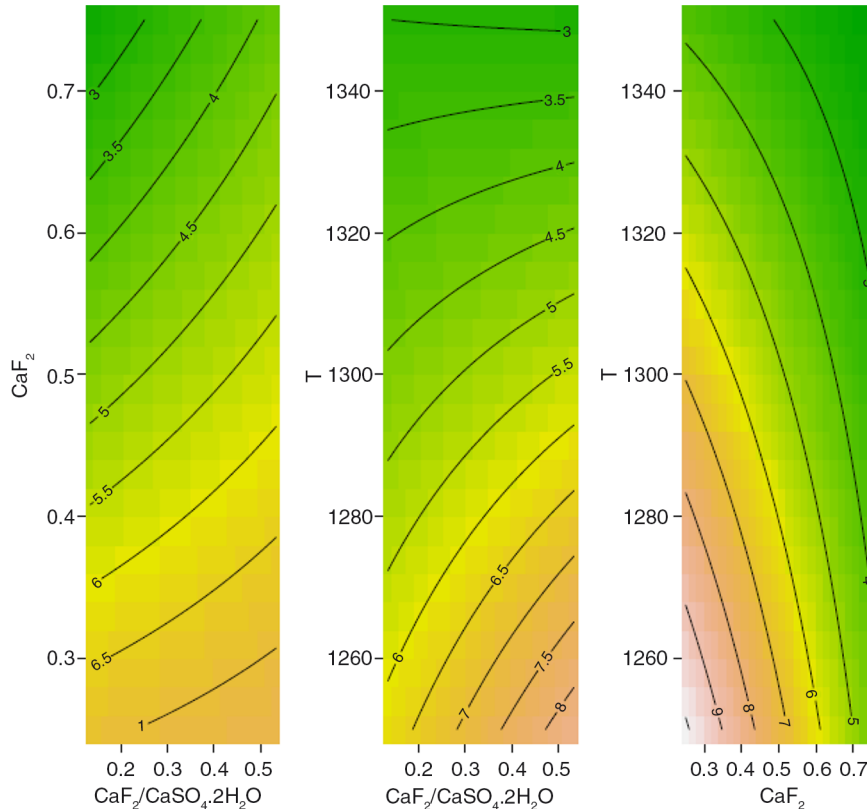


FIGURE 13. Boundary curves of the effect of fluorite, gypsum and temperature on free lime in the clinker.

to decreased free lime in the clinker, while the low-est fluorite/gypsum ratio (2/15) improved clinkering (green areas).

4. CONCLUSIONS

By using fluorite and gypsum in the production of Portland cement clinker, it is possible to decrease the clinkering temperature, and thus reduce fuel consumption and emissions.

Petrographic analysis showed the appearance of calcium silicates and calcium aluminates at a lower temperature when mineralizers were incorporated into the raw materials.

The $\text{CaF}_2/\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ratio of 2/15 favored the production of idiomorphic alite in the appropriate particle size and amount and belite α and α' in the mineralized clinker. It showed evidence of a reactive clinker. This could enable cement plants to increase mineral additions to the cement, which is another way to reduce costs and emissions associated with lower clinker consumption.

Mineralizers showed a positive effect on free CaO content in the clinker. At 1300 °C and 1250 °C, all formulations with mineralization had less free CaO than the reference sample, which indicates efficient clinkering.

The clinker formulation presented in test 2 ($\text{CaF}_2/\text{CaSO}_4 \cdot 2\text{H}_2\text{O}=2/15$, temperature=1300 °C, and fluorite=0.75) had an 81% reduction in free CaO compared to the clinker without mineralization at the same temperature. This ratio was the best formulation found, from an energy standpoint. This represents temperature savings of 150 °C compared to a conventional clinker (1450 °C).

Fluorite and gypsum did not have a significant effect at a temperature higher than or equal to 1350 °C.

