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The determination of the influence of pH value of curing conditions on Portland cement hydration

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Abstract

Water composition during cement hydration can be changed due to migration of ions from the cement matrix to the solution. The storage of various materials together can lead to transfer of various ions and distortion of results. This article is aimed on the influence of storage environment on the Portland cement hydration and hydrated samples composition. Test specimens were prepared and stored in different environments. Storage environments were ultrapure water and solutions having alkaline and acidic pH value. The mechanical properties were measured after 1, 7 and 28 days. Composition of samples stored in different environment was tested by X-ray diffraction and DTA analysis.

Keywords: Portland cement; mechanical properties; thermal analysis; X-ray diffraction; pH value

1. Introduction

Kind, time and conditions of treatment have the biggest influence on the strength and other mechanical properties of cement composites. The requirement for proper treatment is the storage in an environment that facilitates to hydration reactions and processes. Cement hydration takes several years. Over time, the reaction slows down due to the lower water content and storage temperature. Cement composite maturation is very important for the development of its strength and durability. Time of treatment for adequate hydration of Portland cement or concrete

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depends mainly on the chemical and mineralogical composition, fineness of the cement and curing conditions [1,2,3].

The hydration reaction contributes to the potential strength and durability of concrete and pastes. There also depends on type and fineness of cement, amount of additional material, water-cement ratio and curing conditions, especially during the early stages of hydration [4].

According to Powers, the minimal humidity required for the hydration of Portland cement is 80%. He also discovered increasing sample surface throughput due to insufficient curing. According to his result, the most effective method for treating is continued exposure of the sample surface to moisture or water spraying [5].

Sajedi et al. studied the influence of environment and softness of the material on the properties of cementitious composites. They compared mechanical properties of samples stored in the air, humid environment and water. Comparison of compressive strengths for the mixes shows that strength at 3 and 7 days in air conditions are higher than those of water conditions, but after 7 days the strengths reduce up to 90 days. At 90 days the strength is minimized and there is strength loss about 7% compared to 56 days. The strengths for water conditions continuously increase at all ages and there is not any strength loss [6].

The aim of this article is the study of environmental influences on the properties of cement composites. Five kinds of environments with different pH were tested. The samples were tested in neutral alkaline and acidic pH. The samples were immersed to the aqueous medium after 1 day. The first stage of hydration reactions are carried out in the air under polethylene foil. The results shows development of cement pastes properties in aqueous media after the first 24 hours.

2. Experimental

2.1. Materials

Cement (CEM I 42.5 R Mokrá, Heidelberg Cement group, Czech Republic) with the following particle size distribution characteristics (the numbers in this parameter means how many percent of the number of particles is smaller than a given percentage (10%, 50%, and 90%)): $d_{10} = 0.47$ µm, $d_{50} = 8.89$ µm, $d_{90} = 34.42$ µm, was used for the preparation of paste mixtures. Particle size distribution of all components was determined by the laser diffraction method.

2.2. Chemicals

For the prepared different treatment was used a solution of sulfuric acid with purity p.a. and concentration of 96%, ammonia solution (25 – 29%) (both from Penta s.r.o., Czech Republic) and white lime CL 90 (Vitošov, Czech Republic).

2.3. Specimen preparation

Test prisms were prepared with water-binder ratio 0.4. The total mixing time was 3 minutes. The resulting mixture was molded and vibrated for one minute. The resulting prisms were 1 day stored under polyethylene bags for reaching a high humidity hydration environment.

2.4. Curing condition

Samples were demoulded after 2 hours and placed in various aqueous environments. Test specimens properties developments in three different environments were studied. A solution of sulfuric acid was used to prepare an acidic solution with pH 2. To cover the neutral pH ultrapure water and tap water were used. Finally, the basic environment (pH 12) was made by ammonia solution and white lime CL 90. Also, the influence of tap water changed every 7 days was measured.

2.5. Test techniques

The influence of curing environment on the mechanical properties of test specimens was monitored after 2, 7 and 28 days. To monitor changes in the aqueous environment the pH value of aqueous solutions was measured. After 28 days of curing, phase composition by X-ray diffraction (XRD) and thermal properties by Differential thermal analysis (DTA) were tested.

3. Results and discussion

3.1. Mechanical properties

Mechanical properties increased with increasing time for all samples. The most noticeable compressive strength increase was recorded between 48 hours and 7 days. Significant increase of flexural strength after 48 hours was detected unlike the compressive strength. The results indicate average values of three measurements for flexural strength and six measurements for compressive strength.

All samples have higher strength measured than reference sample cured in humidity chamber. The highest flexural (13.1 MPa) and compressive strength (90.3 MPa) were measured for samples stored at pH 2. These samples reached the highest strength after 7 and 28 days. After two days the highest strength were measured in ultrapure water. Flexural strengths after long periods of maturation (7 and 28 days) are higher in the altered tap water than in ultrapure water but compressive strengths are comparable. For the samples in an alkaline medium the lowest strength were measured.

