

Effects of the incorporation of aluminum fluoride mineralizers in Portland cement clinker phases

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Abstract

Calcium fluoride can be used as mineralizer in the manufacturing of Portland cement clinker in order to decrease the temperature of clinkerization and/or increase the alite content of clinker. Also, by-products with fluorides could be valorized as mineralizers, for example by-products of the primary aluminum industry. But it is necessary to evaluate and understand the influence of these additions on the composition of the cement phases.

In the present study eight individual single phases of cement clinker have been synthesized (monoclinic-C₃S, triclinic-C₃S, γ -C₂S, δ -C₂S, orthorhombic-C₃A, cubic-C₃A, C₄AF and ferrite with different quantities of aluminum fluoride added to the respective raw meals. And the effect of the fluoride addition has been evaluated by analyzing different physico-chemical characteristics. The chemical composition has been analyzed by XRF, ICP and F-determination. The mineralogy has been determined by XRD. Also, a microstructural and compositional analysis of the phases has been done by BSE-EDX analysis, identifying the possible variations of the microstructure and composition due to the aluminum fluoride mineralizers; and, analyzing the localization of the fluoride in the clinker phases.

According to the results obtained, no adverse influence of the aluminum fluoride addition has been detected in the synthesized single clinker phases. The detected changes are an increase of the crystal size, mainly of the calcium silicates, and a preferential concentration of fluoride in the aluminate phases. These changes would also be expected in clinker mineralized with calcium fluoride according to the literature. These results indicate a possible use of aluminum fluoride as mineralizer in the manufacturing of Portland cement clinker.

Originality

The use of aluminum fluoride as mineralizer in the cement clinker manufacturing is not reported so far at industrial level. The use of such by-products allow a reduction of the energy cost in the clinkerisation process and a valorization of an industrial waste. The present study analyzes the influence of this addition on the single clinker phases to determine the main changes and to verify that there are no adverse effects on clinker formation.

Keywords: mineralizer, aluminum fluoride, clinker phases, physic-chemical characteristics.

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1. Introduction

The well-known mineralising action of fluoride has been applied to cement clinkering with at least partial success. Usually calcium fluoride has been used as mineralizer in the manufacturing of clinker cements. Fluoride lowers temperatures at which liquid develops and, under comparable conditions, the melt viscosity and surface tension of the liquid is reduced (Blanco et al., 1995) (Christensen, 1980) (Klemm et al., 1979) (Older, 1980) (Older, 1980). Thus good theoretical explanations are given for the fluxing action of F (Altun, 1999) (Blanco et al. 1995) (Chen et al., 2010) (Domínguez, 2010) (Klemm et al., 1979) (Kolovos et al., 2001).

However fluoride also behaves as a mineraliser, altering the stability, polymorphism and reactivity of the clinker phases. The many consequences of F mineralisation in multiphase systems can have both favourable and unfavourable consequences. These have generally been identified in the course of studied of isolated compositions and have not generally been systematized to the point where generic conclusions can be adduced and unfavourable effects avoided or mitigated (Altun, 1999) (Blanco et al., 1995) (Castillo, 1990) (Chen et al., 2010) (Domínguez, 2010) (Emanuelson et al. 2003) (Johansen, 1979) (Kacimi et al. 2006) (Older, 1980a) (Raina 1998) (Raina, 1998).

The literature also contains gaps. For example, although the action of CaF₂ is clearly different from that of NaF, the differences between the two, as described in the literature, are largely unquantified (Badanoiu et al., 2010) (Kacimi et al., 2006) (Stanek, 2002).

The use of fluoride with high content of aluminium has been studied by Shame and Glasser, 1987, the fluoride substituted in alite was analysed and they observed that while substitution of fluoride was limited, the two pairs (Al+F) readily replaced silicon, while maintaining an electrostratic balance. It was shown that at or near the maximum substitution, alite could be made at as low as 1075°C. Such alite was the rhombohedral phase. The cement industry usually applies calcium fluoride as mineralizer when manufacturing clinker. Some industrial by-products contain high quantities of fluoride. The manufacturing of the aluminium from bauxite generate wastes with high content of carbon, fluoride and aluminium [Welch, 1999]. In the combined Bayer Process calcination and bauxite calcination red mud is produced and sodium dominate the soluble cations during the storage, decreasing with the time, and different types of heavy metals are produced [Liu et all, 2007].

