

Fast Set and High Early Strength Cement from Limestone, Natural Pozzolan, and Fluorite

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Abstract: Fast set and high early strength cements containing calcium fluoroaluminate phase ($C_{11}A_7CaF_2$) are usually produced by sintering a proportioned raw mix from calcareous and argillaceous components as the main raw materials, at reduced temperatures about 1330 °C. In this work, the possibility of utilizing natural pozzolan as the argillaceous component in the cement raw mix and in order to decrease the sintering temperature of fast set and high early strength cement clinker containing $C_{11}A_7CaF_2$ phase has been investigated. The results reveal that the sintering temperature can be reduced to temperatures as low as 1270 °C by utilizing a suitable natural pozzolan and improving the mix burnability. The experimental results confirm the possibility of achieving final setting times as low as 10 min and 3-day compressive strengths as high as 57 MPa.

Keywords: Fast set cement, High early strength cement, Compressive strength, Natural pozzolan

1. Introduction

Many investigations have been done to develop suitable fast set and high early strength cements for fast construction works. Nowadays, the necessity for accelerating construction works and applications such as repair of airways and highways have provided a basis for production and use of fast set and high early strength cements [1]. In recent decades, fast set and high early strength cements have gained more and more importance as important special inorganic binders. In many developed countries such as USA, Germany, Italy, and Japan, the industrial production and application of these cements have been increased.

Fast setting and quick hardening cements could be produced by one or a combination of the following methods:

- 1) Modifying the mineral phase composition of Portland cement and increasing its fineness.
- 2) Adding special admixtures to Portland cements.
- 3) Producing ternary-component mixtures of

Portland cements, alumina cements, and calcium sulfates.

- 4) Producing cements of specific mineral phase compositions.

Various quick binders are now being obtained by clinkerizing mixtures of minerals or industrial by-products, followed by grinding of the clinker obtained and then adding suitable additives such as anhydrite [1-5]. Different types of clinkers are known for fast set cements such as; clinkers rich in $C_{12}A_7$ phase, with mineral phase composition of C_2S - $C_{12}A_7$ - C_3A - C_4AF , which have been produced since 1976 with the name of Prompt Vicat in Italy and some other countries [5], clinkers containing calcium-aluminosulfate $C_4A_3\bar{S}$ and β - C_2S produced since 1990 in some countries [3], and clinkers containing fluorinated derivatives of $C_{12}A_7$ with mineral composition of C_3S - $C_{11}A_7CaF_2$ - C_2S - C_4AF that are known on the USA market since 1970 as regulated set cements [6-9].

The Japanese quick binder called Jet cement (regulated set cement of U.S.) has introduced new standards due to its rapid hardening. These cements exhibit a compressive strength of nearly 4 MPa at early ages that ordinary Portland cement just shows final setting. Such an early strength enables the prefabricated factories to open molds soon after short time periods [7].

Calcium fluoroaluminate-containing cements were first introduced in the USA. Intensive

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investigations done by Japanese researchers finally led to the production of these cements at industrial scale from 1971 [7]. In 1972, Uchikawa and Uchida [10] investigated the hydration of $C_{11}A_7CaF_2$ ($11CaO \cdot 7Al_2O_3 \cdot CaF_2$) phase with different additives for interpretation of the mechanism of setting and hardening of regulated set cement. In 1973, Uchikawa and Tsukiyama [9] investigated two types of Jet cements to clarify the effect of different methods of set regulation on the physical properties of Jet cement paste and mortars. In 1974, Uchikawa [8] invented a process for manufacturing modified rapid hardening Portland cement with a clinker that mainly consists of calcium fluoroaluminate. In 1999, Costa [4] investigated a particular quick-setting Portland cement clinker containing calcium fluoroaluminate mixed with lime. In 2003, Costa [11] invented quick-setting cement made from a clinker containing calcium fluoroaluminate to which sodium aluminate, lime, and optionally sodium bicarbonate were added.

Nowadays, the production and utilization of Jet cement in Japan is quite usual and everyday it gains more and more confidence. During the years 1984 to 1987 that production of all Portland cements shows an average annual reduction of approximately two million tones, the production of Jet cement was increased by nearly 2% [7].

