

Article

Natural Fluorite from Órgiva Deposit (Spain). A Study of Its Pozzolanic and Mechanical Properties

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Abstract: This work presents the results of the partial substitution of Portland cement (PC) by natural fluorite (NF) and calcined fluorite (CF) in mortars, at 10%, 25% and 40%. To meet these objectives, a sample of fluorite was initially studied by XRD, SEM and Raman Spectroscopy (RS). A chemical quality analysis (CQA) and a chemical pozzolanicity test (CPT) at 8 and 15 days were carried out in a second stage to establish the pozzolanic properties of the investigated sample. Finally, a mechanical compressive strength test (MCST) at 7, 28 and 90 days was carried out on specimens made up with PC/NF and PC/CF mixes, at a ratio of 10%, 25% and 40%. XRD, SEM and RS results indicated fluorite as the major mineralogical phase. The CPT and CQA showed an increase in the pozzolanicity of the samples from 8 to 15 days. The MCST showed an increase in compressive strength from 7 to 90 days for both PC/NF and PC/CF specimens. The results obtained establish that fluorite produces positive effects in the mortar and contributes to the gain of mechanical strength over time, being a suitable material for the manufacture of cements with pozzolanic addition with a reduction of CO₂ emissions, and by reducing the energy costs of production.

Keywords: fluorite; cement; pozzolan; mortar; mechanical strength; reduction of CO₂ emissions



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1. Introduction

The use of fluorite in the making of cement has been known for several decades. In studies such as those presented by Gilvonio and Dominguez [1] the use of fluorite as a flux in the clinkerization process is mentioned; this significantly reduces the clinkerization temperature and obtains cements with greater mechanical strength, which contributes to the reduction of high energy costs during the production of Portland cement [2]. Fluorite has been used in the manufacture of cement with special characteristics, such as fast setting and high initial strength, as demonstrated by Najafi Kanil and Allahverdi [3]. Dominguez et al. [4] and Endzhievskaya et al. [5] have used natural fluorite in the characterization of the clinker sintering process, concluding that phase transformation and, above all, the presence of alite, occur at lower temperatures than usual when this mineral is incorporated. Other researchers, such as Fridrichova et al. [6], have managed to raise the reactivity of the common included of Portland clinker by the controlled addition of natural fluorite. Additionally, Zeta-Garcia et al. [7] have recently shown that the addition of fluorite in the standard clinker with alite, belite and ye'elimitite (ABY) causes an increase

in the mechanical strength of mortars and favourably affects the production of “ecological cements”. Recently, the use of natural fluorite residues as substitutes for traditional aggregates in concrete has been used in proportions of 5%, 10% and 20%, achieving an improvement in mechanical properties [8]. The works of Zhu et al. [9] mention the use of waste from the mining of serpentine and kaolin by means of mixtures with fluorite slurry, obtaining mechanical strength of up to 150 MPa. Achmania et al. [10] detail the uses of fluorite in other fields, such as steel, aluminium metallurgy, the manufacture of plastics, solvents, refrigerants, welding and glass manufacturing, as well as pointing out the use of this mineral in the cement industry. It is pertinent to mention that the fluorite has been used as an index mineral for locating possible deposits of rare earth (REE) elements and niobium, related to carbonatites, as established by Makin et al. [11].

This research aims to demonstrate the efficacy of natural fluorite from a site in the province of Granada, south of the Iberian Peninsula (Spain). For this, natural and calcinated fluorite have been used to partially replace the Portland cement in the mortars, and to establish two fundamental parameters: the proportion of PC/NF and PC/CF mixtures, as well as the ideal calcination temperature threshold of the samples, in order to achieve optimal compression strength.

This work has been structured and developed in two phases: first, natural fluorite has been characterized by XRD, SEM and Raman Spectroscopy (RS) to determine the constitution and morphology of the mineralogical phases present in the sample; secondly, a study was carried out to establish technological quality through calcination tests, chemical analysis, pozzolanicity and compression strength at different ages.

This work is considered novel for several reasons, such as obtaining resistant mortars, the possible manufacture of cements with more environmentally friendly pozzolanic additions, the inclusion of fluorite and its residues within the circular economy cycle and the revitalization of the local industry.

2. Materials and Methods

2.1. Materials

The materials used in this research consist of natural fluorite, Portland cement and standardized sand. Natural fluorite comes from the Órgiva deposit, located in the Province of Granada, in the south of the Iberian Peninsula. The Órgiva Mining Company exploits the deposit. A volumetric sample of fluorite of 50 kg was taken from the La Candelaria mine, by lithochemical fragment sampling.

A Portland cement (PC) type 1, 42.5 N, of normal resistance, with the characteristics and parameters indicated in the standard UNE-EN 197-1:2011 [12], was used in this research.

