Study of Effects of Natural Pozzolan on Properties of Cement Mortars

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Abstract: Natural pozzolans, also known as trass, can be used in cement manufacturing due to their cementitious properties after reaction with calcium hydroxide. At different mixture proportions, the strength, setting time, workability, and soundness of the cement mortar made will differ. In this paper, cement mortars with six different natural pozzolan additions (ranging from 0 to 35%) were employed while using one type of natural pozzolan. As the experimental results show, increase in a natural pozzolan addition decreases the early age strength of cement significantly as expected and decreases the soundness of mortar by two-thirds. In addition, the workability conditions relatively improve and the settings delay for awhile.

DOI: 10.1061/(ASCE)0899-1561(2006)18:6(813)

CE Database subject headings: Cements; Compressive strength; Volume change.

Introduction

ASTM C125 defines pozzolan as "a siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious value, but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties." Pozzolans can be added to cement during the production process or mixed directly into concrete.

Turkey is rich in natural pozzolan sources (Çavdar and Yetgin 2004a; Türkmenoğlu and Tankut 2002); almost one-third of the total production there in recent years was "trass cement" TS (1975), which is a portland-pozzolan cement (Tokyay and Munlafalioğlu 1997). In most Mediterranean countries, the situation is also the same (Türkmenoğlu and Tankut 2002). Therefore, the writers decided to investigate the properties of blended cements containing different contents of natural pozzolan from one Turkish deposit and to test their strength-development characteristics.

Previous studies (Canpolat et al. 2003; Çavdar and Yetgin 2004b) say that the harmful materials in cements such as CaO, MgO, and SO_3 can damage volume stability. The ratio of these materials in cement mixtures should be kept under some values. The amount of CaO is less than 2% (by mass) and the ratio of MgO is less than 5% (by mass), and furthermore, it is known that addition of natural pozzolan materials decreased the amount of "harmful materials" by reaction with them, depending on the fineness, of the natural pozzolan.

In addition, thanks to their abilities to divide easily, natural pozzolans can fill the micropores in the cement matrix and increase the durability of cements significantly by changing the framework of the matrix (Sabir et al. 2001; Shannag 2000; Pan et al. 2003). Natural pozzolans also have lubricant effects on cement mortar or concrete because of their fine grain size; they improve the consistency and thus the workability conditions of the concrete (Pan et al. 2003). However, besides this, natural pozzolans can be expected to increase the water requirement a little, since they increase the total cement surface (Vu et al. 2001).

Studies also state that in mortars and concretes, where portland cement and natural pozzolan are applied together as a mixture, setting times depend on the replacement amount, fineness, and reactivity of pozzolan compared with portland cement (Taşdemir 2003; Erdoğdu et al. 2001; Öner et al. 2003).

The object of this study is to examine the effects of the change in pozzolan content upon the compressive strength, workability, setting times, and soundness properties of cement containing pozzolan. For this aim, cements including five different amounts of pozzolan were prepared by fixing a natural pozzolan type as constant while related experiments were tested. In addition, the natural pozzolan sample taken from Macka (Trabzon/Turkey) was investigated for its ability to be used in the cement industry.

Materials and Experimental Method

Natural Pozzolan

The natural pozzolan used in the experiments is taken from the Macka/Trabzon district (in northeast Turkey). Mineralogical and petrographical properties of the natural pozzolan samples were identified under the polarizing microscope by using their thin sections (Fig. 1), and X-ray powder diffraction (XRD) analysis of the powdered bulk samples was carried out (Fig. 2). A major element analysis of the samples comprising SiO_2, TiO_2, $A1_2O_3$, Fe_2O_3, MgO, CaO, Na_2O, and K_2O was carried out by means of wet chemical analysis (Table 1). The pozzolanic activity (Table 2),

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Note. Associate Editor: Baoshan Huang. Discussion open until May 1, 2007. Separate discussions must be submitted for individual papers. To extend the closing date by one month, a written request must be filed with the ASCE Managing Editor. The manuscript for this paper was submitted for review and possible publication on May 24, 2005; approved on November 4, 2005. This paper is part of the ***Journal of Materials in Civil Engineering***, Vol. 18, No. 6, December 1, 2006. ©ASCE, ISSN 0899-1561/2006/6-813–816/$25.00.