Clinkers with a mineral phase composition of C_3S - $C_{11}A_7CaF_2$ - C_2S - C_4AF are usually produced from a proportioned raw mix prepared from a calcareous material, e.g. limestone or lime-marl, an argillaceous or a mixture of argillaceous materials, e.g. clay, kaolinite-clay, bauxite, and a fluoride-containing mineral, e.g. fluorite. The temperature reported in the literature for sintering such a raw mix is 1330 °C [4, 8, 11] that is quite lower than the sintering temperature for ordinary Portland cement. An important advantage of this cement compared to ordinary Portland cement is therefore a lower sintering temperature resulting in significant energy conservation in the sintering process. The need for energy conservation could economically be accomplished by promoting the clinker formation reactions at relatively lower temperatures. The use of alternative raw materials in cement industry, in order to improve

the reactivity of the raw mix is therefore expected to attract more attention in the future. The effectiveness of the use of partially calcined or amorphous alternative raw materials in production of Portland cement at the expense of lower rates of energy consumption has been well studied and practiced [12-16]. It is hypothesized that the sintering temperature of the fast set and high early strength cement can probably be still reduced by application of partially calcined or amorphous alternative raw materials. In such a case, there will be two reasons for an effectively lower sintering temperature compared to Portland cement. One is the mineralizing effect of fluoride-containing mineral and the other relatively higher chemical reactivity of the raw mix [17, 18]. In this work, the possibility of utilizing natural pozzolan as the argillaceous component in the cement raw mix and in order to decrease the sintering temperature has been investigated.

2. Experimental

2.1. Raw Materials

Suitable raw materials including limestone, fluorite, and natural pozzolan were prepared at first. Natural pozzolan, used in this work, was pumice obtained from Taftan mountain, located at the south east of Iran. The obtained pozzolan was firstly characterized for its chemical and mineralogical compositions and also its pozzolanic activity. The results of chemical

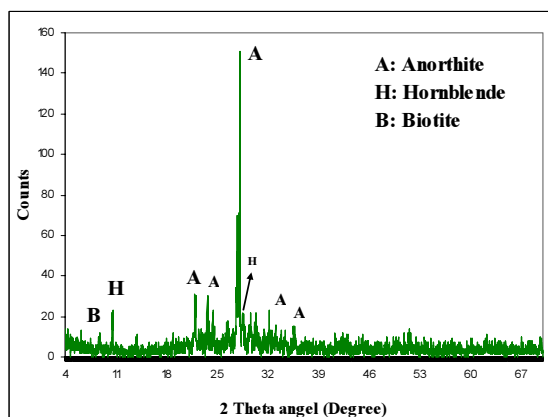


Fig. 1. X-ray diffraction pattern of pozzolan

Table 1. Chemical compositions of raw materials and raw mix proportions (wt %)

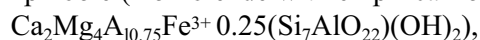
	Na ₂ O								Proportion	
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	+	F ⁻	L.O.I	in raw mix
	K ₂ O									
Pozzolan	61.25	17.94	5.00	6.70	2.52	0.11	3.65	-	2.40	22.58
Limestone	0.92	0.57	0.18	54.32	0.10	0.05	0.37	-	42.56	72.67
Fluorite	0.41	3.27	0.68	58.40	1.40	0.30	0.40	32.98	1.43	4.74
Raw mix	14.06	4.46	1.23	39.73	0.70	0.10	0.20	1.56	38.13	100

analysis determined according to ASTM standard C311 is shown in table 1. As seen, this natural pozzolan is a relatively highly siliceous material and according to ASTM standard C618, it could chemically be considered as a relatively good natural pozzolan. Figure 1 shows the X-ray diffraction pattern of Taftan pozzolan. The crystalline mineral phases present in Taftan pozzolan therefore include:

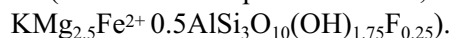
Feldspar (Anorthite with empirical formula;



Amphibole (Hornblende with empirical formula;



Mica (Biotite with empirical formula;



The pozzolanic activity of Taftan pozzolan was also evaluated by determining its strength activity index with Portland cement at 7 and 28 days (ASTM C311). The obtained results were 83.2 and 86.8 percent of control respectively for 7 and 28 days that show a relatively good pozzolanic activity in accordance with ASTM standard C618. A mix was designed according to calculations based on reaction stoichiometry. The selected raw materials were then mixed proportionally and the mix was ground and homogenized in a laboratory ball mill to a fineness of 12 per cent by weight on 90 μm sieve,

i.e. the usual norm for Portland cement raw mix. Chemical compositions of raw materials and raw mix proportion are shown in table 1.

