CHEMICAL ACTIVATION AND SET ACCELERATION OF LIME-NATURAL POZZOLAN CEMENT

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In order to shorten the setting time and to fasten the strength development of lime pozzolan cements, different methods including calcinations, acid treatment, prolonged grinding, elevated temperature of curing and addition of chemical activators have been tried to improve the pozzolanic reactivity of natural pozzolan. In this work, the effects of some chemical activators and set accelerators on set and strength behaviours of a lime-natural pozzolan cement containing 70% natural pozzolan of the type pumice and 30% hydrated lime (by mass) have been investigated. Results obtained show that addition of alkaline compounds and Portland cement clinker can improve the set and strength behaviours of lime-natural pozzolan cements. Sodium sulfate is the most effective chemical activator for lime-natural pozzolan cements compared to Na_2CO_3, NaOH, $CaCl_2 \cdot 2H_2O$, and ordinary Portland cement-clinker. The most effective set accelerator for the studied lime-natural pozzolan cement however is sodium hydroxide compared to Na_2SO_4, Na_2CO_3, NaCl, $CaCl_2 \cdot 2H_2O$ and ordinary Portland cement-clinker. Addition of 6 wt.% Na_2SO_4 could noticeably increase 90-day compressive strength and presence of 4% NaOH as a set accelerator could effectively decrease both initial and final setting times.

INTRODUCTION

Lime-natural pozzolan cements were widely used for all kinds of construction as the earliest important building materials. The invention of lime and lime-natural pozzolan cements backs to the Neolithic period (7000 BC). They were widely used in the masonry construction of aqueducts, arch bridges, retaining walls and buildings during Roman times. The use of lime-natural pozzolan cements however has not been continued during the history of inorganic binders due to their important disadvantages including long setting time along with low early-age strength. In practice, it is important for cement to reach satisfactory strength within a short period of time. On the other hand, lime-natural pozzolan cements have a number of advantages including low cost and more importantly long-term engineering properties such as very low heat evolution, decreased permeability and increased chemical resistance.

The invention of Portland cement in the 19^{th} century resulted in a drastic reduction in use of lime-natural pozzolan cement because of the faster setting time and higher early-age strength of Portland cements. In the past 50 years, the shortage of Portland cements and the environmental side-effects of its production process have caused a growing interest in the demand of lime-natural pozzolan cements.

In order to have lime-natural pozzolan cements with shorter setting time and faster strength development, different methods have been tried to improve the pozzolanic reactivity of natural pozzolan, which include calcinations [1-4], acid treatment [5-7], prolonged grinding [8-10], elevated temperature of curing [11, 12] and addition of chemical activators [13-17]. However, some methods are too expensive to be used practically, and some do not show a significant efficiency [18].

In previous studies, it has been found that addition of some chemicals to lime-natural pozzolan cements can significantly increase the pozzolanic reaction rate resulting in shorter setting times, faster strength gain and higher ultimate strengths [15-17].

A previous study [19] has indicated that the presence of 4% $CaCl_2 \cdot 2H_2O$ increased the apparent activation of lime-pozzolan cement greatly. According to a comparison based on strength development and cost, Shi C. [20] has shown that addition of Na_2SO_4 or $CaCl_2$ is much more effective than prolonged grinding of natural pozzolans or elevated-temperature curing of lime-pozzolan pastes. In an experimental work [16], it is concluded that addition of 4% Na_2SO_4 increased both the early and later strength of lime-pozzolan cement pastes from 23 to 65°C. Addition of 4% $CaCl_2 \cdot 2H_2O$ lowered the early strength but increased the later strength at 23°C, and increased both the early and later strengths from 35 to 65°C [16].

In this work, we have studied the effect of some chemicals including a number of set accelerators and some chemical activators of Portland cements on set and early-age strength behaviours of lime-natural pozzolan cement consisting of 70% by weight natural pozzolan of the type pumice and 30% hydrated lime.

EXPERIMENTAL

Raw Materials

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 analysis determined according to ASTM standard C311 [21] and the value of specific surface area determined by Blain air-permeability apparatus are shown in table 1. As seen, this natural pozzolan is a relatively highly siliceous and according to ASTM standard C618 [22], chemically it could 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 Anorthite, Hornblende and Quartz.

