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Effect of protein additive on properties of mortar

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Abstract

Test results presented in the article describe the impact of a protein additive (powdered red blood cells) on selected physical properties of cement paste, fresh mortar and physical and mechanical properties of hardened mortar. The protein additive is achieved as a result of industrial processing of animal blood. The research was made in the laboratory of the Institute of Structural Engineering of Poznan University of Technology.

The analysis of the test results achieved showed that the protein included in the preparation added to the mortar leads to intensive air entraining, which has a significant effect on the most basic of physical properties both of the fresh mortar (consistence, plasticity, volumetric density) and hardened mortar (bending strength, shrinkage, volumetric density and frost resistance). The intensity of this influence, calculated in relation to the mass of the protein preparation added to the mortar, for most of the tested properties, is much higher than in the case of currently used air entraining agents [Chatterji S. Freezing of air-entrained cement-based materials and specific actions of air-entraining agents. Cem Concr Compos 2003;25:759–65, Du Lianxiang, Folliard KJ. Mechanisms of air entrainment in concrete. Cem Concr Res 2005;35:1463–71, Neville AM. Properties of concrete. 4th and final ed. London: Longman Group Limited, 1995. p. 844].

Keywords: Protein additive; Air entraining agent; Modified cement paste and mortar

1. Introduction

The use of various additives, aimed at improving selected concrete properties, is as old as concrete itself. It was the ancient Egyptians, Greeks, Romans, who started using various natural protein substances such as blood, animal fat or milk [2,3,5,7,10]. In the second half of the 20th century, better products of chemical synthesis completely displaced all natural substances which had been used before [8,9]. In recent years, following ecological trends in building materials, an interest in former technologies and materials has been observed [1,2]. Powdered blood used to be added to concrete as an air entraining agent in the 1970s in the USSR [9]. In concrete, a small quantity of powdered blood—approximately 0.2–1‰ of the cement weight is sufficient to entrain 5–25% of air. Air bubbles are small, well distributed, separated from each other and modify the behaviour of both wet and hardened material. Also in recent years, powdered protein for air entraining of clay–cement mixtures has been used in Rennes University [1]. Test results, presented in this article, concerning air entraining properties of animal protein in cement mortar, demonstrate that the performance of additives formerly used in mortar and concrete may still take us by surprise.

The substance is added to cement in a quantity lower than 5%. The aim is to modify physical or chemical properties of one or more properties of hardened mortar. When mixing the ingredients, air entraining additives have foaming properties, improve the dispersion of cement grains and create air bubbles of 20–250 μm which are well distributed in the whole mortar. During hardening of the cement, bubbles partly get mineralised and become a stable component of the mortar. Air entraining admixtures increase the workability of the fresh mortar, increase its waterproofing and

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freeze-thaw properties as well as its resistance to corrosion causing factors [4,6]. One of the areas where air entrained concrete can find a wide use is in lower layers of substrates for road construction.

2. The aim and scope of the research

Tests have been carried out in the laboratory of the Institute of Structural Engineering at Poznan University of Technology. The aim of the tests was to check the influence of added powdered protein on some selected physical properties of cement paste, fresh mortar and physical and mechanical properties of hardened mortar.

The powdered protein used is received as a result of industrial processing of pig's and cow's blood. The main component of the substance is red blood cells. The preparation in the form of fine powder and in over 99% of its volume consists of animal protein.

As a result of literature studies and preliminary research, the content of the protein preparation in test samples was at the levels of 0.05%, 0.1% and 0.2% of the cement in volume terms. Two types of cement were used [12]: Portland cement CEM I 32.5 R (marked on the samples: "I") and one of the cheapest and therefore the most popular types of multi-component Portland cement containing siliceous fly ashes—CEM II/B-V 32.5 R (marking on the samples: "II").[1] The aim of such a selection of cement was to get to know a possible impact of the main components of cement, apart from clinker, on the characteristics of mortar modified with protein additive.

The tests were carried out on standard prisms of $4 \times 4 \times 16$ cm. To prepare the mortar, standard silicon sand was used (according to norm PN EN 196-1 [13]). During the test time, the samples were stored in laboratory conditions of 18 °C and relative air humidity of >90%. The following scope of laboratory tests were performed:

(a) Testing the time of the beginning and the end of setting.
(b) Testing fresh mortar:
- Consistency measurement.
- Plasticity measurement.
- Volumetric density measurement.