A standardized sand (NS) of Normsand-CEN EN 196-1 typology, consisting of 98% silica, was used in this work as a fine aggregate.

2.2. Methods

2.2.1. Preparation of the Sample

The sample was crushed in two phases. In the first, a reduction in the size of the particles was made up to 3 cm in diameter, with the help of a crusher model Alas. In the second phase, the size of the particles was reduced to 1 cm, by using the Controls brand crusher. The sample was then ground in a Siebtechnik mill model Scheibenschwingmühle TS 1000 in order to obtain two different particle sizes or blaine fineness (BPF): 2000 cm²/g and 5000 cm²/g, respectively. To obtain the BPF of 2000 cm²/g the sample was ground for 50 s, whereas for the fraction 5000 cm²/g the time was 30 s.

2.2.2. Calcination Test

Two subsamples, CF-01 and CF-02, representative of both particle sizes 2000 cm²/g and 5000 cm²/g, were calcinated. The calcination process was carried out at a temperature of 900 °C, for one hour, with the use of a Binder stove, model 9010-0101 ED240; Serial

number: 206493; Measuring range and scale division: 1300 °C/1 °C; Electrical power and connection voltage: 100–240 V; Measuring accuracy: ± 3 °C; Made in Germany. After the heating treatment, the samples were crushed again for 40 s, following the procedure described in Section 2.2.1, to remove the compaction produced during the calcination process. All the materials and instruments used in this research belong to the laboratories of the Escuela Técnica Superior de Ingenieros de Minas y Energía and the Laboratorio Oficial para Ensayos de Materiales de Construcción (LOEMCO), both of the Universidad Politécnica de Madrid, Spain.

2.2.3. X-ray Diffraction Analysis (XRD)

A study to determine the mineralogical phases present in the natural fluorite sample was performed by X-ray diffraction (XRD) (All the materials and instruments used in this research belong to the laboratories of the Escuela Técnica Superior de Ingenieros de Minas y Energía and the Laboratorio Oficial para Ensayos de Materiales de Construcción (LOEMCO), both of the Universidad Politécnica de Madrid, Madrid, Spain). The equipment used consisted of a Rigaku Miniflex-600, with the capacity to carry out qualitative and quantitative tests. It is equipped with an X-ray tube operating at 600 w, plus a graphite monochromator and a standard scintillation counter. The diffractometer contains a six-position automatic sampler, and has a HyPix-400 MF-2DHPAD, as well as a ShapeFlex Brand sample stand. The software used was the SmartLab Studio II. This equipment has an interface for profile views, data view, 3D views, and view of the crystal structure of the sample. The power used in the analysis process is 1 \emptyset , 100–240 V and 50/60 Hz. About 500 mg for each sample were weighed, ground up and screened to a fineness of 74 μm . The standard tablets were then manufactured in their respective moulds and then placed on the sample holder for analysis.

2.2.4. Scanning Electron Microscopy (SEM)

A Hitachi S-570 scanning electron microscope from the Laboratorio Centralizado of the Escuela Técnica Superior de Ingenieros de Minas y Energía of the Universidad Politécnica de Madrid was used in the characterization of the morphological properties of the investigated sample.

The equipment has a Kevex-1728 analyser, a Polaron BIORAD, a power supply for evaporation and a Polaron SEM coating system. The equipment attains a resolution of 200×10^3 . Other components are part of the Scanning Electron microscope such as: a lithium-doped silicon, a liquid nitrogen reservoir, an electronic cannon, a filament chamber, control panel for placing the sample in the high vacuum chamber and for varying the angles of the sample position, and an interface module to display the image during electronic scanning of samples.

The equipment operates with two pieces of software, Winshell and Printerface, to handle the information obtained during the study of the analysed sample and to take microphotographs, respectively. To perform the analysis by SEM, the samples in their natural state were previously reduced to a particle diameter of 0.2–0.5 cm; they were then placed on a graphite adhesive tape and later on the sample holder. Next, samples were covered with a layer of vacuum graphite and then placed in the sample holder of the scanning electron microscope.

2.2.5. Raman Spectroscopy (RS)

Raman Spectroscopy is a non-destructive analytical technique that is based on the analysis of scattered light and molecular vibrations produced by the incidence of monochromatic light on the surface of the sample, which yields information on the chemical and structural composition.

The sample was analysed using a Spectrometer brand Gemmo Raman-532, Class 1, Laser product, Reference No. 18-Raman/PL Broad Scan with spectral artifacts-Sinhalite, Brownish Yellow. The equipment also has a laser cannon for the concentration of displaced

photons; a filter to separate elastic scattered light from inelastic light, a monochromator to separate the wavelengths of inelastically scattered light and a detector that collects and digitizes the signal of the different wavelengths.