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 results obtained, i.e. 83.2 and 86.8 percent of control respectively for 7 and 28 days, show a relatively good pozzolanic activity in accordance with ASTM standard C618.

Knowing that particle size distribution of pozzolan powder could effectively affect both wet and dry properties of the lime-natural pozzolan cement, the pozzolan was ground in an industrial closed mill to obtain a relatively highly fine powder with a suitable particle size distribution. The particle size distribution of the pozzolan powder was determined by a laser particle size analyzer. The RRSB curves of particle size distribution for pozzolan powder presented in figure 2, shows a relatively suitable ground powder. The uniformity factor and the mean particle size are 0.95 and 22.63 μm respectively.

A commercial hydrated lime of relatively high purity was also prepared. Chemical composition and Blaine fineness of the hydrated lime were determined in accordance with ASTM Standard C25 [23] and C204 [24]. The Suitability of the hydrated lime was evaluated in accordance with ASTM Standard C821 [25]. Table 2 shows the chemical and physical specification of the hydrated lime and the corresponding requirements of ASTM standard.

Many chemical admixtures can be used to activate lime-natural pozzolan cements. The previous results indicated that the addition of alkaline compounds can significantly increase the strength of lime-natural pozzolan cements [15-17]. Some substances, however, are

Table 2. Chemical and physical specification of the hydrated lime and the corresponding requirements of ASTM standard C821.

Specification	Hydrated Lime	ASTM C821
$Ca(OH)_2$	98.20 %	-
$Mg(OH)_2$	1.32 %	-
Impurities	0.48 %	-
Chmical Factor	74.31	50 min
Blaine Fineness (m^2/kg)	1368	1000 min
Pozzolanic Receptivity Index	102.21	100 min

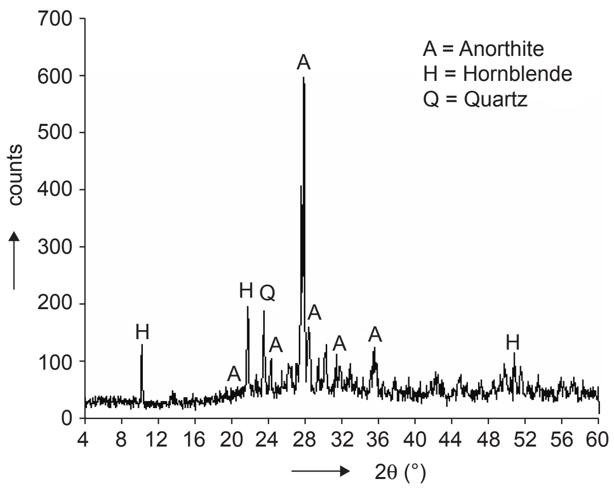

Figure 1. X-ray diffraction pattern of Taftan pozzolan.

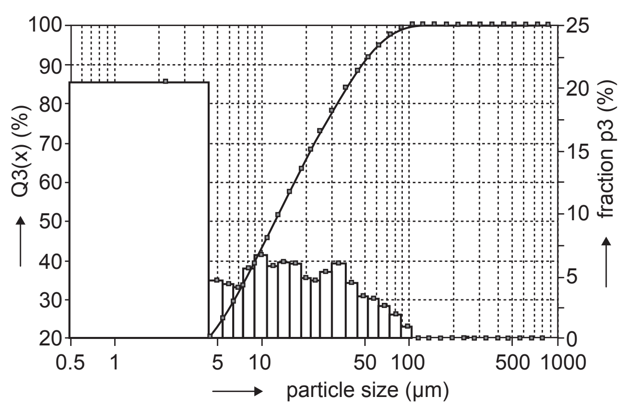

Figure 2. RRSB-curve of particle size distribution of ground Taftan pozzolan.

Table 1. Chemical composition and Blaine fineness of the ground Taftan pumice-type pozzolan.