(c) Testing hardened mortar:
- Testing bending strength (after 7 and 28 days of curing).
- Ultimate compressive strength (after 7 and 28 days of curing).
- Shrinkage of mortar.
- Volumetric density measurement.
- Testing absorbability.
- Frost proof test.
- Microscope observation.

[1] Example of sample marking: II/0.5—sample made of cement CEM II/B-V 32.5 R and 0.5‰ of protein additive (in relation to mass of cement).

3. Tests of the cement paste and fresh mortar

Test results presented in Table 1 are the arithmetical average of two measurements. The measurements were made after 15 min from cement paste and fresh mortar preparation (according to standard [11]). The dependence of the volumetric density of fresh mortar and the content of the protein additive is described by the following functions:

(a) for cement "I" $y = \frac{1}{0.475+0.052x}$ where the correlation coefficient $k = 0.941$,
(b) for cement "II" $y = \frac{1}{0.469+0.064x}$ where the correlation coefficient $k = 0.952$,

where x signifies the content of protein additive per ml, y is the volumetric density in kg/dm^3.

Graphs of the both functions are presented in Fig. 1.

4. Tests of the hardened mortar

4.1. Bending strength and ultimate compressive strength

Tests of the bending strength (measurements on six samples) and ultimate compressive strength (measurements on twelve samples) were carried out after 7 and 28 days of curing [11]. Test results obtained are presented in Tables 2 and 3. Standard deviation of the results of both the bending strength and ultimate compressive strength does not exceed 9%.

The dependence between the bending strength after 28 days of curing and the content of the protein additive are described by the following functions:

(a) for cement "I" $y = \frac{1}{0.157+0.307x-0.075x^2}$ where the correlation coefficient $k = 0.975$,
(b) for cement "II" $y = \frac{1}{0.217+0.214x-0.049x^2}$ where the correlation coefficient $k = 0.974$,

where x is the content of protein additive expressed per ml, y is the bending strength in N/mm^2.

Graphs of the both functions are shown in Fig. 2.

The dependence of the ultimate compressive strength after 28 days of curing and the content of the protein additive are described by the following functions:

(a) for cement "I" $y = \frac{1}{0.022+0.068x-0.017x^2}$ where the correlation coefficient $k = 0.952$,
(b) for cement "II" $y = \frac{1}{0.024+0.063x-0.013x^2}$ where the correlation coefficient $k = 0.947$,

where x is the content of the protein additive in per mille, y is the bending strength in N/mm^2.

Graphs of the both functions are presented in Fig. 3.

Table 1
Test results of selected physical properties of cement paste and fresh mortar (average of two measurements)

Tested characteristics	Content of protein additive (‰) in relation to cement volume							
	CEM I/32.5 R				CEM II/B-V 32.5 R			
	0	0.5	1	2	0	0.5	1	2
Time of the start and end of setting	1 h 25′	1 h 30′	1 h 15′	1 h 10′	3 h 20′	4 h 20′	3 h 15′	4 h 20′
	4 h 25′	6 h 05′	6 h 25′	6 h 20′	5 h 40′	7 h 05′	6 h 55′	8 h 35′
Consistency (cm)	4.25	7.00	6.35	5.90	5.20	5.50	5.30	8.50
Workability (cm)	13.0	16.1	14.8	13.9	13.3	14.9	13.7	15.7
Volumetric density (kg/dm^3)	2.18	1.93	1.87	1.75	2.17	2.03	1.78	1.71

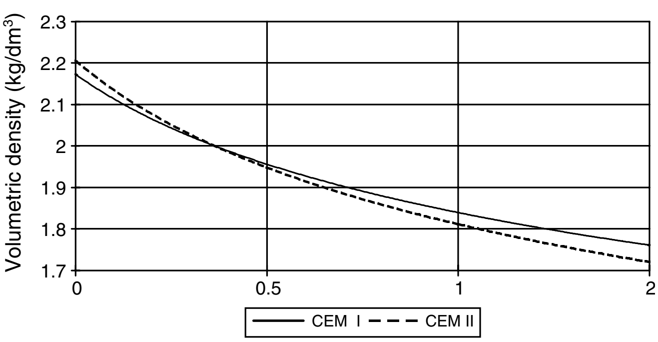

Fig. 1. Impact of protein additive content on apparent density of fresh mortar, using cement "I" (correlation coefficient $k = 0.941$) and cement "II" (correlation coefficient $k = 0.952$).