2.2. Raw Mix Sintering

For sintering the prepared raw mix, it was necessary to shape the mix into pills of proper size. The mix was therefore moistened by adding enough water (16% by weight). Then 40 g of the moist powder was poured into a cylindrical mold and pressed at a pressure of 4 MPa to shape it into a circular pill of 40 mm in diameter and 10 mm in thickness.

The pills were then dried at 110°C, and put on a zirconium refractory plate in a programmable laboratory furnace. To determine the optimum time-temperature-program for sintering process and the minimum possible sintering temperature, a series of burnability tests were designed and carried out. The pills were heated up to 900 °C during 50 minutes and allowed for being completely calcined at the same temperature. The burning temperature was then sharply increased to its maximum value during 20 minutes, and the pills were held at the maximum temperature for 1 h. Figure 2 shows the lime-combinability of the raw mix at different temperatures. The optimum time-temperature-program, was designed based on the results of burnability test and the minimum temperature required for the appearance of the

Table 2. Chemical composition of clinker produced at 1270°C (wt %)

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O+K ₂ O	F ⁻	L.O.I	Free CaO
21.50	6.91	1.91	66.10	1.08	0.16	0.30	1.40	0.17	0.16

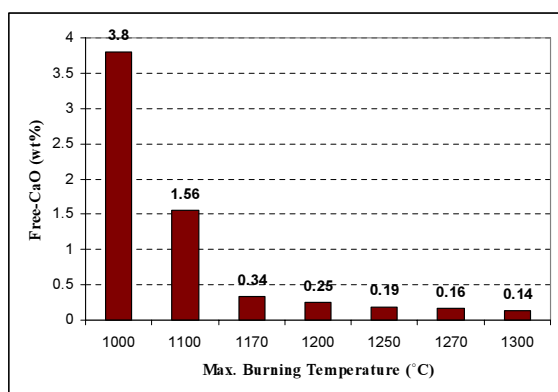


Fig. 2. Free-lime content of the raw mix at different maximum burning temperatures (burning time; 1h)

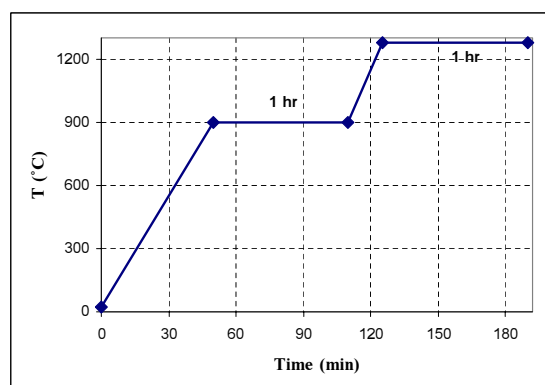


Fig. 3. Time-temperature-program for sintering process of raw mix

mineral phase $C_{11}A_7CaF_2$. Figure 3 shows the designed time-temperature-program for sintering process of the raw mix.

The pills were then burned according to the optimum program and for a total sintering time of nearly 3 h. After sintering, the produced clinker was cooled at ambient temperature. Chemical composition of the produced clinker is shown in table 2.

2.3. Preparation of Fast Set and Very High Early Strength Cement

Calcium sulfate is an important constituent in fast set and high early strength cements containing $C_{11}A_7CaF_2$ mineral phase. The presence of calcium sulfate is necessary because of its participation and its role in hydration mechanism resulting in fast setting and quick hardening behaviors. Natural gypsum was prepared as the source of calcium sulfate required. Chemical composition of the natural gypsum is shown in table 3. Part of the prepared natural gypsum was burned at 950°C for one hour to produce anhydrite.

Fast set and high early strength cement samples were designed and produced by intergrinding the produced clinker with anhydrite

or a mixture of anhydrite and gypsum to a Blaine specific surface area of nearly 5500 cm²/g using a laboratory ball mill. The amount of calcium sulfate added was adjusted to control a weight-ratio of Al_2O_3/SO_3 in cement in the range 0.6-1.8 that is reported to be optimum [8].