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	Cl	LOI	Moisture	Blaine (m^2/kg)
wt.%	61.57	18.00	4.93	6.69	2.63	0.10	1.95	1.65	0.04	2.15	0.51	309

too expensive to be practically used. Based on the information in the literature and economic analysis, six relatively inexpensive chemicals including Na_2SO_4, Na_2CO_3, NaOH, NaCl, $CaCl_2 \cdot 2H_2O$, and ordinary Portland cement-clinker was chosen. They were added at three different dosages of 2, 4 and 6 wt.% by dissolving them into the mixing water, except ordinary Portland cement-clinker which was thoroughly mixed with dry binder. Table 3 shows the chemical composition of the ordinary Portland cement-clinker used.

Preparation of Specimens

Mixtures of ground pozzolan and hydrated lime at given proportions were homogenized using a domestic grinder of the type SANA SCG-3001 (180W) and grinding each system separately for a few minutes (1 to 2). Water-to-dry binder ratios were determined for an approximately the same workability in all the pastes using a flow table. Water-to-dry binder ratios of different systems are given in table 4. After enough mixing, the pastes were cast into specimens of 2×2×2 cm in size, and the moulds were placed into a bath of more than 95% relative humidity. The moulds were opened when the specimens were strong enough and the specimens were then stored in the humid bath for further curing.

Test Procedure

Attempts were made to measure the compressive strength of the specimens at different ages. However, the results obtained were not reliable because most of the specimens seemed to be quite sound and without any crack after the test. Such a different behaviour compared to specimens made from Portland cement is due to difference in the brittleness of the two materials. Hardened paste of Portland cement is brittle whereas that of lime-natural pozzolan mixture is to some extent elastic. To overcome such a difficulty, the specimens were firstly dried for 12 hours at 50°C for making them brittle, and then tested for their compressive strength at the designated testing ages. It was considered that such a drying stage could result in an increase in compressive strengths both due to acceleration of pozzolanic reaction and enhancement of Van der Waals forces in the microstructure of the hardened pastes. A comparison between the results of compressive strengths obtained with and without drying however confirmed a maximum difference of nearly 7% which could be taken into account.

For each system, three specimens were used for determining compressive strength. The average of the three results was reported as the compressive strength of the system. Initial and final setting times of all the systems were measured using Vicat needle in accordance with ASTM standard C191-82 [26]. X-ray diffraction (XRD, Philips Expert System, CuK_α-radiation and Ni-filter) and scanning electron microscopy (SEM, Philips XL30) were the principle laboratory techniques used to study the systems. For studying with SEM, a number of specimens were cut into halves to expose internal regions. Suitable halves were then impregnated with epoxy resin, polished and coated with carbon.

RESULTS AND DISCUSSION

Determination of the proper lime-natural pozzolan proportion

For determining the proper proportion of the lime-natural pozzolan, a number of differently proportioned dry binders were designed, prepared, and tested for their 50- and 90-day compressive strengths. The results obtained for 50- and 90-day compressive strengths are shown in table 5. As seen, the system consisting of 70% pozzolan and 30% hydrated lime (by weight) exhibits the highest 50- and 90-day compressive strengths, i.e. 7.25 and 10.03 MPa respectively. This optimum proportion of lime-natural pozzolan showing the best strength behaviour was chosen for the rest of the work.

Chemical Activation and Set Acceleration

Figures 3 and 4 show the effects of chemical admixtures on 50- and 90-day compressive strengths of the studied lime-natural pozzolan cement respectively.

Table 3. Chemical composition of ordinary Portland cement clinker.

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	Cl	LOI	Free-CaO
wt.%	21.88	5.56	3.81	64.73	2.30	0.21	0.42	0.19	-	0.18	0.85

Table 4. Water-to-dry binder ratio for lime-natural pozzolan cements.

Lime-pozzolan proportion (wt.%)	10-90	20-80	30-70	40-60	50-50	60-40
Water-to-dry binder ratio (%)	43	43	44	44	45	45

The 90-day compressive strength of the system without any chemical admixture was 10.03 MPa. As seen, all the chemical admixtures used behave as activators and could more or less improve the strength behaviour of the lime-natural pozzolan cement. The higher the dosage of the activator, the higher the 50- and 90-day compressive strengths. The introduction of 6 wt.% Na_2SO_4 however noticeably improves the strength of lime-natural pozzolan cement. It has increased the 90-day compressive strength of the lime-natural pozzolan cement up to 19.83 MPa, i.e. nearly twice. The effect of Na_2SO_4 was also studied by other researchers [14-16] and they claimed that addition of 4% Na_2SO_4 can significantly improve the early strength of this cement.