4.2. Shrinkage

For each of the eight tested recipes (see Table 4), three samples of $4 \times 4 \times 16$ cm were prepared. Measurements of shrinkage were made after 1, 3, 7, 14 and 28 days of curing. During the whole period of making measurements the samples were stored under laboratory conditions (18 °C, air humidity 55–65%). The measurements were made with on accuracy of up to ±0.005 mm. Changes of the shrinkage in the first 28 days of curing for each of tested recipes were described by the function $y = a + b/x + c/x^2$. For calculated functions, correlation coefficients of 0.96–0.99 between the shrinkage and the curing time were received. In Table 4 and in Fig. 4 the average 28-day shrinkage for tested samples was presented, calculated on the basis of the mentioned functions.

4.3. Volumetric density of the dry mortar

Tests were made using the drying and weighing method for samples of $4 \times 4 \times 16$ cm, after 28 days of curing. All results shown in Table 5 are the arithmetical average from the six tested samples. The maximum value of the standard deviation of the test results is lower than 4.5%. The dependence of the volumetric density of the dry mortar after 28 days of curing and the content of the protein additive is described by the following functions:

(a) for cement "I" $y = \frac{1}{0.472+0.043x}$ where the correlation coefficient $k = 0.942$,
(b) for cement "II" $y = \frac{1}{0.468+0.057x}$ where the correlation coefficient $k = 0.965$,

Table 2
Test results of bending strength (average of six measurements) of cement prisms (N/mm^2)

Days of mortar curing	Content of protein additive (‰) in relation to cement volume							
	CEM I/32.5 R				CEM II/B-V 32.5 R			
	0	0.5	1	2	0	0.5	1	2
7	3.9 ± 0.1[a]	2.5 ± 0.2	2.1 ± 0.1	1.2 ± 0.1	4.6 ± 0.3	2.7 ± 0.2	1.8 ± 0.1	0.9 ± 0.1
28	7.1 ± 0.3	3.0 ± 0.2	2.8 ± 0.2	2.1 ± 0.1	4.9 ± 0.2	2.9 ± 0.1	2.8 ± 0.1	2.2 ± 0.2

[a] Standard deviation of achieved results (N/mm^2).

Table 3
Test results of ultimate compressive strength (average of 12 measurements) of cement prisms (N/mm^2)

Days of mortar curing	Content of protein additive (‰) in relation to cement volume							
	CEM I/32.5 R				CEM II/B-V 32.5 R			
	0	0.5	1	2	0	0.5	1	2
7	30.4 ± 1.8[a]	17.2 ± 0.8	15.5 ± 1.0	12.4 ± 0.9	25.0 ± 1.1	15.6 ± 1.0	11.8 ± 0.9	6.8 ± 0.4
28	40.3 ± 2.2	23.2 ± 1.4	12.6 ± 0.9	11.5 ± 0.9	36.6 ± 1.5	23.3 ± 1.3	12.4 ± 1.0	10.3 ± 0.9

[a] Standard deviation of achieved results (N/mm^2).

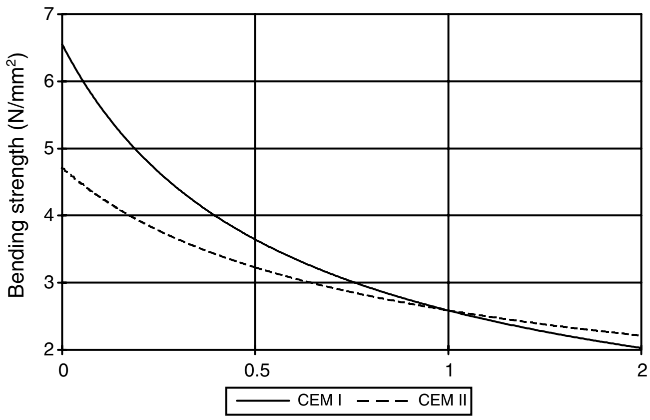

Fig. 2. Impact of protein additive content on bending strength after 28 days of mortar curing, using cement "I" (correlation coefficient $k = 0.975$) and cement "II" (correlation coefficient $k = 0.974$).