Higher compressive strength of the samples stored in water may be attributed to the formation of compact microstructure, but also thanks to the formation of lower amounts of portlandite ($Ca(OH)_2$) which can be leached into the surrounding solution.

Mechanical properties measured are visible in the Table 1.

Table 1. Mechanical properties of samples stored in different environment.

Sample	Sample age (*day*)	Flexural strength (*MPa*)	Compressive strength (*MPa*)
Humidity chamber	1	5.7 ± 0.6	25.8 ± 1.4
	7	5.6 ± 0.5	55.8 ± 3.5
	28	6.0 ± 0.4	61.7 ± 4.7
Ultrapure water	2	6.9 ± 0.4	32.2 ± 1.6
	7	6.6 ± 0.5	72.7 ± 2.4
	28	8.9 ± 0.5	83.3 ± 4.6
Changed tap water	2	5.3 ± 0.4	30.4 ± 3.2
	7	9.8 ± 0.4	67.3 ± 5.5
	28	12.0 ± 0.4	87.5 ± 3.0
H_2SO_4 solution	2	6.0 ± 0.4	29.1 ± 3.6
	7	11.5 ± 0.7	72.4 ± 4.6
	28	13.1 ± 0.9	90.3 ± 2.3
NH_3 solution	2	5.9 ± 0.0	25.8 ± 2.6
	7	7.9 ± 0.0	66.9 ± 4.6
	28	8.6 ± 0.4	71.5 ± 1.8
CaO	2	6.5 ± 0.0	24.4 ± 3.1
	7	9.3 ± 0.7	72.5 ± 4.7
	28	9.8 ± 1.0	75.7 ± 4.2

3.2. The pH values changes during storing

The pH value of samples stored in tap water was measured each time before changing the water. The most obvious increase in pH was observed during the first 7 days due to intense hydration reactions. During these reactions, clinker minerals are forming new hydration products with water. This leads to the release of alkali metal ions into the surrounding solution and the pH value is increasing. The migration of these ions is slowing in later stage due to the formation of stable hydrates. Release of other elements is controlled by diffusion in this stage and increasing of pH value is not so significant.

The pH value after 7 days in all aqueous environments where the pH was changed by foreign compounds was higher than 12. In the acidic environment, pH value is slightly increased during the first 4 days. Then, during the next three days, there was a very significant increase in pH, which does not significantly increase in later stage. This result correspond to samples in the water, where is also very small increase of pH value between 7 and 14 days. There was only little change of pH value in the alkaline environment thanks to high values in the first stage of hydration.

The pH values after 28 days were comparable for all samples stored without changing environments throughout maturation. Surprisingly, the lowest pH after 14 days was achieved in a solution containing CaO. In this environment, the highest detected pH corresponds to the pH value of portlandite precipitation. The pH value may be also affected by precipitation of calcite ($CaCO_3$). The pH is in the slightly higher values for all other samples. In all investigated environments excluding H_2SO_4, the pH value above 12.5 were detected after 14 days. The slight lowering of pH may be due to portlandite and calcite precipitation.

All pH values measured are visible in the Table 2.

Table 2. The pH values of all aqueous environment.

Time (*day*)	pH value				
	Ultrapure water	Changing tap water	H_2SO_4	CaO	NH_3
0	7.0	7.7	2.0	12.0	12.0
4	12.1	12.4	3.3	-	-
7	12.0	11.7	12.4	12.4	12.7
14	12.6	11.1	12.5	12.4	12.7
28	12.7	10.8	12.6	12.4	12.6
33	12.7	8.7	12.7	12.3	12.6

Due to the reaction of calcium ions with CO_2 from the air, calcite was detected in the thin layer covering the surface of liquids in all samples after a certain time. According to assumptions, the highest amount of portlandite was precipitated in an alkaline medium and the lowest amount in an acidic media. The largest crystals have been precipitated in the water environment.

3.3. XRD

The results were obtained by using of Rietveld Analysis. Although this type of analysis is burdened by specific mistakes, certain trends were found there.

There was measured very similar amount of residual clinker minerals in all studied environments: 20 – 26% of alite, 8 – 10% of belite and 4 – 6% of brownmillerite. The smallest amount of alite was found in the sample stored in tap water which is changed every week. This result would correspond to very intensive dissolution of the silicate phase and re-saturation of the surrounding solution ions.