The effects of the same chemical admixtures on the set behaviour of the lime-natural pozzolan cement were also studied. Figures 5 and 6 show initial and final set-

Table 5. 50- and 90-day compressive strengths of the plain lime-natural pozzolan cements at different proportions.

Lime-natural pozzolan proportion (wt.%)	10-90	20-80	30-70	40-60	50-50	60-40
50-day Compressive Strength (MPa)	5.15	6.64	7.25	6.67	6.42	5.96
90-day Compressive Strength (MPa)	7.15	9.20	10.03	9.13	8.85	8.23

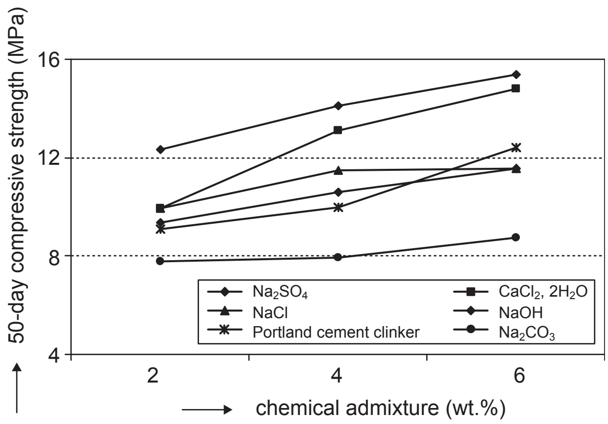

Figure 3. 50-day Compressive Strength of the studied lime-natural pozzolan cement with chemical activators at different dosages.

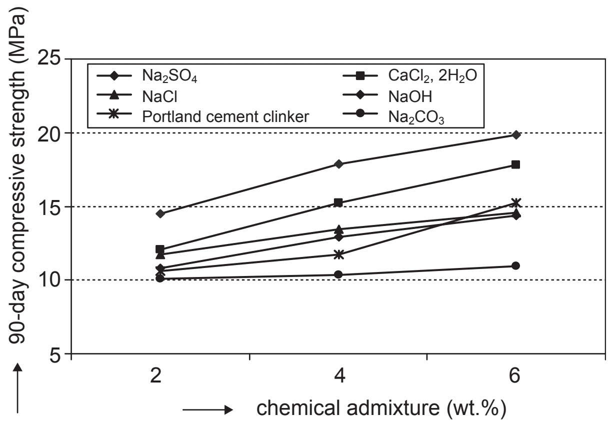

Figure 4. 90-day Compressive Strength of the studied lime-natural pozzolan cement with chemical activators at different dosages.

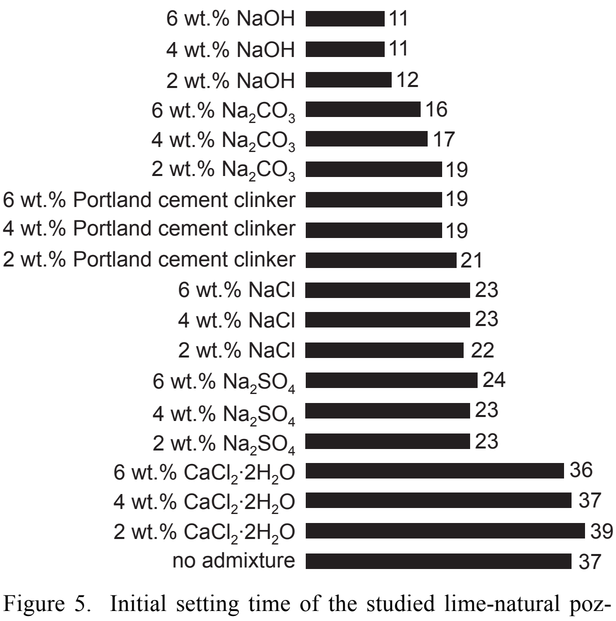

Figure 5. Initial setting time of the studied lime-natural pozzolan cement without and with chemical admixture (h).