In the present study the use of by-products from the manufacturing of aluminium (HiCal) as mineralizers is done. Different proportions of fluoride has been added to the Portland cement clinker phases, C₃S, C₂S, C₃A, C₄AF and ferrite, to analyse the modification produced by adding of this product. These clinker phases have been studied by different techniques to observe the modification of different properties due to the adding of fluoride.

2. Experimental

2.1. High Fluoride By-product

The HiCal product, from the manufacturing of aluminium, is a ground grey powder. The chemical composition of HiCal showed a high content in carbon, aluminium, fluoride, silicon, iron and calcium and less quantity of alkalis and metals. The chemical composition has been analysed by different techniques, total organic carbon with a Leco CS230, mayor compounds by X-ray fluorescence with a S8 Tiger Bruker, minor compounds by inductively coupled plasma with a Varian model 725-ES and chlorines by potentiometry. In table 1 the chemical composition is shown. Also, the mineralogical composition of HiCal, analysed by X-ray diffraction with equipment D8 Bruker, is graphite, cryolite, villiamite, corundum and diaoyudaoite. The proportions of these compounds are shown in table 2.

Tab. 1 Chemical compositions of HiCal /%

Composit.	TOC	Al ₂ O ₃	F	SiO ₂	Fe ₂ O ₃	SO ₃	CaO	V ₂ O ₅	ZrO ₂	Ga ₂ O ₃	Na ₂ O	K ₂ O	
%	38.62	16.036	12.83	6.177	4.534	2.115	1.839	0.037	0.005	0.003	16.656	0.35	
Composit.	MgO	TiO ₂	ZnO	MnO ₂	NiO	CuO	P ₂ O ₅	Cr ₂ O ₃	BaO	PbO ₂	SrO	CdO	Cl ⁻
%	0.353	0.109	0.077	0.055	0.043	0.033	0.033	0.029	0.018	0.014	0.009	0.001	0.03

Tab. 2 Mineralogical composition of HiCal /%

Graphite (C)	18.40%
Cryolite (Na ₃ AlF ₆)	17.52%
Villiamite (NaF)	9.43%
Corundum (Al ₂ O ₃)	7.00%

Gibbsite (Al(OH) ₃)	5.09%
Diaoyudaoite (NaAl ₁₁ O ₁₇)	3.04%
Fluorite (CaF ₂)	2.44%
Amorphous	39.06%

The analysis of HiCal by-product is showing a high content of organic carbon and amorphous material. With respect to the mineralogy is observed different types of aluminium compounds and calcium and sodium fluoride.

2.2. Synthesis of Clinker Phases

Eight different clinker phases have been synthesized without of fluoride and with 0.25% and 0.50% of fluoride, calculating the amount of HiCal to added according with their fluoride content. The phase's synthesized are: C₃S triclinic, C₃S monoclinic, C₂S alpha, C₂S beta, C₃A cubic, C₃A orthorhombic, C₄AF and ferrite. The C₃S phases are synthesized 2h heating ramp to 1495°C, holding for 2h and fast cooling. The -C₂S is synthesized 1 h 45 min heating ramp to 1250°C, holding for 7h and fast cooling. The -C₂S is synthesized 1 h 45 min heating ramp to 1450°C, holding for 4h and fast cooling. The C₃A cubic and C₃A orthorhombic are synthesized 1 h 45 min heating ramp to 1450°C, holding for 3h and slow cooling. And finally, C₄AF and ferrite have been synthesized 1h 30 min heating to reach 1300°C, then holding for 2h and fast cooling. The synthesis of these clinker phases has been done according the procedures described by Wesselsky and Jensen, 2009. During the treatments, partial melting could be occurs.

A total of twenty four clinker phases are studied in the present work. Three percentages of fluoride (0%, 0.25% and 0.50%) of each eight phase.