2.2.6. Chemical Pozzolanicity Test (CPT)

Pozzolanicity is the property of certain materials to react with $\text{Ca}(\text{OH})_2$ in solution when these materials have a very fine particle size, usually below 50 microns [13]. Pozzolans can be of natural origin [14] as well as artificial [15]. Two samples of fluorite, one in its natural state (NF) and the other calcinated (CF), were analysed by CPT to determine their pozzolanic properties, following the indications of the standard UNE-EN 196-5:2011 [13] at 8 and 15 days. A portion equivalent to 100 mL of demineralized water was heated to 40 °C for 60 s; then 20 g of a mixture of PC/NF and PC/CF, respectively, were added to this solution. Once the 8 days had elapsed, the solutions were filtered. This procedure was also repeated for a period of 15 days. The concentration of hydroxyl ions $[\text{OH}^-]$ was calculated using the following equation:

$$[\text{OH}^-] = \frac{1000 \times 0.1 \times V_3 \times f_2}{50} = 2 \times V_3 \times f_2 \quad (1)$$

where:

- $[\text{OH}^-]$: is the concentration in hydroxyl ions (mmol/L).
- V_3 : is the volume of the hydrochloric acid solution (0.1 mol/L).
- f_2 : is the factor of the hydrochloric acid solution (0.1 mol/L).

The concentration of calcium oxide (CaO) was calculated with the following equation:

$$[\text{CaO}] = \frac{1000 \times 0.025 \times V_4 \times f_1}{50} = 2 \times V_4 \times f_1 \quad (2)$$

where:

- $[\text{CaO}]$: is the concentration in calcium oxide (mmol/L).
- V_4 : is the volume of EDTA solution used in the titration.
- f_1 : is the factor of the EDTA solution.

The pozzolanicity test is positive when the hydroxide concentration of calcium in dissolution is lower than the saturation concentration [13]. The results are seen in the graph, where all samples below the solubility isotherm curve are considered as pozzolan.

2.2.7. Chemical Quality Analysis (CQA)

A chemical quality analysis (CQA) was carried out to determine the main major compounds of the natural fluorite (NF) sample analysed in this research; in addition, to determine its quality as a natural aggregate of pozzolanic cement. The different stages of the test were developed following the parameters of the standard UNE-EN 196-2:2014 [16]. The main compounds determined were the following: Total SiO_2 (TS), reactive SiO_2 (RS), total CaO (TC), reactive calcium (RC), MgO, Al_2O_3 and Fe_2O_3 . In addition, the insoluble residue (I.R.) was calculated in a standardized solution of hydrochloric acid [16].

2.2.8. Mechanical Strength Test (MST)

This method was carried out to determine the compression strength of specimens cured at 7, 28 and 90 days, using the procedures indicated in the standard UNE-EN 196-1 [17]. The specimens were developed with standardized mixtures of PC/NF and PC/CF. The percentage of PC replacement by NF and CF, respectively, was 10, 25 and 40%. In addition in the manufacture of the specimens, two blaine particles fineness (BPF) were taken into account: 2000 and 5000 cm^2/g , for both NF and CF. A total of 12 samples of specimens were prepared for the mechanical strength test, with three PC/NF-CF replacement ratios (10, 25 and 40%) and two types of BPF (2000 and 5000 cm^2/g). All data referring to the preparation and proportion of the components of the specimens are presented in Table 1.

Table 1. Proportions of mixtures of PC, NF, CF and NS used in the preparation of the specimens.