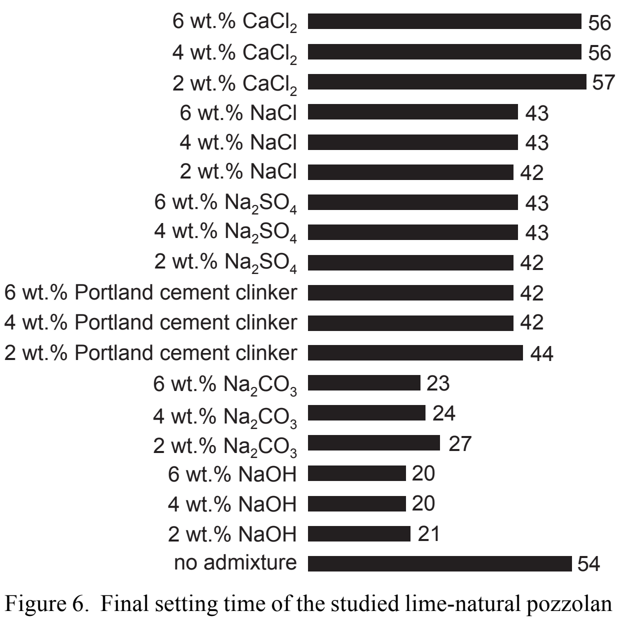

Figure 6. Final setting time of the studied lime-natural pozzolan cement without and with chemical admixture (h).

ting times of the studied lime-natural pozzolan cement without and with chemical admixtures at different dosages of 2, 4, and 6 % by weight respectively. The initial and final setting times of the lime-natural pozzolan cement without chemical admixture were 37 and 54 hours respectively at an atmosphere of more than 95% relative humidity and at 25°C. As seen, all the used chemical admixtures are effective and can more or less decrease both initial and final setting times, except calcium chloride. Sodium hydroxide however is the most effective set accelerator. Addition of 4% NaOH can decrease the initial and final setting times of the lime-natural pozzolan cement to 11 and 20 hours respectively at an atmosphere of more than 95 % relative humidity and at 25°C.

X-Ray Diffractometry

Taftan pozzolan, 50-day hardened paste of lime-natural pozzolan cement, and 50-day hardened paste of lime-natural pozzolan cement containing 6 wt.% Na_2SO_4 were studied with X-ray diffractometry technique to identify their crystalline mineral phases. The X-ray diffraction patterns of the hardened paste of lime-natural pozzolan cement, and hardened paste of lime-natural pozzolan cement containing 6 wt.% Na_2SO_4 are presented in figures 7 and 8. The crystalline mineral phases identified are as follows;

1-Taftan pozzolan:
- Anorthite with empirical formula;
  $Na_{0.05}Ca_{0.95}Al_{1.95}Si_{2.05}O_8$
- Hornblende with empirical formula;
  $Ca_2Mg_4Al_{0.75}Fe^{3+}{}_{0.25}(Si_7AlO_{22})(OH)_2$
- Quartz; SiO_2

2-Hardened paste of lime-natural pozzolan cement:
- Portlandite with empirical formula;
  $Ca(OH)_2$
- Actinolite with empirical formula;
  $Ca_2Mg_3Si_8O_{22}(OH)_2Fe^{2+}{}_2$
- Anorthite

3-Hardened paste of lime-natural pozzolan cement containing 6 wt.% Na_2SO_4:
- Albite with empirical formula;
  $Na_{0.95}Ca_{0.05}Al_{1.05}Si_{2.95}O_8$
- Portlandite
- Actinolite

According to the results obtained both hardened pastes of lime-natural pozzolan cement without and with chemical admixture have the same crystalline mineral phases except the two phases Anorthite and Albite. These two phases belong to the feldspar group of minerals and posses almost the same properties, so that such a difference in the crystalline phases of the two cement systems is less probable to be responsible for the difference observed in their strength behaviours. Knowing that the compressive behaviour of the lime-natural pozzolan material is mainly due to formation of gel-like C–S–H type hydrates, the compressive strength improvement with addition of 6 wt.% Na_2SO_4 therefore is due to higher contents of amorphous C–S–H gels and/or less probably different amorphous binding phases not detectable by X-ray diffractometry. The results obtained by TG-DTA laboratory technique and the effects of Na_2SO_4 on the kinetics of the pozzolanic reaction of the studied lime-natural pozzolan material will be presented and discussed in a future publication.