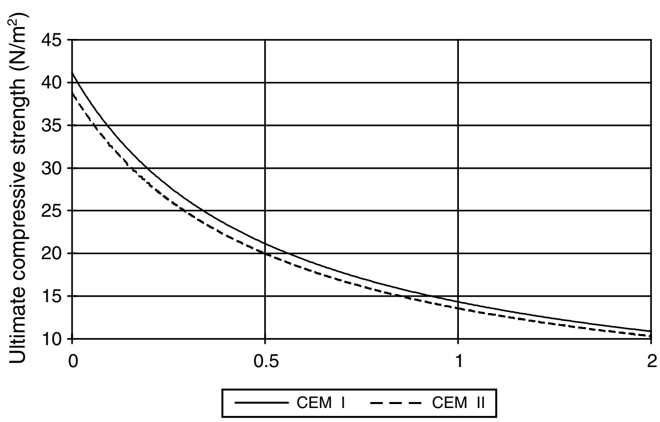

Fig. 3. Impact of protein additive content on ultimate compressive strength after 28 days of mortar curing, using cement "I" (correlation coefficient $k = 0.952$) and cement "II" (correlation coefficient = 0.947).

where x is the content of red blood cells expressed per ml, y is the volumetric density of the dry mortar in kg/dm^3.

Graphs of the above functions are presented in Fig. 5.

4.4. Absorbability

Tests were made according to drying and weighing method for samples of $4 \times 4 \times 16$ cm, after 28 days of curing. All results presented in Table 6 are the arithmetical average of the six tested samples. The maximum value of standard deviation of the test results is lower than 2.5%.

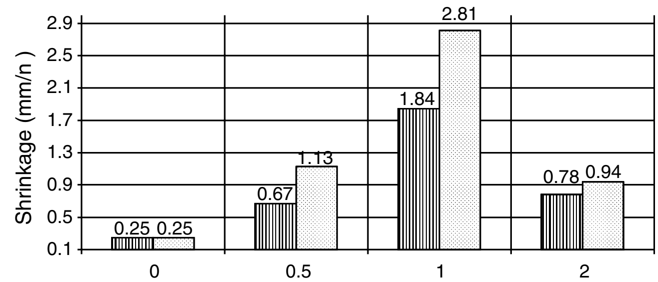

Fig. 4. Twenty eight-day shrinkage for mortars made with CEM I and CEM II, depending on protein additive content. Measurement error is ±0.031 mm/m.

4.5. Freeze- thaw resistance

Tests were made after 28 days of curing on 12 standard prisms of $4 \times 4 \times 16$ cm. For each recipe, six samples were subject to 25 cycles of freezing at −20 °C and defrosting in +20 °C. The remaining samples left for controlled tests were stored in water. After performing the tests, macroscopic estimation of damage was made as well as the measurement of mass decrease and fall in resistance. The arithmetical average of the test results is presented in Table 7.

5. Analysis of the test results

5.1. Testing the time of the beginning and the end of setting

The powdered protein added to a standard cement paste does not have an observable impact on the time of the beginning of its setting (Table 1). The time at the end of setting is lengthened by approximately 50% when 0.5‰ additive of red blood cells is added. When the quantity of the additive is increased, the time of the end of setting still lengthens, although at a much slower pace.

5.2. Testing fresh mortar

Consistency measurements. For mortars made of CEM I, 0.5‰ additive of protein preparation causes the decrease of the consistence measured by a cone (described in standard [11]) by approximately 50% (from 4.25 to 7 cm), then it becomes more stable when more additive is used. In case of using CEM II, a considerable decrease of consistence (from 5.2 to 8.5 cm) was observed when 2‰ red blood cells additive was added.