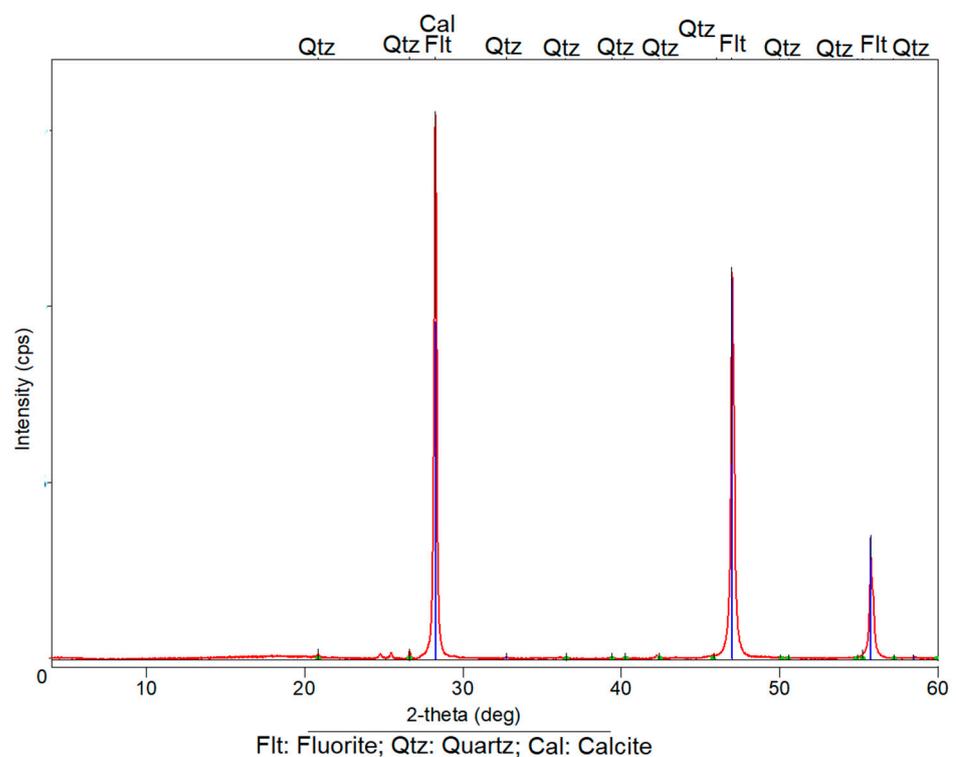
Sample	Proportion (Ratios)				Temperature of Calcination (°C)	Blaine Particle Fineness (BPF) for NF and CF (cm ² /g)
	PC ¹ :NF ² (%)	PC:CF ³ (%)	NS ⁴ (g)	DW ⁵ (g)		
PC/NF-01	90:10					
PC/NF-02	75:25					2000
PC/NF-03	60:40	-	1350	225	-	
PC/NF-04	90:10					
PC/NF-05	75:25					5000
PC/NF-06	60:40					
PC/CF-07		90:10				
PC/CF-08		75:25				2000
PC/CF-09	-	60:40	1350	225	900	
PC/CF-10		90:10				
PC/CF-11		75:25				5000
PC/CF-12		60:40				

¹ Portlan cement; ² Natural fluorite; ³ Calcined fluorite; ⁴ Normalised sand; ⁵ Distilled water.

3. Results and Discussion

3.1. X-ray Diffraction (XRD)

The study of the mineralogical phases determined that the analysed sample is composed of a main phase of fluorite, of up to 98.3%; it also has subordinate secondary phases of quartz and calcite, indicating that the ore is practically monomineral (Figure 1). The study detected the three main peaks of fluorite at the following 2θ angular positions: $2\theta = 28.2508$ /Intensity Cps = 50.766 (peak 5); $2\theta = 46.9905$ /Intensity Cps = 47.552 (peak 17); $2\theta = 55.7479$ /Intensity Cps = 14.129 (peak 19) and $2\theta = 26.61$ /Intensity Cps = 235 (peak 4) (Figure 1).

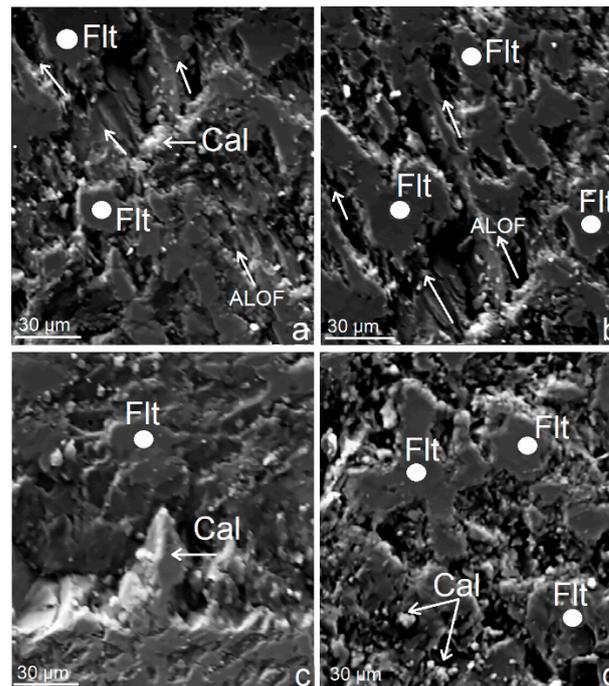
**Figure 1.** X-ray diffraction patterns of the natural fluorite from the research area.

The peaks of quartz and calcite have low intensity and are confined to the background of the X-ray diffraction patterns. The major presence of fluorite in the investigated

sample has been confirmed by the analyses of SEM and Raman Spectroscopy (RS) in Sections 3.2 and 3.3.

3.2. Scanning Electron Microscopy (SEM)

The analysis of the sample under study shows a majority of fluorite, as shown in Figures 2a–d and 3a–d. In Figure 2a–d the fluorite crystals are large and they usually have a typical orientation that provides an apparent banding. This orientation was possibly caused by tectonics. The direction of accretion and orientation of the fluorite crystals are indicated by arrows in Figure 2a,b.



