Pergamon

Cement and Concrete Research, Vol. 26, No. 5, pp. 701-705, 1996

0008-8846/96 $15.00 + .00

PII S0008-8846(96)00060-9

THE INFLUENCE OF ETHANOLAMINES ON THE HYDRATION AND MECHANICAL PROPERTIES OF PORTLAND CEMENT

Z. Heren and H. Ölmez
Department of Chemistry, Ondokuz Mayıs University
55139 Kurupelit, Samsun - Turkey

(Refereed)
(Received November 10, 1995; in final form March 22, 1996)

ABSTRACT

The effect of ethanolamines—monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA)—on the hydration, mechanical and surface properties of the white Portland cement pastes (white PC) has been investigated. The cement pastes with and without admixtures were cured at various hydration times ranging from 1 day to 90 days. Hydration development of cement pastes were followed by setting times, flexural and compressive strengths, specific surface area measurements and thermal analysis techniques. The measurements showed that all these admixtures retard the hydration of white Portland cement in order TEA>DEA>MEA.

Introduction

Admixtures are generally used to improve the quality of plastic concrete, such as increased workability or water reduction, and the quality of hardened concrete (1).

Yılmaz and Işıldak investigated the influence of some set accelerating admixtures on the hydration of Portland cement containing phosphogypsum (2).

Ethanolamines are generally organic bases and probably the most popular of ethanolamines is TEA. Depending on the cement type and addition rate TEA can produce either set acceleration or retardation. An addition rate of 0.02% to the type I Portland cement, TEA acts as a set accelerator, at 0.25% as a mild set retarder and at 0.5% a severe retarder and at 1% a very strong accelerator (3–5).

There is not any published data for MEA and DEA. In this study the effects of ethanolamines; MEA, DEA and TEA at various addition rates, on the hydration of white Portland cement were investigated using setting times, strength measurements and thermal analysis techniques. The specific surface areas of the same samples were also determined.

Experimental

The specimens were prepared with white PC and tapwater. The chemical composition of the white PC used is given in Table 1. The water to cement ratio was chosen as 0.4. The admixtures

TABLE 1

The Chemical Composition of White PC (wt%)

Oxide composition							
CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	$K_2O + Na_2O$	Free CaO
65.67	22.29	4.60	0.28	0.54	2.43	0.32	2.10

Mineral composition			
C_3S	C_2S	C_3A	C_4AF
51.16	27.55	12.14	0.88

Blaine surface area: 4000 cm^2/g

MEA(Merck), DEA(Merck), TEA(Merck) were dissolved in the mix water, the addition rate was 0.1, 0.5 and 1% by weight of cement. The cement-water mixtures with and without admixture were stirred for three minutes, the specimens were cast into 40 × 40 × 60mm prism molds and vibrated for 2 minutes on a shaker table to aid in consolidation. The specimens were then cured at room temperature (~20°C) for one day and after that placed in tapwater and cured up to 90 days (6). According to Turkish standards setting times were determined by using a vicat apparatus.

For the thermal analysis and surface area measurements, the hydration process was stopped by grinding the cement pastes with acetone, filtering off the suspension and washing the residue several times with more acetone. The samples were then dried in vacuum.

The amount of calcium hydroxide formed at different hydration periods was determined by measuring the weight loss of calcium hydroxide on decomposition. DTA and TG curves of the specimens were obtained using a Rigaku TG 8110 simultaneous thermal analyser at a uniform heating rate of 10°C/min in a nitrogen atmosphere with a flowing rate of 80 ml/min.

The specific surface areas of the specimens were determined using the BET volumetric adsorption apparatus by nitrogen gas adsorption at 77 K (7).

For flexural strength tests three measurements and for compressive strength tests five measurements were performed for each sample and averaged to obtain the mean flexural and compressive strength values.

TABLE 2

Setting Times of Cement Pastes, min

Cement Samples	*Initial setting times*	*Final setting times*
Control	270	378
MEA 0.1%	270	381
0.5%	260	410
1%	270	600
DEA 0.1%	254	378
0.5%	261	405
1%	280	650
TEA 0.1%	270	400
0.5%	340	510
1%	360	720

TABLE 3

$Ca(OH)_2$ Contents (wt%) of
Hydrated Cement Pastes Determined by TG

Cement Samples		*1 d.*	*3 d.*	*7 d.*	*28 d.*	*90 d.*
Control		8.6	11.5	14.6	15.4	15.6
MEA	0.1%	8.7	11.5	14.4	15.4	16.2
	0.5%	8.4	10.8	13.5	14.5	15.8
	1%	7.7	10.5	11.4	15.0	15.7
DEA	0.1%	9.0	11.9	14.4	15.4	15.5
	0.5%	8.9	12.0	14.0	15.4	15.5
	1%	4.5	10.4	11.9	12.5	13.5
TEA	0.1%	7.8	10.6	13.3	15.5	15.6
	0.5%	6.4	10.5	13.0	14.8	15.0
	1%	3.3	7.5	8.6	9.9	10.6

Results and Discussion

Setting Times. The setting times of the pastes with and without ethanolamines are given in Table 2.

At the addition rate of 0.1% and 0.5% MEA and DEA did not show any significant effect the on the initial setting times but, final setting times were slightly retarded. However, 0.1% TEA influenced the final setting time rarely.

Depending on the addition rate, all of the admixtures significiantly increased the final setting times and therefore retarded the hydration of cement pastes. Among the three admixtures DEA and TEA showed more marked effect on both the initial and final setting times although the MEA addition influenced only the final setting times.