Table 4
Twenty eight-day shrinkage—average of three measurements (mm/m)

Days of mortar curing	Content of protein additive (‰) in relation to cement volume							
	CEM I/32.5 R				CEM II/B-V 32.5 R			
	0	0.5	1	2	0	0.5	1	2
28	0.2500	0.6688	1.8438	0.7750	0.2500	1.1250	2.8125	0.9375

Table 5
Test results of volumetric density (average of six measurements) of cement prisms (kg/dm^3)

Days of mortar curing	Content of protein additive (‰) in relation to cement volume							
	CEM I/32.5 R				CEM II/B-V 32.5 R			
	0	0.5	1	2	0	0.5	1	2
28	2.180 ± 0.081[a]	1.943 ± 0.072	1.892 ± 0.080	1.822 ± 0.055	2.176 ± 0.051	2.019 ± 0.067	1.832 ± 0.050	1.746 ± 0.076

[a] Standard deviation of achieved results (kg/dm^3).

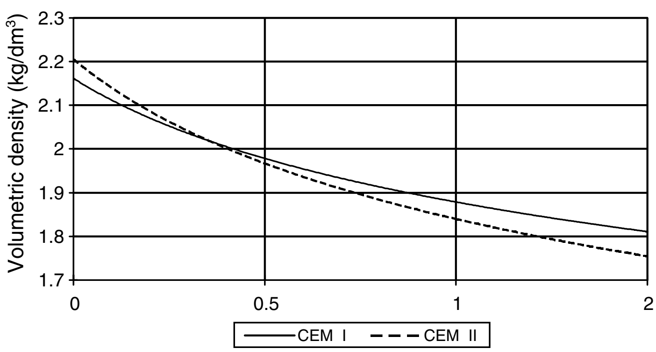

Fig. 5. Impact of protein additive on apparent density of dry mortar after 28 days of curing, using cement "I" (correlation coefficient $k = 0.942$) and cement "II" (correlation coefficient $k = 0.965$).

Workability measurement (flow test). No clear correlation between the quantity of added protein preparation and the diameter of the sample spread on a flow table was observed. The existing differences (Table 1) are within the limits of the measuring error.

Measurement of volumetric density. There is a close correlation between the quantity of the protein additive and the density of the achieved mortar (Fig. 1). The dependence has a form of the function $y = 1/(a + bx)$. The achieved correlation level is included between 0.94 (CEM I) and 0.95 (for CEM II).

5.3. Testing hardened mortar

Testing the bending strength and ultimate compressive strength. Both the results of bending strength tests (Table 2) as well as the results of ultimate compressive strength tests (Table 3) are in a close correlation with the quantity of the protein preparation in the mortar (Figs. 2 and 3). The dependence is described by the function $y = 1/(a + bx + cx^2)$. The achieved correlation level is approximately 0.97 for bending strength (both for CEM I and for CEM II) and 0.95 (for CEM I and CEM II) for ultimate compressive strength.

Measurement of mortar shrinkage. Both for the mortar made of CEM I and the one made of CEM II (Table 4 and Fig. 4) their 28-day shrinkage increases considerably, proportionally to the quantity of red blood cells, from 0‰ to 1‰ (for CEM I: 7-fold increase and for CEM II: 11-fold). Then, for 2‰ content of red blood cells there is a clear decrease of the shrinkage (compared to 1‰ content, it is a decrease of approximately one half).

Table 6
Test results of absorbability (average of six measurements) of cement mortar (%)

Days of mortar curing	Content of protein additive (‰) in relation to cement volume							
	CEM I/32.5 R				CEM II/B-V 32.5 R			
	0	0.5	1	2	0	0.5	1	2
28	7.4 ± 0.1[a]	8.8 ± 0.1	8.1 ± 0.2	8.8 ± 0.1	8.4 ± 0.2	8.7 ± 0.1	8.5 ± 0.1	9.0 ± 0.1

[a] Standard deviation of achieved results (%).

