J Mater Sci (2006) 41:6965–6972
DOI 10.1007/s10853-006-0227-0

Mechanical and durability properties of cement mortar with Algerian natural pozzolana

M. Ghrici · S. Kenai · E. Meziane

Received: 10 April 2003 / Accepted: 19 February 2005 / Published online: 16 September 2006

Abstract This paper presents a study of the properties and behaviour of cement mortar with natural pozzolana from Algeria. The effect of level of addition of natural pozzolana (0, 10, 20, 30, and 40%) on the mechanical properties of mortars at different ages as well as the effect of curing environment and the period of initial curing on the mechanical properties were investigated. The performance of natural pozzolana cement exposed to three aggressive solutions (acids, sulphate, and chloride) is also analysed. The results indicate that the strength of pozzolanic cement is lower than that of plain Portland cement at early ages, but can reach the same order of strength at longer curing periods. The enhancement of the resistance to acid and sulphate attack as well as to chloride ion penetration of natural pozzolanic cement is also demonstrated.

Introduction

Most cement plants consume large amounts of energy and produce a number of undesirable products which negatively affect the environment. In order to reduce energy consumption, CO_2 emission and increase production, cement manufacturers are blending or intergrinding mineral additives such as slag, natural pozzolana, sand and limestone into the cement.

M. Ghrici
Civil Engineering Department, University of Chlef, Chlef, Algeria

M. Ghrici
Civil Engineering Department, USTO University, Oran, Algeria

S. Kenai (✉) · E. Meziane
Geomaterials Laboratory, Civil Engineering Department, University of Blida, 270, Blida, Algeria
e-mail: sdkenai@yahoo.com

Durability of structural concrete has received increasing attention in modern concrete technology and pozzolanic cementitious materials are known for their beneficial effect on durability of concrete structures [1]. When used as a concrete additive, these materials react with calcium hydroxide liberated during the hydration of cement to form additional cementitious compound, namely calcium silicate hydrate (CSH). The resultant binder matrix is more chemically resistant, mainly by virtue of its more refined microscopic pore structure [2].

A number of studies have shown that natural pozzolana have been widely used as a substitute for Portland cement in many applications because of their advantageous properties. These include environmental and economical benefits, decreased permeability, increased chemical resistance and the improvement of the properties of fresh concrete [3–8].

In Algeria, most of the cement is blended with additions such as slag and limestone. Volcanic sediments of natural pozzolana occur only in the western region of Beni-Saf and are used for cement manufacture by at least 6 of the 12 Algerian cement plants. These cement plants usually add about 15% of natural pozzolana as cement replacement by weight and hence less than 500,000 tonnes is exploited annually. Apart from the internal quality control testing for conformity to standards requirements, no detailed investigation has been done to evaluate the performance of natural pozzolana cement mortar and concrete under local environmental conditions. In addition, deterioration of concrete structures by sulphate attack is commonly observed in buildings foundations and other structures exposed to soils or ground water with high concentration of sulphate ions in the west and south regions of Algeria. Natural pozzolana addition has been found to improve sulphate performance of ordinary Portland cement [9]. Natural pozzolana addition could also be useful in hot climate regions due to its reduction of the heat of hydration.

The objective of this paper is to report a part of an ongoing project on the effect of different amounts of natural pozzolana on the physical, mechanical properties and durability of mortar and concrete.

Experimentation

Material used

A local ordinary Portland cement with a fineness of 350 m^2/kg was used for all the mixes. The natural pozzolana used in this work was from Beni-Saf quarry in the west of Algeria. The pozzolana was ground in a laboratory mill to a specific surface of 420 m^2/kg. The chemical composition of the cement and natural pozzolana are given in Table 1. The mineralogical composition of the natural pozzolana was determined by X-ray diffraction and is summarised in Table 2. The sand used in mortar mixes was a standard sand of 2 mm maximum particle size. A concrete mix was used only for chloride penetration tests. Crushed limestone coarse aggregates with a nominal size of 12 mm, and a specific gravity of 2.65, and natural sand with a specific gravity of 2.59 were used for the concrete samples. The superplastciser used in the concrete mix is based on naphthalene sulphonates and modified lignosulphonates with specific gravity of 1.20.