Thermal Analysis Studies. The $Ca(OH)_2$ contents of the white PC pastes cured up to 90 days are given in Table 3. The cement pastes containing MEA and 0.1% and 0.5% DEA produced

TABLE 4

Flexural Strengths of Cement Pastes, MPa

Cement Pastes		*3 d.*	*7 d.*	*28 d.*	*90 d.*
Control		8.0	9.0	10.1	10.3
MEA	0.1%	5.7	9.0	9.2	10.0
	0.5%	5.5	8.0	8.9	10.0
	1%	5.5	7.0	10.3	10.7
DEA	0.1%	7.8	8.8	9.9	10.0
	0.5%	7.8	8.7	9.9	10.0
	1%	7.6	8.5	9.3	9.6
TEA	0.1%	5.4	7.7	10.5	10.6
	0.5%	5.3	7.4	9.0	9.3
	1%	5.3	6.9	8.6	8.7

TABLE 5

Compressive Strengths of Cement Pastes, MPa

Cement Pastes	*3 d.*	*7 d.*	*28 d.*	*90 d.*
Control	35.0	51.1	72.6	92.6
MEA 0.1%	29.4	49.3	73.1	92.9
0.5%	27.3	43.7	70.0	93.2
1%	26.2	42.9	77.5	90.9
DEA 0.1%	36.9	47.5	73.1	80.6
0.5%	37.5	44.3	72.4	79.0
1%	32.5	41.9	68.6	73.5
TEA 0.1%	27.5	43.4	82.0	90.6
0.5%	25.5	40.6	62.3	78.3
1%	25.0	40.2	51.9	68.1

nearly the same amount of $Ca(OH)_2$ with control paste at all ages.

The amount of calcium hydroxide of the cement pastes containing TEA and 1% DEA was found to be much lower than that of the control samples. This also shows the redardation effect of these admixtures.

Strengths. The effect of the admixtures on the strength development of the cement pastes are shown inTable 4 and 5, respectively.

Although MEA and TEA lowered the early strengths of the cement pastes, the early strengths of the cement pastes containing DEA were very close to that of the control sample. Due to retardation effect of the admixtures, the early strengths of cement pastes with MEA and TEA were found to be lower than that of the control sample. After 28 days, the effect of the admixtures changes depending on the admixtures type and addition rates. For example, the addition of MEA did not change the strengths of the cement pastes in relation to the control paste at 28 and 90 days. However, the strengths of the pastes with DEA and TEA were lower

TABLE 6

The Specific Surface Areas of Cement Pastes, m^2/g

Cement Pastes	*1 d.*	*3 d.*	*7 d.*	*28 d.*	*90 d.*
Control	10.5	19.3	24.8	70.2	89.4
MEA 0.1%	10.5	20.5	24.0	70.2	90.0
0.5%	10.0	19.0	23.0	55.8	83.3
1%	10.5	19.0	22.5	68.0	87.0
DEA 0.1%	11.3	20.0	24.3	72.3	88.1
0.5%	10.8	20.0	24.5	72.0	85.0
1%	6.3	16.1	21.0	60.7	80.0
TEA 0.1%	10.1	19.5	23.0	71.7	88.2
0.5%	9.2	19.5	23.1	62.2	86.4
1%	5.7	10.9	15.3	50.5	73.4

than that of the control paste at 28 and 90 days.

Specific Surface Areas. The specific surface areas of cement pastes with and without admixture are given in Table 6. The specific surface areas increased with hydration time for all the samples, as expected. The highest specific surface area values obtained with control sample and paste with 0.1% MEA. For the cement pastes with DEA and TEA the specific surface area values decreased with increasing admixture concentrations, although, the cement pastes with TEA gave the lowest values.

Conclusions

The effect of the various concentrations of the ethanolamine admixtures on the hydration of white Portland cement were investigated. The setting times, the $Ca(OH)_2$ content, flexural and compressive strength measurements and specific surface areas showed that among these admixtures MEA and DEA at low concentrations have slightly retardation effect while the retardation of 1% DEA and TEA was found to be significant. From the present results, TEA is the most effective set retarder but it produced low strength development at early and late stages of white PC hydration. However, MEA showing a slight retardation gave the highest strength values at 90 days.

Acknowledgement

We thank Ondokuz Mayıs University Research Fund for the financial support given to the research project.

References

1. Rixom, M.R. and Mailvaganam, N.P. (editor), Chemical Admixtures for Concrete, 306p, E.&F.N. Spon Ltd., New York (1986).
2. Yılmaz, V. T., Işıldak, Ö., "Influence of Some Set Accelerating Admixtures on the Hydration of Portland Cement Containing Phosphogypsum", Advances in Cement Research, 20, 147–150 (1993).
3. Ramachandran, V.S. "Influence of Triethanolamine on the Hydration Characteristics of Tricalcium Silicate", Journal of Applied Chemistry and Biotechnology, Vol.22, 1125–1138 (1972).
4. Ramachandran, V.S. "Action of Triethanolamine on the Hydration of Tricalcium Aluminate", Cement and Concrete Research, Vol.3, 41–54 (1973).
5. Dodson V.H., Concrete Admixtures, 211p, Van Nostrand Reinhold, New York, (1990).
6. Turkish Standard Institution, Physical Testing Methods of Cement, TS-24, TSE, (1974).
7. Brunauer, S., Emmett, P.H., Teller E.S., Am. Chem. Soc., 60, 309 (1938).