In addition of these clinker phases, samples of C₃S triclinic, C₃S monoclinic, C₂S alpha, C₂S beta, C₃A cubic, C₃A orthorhombic, C₄AF and ferrite with 1.40% and 2.70% of fluoride have been synthesized to analyse the distribution of fluoride in these phases by scanning electron microscopy combined with X-ray microanalysis.

2.3. Experimental Analysis

The variation clinker phases due to add of fluoride has analysed using different instrumental techniques, to evaluate de modification of chemical, mineralogical, microstructural and compositional characteristics.

The chemical composition of the clinker phases has analysed using X-ray fluorescence (S8 Triger Bruker equipment), for major compounds, inductively coupled plasma (Varian mod 425ES), for minor compounds and selective ion for analysis of small quantities of fluoride.

The mineralogical compounds of the synthesized phases have done using X-ray diffraction (D8 Bruker) and the quantitative analysis of these compounds has done by Rietvelt refined software Topas 3.0.

Also, the microstructural analysis of clinker phases has done by electron microscopic techniques. Fracture samples have been observed and analysed using scanning electron microscopy combined with X-ray dispersive energy microanalysis. And, polish samples have been observed and analysed using backscattering electron microscopy combined with X-ray dispersive energy microanalysis. The equipment's used are an electron microscopy Hitachi S-4800 and X-ray microanalysis Bruker Nano X-Flash detector 50300.

3. Results and Discussion

3.1. Chemical Composition

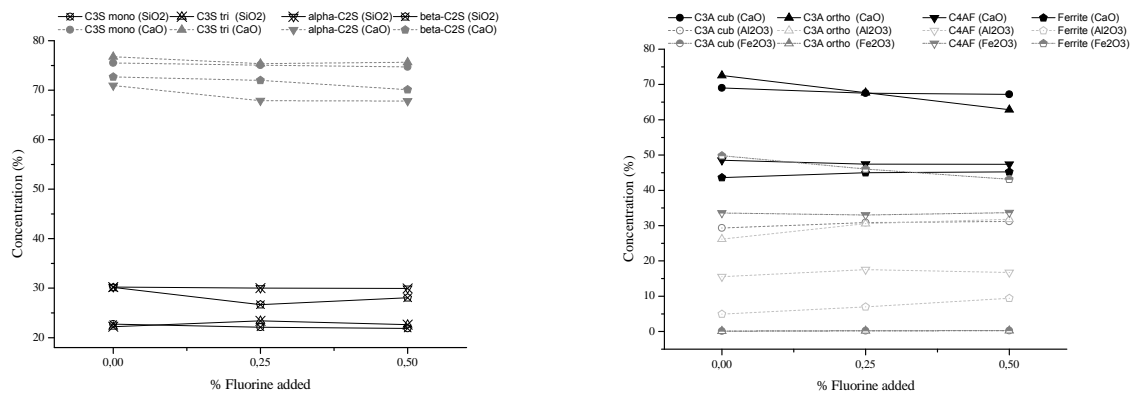
The chemical composition of clinker phases with incorporation of aluminium fluoride (HiCal) shown small variation with respect to the original clinker phases without any fluoride addition.

In the calcium silicate phases (C₃S and C₂S) a slight decrease of calcium is observed both in alite and belite with the addition of fluoride, as can be seen in the figure 1(a). With respect to the silicon a slight decrease in the alite phases (C₃S tri and C₃S mono) while an slight increase in the belite phases (-C₂S and -C₂S) is produced with the addition of fluoride (figure 1(b)). These effects are associated with the increase of content of aluminium and iron due to the composition of HiCal product.

With respect to the aluminium phases, C₃A cubic, C₃A ortho, C₄AF and ferrite, a decrease of calcium is observed in the C₃A phase with the adding of fluoride, while a slight decrease of calcium of calcium

is observed in the C_4AF phases with the adding of fluoride. With respect to the aluminium and iron, these are increasing in all aluminate phases (C_3A cubic, C_3A ortho, C_4AF and ferrite).