Flt: Fluorite / Cal: Calcite

ALOF: Accretion lines and orientation of fluorite crystals

Figure 2. Microphotographs (a–d) of the natural fluorite (NF) sample investigated, showing typical banding.

The crystals are enlarged and show an anomalous increase in size, possibly by recrystallization. They form compact crystalline aggregates of zebra appearance that are reflected in the sample as list or bands. Sometimes these aggregates are in the form of impregnations and granular compact masses.

According to the Figures 2a–d and 3a–d, it seems that fluorite comes from two origins: a primary one, prior to tectonic deformation processes (Figure 2a–d), and a posttectonic one, with the formation of new generation fluorite, in which the crystals are well preserved (Figure 3a–d).

Calcite forms small aggregates of rhombohedral shapes in empty spaces, as well as druses that develop greater in fractures (Figure 2c). Calcite is very scarce in the samples analysed.

The microphotographs, in Figure 3a–d, show compact crystalline aggregates of fluorite without deformation. Its origin may be related to hydrothermal solutions caused by autometamorphism [18]. All the crystals grow and are arranged in a very tight way, without spaces or pores, it is common to see interpenetrations and minerals twins. Figure 3a–d shows poorly developed calcite crystals.

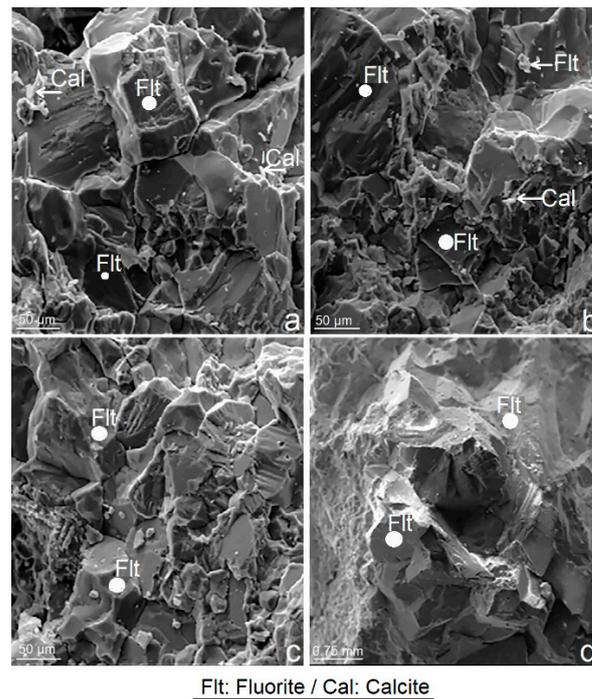


Figure 3. Microphotographs (a–d) of the investigated natural fluorite sample without banding.

3.3. Raman Spectroscopy (RS)

Figure 4 indicates the presence of virtually pure natural fluorite (NF) in the Raman fingerprint zone to the left of the diagram. The intensity of the peak of the NF exceeds 5500 counts, while the wavelength is 541 nm. The application of the Raman spectroscopy method in this research confirms the results obtained by XRD and SEM, Section 3.1 and Section 3.2, respectively, where the fluorite phase was determined to be the major presence; thus, it was established that the methods used are adequate and complement each other.