Scanning Electron Microscopy

Morphology of the microstructures of the two 50-day hardened pastes without any chemical admixture and with 6 wt.% Na_2SO_4 was studied with scanning

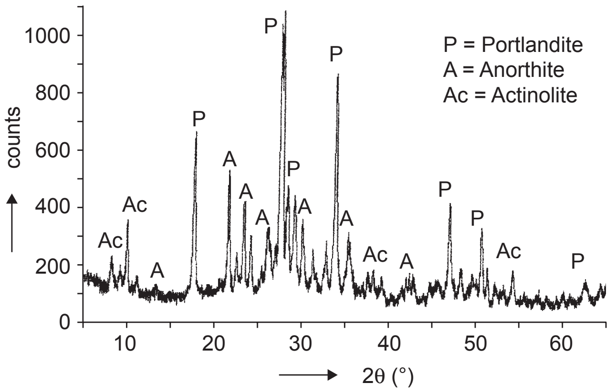

Figure 7. X-ray diffraction pattern of the 50-day hardened paste of lime-natural pozzolan cement without any chemical admixture.

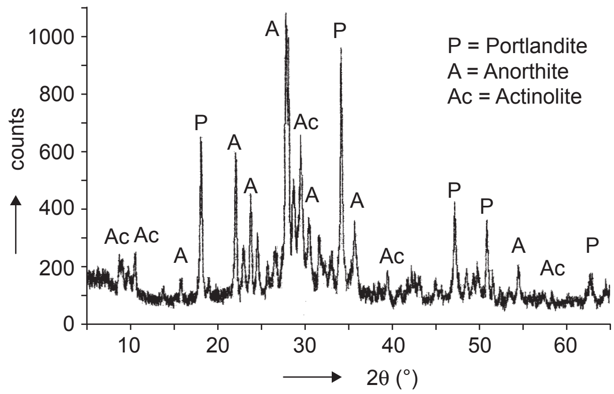

Figure 8. X-ray diffraction pattern of the 50-day hardened paste of lime-natural pozzolan cement containing 6 wt.% Na_2SO_4.

electron microscope. Figures 9 and 10 show SEM-images taken from the microstructure of the two hardened pastes without any chemical admixture and with 6 wt.% Na_2SO_4 respectively. Observations by SEM revealed that the microstructure of the two hardened pastes were quite similar. They consisted of mostly amorphous phases along with few microcrystalline phases observable only at relatively high magnifications. EDAX analysis using ZAF-correction clearly confirmed the presence of relatively large Portlandite crystals accumulated around small voids in both hardened pastes. Figure 10 shows a number of relatively large Portlandite crystals precipitated around a small void in the microstructure of the 50-day hardened paste of lime-natural pozzolan cement with 6 wt.% Na_2SO_4.

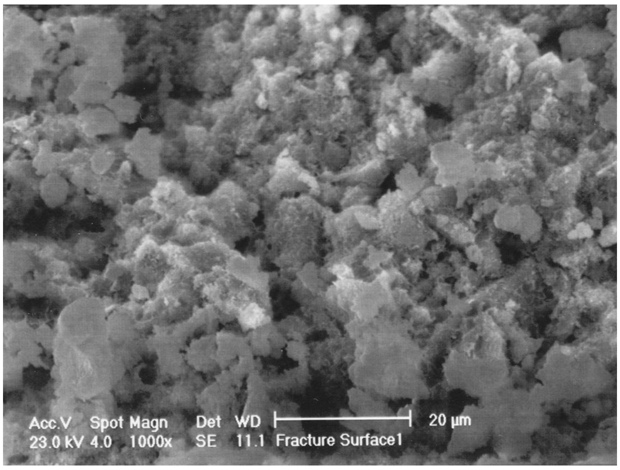

Figure 9. SEM-image of the microstructure of 50-day hardened paste of lime-natural pozzolan cement without any chemical admixture.