The most important phase for higher strength of cement clinker is dissolution product of C_3S phase. In case of more significant dissolution of this phase, the mechanical properties of tested cement specimens should increase. This effect was observed by significant increase of tensile strength after 7 days. The compressive strength was only slightly higher in comparison to other aqueous environments without the addition of substances. In contrast, there is

very slow alit phase dissolution for the samples immersed in sulfuric acid. In an acidic environment, the formation of gypsum according to this equation might result:

$$Ca(OH)_2 + SO_4^{2-} \rightarrow CaSO_4 \cdot 2H_2O + 2OH^- \tag{1}$$

In suitable conditions, the gypsum can be recrystallized to ettringite. This ettringite arises in hardened cement unlike ettringite which causes retardation of fresh cement paste.

$$3CaO \cdot Al_2O_3 \cdot 6H_2O + 3(CaSO_4 \cdot 2H_2O) + 19H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 32H_2O \tag{2}$$

The quantity of ettringite in the samples was between 8 and 12 %. The highest amount of ettringite was detected in a sample immersed in tap water that was changed periodically. This result is related to the release of various ions into the surrounding solution. Also, the amount portlandite not differ significantly and ranging from 35 to 42 wt. %.

However, these values may be influenced by inhomogeneity of the material. Calcite was discovered in each sample. Calcite may arise during solidification in the molds of samples before they were placed to the test environment. Amount of calcite is similar for all samples (8 – 10 wt. %). Gypsum was detected in some samples. Gypsum probably comes from fresh cement.

Table 3. Amount of different substances in the samples stored in different environments according to XRD.

Amount (*wt. %*)	C_2S	C_3S	C_4AF	$Ca(CO_3)$	$Ca(OH)_2$	ettringite	SiO_2	$CaSO_4.2H_2O$
Ultrapure water	8	26	5	9	41	8	2	1
Changed tap water	9	20	5	10	39	12	3	1
H_2SO_4	9	26	4	9	38	11	2	-
CaO	10	22	4	10	42	9	3	-
NH_3	10	22	4	8	42	9	5	-

3.4. DTA

In the picture below you can see the gradual samples weight decreasing during heating. The sharp mass drop around 100 °C is caused by the release of free water from the samples. The water in samples may remain as capillary water, or as part of CSH gel, ettringite or hydrates despite the crushing of the sample and washing with acetone. In the right figure we can observe the endothermic reactions that take place in the systems. The small endothermic peak around 370 °C could be due to complete loss of free water. This water cannot be present after exceeding the temperature of 374 °C. Another visible mass loss was observed above 400 °C, where is the thermal decomposition of portlandite. Portlandite contents in the samples were calculated by using of directives lines. The largest amount of portlandite was detected in the sample stored in the alkaline solution of CaO, which is probably caused by a large amount of calcium ions. In other environments, the amount of portlandite measured was very similar. Difference was only 0.3%.
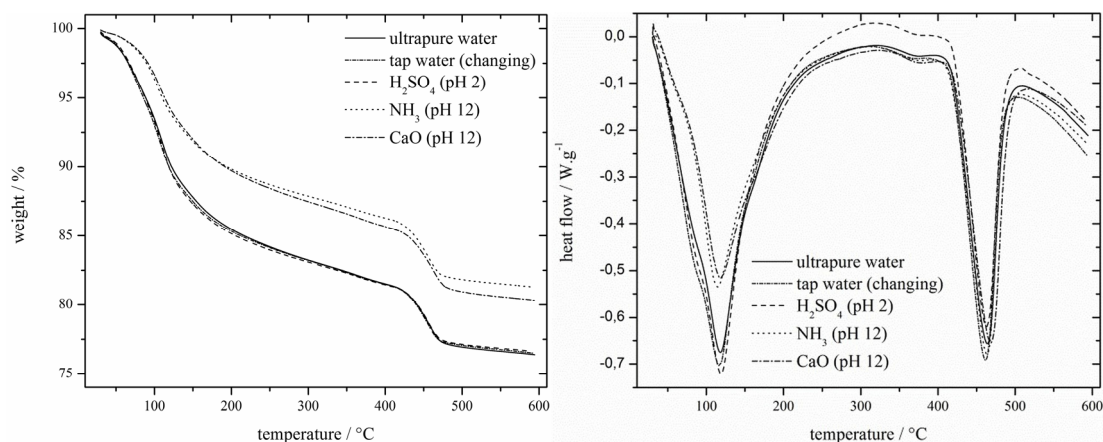
Fig. 1. Sample weight loss and heat flow evolution with temperature increase.

Table 4. Portlandite content.