Mixes used

The mortar mixes had proportions of 1 binder: 3 Sand. The binder consisted of cement and natural pozzolana. The cement was partially replaced by 0, 10, 20, 30, or 40% of natural pozzolana. All replacement was made by mass of cement. The water: binder ratio was kept constant at 0.5. The concrete mix had a total binder content of 400 kg/m^3, fine aggregate content of 720 kg/m^3, and coarse aggregate content of 1130 kg/m^3. The superplastciser was added with a dosage of 1 l per 100 kg cement to improve workability.

Specimen preparation, curing and testing

The physical properties of the pastes and the strength of mortars were determined in accordance with EN 196-3 [10] and EN 196-1 [11] respectively. The mortar was placed in prismatic steel moulds having dimensions of $40 \times 40 \times 160$ mm. After casting, specimens were left covered with a plastic sheet. After removal from the moulds at 24 h of age, mortar specimens were cured under the following conditions:

- Standard water curing: specimens immersed in water saturated with lime at 20°C until the age of testing;
- Air laboratory curing: specimens were air cured in a laboratory environment with temperature and relative humidity controlled at 23 ± 2°C and 60 ± 10% respectively.
- Hot climate: specimens were cured outside the laboratory under atmospheric conditions with a daily average temperature and relative humidity of 38 ± 2°C and 35 ± 10% respectively.

Compression and bending tests were conducted at 2, 7, 28, and 90 days of age. The results reported are the average of three flexural specimens and six compression tests.

The resistance to acid attack was determined in accordance with ASTM C-267 [12]. The mortar specimens were cured in water at 23 ± 2°C for 30 days before being subjected to acid attack. Three specimen of each mortar mix were immersed either in 1% sulphuric acid (H_2SO_4) or in 1% hydrochloric acid (HCl). After being subject to acid attack, the mortar specimens were cleaned with deionised water and then the acid attack evaluated through measurement of the weight loss of the specimens determined as follows:

Table 1 Chemical composition (%) of the cement and natural pozolana used

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	CaO(free)	SO_3	IR*	LOI**
Cement	23.7	6.58	4.0	64.95	0.32	0.33	–	–	–
Pozzolana	46.86	16.62	9.37	9.38	2.84	–	0.36	–	5.79

* Insoluble residue

** Loss on ignition

Table 2 Mineralogical composition of the natural pozzolana

Mineral	Plagioclase	Augite	Analcine	Chlorite	Haematite	Glass content	Other
Percentage	40	15	12	6	8	14	8

$$\text{Weight loss}(\%) = [(W_1 - W_2)/W_1] \times 100 \quad (1)$$

where W_1 is the weight of the specimen before immersion and W_2 is the weight of the cleaned specimen after immersion. The solution was renewed every 15 days and the weight loss of the specimens measured.

For the sulphate attack tests, the mortar specimens were cured in water at 23 ± 2°C for 30 days before being immersed in 5% sodium sulphate (Na_2SO_4) which was renewed every 30 days. The sulphate attack was evaluated through the measurement of the compressive strength of three specimen for each mix.

The rapid chloride permeability test was conducted in accordance with ASTM C-1202 [13]. Three specimens of 100 mm in diameter and 50 mm in thickness conditioned according to these standards were subjected to 60-V potential for 6 h. The total charge passed through the concrete specimens was determined and used to evaluate the chloride permeability of each concrete mixture.

Results and discussion

Physical properties

The chemical analysis of the pozzolana used and reported in Table 1 shows that the total percentage of (Al_2O_3 + SiO_2 + Fe_2O_3) is 72,85%, which is greater than the minimum (70%) specified in ASTM C-618 [14]. The mineralogical composition by X-ray analysis (Table 2) shows that plagioclase is the main crystalline component.