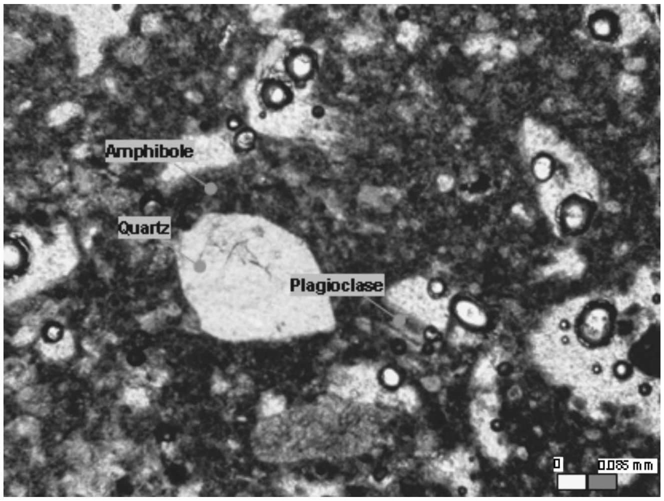

Fig. 1. Thin section of natural pozzolan

that is, the behavior of pozzolan in mortar, was determined according to the Turkish standards; TS 25 (similar to ASTM C 311).

Previous studies (Çavdar and Yetgin 2004a) say that high SiO_2 content of natural pozzolan implies high pozzolanic activity (strength). High SiO_2 content can be seen in Table 1, especially from quartz (Figs. 1 and 2). Besides, there are clay group minerals (Figs. 1 and 2) and a little zeolitization (Fig. 2) in the natural pozzolan sample.

Cement Samples

For this study, five different types of cement mixtures containing different amounts of natural pozzolan were designed, and also one sample, NP00, was produced without natural pozzolan to compare. Mixing proportions of these mixtures are 97:0:3 (NP00), 87:10:3 (NP10), 77:20:3 (NP20), 72:25:3 (NP25), 67:30:3 (NP30), and 62:35:3 (NP35) for clinker:natural pozzolan:gypsum. These cements are in the portland pozzolan cement class (CEM II/A-P, CEM II/B-P) with their natural pozzolan amounts according to EN 197, except for sample NP00, CEM I.

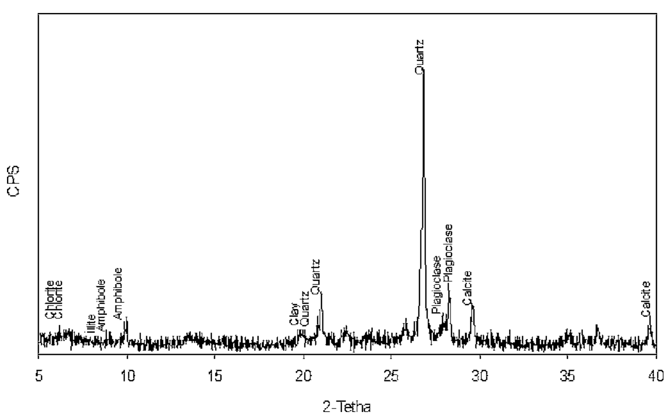

Fig. 2. XRD of natural pozzolan

Table 3. Physical Properties

	NP00	NP10	NP20	NP25	NP30	NP35
Specific gravity (g/cm^3)	3.12	3.10	3.03	3.06	3.05	2.86
Remain 90μ sieve (%)	0.20	0.20	0.20	0.30	0.20	0.20
Remain 200μ sieve (%)	4.80	4.70	4.70	4.50	4.30	5.00
Specific surface (cm^2/g)	2,880	3,596	3,770	4,103	4,310	4,392

Each mixture was prepared by grinding it together for 90 min. Since only the effect of the natural pozzolan ratio on the cement property is investigated in this study, natural pozzolan fineness should be kept fixed. However, especially due to the difference in the natural pozzolan ratios, it was not possible to keep the fineness of cement samples constant (Table 3). As also mentioned in the previous studies (Çavdar and Yetgin 2004b; Pan et al. 2003; Taşdemir 2003; Czernin 1962), it is known that the fineness has an effect on strength, volume change, and setting times of cements.

Such an explanation can be made for this subject: Natural pozzolan and clinkers have different grinding properties. Actually, it can be clearly observed and indicated in the sources that natural pozzolan can be more finely grained ($\geq$6,000 cm^2/g) than clinker. Therefore, as the ratio of natural pozzolan present in the cement increased, natural pozzolan became the dominant factor determining the fineness of the cement, and therefore the main factor affecting the tests' results was the natural pozzolan amount rather than the cement fineness.

The physical properties (Table 3) of chemical compounds (Table 4) of the cement samples containing the mentioned amount of natural pozzolan were determined, and these properties were presented with tables. As seen from Table 3, as the natural pozzolan amount increased, especially, the CaO component's content dropped significantly and therefore the free CaO amount decreased. Thus, concrete that is more durable may be obtained. In addition, SiO_2 and Al_2O_3 content also increased, but Fe_2O_3 content decreased. Besides, as seen from Table 4, as natural pozzolan ratio increases, specific surface also increases.