The quantity of fluoride has been determined in each of the sixteen samples with fluoride addition using a selective ion electrode. Previously the clinker phase samples have been attacked using a specific procedure se for cement materials [Zimmermann, 2014]. In all the case a higher quantity of fluoride is observed with the higher content of fluoride added. Although, the proportion of fluoride measurement are less than the 50% of the theoretical quantity added to the samples. It is necessary to consider that the procedure to determine the fluoride quantity is different to the procedure to characterize the composition of HiCal. The fluoride is fix mainly in C_3S phases (C_3S mono and C_3S tri) while the rest of clinker phases shown amounts smaller than 0,08% of fluoride. The amounts of fluoride in each clinker phase are shown in figure 2.



(a) SiO₂ and CaO in calcium silicate phases. (b) CaO, Al₂O₃ and Fe₂O₃ in aluminium phases.
Figure 1 Variation of compounds in clinker phases due to adding of HiCal product (aluminium fluoride).

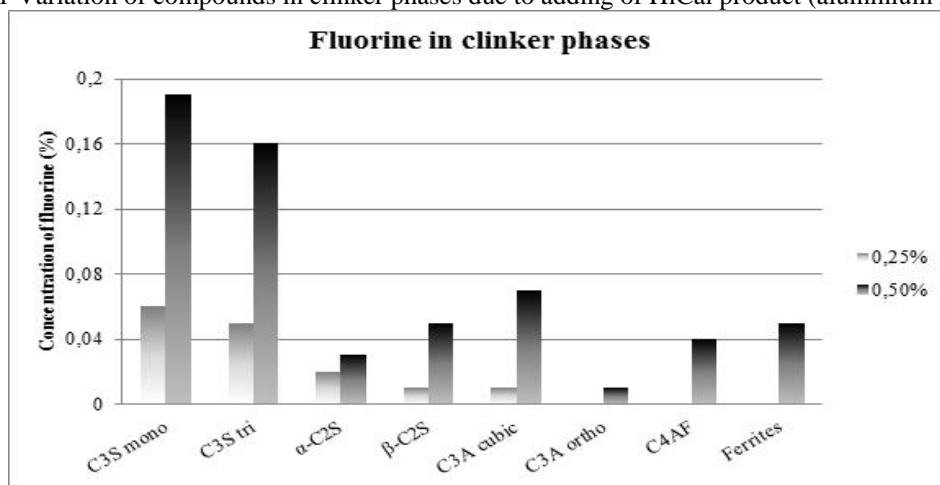


Figure 2 Increase in fluoride due to the adding of HiCal product (aluminium fluoride).

All the changes in composition aren't significant and are associated with the composition of HiCal product and their addition. The fluoride fixed in the clinker phases in small than 0.2% in all cases and appearance mainly in C_3S phases (C_3S mono and C_3S tri) and C_3A cubic. The techniques to quantify the fluoride content in the HiCal and in the synthetized phases are different, although a partial volatility of fluoride seems occurs.

3.2. Mineralogical Composition

The crystalline phases have been analysed by X-ray diffraction. And, the quantity of C_3S , C_2S , C_3A and C_4AF is determined using Rietvelt refinement, for each of the single phase's synthesized. In figure 3 the percentage of C_3S , C_2S , C_3A , C_4AF and ferrite phases is shown.

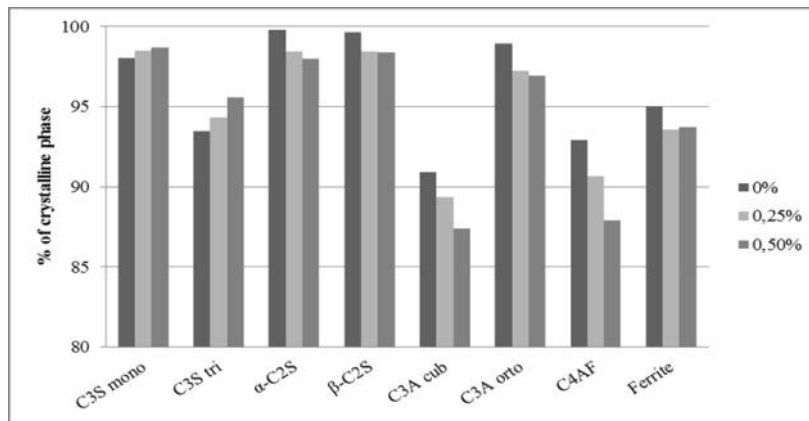


Figure 3 Variation of quantities of C_3S , C_2S , C_3A and C_4AF due to the adding of HiCal product (aluminium fluoride).