REFERENCES

- Taylor, H.F.W. (1990) Cement Chemistry, Academia Press, Inc. New York.
- Hasanbeigi, A.; Price, L.; Lin, E. (2012) Emerging energy-efficiency and CO₂ emission-reduction technologies for cement and concrete production: A technical review. *Renewable and Sustainable Energy Reviews* 16, 6220–6238. <http://dx.doi.org/10.1016/j.rser.2012.07.019>.
- Lawrence, C. (1988) Lea's chemistry of cement and concrete. Cap 9: Production of Low-Energy Cements. 4th ed.
- Chatterjee, A.K. (2011) Chemistry and engineering of the clinkerization process — Incremental advances and lack of breakthroughs. *Cem. Concr. Res.* 41, 624–641. <http://dx.doi.org/10.1016/j.cemconres.2011.03.020>.
- Van Oss, H.G.; Padovani, A.C. (2003) Cement manufacture and the environment, part II: environmental challenges and opportunities. *J. Ind. Ecol.* 7, 93–126. <http://dx.doi.org/10.1162/108819803766729212>.
- Puertas, F.; García-Díaz, I.; Barba, A.; Gazulla, M.F.; Palacios, M.; Gómez, M.P.; Martínez-Ramírez, S. (2008) Ceramic wastes as alternative raw materials for Portland cement clinker production. *Cem. Concr. Comp.* 30, 798–805. <http://dx.doi.org/10.1016/j.cemconcomp.2008.06.003>.
- Garnet, E. (2004) Industrially interesting approaches to “low CO₂” cements. *Cem. Concr. Res.* 34, 1489–98. <http://dx.doi.org/10.1016/j.cemconres.2004.01.021>.
- World Business Council for Sustainable Development (WBCSD)/International Energy Agency (IEA). (2009a) Cement Technology Roadmap 2009—Carbon emissions reductions up to 2050. Available: www.iea.org/papers/2009/Cement_Roadmap.pdf.
- Gineys, N.; Aouad, G.; Sorrentino, F.; Damidot, D. (2011) Incorporation of trace elements in Portland cement clinker: Thresholds limits for Cu, Ni, Sn or Zn. *Cem. Concr. Res.* 41, 1177–1184. <http://dx.doi.org/10.1016/j.cemconres.2011.07.006>.
- García-Díaz, I.; Palomo, J.G.; Puertas, F. (2011) Belite cements obtained from ceramic wastes and the mineral pair $\text{CaF}_2/\text{CaSO}_4$. *Cem. Concr. Comp.* 33, 1063–1070. <http://dx.doi.org/10.1016/j.cemconcomp.2011.06.003>.
- Ying-Liang Chen; Juu-En Chang; Pai-Huang Shih; Ming-Sheng Ko; Yi-Kuo Chang; Li-Choung Chiang. (2010) Reusing pretreated desulfurization slag to improve clinkerization and clinker grindability for energy conservation in cement manufacture. *J. Env. Manag.* 91, 1892–1897. <http://dx.doi.org/10.1016/j.jenvman.2010.04.006>.
- Emanuelson, A.; Hansen, S.; Viggø, E. (2003) A comparative study of ordinary and mineralised Portland cement clinker from two different production units Part I: Composition and hydration of the clinkers. *Cem. Concr. Res.* 33 [10] 1613–1621. [http://dx.doi.org/10.1016/S0008-8846\(03\)00115-7](http://dx.doi.org/10.1016/S0008-8846(03)00115-7).
- Emanuelson, A.; Landa-Cánovas, A.; Hansen, S. (2003) A comparative study of ordinary and mineralized Portland cement clinker from two different production units Part II: Characteristics of the calcium silicates. *Cem. Concr. Res.* 33, 1623–1630. [http://dx.doi.org/10.1016/S0008-8846\(03\)00114-5](http://dx.doi.org/10.1016/S0008-8846(03)00114-5).
- Tongsheng Zhang; Xiangyang Liu; Jiangxiang Wei; Qijun Yu. (2014) Influence of preparation method on the performance of ternary blended cements. *Cem. Concr. Comp.* 52, 18–26. <http://dx.doi.org/10.1016/j.cemconcomp.2014.04.005>.
- Komnitsas, K.; Zaharaki, D. (2007) Geopolymerisation: A review and prospects for the minerals industry. *Minerals Engineering*. 20, 1261–1277. <http://dx.doi.org/10.1016/j.mineng.2007.07.011>.
- Péra, J.; Ambroise, J. (2004) New applications of calcium sulfoaluminate cement. *Cem. Concr. Res.* 34, 671–676. <http://dx.doi.org/10.1016/j.cemconres.2003.10.019>.
- Ghafari, E.; Costa, H.; Júlio, E.; Portugal, A.; Duraes, L. (2014) The effect of nanosilica addition on flowability, strength and transport properties of ultra high performance concrete. *Mat. Design.* 59, 1–9. <http://dx.doi.org/10.1016/j.matdes.2014.02.051>.
- Moir, G.K.; Glasser, F.P. (1992) Mineralisers, modifiers and activators in the clinkering process, Proceedings of the 9th International Congress on the Chemistry of Cement, New Delhi 1992, vol. 1, National Council for Cement and Building Materials, New Delhi, 25–152.
- Stephan, D.; Mallmann, R.; Knöfel, D.; Härdtl, R. (1999) High intakes of Cr, Ni, and Zn in clinker art I. Influence on burning process and formation of phases. *Cem. Concr. Res.* 29, 1949–1957. [http://dx.doi.org/10.1016/S0008-8846\(99\)00195-7](http://dx.doi.org/10.1016/S0008-8846(99)00195-7).
- Kolovos, K.; Tsvivilis, S.; Kakali, G. (2002) The effect of foreign ions on the reactivity of the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ system Part II: Cations. *Cem. Concr. Res.* 32, 463–469. [http://dx.doi.org/10.1016/S0008-8846\(01\)00705-0](http://dx.doi.org/10.1016/S0008-8846(01)00705-0).
- Trezza, M.A.; Scian, A.N. (2007) Waste with chrome in the Portland cement clinker production. *J. Haz. Mat.* 147, 188–196. <http://dx.doi.org/10.1016/j.jhazmat.2006.12.082>.
- Xian-Wei Ma; Hu-Xing Chen; Pei-Ming Wang. (2010) Effect of CuO on the formation of clinker minerals and the hydration properties. *Cem. Concr. Res.* 40, 1681–1687. <http://dx.doi.org/10.1016/j.cemconres.2010.08.009>.
- Kacimi, L.; Simon-Masseron, A.; Ghomari, A.; Derriche, Z. (2006) Reduction of clinkerization temperature by using phosphogypsum. *J. Haz. Mat.* B137, 129–137. <http://dx.doi.org/10.1016/j.jhazmat.2005.12.053>.
- Kacimi, L.; Simon-Masseron, A.; Ghomari, A.; Derriche, Z. (2006) Influence of NaF, KF and CaF_2 addition on the clinker burning temperature and its properties. *C. R. Chimie*. 9, 154–163. <http://dx.doi.org/10.1016/j.crci.2005.10.001>.