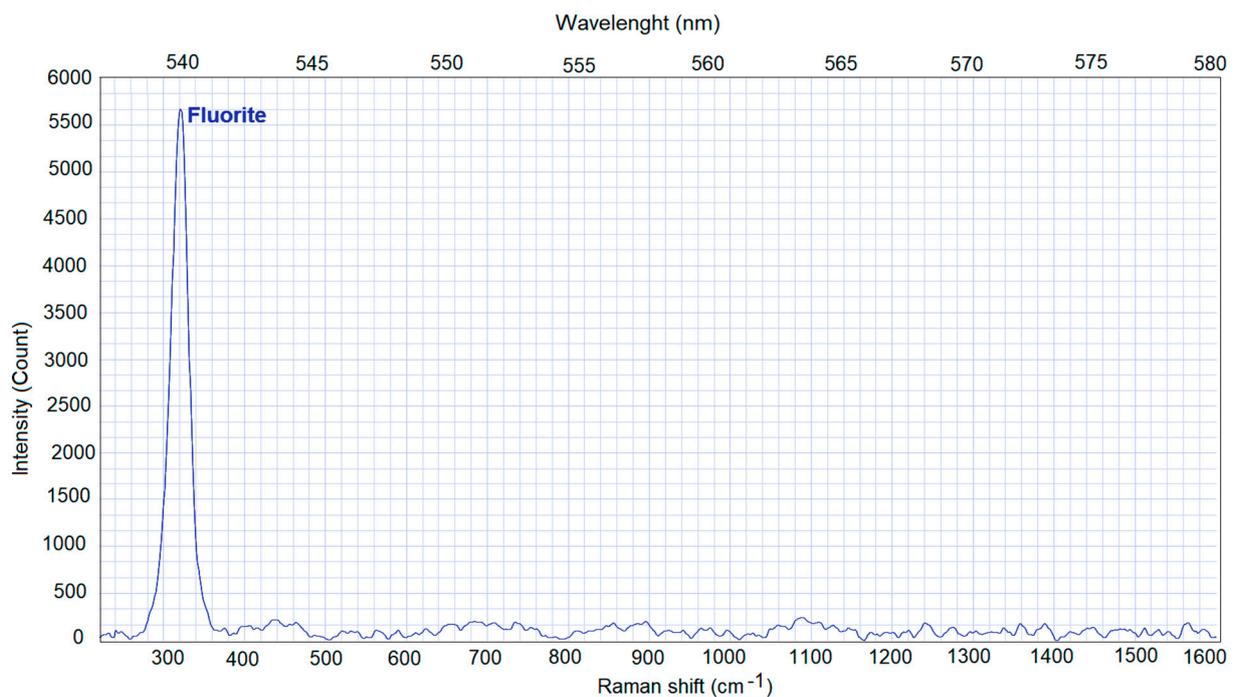


Figure 4. Results obtained from the analysis of the NF sample by Raman Spectroscopy.

3.4. Pozzolanicity Test (CPT) at 8 and 15 Days

Figure 5a,b demonstrates the pozzolanic character of the natural fluorite (NF) and calcinated (CF) samples investigated. The 8-day test (Figure 5a) fixes both samples immediately below the isothermal solubility curve at 40 °C, indicating an adequate pozzolanic reaction.

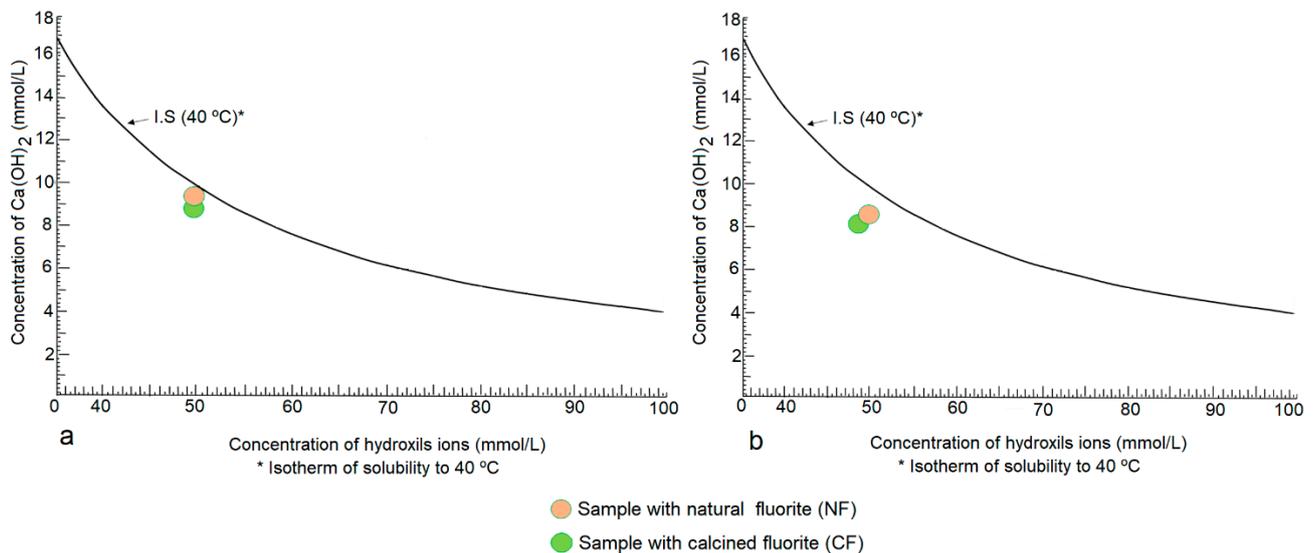


Figure 5. Evolution of the pozzolanic behaviour of the NF and CF samples analysed: (a) at 8 days; (b) at 15 days.

After 15 days of testing, both samples varied their position under the isotherm, which is interpreted as an increase in pozzolanic reactivity over time. It follows that the factors that caused this trend are the percentages of reactive SiO₂ and CaO present in the composition of both samples, as shown in Table 2.

Table 2. Chemical composition of the NF and CF samples investigated.