It is observe that the C_3S phases (monoclinic and triclinic) are increased due to the addition of HiCal, while the percentage of C_2S phases (and), C_3A (cubic and orthorhombic) and C_4AF phases are decreased with the addition of fluoride. And, ferrite phase shows a variable behaviour. With respect to the C_3S triclinic a significant decrease of larnite is observed with the addition of HiCal product, with percentages of 5,39%, 3,22% and 1,67% of larnite with 0%, 0.25% and 0.50% of fluoride. Apart of these phase $C_{12}A_7$ has been detected in C_3A cubic, with percentages of 6.68%, 8.32% and 10.08% with 0%, 0.25% or 0.50% of fluoride, respectively; while $C_{12}A_7$ is not observed in C_3A orthorhombic. Also, formation of $C_{12}A_7$ is observed in C_4AF and Ferrite, with an increase in their percentages with the increasing of the HiCal addition. The percentages are 3.37%, 6.89% and 9.33% for C_4AF and 2.63%, 3.08% and 3.49% for ferrite; with 0%, 0.25% and 0.50%, respectively.

3.3. Microstructural and Compositional Analysis

3.2.1 SEM-EDS analysis. Distribution of Fluoride in the Phases

In order to analyse the distribution of fluoride in the clinker single phases a high quantity of HiCal product has been added, until have 1.4% and 2.7% in the crude mixes. A significant variation of microstructure in clinker phases had observed with the addition of fluoride. Examples of the microstructure of each clinker phase without fluoride, 1.4% and 2.70% is shown in figure 4.