The physical properties of the cement paste containing different replacement levels of natural pozzolana are given in Table 3. The water requirement and setting time were determined by Vicat Probe and Vicat needle apparatus. The effect of replacement of 10–40% of cement with natural pozzolana is an increase in the water demand necessary for maintaining consistency. This might be due to the relatively high fineness and flocculent structure of the natural pozzolana. The increase in natural pozzolana content slightly reduces the initial setting time. This is contrary to expectation and is difficult to explain. However, a negligible effect is also reported by other researchers for low cement replacement levels (up to 20%) using a higher activity natural pozzolana [15]. The soundness of the samples show a gradual increase with the increase in replacement level, but the values measured are less than the maximum of 10 mm tolerated by the European standard specifications [10].

Development of the compressive and flexural strength

The development of the compressive strength with age of blended cement with different levels of cement substitution is shown in Fig. 1 whereas that of the flexural strength is given in Table 4. As expected, the compressive strength of the mortar increases with age with a high rate of strength gain at early ages which gradually decreases at longer ages. Plain mortar specimens have a high compressive strength at any age in comparison with that of pozzolanic mortars. This diminution of strength of natural pozzolana (NP) specimens is higher at early age and increases with the percentage of pozzolana. The compressive strength at 7 days decreases from 45 to 28 MPa when the natural pozzolana content increases from 10 to 40%. The relative compressive strength at 2 days of age for specimens with 30% of natural pozzolana is only 53% of that of OPC specimens. This could be explained by the slowness of the pozzolanic reactions between the glassy particles in the natural pozzolana with the CH released during cement hydration. However, due to the continuation of this reaction and the formation of a secondary C–S–H that enhances the paste-aggregate interface and decreases the capillary porosity of the mortar, a greater degree of hydration is achieved resulting in strengths at 90 days of age which are comparable to those of ordinary Portland cement specimens. Nevertheless, it should be noted that the decrease in strength at early age could be compensated by prolonged grinding, elevated temperature curing or the use of chemical activators. Prolonged grinding has been found to increase the compressive strength of natural pozzolana cement mortar by 50–130% at 3 days and 10–50% thereafter [16].

Flexural strength test results (Table 4) shows a similar trend to those of the compressive strength. However, the decrease in flexural strength at early ages was relatively less significant for higher cement replacement levels than that for compressive strength.

Table 3 Physical properties of the mixed used

	Natural pozzolana (%)				
	0	10	20	30	40
Water demand for standard consistency (%)	27.6	28	28.5	30.6	31.5
Initial setting time (min)	152	146	143	137	109
Final setting time (min)	257	225	200	192	185
Soundness (mm)	0.50	0.55	0.60	0.70	0.90