The prepared cements were then characterized and studied by X-ray diffractometry (XRD, Philips Expert System, CuK α -radiation and Ni-filter) and scanning electron microscopy (SEM, Philips XL30) techniques and measuring their setting times and early age-compressive strength. The initial and final setting times of the systems were measured by using Vicat needle in accordance to ASTM C191-82 and with a constant water/cement ratio of 0.3. The required water for a constant consistency was measured in accordance with ASTM C187-86. Early age compressive strengths were measured using mortar cube specimens of the size 50×50×50 mm in accordance with ASTM C109. The specimens were all prepared with constant water/cement ratio of 0.485 and sand/cement ratio of 2.75:1. The molds were opened after keeping them for 2 h in an atmosphere of more than 95% relative humidity at 24°C. The specimens were then cured in water at 24°C for measuring their compressive strength.

3. Results and Discussion

As seen in figure 2, the free-lime content of the raw mix can easily be reduced to quite low values after burning for one hour at temperatures in the

Table 3. Chemical composition of natural gypsum (wt %)

SiO ₂ +R ₂ O ₃	CaO	SO ₃	L.O.I	Total
1.9	31.8	44.8	21.1	99.6

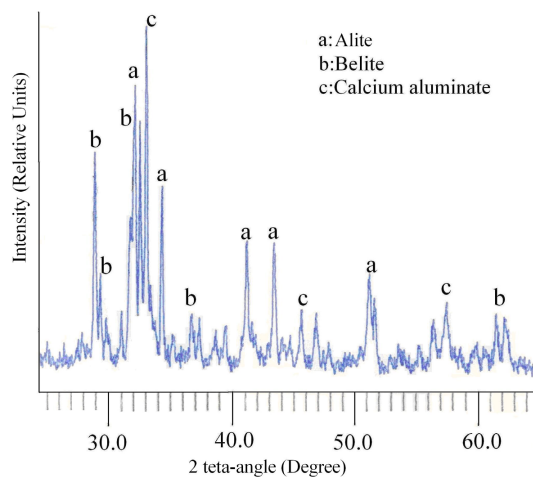


Fig. 4. X-ray diffraction pattern of clinker sample produced at 1200°C

range of 1100°C to 1300°C. This shows that the mix has a good burnability compared to Portland cement raw mix that requires sintering at quite higher temperatures. Such good burnability is due to both the mineralizing effect of calcium fluoride and the relatively high reactivity of the utilized natural pozzolan as the argillaceous component of the raw mix [12-20].

As seen, at temperatures higher than 1100°C, free-lime is less than 1%, which seems to be suitable. However, investigations done by X-ray diffraction revealed that burning at maximum heating temperatures lower than 1270°C does not result in the formation of the desired phase composition. Figure 4 presents X-ray diffraction

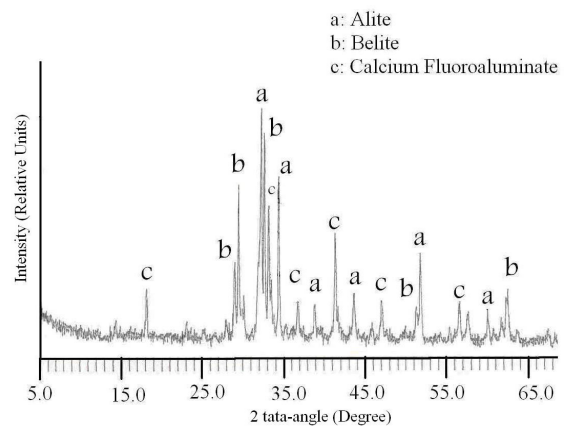


Fig. 5. X-ray diffraction pattern of clinker sample produced at 1270 °C

pattern of the clinker sample prepared by heating at the maximum temperature of 1200°C for 1 hour. As seen, the phase composition comprising of C_3A , C_2S and C_3S does not include the phase $C_{11}A_7CaF_2$.

X-ray diffraction pattern of the clinker sample produced at 1270°C is shown in figure 5. As seen, the mineral phase composition of clinker consists of the four phases; alite, belite, calcium fluoroaluminate, and ferrite in the order of decreasing content respectively. This shows the possibility of synthesizing a mineral phase composition of alite, belite, calcium fluoroaluminate, and ferrite containing relatively high quantities of alite by clinkerizing a

Table 4. Results of setting times and early-age compressive strengths

Cement Sample	Cement sample content	Setting time		Compressive strength			
		(min)		(MPa)			
		Initial	Final	3 h	6 h	1 day	3 days
1	100% Clinker	5	10	2.44	2.52	4.30	24.63
2	87.5% Clinker + 12.5% Anhydrite	8	14	3.66	4.95	15.57	45.49
3	90% Clinker + 2% Gypsum + 8% Anhydrite	13	21	5.17	6.64	12.15	46.95
4	90% Clinker + 10% Anhydrite	12	16	4.32	5.29	18.84	57.45