Fluoride content	0%	1.4%	2.7%
C_3S mono			
C_3S tri			
α - C_2S			

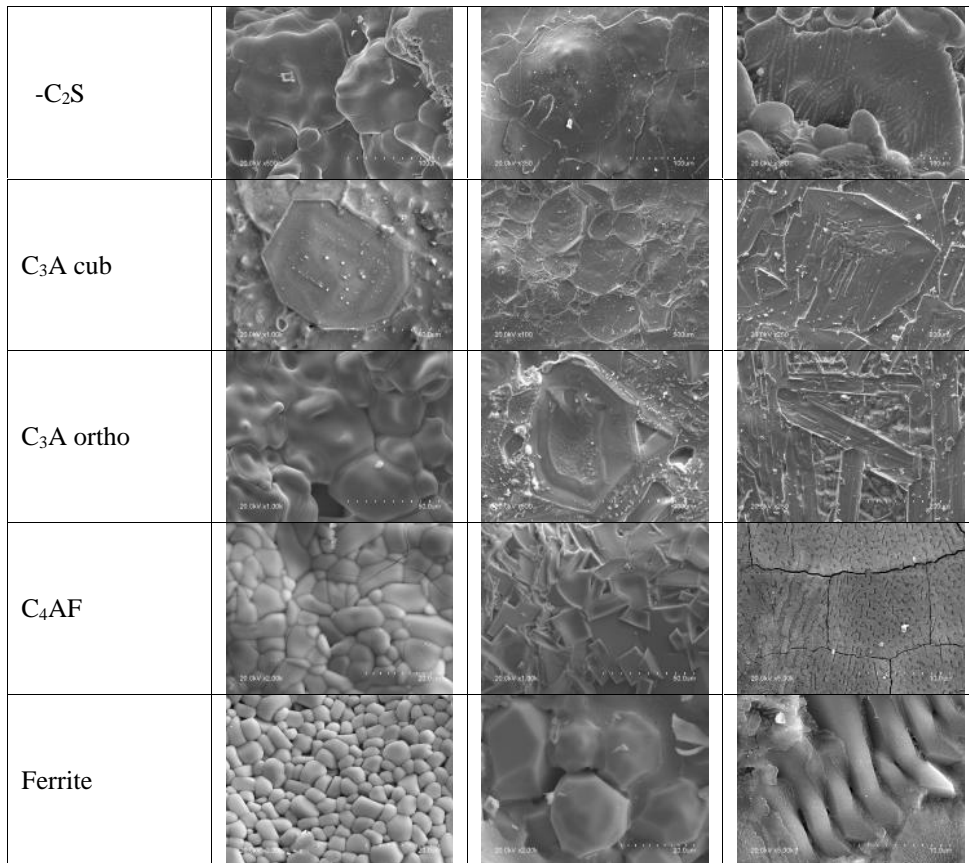


Figure 4 Variation of microstructure with the addition of fluoride in each clinker phase.

With the addition of the HiCal product and increase of fluoride, the C₃S phases (monoclinic and triclinic) increase the density and the crystal size. The C₂S phases (and) mainly showed a modification of shape and a densification. The C₃A (cubic and orthorhombic), C₄AF and ferrite phases are showing mainly a variation of shape, with a more angular form instead of the rounded initial form. Also, is observed a modification of the interfaces between grains with the adding of the fluoride. An example of the aspect of interfaces in clinker phases with 2.70% is observed in figure 5. In general, different types of crystals are observed in the interfaces.

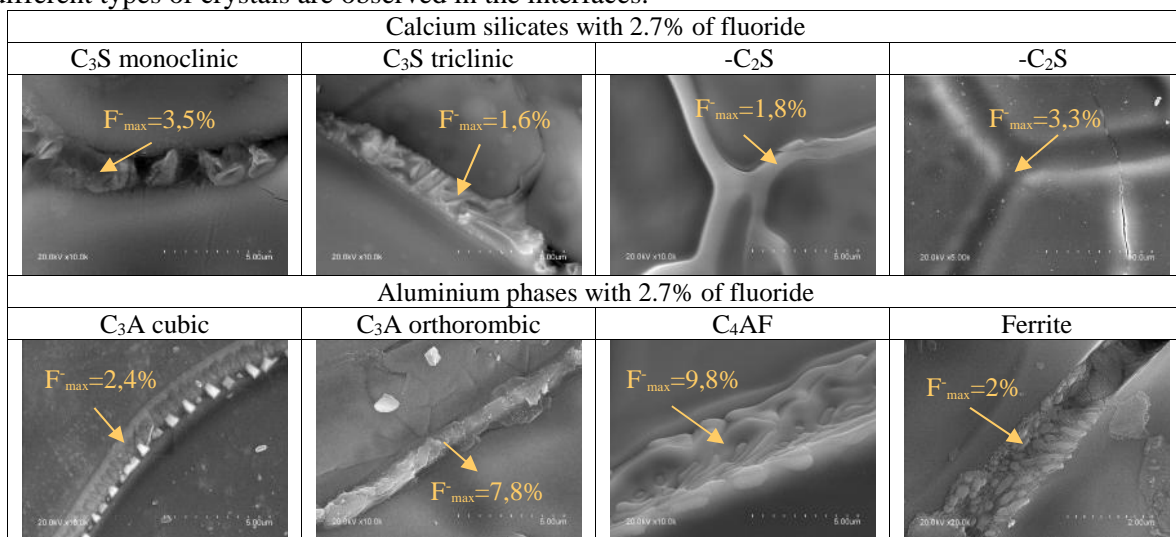


Figure 5 Aspect of the interphase of the grains in samples with 2.70%.

With respect to the distribution of fluoride in the clinker phases this has been observed mainly in the interfaces. But the distribution in the different phases and with the different addition of fluoride is

variable. With the addition of fluoride a partial melting seems occurs and the formation of interphase products is observed and in this case the fluoride has the opportunity to fractionate into the melt phases.

Several punctual analyses have been done in the different types of crystals and in the interphases. In Figure 6 the dispersion of values of fluoride content is shown. These values are punctual analysis taken in the different microstructures observed in each single clinker phases.