Compounds	Samples	
	Natural Fluorite (NF) (%)	Calcined Fluorite (CF) (%)
Total SiO ₂	53.28	56.70
Reactive SiO ₂	51.36	55.75
MgO	0.02	0.06
Total CaO	30.34	28.66
Reactive CaO	28.58	28.40
Fe ₂ O ₃	0.10	0.15
Al ₂ O ₃	0.23	0.15
I.R. *	3.85	2.84
SiO ₂ /(CaO + MgO)	1.86	1.99

* Insoluble residue.

Another factor that can determine the pozzolanic capacity of the researched fluorite is its electrical conductivity (EC); in this sense, Liu et al. [19] have determined that the EC is dominated by the fluorine ion, reaching ~0.01 S/m at 650 °C and is potentially important as a carrier of electric charge. Costafreda et al. [20] have demonstrated a similar situation in their study on the electrical conductivity of altered volcanic tuffs. In the works of Rosell et al. [21] it is established that by means of electrical conductivity the index of pozzolanic activity of the materials can be rigorously evaluated.

3.5. Chemical Quality Analysis (CQA)

Table 2 shows the result of the chemical analysis of two fluorite samples, one in the natural state (NF), which has already been described in Sections 3.1–3.3, and the other calcinated (CF). Virtually all silica in the NF sample is reactive (51.36%). A similar case occurs with reactive CaO (28.38%). Compounds such as MgO, Fe₂O₃ and Al₂O₃ are exceptionally low. The contents of I.R. are moderate with a tendency to reach the limit indicated by the standard UNE EN 196-2:2014 [16] and UNE-EN 197-1:2011 [12].

However, the analysis of the CF sample indicates an increase in reactive SiO₂ and reactive CaO of 55.70% and 28.40%, respectively; a similar case has been demonstrated in the work of Pei et al. [22]. In addition, the I.R. is comparatively lower in the CF, which is caused by the influence of the increase in temperature and the elimination of the most unstable residues [16].

The percentages of reactive SiO₂ and reactive CaO indicated in Table 2 confirm the pozzolanic character of both samples, both calcinated and in their natural state, which is reinforced by what was discussed in Sections 3.4 and 3.6.

3.6. Mechanical Strength Test (MST)

The results shown in Figure 6a,b and Figure 7a,b indicate an evident increase in mechanical compressive strength, both for specimens made with PC/NF and those with PC/CF, over the investigation period between 7 and 90 days of curing. Note how the values of compressive strength vary depending on two fundamental factors: the BPF of the NF and CF particles (2000 and 5000 cm²/g) and the degree of substitution of the PC by natural and calcinated fluorite. First, it considers the specific case of the PC/NF-01 to 06 sample series; within this series, the PC/NF-01 to 03 samples replace the PC in the specimens in 10, 25 and 40% with the BPF of the NF particles equal to 2000 cm²/g. The PC/NF-04 to 06 series has the same PC/NF ratios as the above-mentioned series, but the NF BPF is 5000 cm²/g. A substantial increase in mechanical strength is observed in specimens containing 10% NF and BPF 2000 cm²/g, and this increase is even more noticeable in specimens made with BPF of NF equal to 5000 cm²/g, as is the case with the PC/NF-04 to 06 specimen series. According to these results, it can be established that the mechanical strength increases as the portion of NF in the specimen decreases, and when the BPF is reduced from 2000 cm²/g to 5000 cm²/g [23].

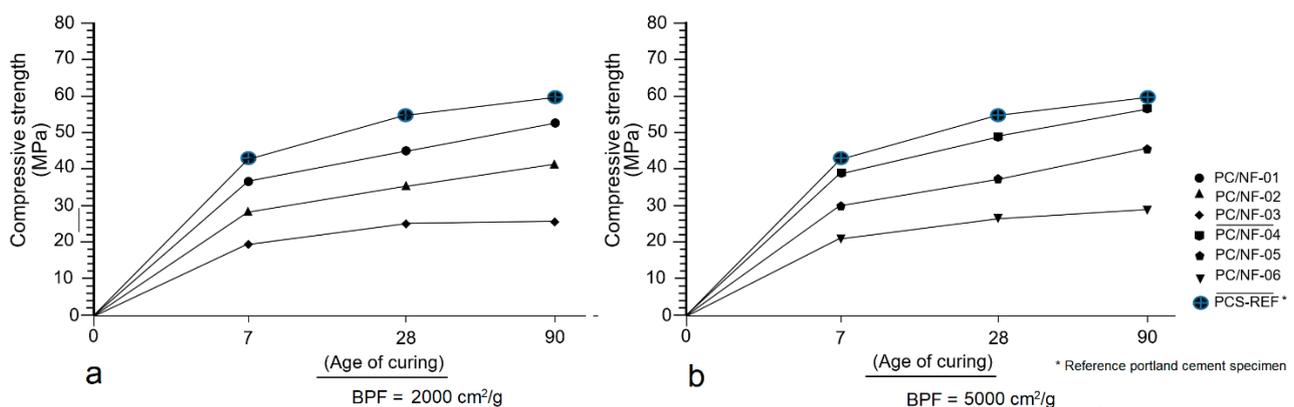


Figure 6. Behaviour of the mechanical strength of specimens elaborated with substitution of PC by NF in 10, 25 and 40%. In (a) the specimens have BPF of fluorite of 2000 cm²/g, while in (b) the BPF is 5000 cm²/g.