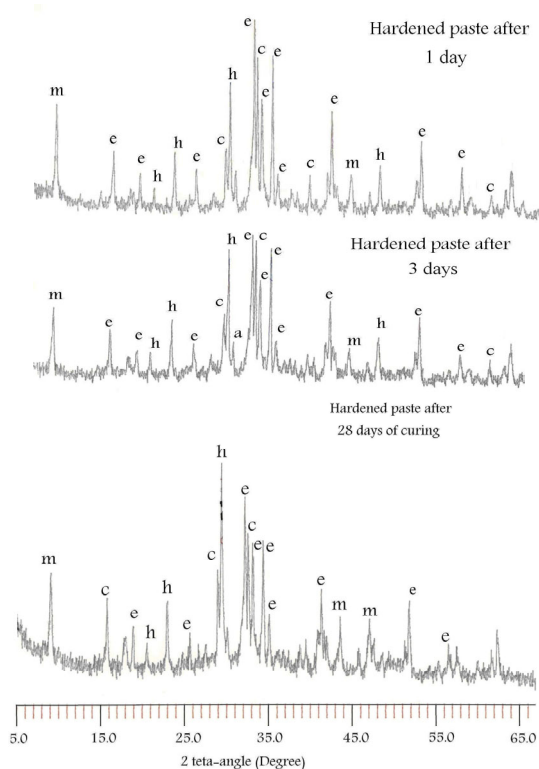


Fig. 6. X-ray diffraction patterns of 1-, 3-, and 28-day cured hardened pastes of cement sample containing 10% anhydrite (h: Calcium silicate hydrate, e: Ettringite, c: Calcium hydroxide, m: Monosulfate hydrate)

proportioned raw mix of limestone, fluorine, and natural pozzolan at a temperature as low as 1270°C.

Results obtained for setting times and early-age compressive strengths, which are comparable to those reported in the literature [7-11], are presented in table 4. As seen, initial and final setting times as low as 5 and 10 minutes could be obtained respectively. Samples containing different amounts and different forms of calcium sulfate exhibit maximum compressive strengths as high as 5.17, 6.64, 18.84, and 57.45 MPa at different ages of 3 h, 6 h, 1 day, and 3 days. The hydration kinetics of the phase calcium fluoroaluminate strongly depends on the type and the amount of calcium sulfate added [8]. The compressive strength gain of the prepared cement samples at early ages therefore significantly varies with the amount and the type of calcium sulfate.

At very early ages, e.g. after 3 and 6 h, sample No. 3 shows the highest compressive strength, i.e. 5.17 and 6.64 MPa. After 1 day however, this

is sample No. 4 that provides the highest results for compressive strength. The compressive strength values obtained for sample No. 1 are exceptionally low confirming the necessary role of calcium sulfate for high early strength behavior. As seen, system No. 4 exhibits the highest 1-day and 3-day compressive strengths, i.e. 18.84 MPa and 57.45 MPa respectively.

Knowing that the fineness of the prepared cement samples was taken constant and almost equal to those reported in the literature, the reason for such high 1- and 3-day strengths can be attributed to probably relatively higher amount of $C_{11}A_7CaF_2$ phase in the studied cement samples. Investigations have shown that this is the hydration of $C_{11}A_7CaF_2$ phase in the presence of calcium sulfate that effectively improves the strength behavior of these cements. The weight ratio of $C_{11}A_7CaF_2$ to calcium sulfate is also quite an important influencing parameter [9].

X-ray diffraction patterns of 1-, 3-, and 28-day cured hardened paste of the produced cement containing 10% anhydrite (sample No. 4) are shown in figure 6. Properties of the hardened paste are influenced by the type, size, and shape of hydration products and the structure of the hardened paste. As seen in figure 6, the main hydration product at early ages of 1 to 3 days is ettringite. The more the amount of ettringite produced, the higher the early age compressive strengths obtained. Theoretically, compressive strength of ettringite is twice as high as that of monosulfate hydrate, so that the amount of ettringite produced is one of the most important factors governing the compressive strength development at earlier ages [9]. Calcium silicate hydrate, which is the hydration product of calcium silicates (C_3S , C_2S) shows relatively lower quantities at early ages. After 28 days of curing however, the content of calcium silicate hydrates increases to the highest. The rate of hydration of alite estimated from stoichiometry of hydration reactions is reported to be twice as fast as monoclinic alite in Portland cement [9].