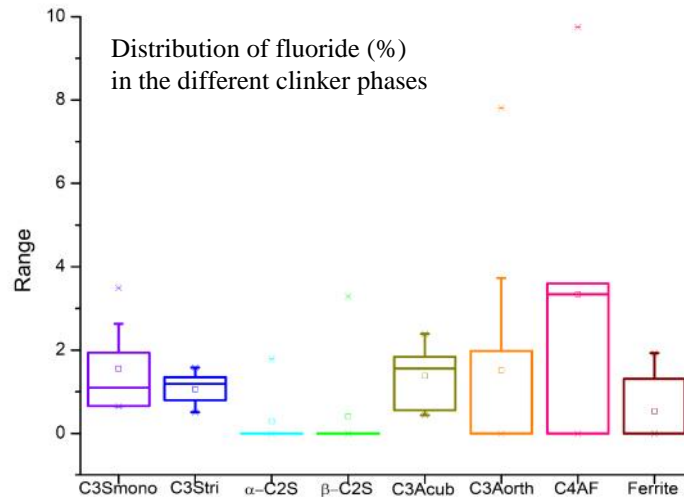


Figure 6 Fluoride content in punctual analysis of different clinker phases.

3.2.2 BSE-EDS analysis

Polished samples of each clinker single phase's synthesized with 0%, 0.25% and 0.50% of fluoride have been analysed to see the modification of the microstructure and to analyse their chemical composition.

In general, a densification and an increase of the clinker size have been observed with the addition of fluoride. In figure 7 a general aspect of the C₃S mono, C₃S tri, -C₂S, -C₂S, C₃A cubic, C₃A ortho, C₄AF and ferrite is collected.

Also, the chemical composition has determined as a mean value of around fourth areas analysis. The CaO – SiO₂ – Al₂O₃ ratio of the samples with different fluoride addition has been represented in the ternary diagram in figures 8 and 9. On the other hand, the fluoride is not well detected in the area analysis due to resolution limit of this element in very small quantities.