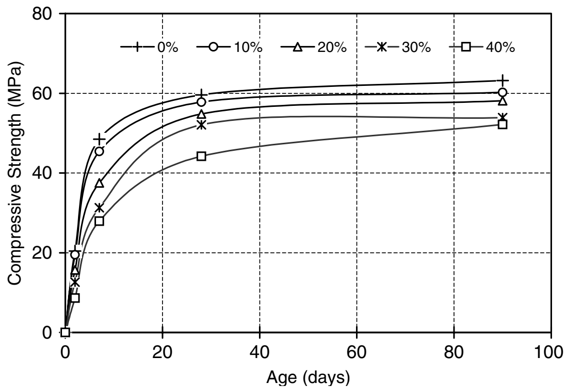


Fig. 1 Development of the compressive strength under standard water curing

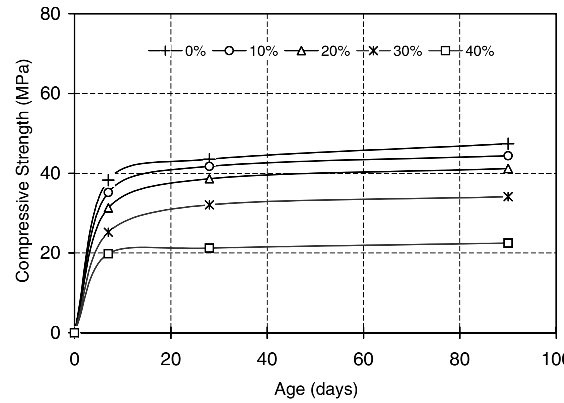


Fig. 2 Development of the compressive strength under air laboratory curing

Effect of curing environment

The effect of air laboratory curing environment on compressive strength is shown in Fig. 2. The air laboratory temperature is similar to that of water curing. However, the relative humidity is lower and this causes a higher rate of water evaporation from the mortar surface and a more rapid cessation of hydration especially on the skin of the specimens. The compressive strength at 28 days in laboratory air curing was about 72% of that of water curing for both OPC and NP specimens at 10–20% replacement level. For higher replacement level, the relative strength was lower (48–62%) showing the sensitivity of blended cement specimens to the lack of moist curing. Only a slight relative gain in strength after 7 days was observed for all specimens indicating a cessation of the hydration by lack of humidity.

The negative effect of hot climate conditions on the compressive strength is shown in Fig. 3. The reduction in strength was higher than that of air laboratory curing specimens. The compressive strength development seems to stop at 7 days. The ultimate strength at 90 days of age was only about 52% of that under water curing. This is due to the fact that drying at high temperature leads to higher water evaporation from the surface leading to micro-cracks and restricted hydration, therefore higher porosity and permeability and lower strength are expected [17].

Flexural strength test results under different curing environments are summarised in Table 4. A reduction in the flexural strength is observed under both air laboratory and outdoor curing. However, the reduction in the flexural strength was slightly lower especially under air laboratory curing environment.

Effect of period of initial moist curing

In order to analyse the effect of duration of initial curing on the compressive and flexural strengths, specimens were cured for 1, 3, 7, or 14 days before being left in the outdoor hot environment until the age of testing of either 28 or 90 days. The effect of duration of curing is summarised in Table 5 and Fig. 4. It seems that the period of initial moist curing has a significant effect on the mechanical properties as natural pozzolana does not react as rapidly as the cement. Longer curing periods allow sufficient moisture for continued hydration resulting in higher strength. A curing period of 7 days improved the compressive strength at 90 days of age up to 82% of that of continuous humid curing of mortars containing 30% of natural pozzolana as compared to only 53% with one day curing. This shows the importance of proper curing for strength development especially in concretes containing pozzolans as cement extenders.

However, the increase of compressive strength when the period of initial moist curing increase from 7 to 14 days, is negligible and one can conclude that a minimal period of

Table 4 Effect of curing environment on the flexural strength in MPa

	Standard water curing				Air laboratory curing				Hot climate curing			
	2 day	7 day	28 day	90 day	2 day	7 day	28 day	90 day	2 day	7 day	28 day	90 day
0%	4.84	6.65	7.87	8.13	4.54	6.01	6.77	6.79	4.46	4.49	5.28	5.52
10%	4.10	6.29	7.39	8.52	3.82	5.82	6.53	6.83	3.64	4.40	5.22	4.90
20%	3.23	6.13	6.8	7.65	3.53	5.14	6.51	6.63	2.83	3.72	4.78	4.00
30%	2.45	5.34	6.75	7.07	2.69	4.24	4.96	6.65	2.57	3.05	7.06	3.35
40%	2.09	4.38	6.55	7.00	1.91	2.93	3.66	3.08	1.61	2.61	3.76	2.39