Table 7
Test results of frost resistance of cement mortar

Test type	Content of protein additive (‰) in relation to cement volume							
	CEM I/32.5 R				CEM II/B-V 32.5 R			
	0	0.5	1	2	0	0.5	1	2
Macroscopic estimation after the test	No changes	No changes	No changes	No changes	No changes	No changes	No changes	No changes
Loss of mass (%)	0.2	<0.1	<0.1	<0.1	0.3	<0.1	<0.1	<0.1
Ultimate compressive strength of samples (N/mm^2)	49.6	24.4	21.6	17.6	39.7	28.5	19.0	12.5
Ultimate compressive strength of frozen samples (N/mm^2)	39.9	24.0	20.8	17.0	20.7	27.5	19.4	11.4
Loss of ultimate compressive strength (%)	−19.6	−1.6	−3.7	−3.4	−47.9	−3.5	+2.1	−8.8
Bending strength of samples (N/mm^2)	9.6	4.7	4.5	3.2	8.1	5.5	3.4	3.1
Bending strength of frozen samples (N/mm^2)	4.8	4.4	4.2	3.2	2.6	5.6	3.5	2.8
Loss of bending strength (%)	−50.0	−6.4	−6.7	0	−67.9	+1.8	+2.9	−9.6

Testing volumetric density. There is a close correlation between the volumetric density of the dry mortar after 28 days of curing and the content of the protein additive (Fig. 5). The dependence has a form of the function $y = 1/(a + bx)$. The achieved correlation level is included between 0.94 (CEM I) and 0.97 (for CEM II).

Absorbability test. The absorbability of the achieved mortar goes up slightly (Table 6), proportionally to the quantity of the protein preparation. The average increase of the absorbability in case of the increase of the protein preparation from 0‰ to 2‰ was approximately 9.5% for the samples made of CEM I (increase from 7.4% to 8.8%) and approximately 7.2% for CEM II (increase from 8.4% to 9%).

Freezing-thaw resistance. Macroscopic estimation of the samples, after a frost proof test, did not reveal any visible

Fig. 6. Appearance (enlargement of approximately 30×) of mortar made with CEM I.

Fig. 7. Appearance (enlargement of approximately 30×) of mortar made with CEM I + 0.2% of protein additive.

damage of the sample surface. There was a slight loss of the mass for samples made without the use of protein preparation (0.2% for CEM I and 0.3% for CEM II). However, in cases of other samples including protein additive, the loss was minimal, on the verge of the measurement limit (<0.1%). The decrease of the resistance of samples prepared without protein additive, subject to 25 cycles of frosting and defrosting was significant (Table 7). The ultimate compressive strength decrease was from 19.6% (for CEM I) to 47.9% (for CEM II). The bending strength went down even more significantly—from 50.0% for CEM I to 67.9% for CEM II. Strong air entraining properties of protein included in red blood cells led to such an effect that only 0.5‰ protein additive suddenly caused an increase of mortar resistance to frost. The decrease of both the bending strength and ultimate compressive strength for all prepared samples was several per cent, independently from the quantity of the protein additive. In some cases there was even a slight (up to 2.9%) increase of frost resistance in comparison to base samples.

5.4. Cement type

The analysis of the data included in Tables 1–7 demonstrated that the type of cement used (CEM I 32.5 R and CEM II/B-V 32.5 R) did not have much impact on the tested properties of both fresh and hardened mortar.

5.5. Microscopic observation

In microscopic pictures (Figs. 6 and 7) an internal structure of mortar samples before and after air entraining is visible. Air bubbles have an average diameter smaller than 100 μm and are evenly distributed in the mortar.

6. Conclusions

As a result of the analysis of test results we can draw a conclusion that the protein included in the preparation added to mortar causes intensive air entrainment of the mortar and has a significant impact on most basic physical properties of both the fresh mortar and physical and mechanical properties of the hardened mortar. The intensity of this influence, compared to the mass of protein powder added to the mortar, is for the majority of tested characteristics to be close to 10-fold higher than in cases of using chemical air entraining substances. This influence is manifested in the following ways:

Fresh paste and fresh mortar:

- significant lengthening of the end of cement setting time,
- clear decrease of the mortar consistency,
- considerable decrease of the volumetric density.

Hardened mortar:

- decrease of the bending strength and ultimate compressive strength, proportionate to the decrease of the volumetric density,
- considerable increase of the shrinkage,
- significant increase of mortar resistance to the destructive impact of frost.

No significant impact of the type of the cement was observed on tested characteristics of both fresh and hardened mortar. Intensity, influence and low price of the tested protein preparation make this additive attractive as a valuable air entraining substance for mortars and concrete blends.

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