Fluoride content	0%	0.25%	0.50%
C ₃ S mono			
C ₃ S tri			
-C ₂ S			

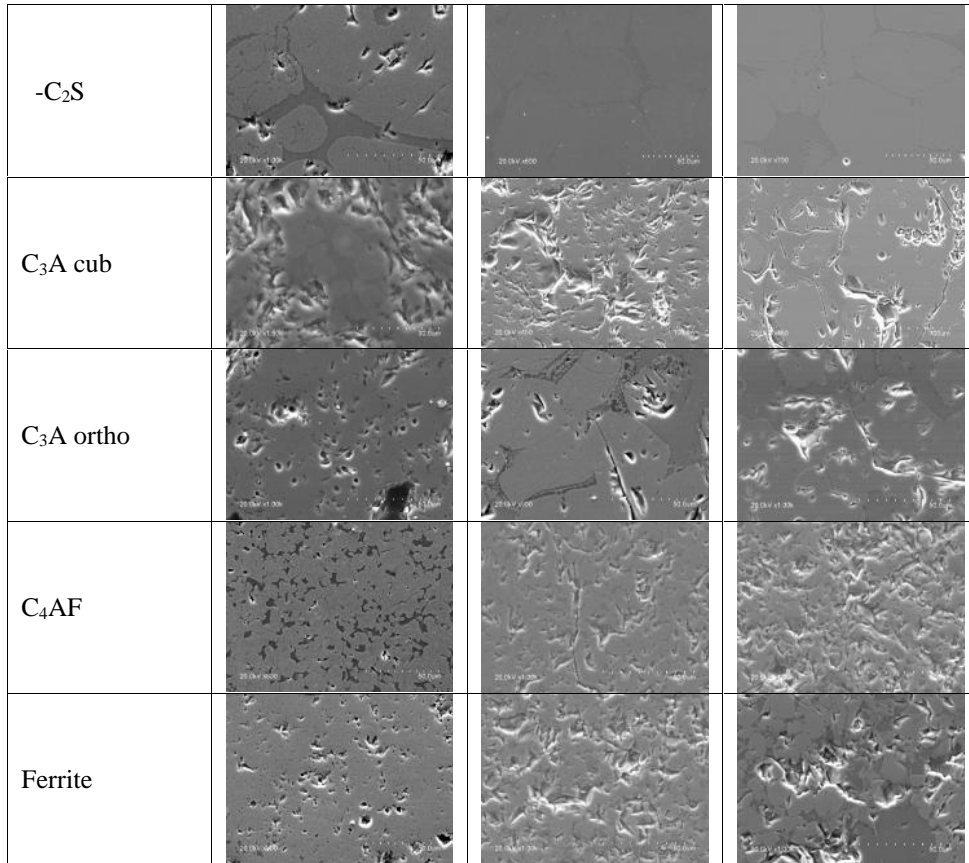


Figure 7 General aspects of the clinker phases with different content of fluoride.

In silicon calcium clinker phases there aren't any significant changes due to the addition of fluoride. Only C₂S- is showing a different composition, but is not associated with fluoride. On the other hand the C₃A cubic, C₃A ortho, C₄AF and ferrite phases are showing similar compositions without and with fluoride. It can be seen from figure 9 that the ferrite has a different composition with respect to the rest of aluminate phases.

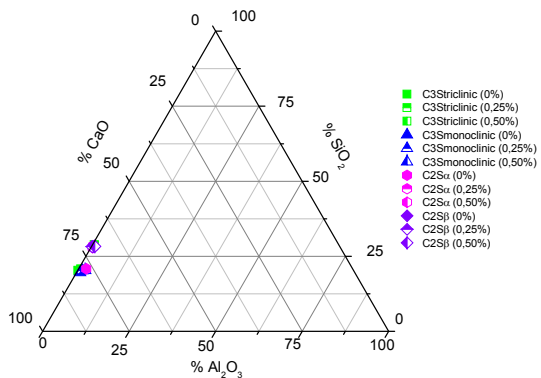


Figure 8 Composition of silicon calcium phases.

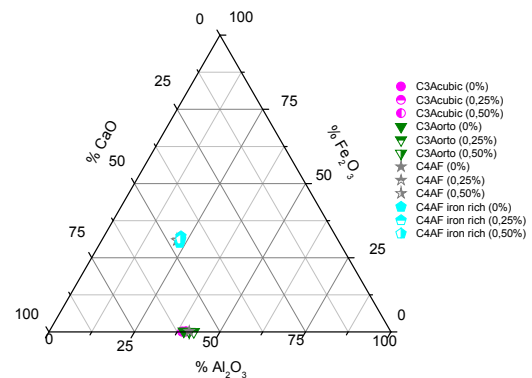


Figure 9 Composition of aluminate phases.

4. Conclusions

The by-products of the aluminium industry can be used as mineralizer in the manufacturing of cement Clinker. Unlike traditionally used mineralizers based on calcium fluoride, these products have a high content of fluoride and aluminium.

The addition of 0.25% and 0.50% of fluoride in the clinker phases haven't significant or adverse modifications in these phases.

The variation in the chemical composition due to the addition of fluoride is slight and it is associated with the own composition of the by-product. With respect to the fluoride the higher incorporation is observed in the C_3S phases and lesser extent in C_3A , C_4AF and ferrite phases. And, in the analysis by electron microscopy combined with X-ray microanalysis is observed that the fluoride is accumulated mainly in the interfaces of the alite phases, in the C_3A phases, C_4AF and ferrite.

The addition of HiCal produced a significant decrease of larnite in the C_3S triclinic phase. But also, an increase of $C_{12}A_7$ is observed in the ferrite-aluminate phases with higher proportion of $C_{12}A_7$ with the increase of fluoride.

The fluoride incorporate to the clinker products are less than the fluoride added to the mixes, this may indicate that have been somewhat volatile.

Also, the increase in the addition of fluoride induces an increase in the crystal size of the clinker phases.

There aren't an appreciable modification of the relative composition of $CaO-SiO_2-Al_2O_3$ in the C_3S and C_2S phases. Neither an important modification can be observed in the relation $CaO-Al_2O_3-Fe_2O_3$ in the C_3A phases, C_4AF and ferrite.

Acknowledgements

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