Higher amounts of $C_{11}A_7CaF_2$ phase and higher reactivity of anhydrite form of calcium sulfate are therefore responsible for accelerating the rate of ettringite formation reaction and thus resulting in the formation of relatively higher

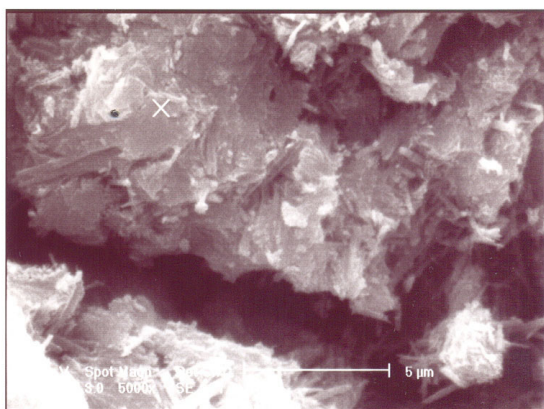


Fig. 7. Microstructure of 28-day hardened paste of cement sample containing 10% anhydrite (Magnification: 5000x)

amount of this binding hydrate.

Investigations done by scanning electron microscopy also confirmed that the microstructure is mainly composed of calcium silicate hydrates and ettringite. Figure 7 presents a typical SEM micrograph prepared from microstructure of the 28-day hardened paste of the cement sample containing 10% anhydrite at a magnification of 5000 times. The results of EDX analyses done on the region shown by a cross sign confirmed the presence of calcium silicate hydrates. Needle-like ettringite crystals are also clearly visible. SEM micrographs presented in Figures 8 and 9 show 5000 and 10000 times magnified images obtained from needle-like ettringite crystals.

Previous studies confirmed a denser microstructure for hardened pastes of fluoroaluminate cements compared to Portland

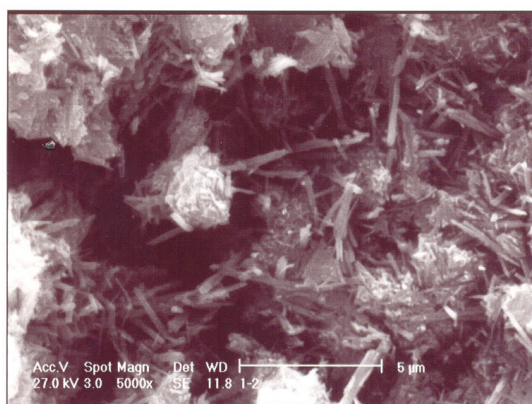


Fig. 8. Needle-like ettringite crystals observed in the microstructure (Magnification: 5000x)

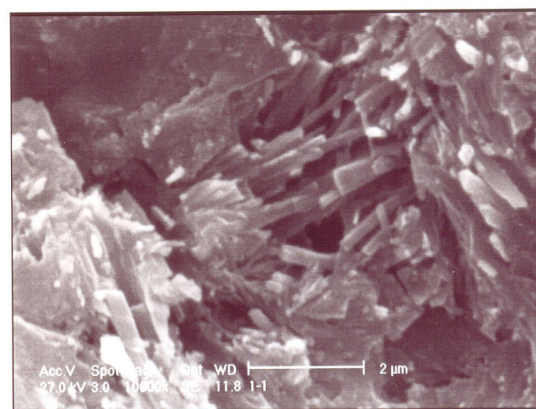


Fig. 9. Needle-like ettringite crystals observed in the microstructure (Magnification: 10000x)

cement [9]. Such a denser microstructure can be attributed not only to the considerably higher fineness of these cements, but also mostly to the expansive nature of ettringite formation reaction. Controlled expansion at early ages can result in an effective decrease in total pore volume and produce a much denser microstructure exhibiting significantly higher compressive strengths. Detailed experimental works and application of suitable laboratory techniques such as mercury intrusion porosimetry are however necessary to investigate the changes happening in the microstructure of the cement paste during the course of hydration.

4. Conclusions

The sintering temperature in fast set and high early strength cement clinker containing calcium fluoroaluminate phase can be reduced to temperatures as low as 1270 °C by utilizing a suitable natural pozzolan as the argillaceous component of the raw mix and improving the mix burnability. The experimental results confirm the possibility of achieving final setting times as low as 10 min and 3-day compressive strengths as high as 57 MPa.

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