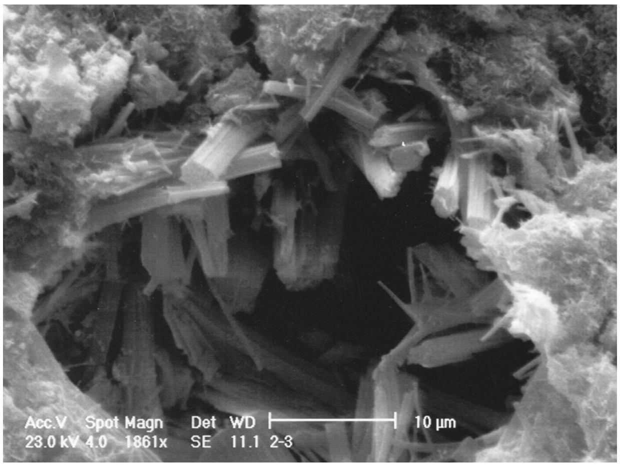

Figure 10. SEM-image of the microstructure of 50-day hardened paste of lime-natural pozzolan cement containing 6 wt.% Na_2SO_4.

CONCLUSION

1. Addition of alkaline compounds and Portland cement clinker can improve the set and strength behaviours of lime-natural pozzolan cements.
2. Sodium sulfate is the most effective chemical activator for the studied lime-natural pozzolan cement compared to Na_2CO_3, NaOH, $CaCl_2 \cdot 2H_2O$ and ordinary Portland cement clinker.
3. Addition of 6 wt.% Na_2SO_4 to the studied lime-natural pozzolan cement consisting of 70 % pumice-type pozzolan and 30% hydrated lime can increase the 90-day compressive strength more than twice.
4. Sodium hydroxide is the most effective set accelerator for the studied lime-natural pozzolan cement compared to Na_2SO_4, Na_2CO_3, NaCl, $CaCl_2 \cdot 2H_2O$ and ordinary Portland cement-clinker.
5. Addition of 4% NaOH to the studied lime-natural pozzolan cement consisting of 70 % pumice-type pozzolan and 30 % hydrated lime can significantly decrease both initial and final setting times.

References

1. Mielenz R. C., Witte L. P., and Glantz O.J . in: *Use of Pozzolanic Materials in Mortars and Concretes*, p. 43-91, Symp. Proc., STP99, American Society for Testing and Materials, Philadelphia, PA, USA 1949.
2. Rossi G. and Forchielli L.: Cemento *73*, 215 (1976).
3. Costa U. and Massazza F.: Cemento *74*, 105 (1977).
4. Shi C. and Day R. L.: Cem.Concr.Res. *23*, 824 (1993).
5. Techner S. and Pernoux T.: Clay Miner. Bull. *1*, 145 (1951).
6. Alexander K. M.: Aust. J.Appl.Sci. *6*, 224 (1955).
7. Hemmings R. T., Berry E. E., Cornelius B. J. and Golden D. M. in: Materials Research Symposium, p. 141-161, Proc. Mater. Res. Soc., 1989.
8. Alexander K. M.: J.Am.Concr.Inst. *57,* 557 (1960).
9. Chatterjee M. K. and Lahiri D.: Trans. Indian Ceram. Soc. *26*, 65 (1967).
10. Day R. L. and Shi C.: Cem.Concr. Res. *24*, 1485 (1994).
11. Collepardi M., Marcialis A., Massidda L., and Sanna U.: Cem.Concr.Res. *6*, 497 (1976).
12. Alexanser K. M. and Wardlaw J.: Aust.J.Appl.Sci. *6*, 334 (1955).
13. Alexander K. M.: Aust.J.Appl.Sci. *6*, 224 (1955).
14. Huizer A., Day R. L., and Shi C. in: 6^{th} Canadian Masonry Symposium, p. 499-507, Proc., vol. 2, Saskatoon 1992.
15. Shi C. and Day R. L.: Cem.Concr.Res. *23*, 1389 (1993).
16. Shi C. and Day R. L.: Cem.Concr.Res. *30*, 51 (2000).
17. Shi C. and Day R. L.: Cem.Concr.Res. *30*, 607 (2000).
18. Shi C. and Day R. L.: Cem.Concr.Res. *31*, 813 (2001).
19. Nanjing Institute of Chemical Technology, Cement Technology, Chinese Construction Press, Beijing 1985.