The mechanical tests were conducted according to the suggested principles in EN 196. The "test mortar" consists of 450 g of the cement mixture, 1,350 g of graded standard sand, and 225 g of water, and consequently the water/cement ratio is 0.50. After the molding process, the molds (with the mortars in them) were placed in the moist room at $23\pm1.7°C$ for 20 to 24 h and

Table 1. Chemical Properties and Mineralogy of Natural Pozzolan

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	LOI	Na_2O	K_2O	Total
Natural pozzolan	70.89	9.08	2.96	5.40	0.62	—	7.23	1.11	1.92	99.21

Table 2. TS 25 Requirements and Mechanic Properties of Natural Pozzolan

	$SiO_2+Al_2O_3+Fe_2O_3$ (%)	MgO (%)	SO_3 (%)	Loss on ignition (%)	7th day flexural strength (MPa)	7th day compressive strength (MPa)
TS 25	>70.00	<5.00	<3.00	<10.00	>1.00	>4.00
Natural pozzolan	82.93	0.62	—	7.23	4.45	11.00

Table 4. Chemical Analysis

Mass ratio (by mass, %)	NP00	NP10	NP20	NP25	NP30	NP35
Insoluble SiO_2	—	8.42	15.20	17.12	28.64	28.53
Total SiO_2	21.49	26.51	30.33	31.68	38.31	38.84
Total Al_2O_3	2.18	4.65	5.23	5.49	6.03	6.27
Total Fe_2O_3	7.27	3.76	3.81	3.81	3.81	3.85
Total CaO	64.26	58.29	52.15	52.12	44.13	43.40
Total MgO	1.11	0.84	1.84	1.20	1.14	1.26
Total SO_3	1.78	1.78	1.86	1.54	1.27	1.35
Loss on ignition	0.72	1.23	1.89	1.94	2.85	2.92
Na_2O	0.20	1.27	1.22	0.41	1.24	0.67
K_2O	0.75	0.96	0.96	1.01	1.18	1.18
Total	99.76	99.29	99.29	99.20	99.96	99.74
Cl^-	—	0.014	0.028	0.035	0.039	—
CO_2	—	0.76	1.03	1.13	1.57	1.61

removed at the end of this period, and the mortar cube specimens were stored in water until the day of testing. Compressive strength tests on the mortar cubes were conducted at either 1, 7, 28 days. Six specimens were tested (Table 5) for each type of mixture at each testing age according to the Rilem-Cembureau method in EN 196. In addition, their setting times (Table 6) and volume expansion (according to the Le Chatelier soundness test) values (Table 6) were determined, and these values were presented in tables and graphics. For setting times, a Vicat apparatus was used in EN 196. Besides, the water demand to obtain the standard consistencies indicated in EN 196 is also given in Table 6.

Results

Availability of Natural Pozzolan Sample in Cement Industry

Both chemical and mechanical properties show that the natural pozzolan is taken from Trabzon (in northeast Turkey), appropriate for the related standard TS 25 (Table 2). Therefore, this sample can be used as natural pozzolan in the mixtures and cement industry.

Effects of Natural Pozzolan Addition Ratio on Compressive Strength

Pozzolans react with $Ca(OH)_2$, which is one product of hydration of clinker in cement. Therefore, after cement is mixed with water, during the collection time of $Ca(OH)_2$ it has a diluting effect on portland cement. However, as $Ca(OH)_2$ is being gathered in the medium, the influences that increase the strength of pozzolan start to emerge, and therefore a fall in the early strength of concrete is expected with pozzolan usage.

As a result, concretes, including pozzolan-blended cement need water to cure for a longer time as compared to concretes, including only portland cement of the same fineness. As can be understood from this, only the ultimate strength of concretes produced with pozzolan-blended cement is expected to reach and even pass the strength of comparison samples prepared with portland cement (Erdoğdu et al. 2001).

Experiments were performed on cement mortars prepared with NP00, NP10, NP20, NP25, NP30, and NP35, and the results obtained from these tests are presented with the help of a table (Table 5). As seen from the compression tests (Table 5), as the natural pozzolan ratio increases, early strength decreases. As a matter of fact, that the ages of the samples were restricted to 28 days may mean that the natural pozzolan in cement mixtures had not yet hydrated completely. The studies performed show that cements including highly ground pozzolan may cause a decrease in the compressive strength because the grinded clinker grains move away from each other (Targan et al. 2003). However, after a longer period, as the pozzolan grains start to react, it can be seen that this strength difference will decrease, and therefore the degree of filling the micrograps of natural pozzolan turns out to be another parameter affecting strength.