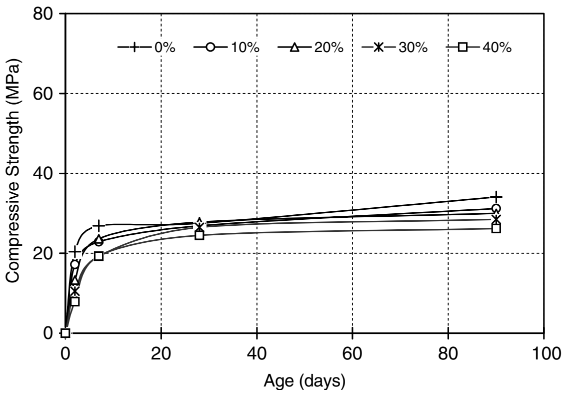


Fig. 3 Development of the compressive strength under external hot climate curing

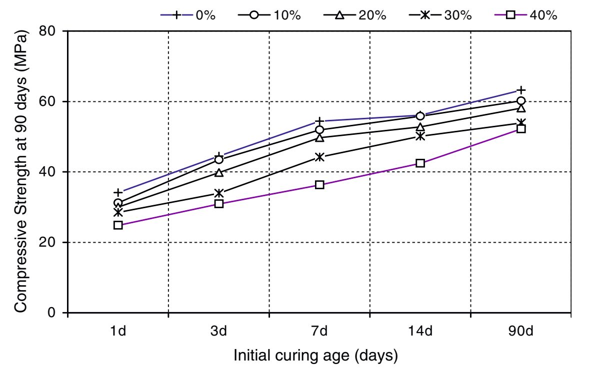


Fig. 4 Effect of the initial curing age on the compressive strength at 90 days

initial moist curing of 7 days could be sufficient. Prolonged moist curing may be required not only to achieve full development of strength but also for durability-related properties as inadequate curing has been found to hinder the refinement of pore structure and reduction of the permeability of concrete and produce a large increase in the absorptivity of concrete [17, 18].

A similar trend to that observed for compressive strength seems to be followed by the flexural strength results. However, the results show that the flexural strength is less sensitive than the compressive strength to inadequate curing.

Correlation between flexural and compressive strength

The relationship between the compressive strength (f_c) and flexural strength (f_t) is given in Fig. 5 and seems to fit well with the relation proposed by some other researchers [19]:

$$f_t = k(f_c)^{\alpha} \tag{2}$$

The correlation between the flexural strength and the compressive strength results were calculated for the entire population of test results and hence the relation obtained is:

$$f_t = 0.45(f_c)^{0.7} \tag{3}$$

With a correlation factor of 0.89

Acid attack

Changes in weight of mortars specimens immersed in acid solutions are presented in Fig. 6. A permanent decrease in weight was found in mortars subjected to 1% HCl solution attack. Before 60 days of immersion, the mortar composition had no significant effect. After 60 days of immersion, the replacement of part of Portland cement by the natural pozzolana increased the mortar's ability to resist to acid attack. For mortars subjected to 1% H_2SO_4 the weight of the mortars increased with age up to 75 days but after that, a permanent decrease in weight was observed. The decrease in weight is due to the dissolution of hydration products leading to a porous concrete. However, the decrease in weight was less with blended cement specimens. These results confirm the increase resistance to acid attack by other pozzolanic materials such as silica fume, metakaolin and fly ash obtained by other researchers [2, 20].

Sulphate attack

The data on strength development in mortar specimens placed in the sulphate solution are shown in Fig. 7. These results indicate a strength gain for plain cement specimens for about 60 days. Beyond this time, a reduction in strength was observed. The increase of strength at early age seems to be due to the continuous hydration of unhydrated cement

Table 5 Effect of initial curing on the flexural strength (MPa) at 28 days and 90 days of age

	Water cured		Exposure in hot environment							
			1 day curing		3 day curing		7 day curing		14 day curing	
	28 day	90 day	28 day	90 day	28 day	90 day	28 day	90 day	28 day	90 day
0%	8.13	8.87	4.28	5.04	5.82	7.47	5.98	7.86	6.32	8.36
10%	8.52	8.82	4.38	5.22	5.46	7.56	6.02	7.96	6.35	8.74
20%	7.65	9.30	3.78	4.78	5.72	7.99	5.82	8.31	6.19	9.10
30%	7.07	7.90	3.11	4.66	4.45	6.19	4.92	7.17	4.56	8.13
40%	7.07	7.65	2.39	2.76	3.01	3.54	3.82	6.17	4.12	7.25