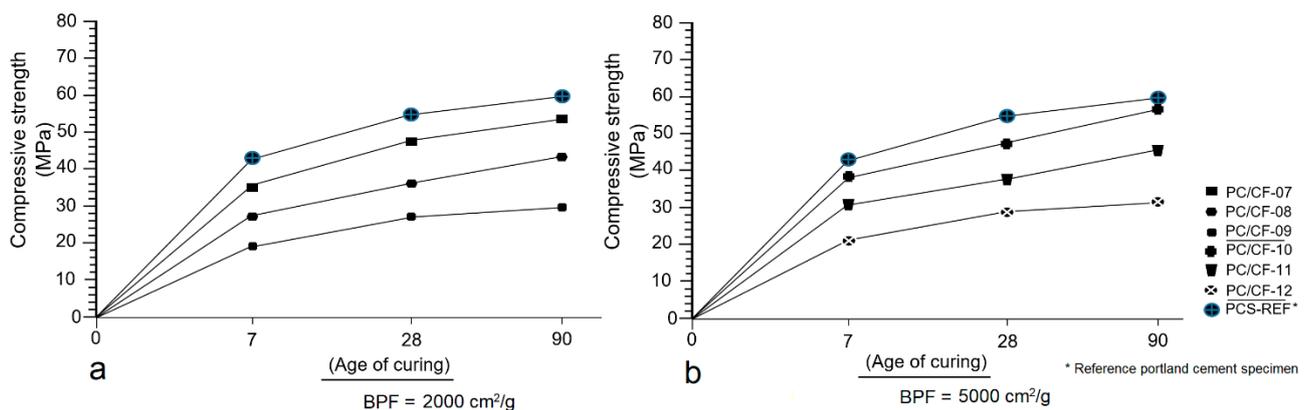


Figure 7. Mechanical strengths of specimens elaborated with replacement of PC by CF in 10, 25 and 40%. The BPF of CF in (a) is 2000 cm²/g, while in (b) it is 5000 cm²/g.

In the specimens made with CF the trend seems to be similar to that seen in Figure 6a,b. An evolution of the compressive strength is observed in the series of specimens PC/CF-07 to 09 and PC/CF-10 to 12, where the highest values correspond to the specimens with the lowest amount of CF and with the lowest BPF (Figure 7a). The analysis carried out in the groups of samples PC/NF-01 to 06 and PC/CF-07 to 12 confirms an increase in mechanical strength from 7 to 90 days in the specimens made with CF and with B.P.F of 2000 cm²/g, with respect to the NF. Similarly, this fact is seen in specimens where the BPF is 5000 cm²/g (Figure 7b).

The comparison of these results with those of the previous subsection shows the relationship that exists between pozzolanicity and mechanical strength [24]. According to Figure 6a,b and Figure 7a,b, in no case were the compressive strength values of the reference Portland cement (PCS-REF) exceeded.

4. Conclusions

The researched fluorite sample has a high degree of purity, according to the results of the XRD, SEM and RS analyses.

Both NF and CF have contents of reactive compounds, such as reactive SiO₂ and reactive CaO, which cause the pozzolanic reactivity of the studied sample; therefore, this is considered a solid argument to establish the pozzolanic character of the fluorite of the Órgiva deposit.

The mechanical strengths obtained are adequate, and this fact has guaranteed that the tested specimens have reached good compressive strengths at 28 and 90 days. However, an increase in resistance can be forecast beyond 90 days. With a view to large-scale industrial processes, the PC/NF ratio of 10% would be the most effective for the manufacture of pozzolanic cements; even the PC/NF ratio of 25% could also be used, which would lead to a significant decrease in production costs. Depending on the economic solvency of the local company, the PC/NF ratio of 40% could be used as a last resort. In the case of calcinated fluorites, the best PC/CF ratio, 10%, would be the most suitable, followed by a PC/CF of 25%. However, since the difference between the compressive strengths of the PC/NF and PC/CF specimens is not very noticeable, it would be recommended to not initially opt for the large-scale fluorite calcination method, due to the high costs that this represents. In this sense, it should also be considered that excessive grinding in the industrial process, with, for example, a BPF equal to 5000 cm²/g, would increase costs significantly.

The results obtained in this research could serve as a guide for the local Mining Company Órgiva, which would have an impact of added value for its fluorite deposits.

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