At the end of 28 days, cement mortars produced with NP00 exhibit 38% better strength when compared to mortar produced by cement containing 35% natural pozzolan by mass (NP35). In addition, this difference is 56% on the first day, 49% on the second day, and 45% on the seventh day. This situation shows that strength-gaining speeds of pozzolan-blended cement samples are less than the speeds of portland cement samples (NP00). However, the first signs that this difference can be overcome are seen, especially as it is known that concretes produced with pozzolan-blended cements need more cure to increase their strength gaining speeds (Kern 1985).

One other result obtained from the compression tests is that although the natural pozzolan amount is raised about 35% (by mass), the cement mortar provides the minimum mechanical properties desired in EN 196 confidently (32.5 MPa). Actually, NP35 that has 35% natural pozzolan by mass shows compressive strength of about 38.0 MPa. This situation indicates that natural pozzolans can be used in high amounts in cement production, especially if they are mixed with high characteristic-strength cements. Thus, this method provides both durability and strength.

Table 5. Compressive Strengths (MPa)

Samples	1st day	2nd day	7th day	28th day
NP00	12.0	21.3	40.1	60.8
NP10	9.9	18.1	36.1	55.2
NP20	7.4	13.2	30.5	49.6
NP25	6.5	11.9	27.2	45.6
NP30	5.9	11.3	23.4	41.7
NP35	5.3	10.8	22.0	37.8

Table 6. Setting Times, Workability, and Le Chatelier Soundness

Cement	Setting times: Initial (min)	Setting times: Final (min)	Water demand for normal consistency (by mass, %)	Soundness (mm)
NP00	115	185	28.00	3.00
NP10	125	190	28.00	3.00
NP20	145	185	31.00	2.00
NP25	125	205	29.00	2.00
NP30	135	195	29.25	1.00
NP35	120	210	31.75	1.00

Effects of Natural Pozzolan Addition Ratio on Workability

As the natural pozzolan addition ratio increased, water demand to obtain the same consistency and workability increases (Table 6) by 13% for a 35% natural pozzolan addition. The reason for this is that the rate of increase of water demand is not as high as the natural pozzolan addition ratio can be, so that natural pozzolan is finely divided and has a lubricant effect on concrete.

Effects of Natural Pozzolan Addition Ratio on Setting Times

Setting properties of cement matrix were affected by the natural pozzolan ratio substituted for cement (Table 6). Experimental results show a proportional delay in the initial set time, depending on the natural pozzolan addition ratio. However, this proportional delay has occurred more clearly at the final set time, which obviously shows that the samples that the natural pozzolan used decrease the hydration speed with setting delay and by decreasing hydration heat, which also implies that they can be effective against the shrinking danger. However, some studies relate this delay in setting times to the increase in the water/cement ratio (Çolak 2002).

Effects of Natural Pozzolan Addition Ratio on Volume Expansion

As mentioned previously, CaO and MgO compounds that exist freely in cement may create a swelling effect, and therefore their presence should be limited. Since the free lime ratio will decrease as the natural pozzolan addition ratio increases, a decrease in the soundness can be expected. Results of the experiments made to see these effects are shown in Table 6.

According to the experimental results, soundness decreases as the natural pozzolan addition ratio increases. The volume expansions (changes) of NP30 or samples having higher amounts of natural pozzolan show a drop of two-thirds compared to NP00, which shows that natural pozzolan samples can make an important contribution to concrete durability.

Conclusions

According to the conclusions drawn from this study, in the early days, although the cements containing natural pozzolan show less compressive strength in comparison with portland cement (NP00), this strength difference decreases gradually in the following days. Especially in applications where the durability of concrete or cement paste is more important than strength, the durability properties can be provided without reducing the minimum strength desired by related standards (32.5 MPa), by adding a relatively high amount of natural pozzolan to the cement (NP00) having high characteristic strength (Table 5). Actually, in the study where this method was applied, the cement with 37.8 MPa average strength and 32.5 MPa characteristic strength could have been obtained from the cement having 60.8 MPa average strength and 52.5 MPa characteristic strength by adding 35% natural pozzolan by mass. Of course these types of pozzolan-blended cements also can be used in ordinary construction work, but the strength-gaining period should be taken into consideration.

On the other hand, as the natural pozzolan addition ratio increase, workability conditions improve and water requirement for obtaining the same consistency increase only relatively. In addition, with the increase of natural pozzolan ratio, probably because the heat evolution is slow, a notable delay (≈20 min) at initial and final setting times and a two-thirds decrease in the volume expansion rate of the cement matrix were seen. This is important evidence that natural pozzolans can make an important contribution to the durability of the concrete.

Acknowledgments

This study is supported by Karadeniz Technical University (Project No. 2002 118.001.1). Thanks are given to the Trabzon Cement Factory for laboratory possibilities.

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