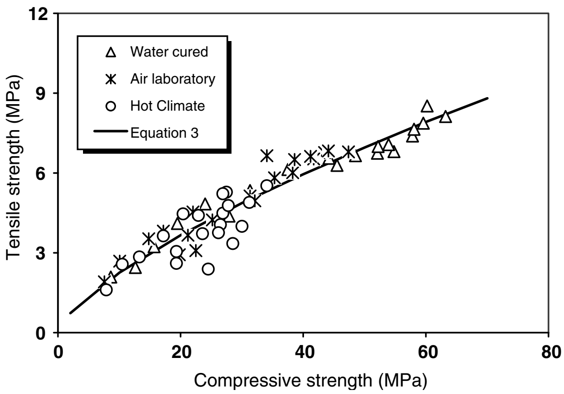


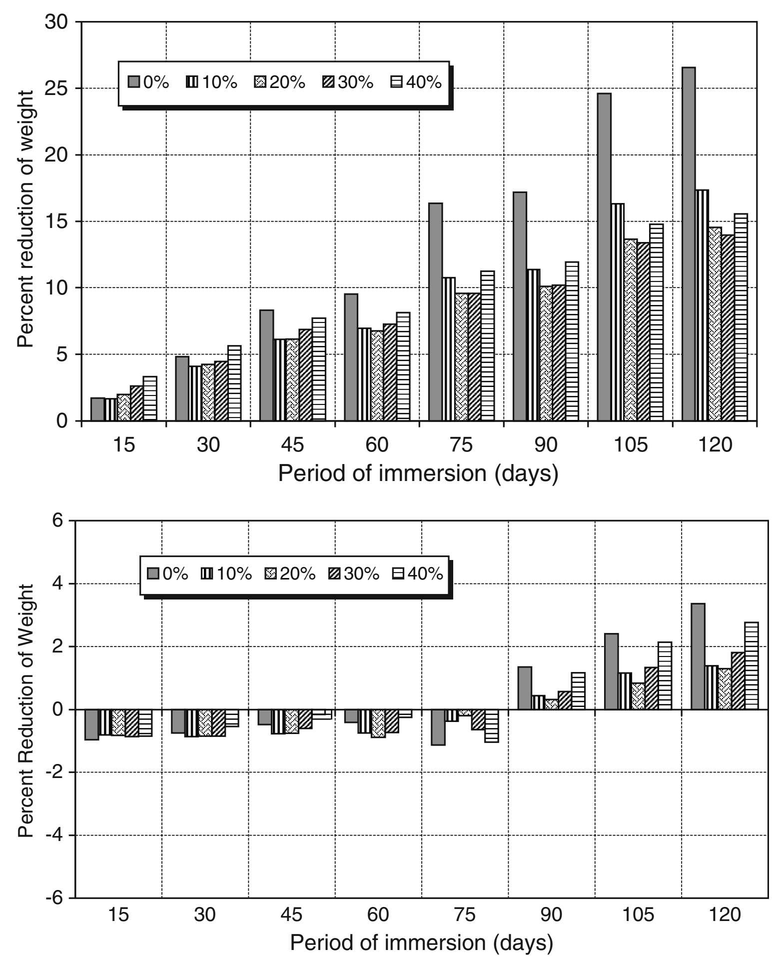
Fig. 5 Relationship between flexural strength and compressive strength

products and the reaction of Na_2SO_4 with $Ca(OH)_2$ to form gypsium and ettringite which fill in the micro-pores leading to a denser structure. The decrease in strength at later ages indicates the expansion effect of the sulphate attack which results in the softening of the material and the formation of micro-cracks [21, 22]. However, mortars containing natural pozzolana generally gained compressive strength during the 180 days of immersion showing its positive effect on sodium sulphate attack. The positive effect of natural pozzolana may be due to its reaction with $Ca(OH)_2$ and the formation of CSH gel. Similar beneficial effect of cement with pozzolanic additions such as straw ash was reported by others [21]. But, it should be noted that the pozzolana used has a high alumina content (>16%) and hence less sulphate resistance as compared to pozzolans with low alumina [7].