25. Syal, S.K.; Kataria, S.S. (1981) Optimization of burning characteristics of raw meal for fuel economy by special mineralizer. *World cement technology*.12 [6], 279–285.
26. Restrepo, O.I.; Tobón, J.I.; Restrepo, O.J. (2007) Efecto de algunas adiciones minerales colombianas en la fabricación de clínker para cemento Pórtland I. *Dyna*. 74 [152], 263–674.
27. Kolovos, K.; Loutsi, P.; Tsvilis, S.; Kakali, G. (2001) The effect of foreign ions on the reactivity of the CaO-SiO₂-Al₂O₃-Fe₂O₃ system Part I. Anions. *Cem. Concr. Res.* 31, 425–429. [http://dx.doi.org/10.1016/S0008-8846\(00\)00461-0](http://dx.doi.org/10.1016/S0008-8846(00)00461-0).
28. Akin A.I. (1999) Effect of CaF₂ and MgO on sintering of cement clinker. *Cem. Concr. Res.* 29, 1847–1850. [http://dx.doi.org/10.1016/S0008-8846\(99\)00151-9](http://dx.doi.org/10.1016/S0008-8846(99)00151-9).
29. Schoon, J.; Vergari, A.; De Buysser, K.; Van Driessche, I.; De Belie, N. (2013) Fines extracted from porphyry and dolomitic limestone aggregates production: MgO as fluxing agent for a sustainable Portland clinker production. *Construc. Build. Mat.* 43, 511–522. <http://dx.doi.org/10.1016/j.conbuildmat.2013.02.046>.
30. Blanco, M.T.; Puertas, F.; Vazquez, T.; Palomo, A. (1996) Modelling of the burnability of white cement raw mixes made with CaF₂ and CaSO₄. *Cem. Concr. Res.* 26 [3], 457–464. [http://dx.doi.org/10.1016/S0008-8846\(96\)85033-2](http://dx.doi.org/10.1016/S0008-8846(96)85033-2).
31. Blanco-Varela, M.T.; Palomo, A.; Puertas, F.; Vázquez, T. (1995) Influencia de la incorporación conjunta del CaF₂ y del CaSO₄ en el proceso de clinkerización. Obtención de nuevos cementos. *Mater. Construcc.* 45 [239], 29–47. <http://dx.doi.org/10.3989/mc.1995.v45.i239.551>.
32. Dominguez, O.; Torres-Castillo, A.; Flores-Velez, L.M.; Torres, R. (2010) Characterization using thermomechanical and differential thermal analysis of the sinterization of Portland clinker doped with CaF₂. *Materials Characterization*. 61, 459–466. <http://dx.doi.org/10.1016/j.matchar.2010.02.002>.
33. Murray, R.J.; Brown, A.W. (1978) Improvements in Hydraulic Cements, U.K. Patent no. 1498057.
34. Grillo-Renó, M.L.; Martins-Torres, F.; Da Silva, R.J.; Conceição Soares Santos, J.J.; Motta Melo, M. (2013) Exergy analyses in cement production applying waste fuel and mineralizer. *Energy Conversion and Management*. 75, 98–104. <http://dx.doi.org/10.1016/j.enconman.2013.05.043>.
35. Blanco-Varela, M.T.; Vázquez, T. (1981) Ahorro de energía en la clinkerización empleando CaF₂ y CaSO₄ como mineralizadores. Estudio de la fluorelestadita (3C₂S.CaSO₄.CaF₂). *Mater. Construcc.* 181, 55–64. <http://dx.doi.org/10.3989/mc.1981.v31.i181.1020>.
36. Giménez-Molina S.; Blanco-Varela, MT. (1995) Solid state phases relationship in the CaO-SiO₂, Al₂O₃, CaF₂-CaSO₄ system. *Cem Concr Res.* 25, 870–82. [http://dx.doi.org/10.1016/0008-8846\(95\)00078-Q](http://dx.doi.org/10.1016/0008-8846(95)00078-Q).
37. Gartner, E.; Hirao, H. (2015) A review of alternative approaches to the reduction of CO₂ emissions associated with the manufacture of the binder phase in concrete. *Cem. Concr. Res.* 78, Part A, 126–142. <http://dx.doi.org/10.1016/j.cemconres.2015.04.012>.