20. Shi C., Activation of natural pozzolans, fly ash and slag, Ph. D. Thesis, The University of Calgary, Canada 1993.
21. ASTM C311-92, Standard Methods of Sampling and Testing Fly Ash or Natural Pozzolans for Use as a Mineral Admixture in Portland Cement Concrete, American Society for Testing and Materials, Annual Book of ASTM Standards, Volume 04.02, West Conshohocken, Pennsylvania, 2005.
22. ASTM C618-92a, Standard Specification for Fly Ash or Raw or Natural Pozzolan for Use as a Mineral Admixture in Portland Cement Concrete, American Society for Testing and Materials, Annual Book of ASTM Standards, Volume 04.02, West Conshohocken, Pennsylvania, 2005.
23. ASTM C25-99, Standard Test Method for Chemical Analysis of Limestone, Quicklime, and Hydrated Lime, American Society for Testing and Materials, Annual Book of ASTM Standards, Volume 04.02, West Conshohocken, Pennsylvania, 1999.
24. ASTM C204, Standard Test Method for Fineness of Hydraulic Cement by Air-Permeability Apparatus, American Society for Testing and Materials, Annual Book of ASTM Standards, Volume 04.02, West Conshohocken, Pennsylvania, 2005.
25. ASTM C821-78, Standard Specification for Lime for Use with Pozzolans, American Society for Testing and Materials, Annual Book of ASTM Standards, Volume 04.02, West Conshohocken, Pennsylvania, 2000.
26. ASTM C191-82, Standard Test Method for Time of Setting of Hydraulic Cement by Vicat Needle, American Society for Testing and Materials, Annual Book of ASTM Standards, Volume 04.02, West Conshohocken, Pennsylvania, 2004.

CHEMICKÁ AKTIVACE A URYCHLENÍ TUHNUTÍ PŘÍRODNÍHO VÁPENCO-PUCOLÁNOVÉHO CEMENTU

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Pro zkrácení doby tuhnutí a urychlení tvrdnutí vápenco-pucolánových cementů byly odzkoušeny různé metody včetně kalcinace, ošetření kyselinami, prodloužené broušení, zvýšení teploty tuhnutí a přidání chemických aktivátorů, které měly přispět k zlepšení pucolánové reaktivity přírodního pucolánu. V této práci jsou vyšetřovány účinky některých chemických aktivátorů a urychlovačů tuhnutí a také je zde zjišťováno pevnostní chování přírodního vápenco-pucolánového cementu obsahujícího 70% přírodního pucolánu typu pemza a 30% hašené vápno (hmotově). Získané výsledky ukazují, že přidání zásaditých složek a slínku portlandského cementu může zlepšit tuhnutí a pevnostní parametry přírodních vápencopucolánových cementů. Nejefektivnějším chemickým aktivátorem pro přírodní vápenco-pucolánové cementy je síran sodný ve srovnání s Na_2CO_3, NaOH, $CaCl_2 \cdot 2H_2O$ a obyčejným slínkem portlandského cementu. Nejúčinnějším urychlovačem tuhnutí studovaného přírodního vápenco-pucolánového cementu je však hydroxid sodný ve srovnání s Na_2SO_4, Na_2CO_3, NaCl, $CaCl_2 \cdot 2H_2O$ a obyčejným slínkem portlandského cementu. Přidání 6 % hmotnostních Na_2SO_4 může výrazně zvýšit 90denní pevnost v tlaku a přítomnost 4% NaOH jako urychlovače může účinně zvýšit počáteční a konečné časy tuhnutí.