Rapid chloride ion permeability

The results of the rapid chloride ion permeability are shown in Fig. 8. In most cases, the chloride permeability of mixtures containing natural pozzolana is lower than that of the reference mixture. Between 28 and 120 days of age, the chloride ion permeability factor for plain concrete and concrete containing 40% of pozzolana diminished from 5950 to 4640 Coulombs and from 2220 to 929 Coulombs, respectively. This may be related to the refined pore structure of these concretes and their reduced electrical conductivity [23]. Results reported elsewhere [8, 24] have

Fig. 6 Weight loss of pozzolana mortar due to the acidic attack (**a**) 1% HCl, (**b**) 1% H_2SO_4



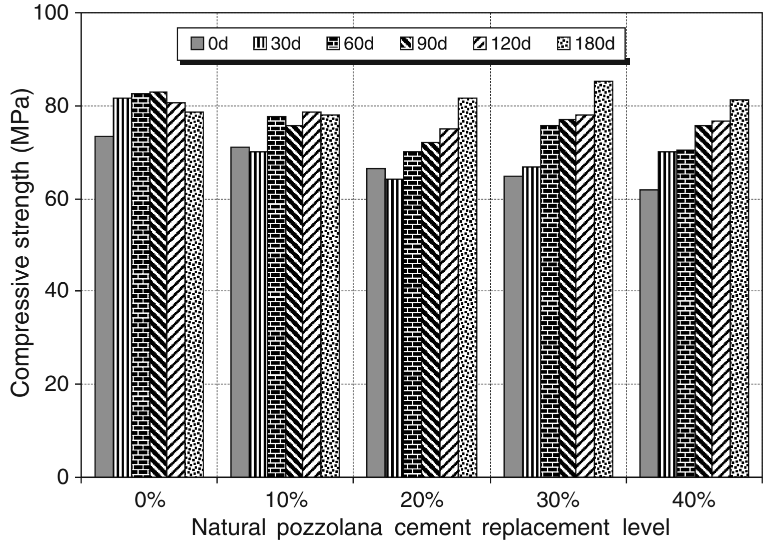


Fig. 7 Relation between compressive strength and exposure time in 5% Na_2SO_4 Solution

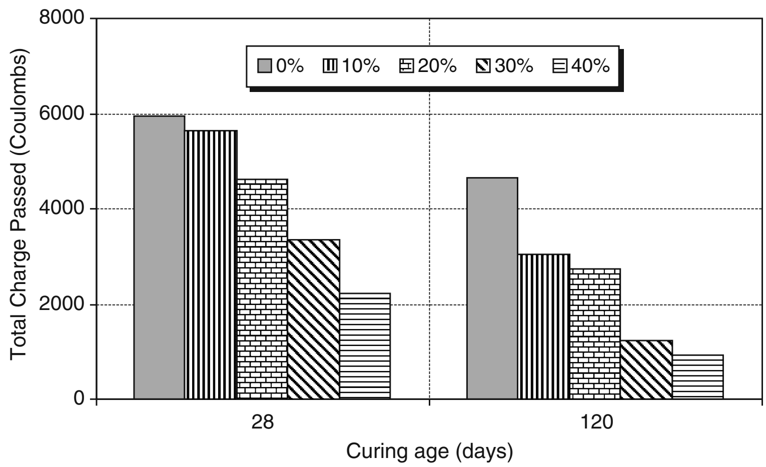


Fig. 8 Influence on natural pozzolana addition on chloride permeability

shown a reduction in the chloride ion permeability with the addition of pozzolanic materials, with further reductions obtained at higher replacement levels and lower water/binder ratios. According to ASTM C1202-97 [13], when the charge passed during a 6 h period is less than 1000°C, the chloride ion permeability is very low. This condition was satisfied only for 120 days curing specimens with 40% replacement levels.

Conclusion

This study was conducted to assess the effect of incorporating natural pozzolana with ordinary Portland cement on the properties of cement, mortar and concrete. The experimental results presented in this paper showed the physical characteristics of the cement containing natural pozzolana are in conformity with the standards requirements and that the strength of pozzolanic cement is lower than the plain Portland cement at early age, but can reach the same order of strength at longer term ages. It seems that the period of initial moist curing has a significant effect and a minimum period of initial moist curing of 7 days is necessary. The improvement of the durability of pozzolanic cement to acid and sulphate attack as well as to chloride ion penetration was demonstrated. Lower weight loss was observed, after immersion in acid solutions, with natural pozzolana cement specimens as compared to OPC specimens. No strength loss was observed with natural pozzolana cement specimens after immersion in sulphate solutions for up to 180 days. A reduction in the chloride ion permeability with the addition of natural pozzolana was observed.

References

1. Swamy RN (2000) In: Proceedings of the CANMET/ACI international symposium on concrete technology for sustainable development. Vancouver, BC, Canada

2. Roy DM, Arjunan P, Silsbee MR (2001) Cem Conc Res 31:1809
3. Mehta PK (1981) Cem Conc Res 11:507
4. Ramezanianpour AA (1987) Engineering properties and morphology of pozzolanic cement-concrete. PhD Thesis, University of Leeds, p 359
5. Massazza F (1993) Cem Conc Comp 15:185
6. Kouloumbi N, Batis G, Panantasopoulou P (1995) Cem Conc Agg 17:18
7. Rodriguez-Camacho RE (1998) In: Proceeding of the 6th international conference on the use of fly ash, silica fume, slag, and natural pozzolan in concrete. Bangkok, ACI SP 178-53
8. Tagnit-Hamou A, Petrov N, Luke K (2003) ACI Mat J 100:73
9. Irassaar EF, Gonzalez M, Rahhal V (2000) Cem Conc Comp 22:361
10. EN 196-3 (1995) Methods of testing cement – Part 3: determination of setting time and soundness. Comité Européen de Normalisation (CEN)
11. EN 196-3 (1995) Methods of testing cement – Part 1: determination of strength. CEN
12. ASTM C-267 (1997) Standard test method for chemical resistance of mortars. Annual Book of ASTM Standards, 04.05
13. ASTM C-1202 (1997) Standard test method for electrical indication of concrete's ability to resist chloride ion penetration. Annual Book of ASTM Standards, 04.02
14. ASTM C-618 (1994) Specification for fly ash and raw or calcined natural pozzolan for use as a admixture in Portland cement concrete. Annual Book of ASTM Standards, 04.02
15. Colak A (2003) Cem Conc Res 33:585
16. Shi C, Day R (2001) Cem Conc Res 31:813
17. Al-Amri AM (1988) Durability of concrete in hot climate. PhD Thesis, University of Leeds, p 261
18. Day RL, Shi C (1994) Cem Conc Res 24:463
19. Neville AM (2000) Propriétés des bétons. Eyrolles, Paris, p 806
20. Janotka I (1999) Ceramics-Silikaty 43:61
21. Biricik H, Akoz F, Turker F, Berktay I (2000) Cem Conc Res 30:1189
22. Janotka I, Krajci L (2000) In: Malhotra VM (ed) Proceedings of the fifth CANMET/ACI international conference on durability of concrete SP-192. p 223
23. Talbot C, Pigeon M, Maarchand M, Hornain J (1995) In: Proceeding of the fifth international conference on the use of fly ash, silica fume, slag, and natural pozzolana in Concrete. Milwaukee, ACI SP 153-8, p 125
24. Feng N, Feng X, Hao T, Xing F (2002) Cem Conc Res 32:623