Sample	Ca(OH)$_2$ (*wt. %*)
Ultrapure water	4.89
Changed tap water	4.72
H$_2$SO$_4$	4.60
NH$_3$	4.77
CaO	5.08

The curves in Figure 2 were made by the weight derivative according to temperature. Two major peaks were detected. The first peak is around 100 °C and the other one around 450 °C. The first peak was deconvoluted by program origin (OriginLab Corporation, Northampton, USA) for the hidden peaks revealing. It was composed from three peaks. The first peak was found around 76 °C. This peak can be attributed to the rest of acetone in the sample or to slow loss of capillary water. The main peak has a maximum at 108 °C where the early dehydration of the cement paste, the release of free water and the decomposition of hydrates occurs. From 80 to 150 °C ettringite dehydration is forthcoming. The last detected peak was found around 145 °C. There is the first phase decomposition of CSH gel. Between 150 °C and 170 °C, gypsum decomposition occurs.
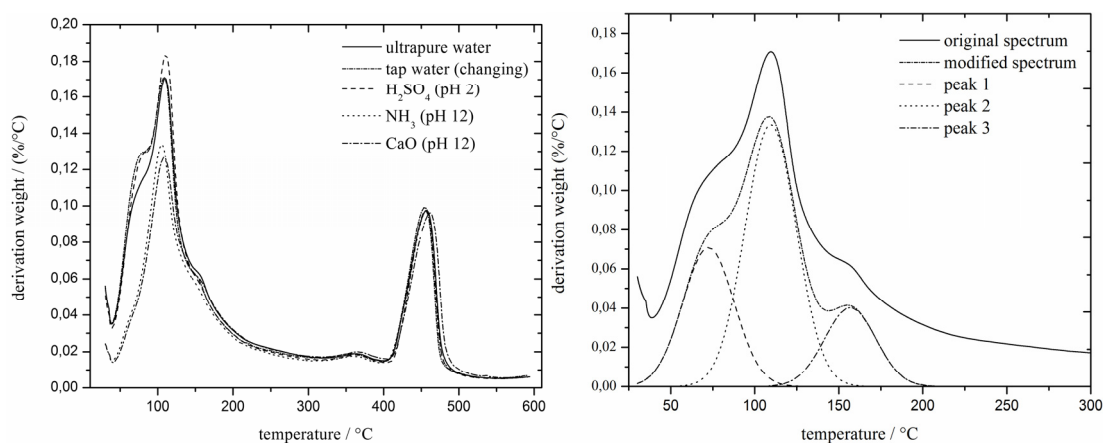

Fig. 2. Mass derivative and spectrum deconvolution around 100 °C.

There was found a little peak below 100 °C for samples stored in an alkaline environment. This peak should correspond to evaporation of capillary bound water or to present of organic solvent used to stop of hydration (acetone). This difference could be attributed to the formation of a denser structure of the paste during cement sample storage in the basic environment. There was detected second peak around 110 °C for all samples. This peak corresponds to the evaporation of free water from the sample. Samples stored at acidic and neutral pH contained a similar amount of free water (7.5 and 7.9 wt. %). There was measured considerably lower quantity of water (about 6.5 wt. %) for samples in basic environment. This fact also imply to faster consumption of water by hydration reactions. These hydration reactions and processes in this environment can be faster due to pH value adjustment. The last peak was discovered around 156 °C. The size was very similar for all samples. This would correspond to a similar quantity of CSH gel decomposed or to gypsum. Minor differences were detected in calculation of their weight. Slightly larger content of CSH, which extends around 156 °C, was calculated for samples immersed in alkaline solutions.

Table 5. The calculated peak area hidden around 100 °C.

		Integral of the area under the peak	Mass (*wt. %*)
Ultrapure water	Peak 1	2.70878	4.11
	Peak 2	5.10616	7.76
	Peak 3	1.53649	2.34
Changed tap water	Peak 1	2.70872	4.87
	Peak 2	5.10616	7.46
	Peak 3	1.53649	2.10
H_2SO_4	Peak 1	3.19725	4.69
	Peak 2	5.38491	7.90
	Peak 3	1.38291	2.03
NH_3	Peak 1	0.73975	1.01
	Peak 2	4.76798	6.61
	Peak 3	1.77335	2.46
CaO	Peak 1	0.76756	1.01
	Peak 2	4.85572	6.51
	Peak 3	1.96352	2.63

4. Conclusions

This work was focused on the monitoring of the effects of different storing environment on cement samples properties. Three environments were tested: acidic (pH 2), neutral and basic (pH 12). The positive influence of test pieces aging in aqueous media on their mechanical properties (compressive and flexural strength) was demonstrated. Slightly lower compressive strength after 28 days were observed for samples immersed in an alkaline environment. This result corresponds to a different effect of pH environment on hydration compared to acidic and neutral media. The pH value 12.4 which is essential for the formation of portlandite ($Ca(OH)_2$) is quickly achieved. The pH value of the aqueous medium is increased with time. The amount of portlandite was decreasing only for sample with changed water. This is causing by formation of stronger links of alkali ions in the cement paste through the advancing hydration reactions and processes. Significant differences in phase composition of the samples after 28 days of storing by XRD were not found. By using of thermal analysis, the highest amount of portlandite in the sample stored in alkaline solution (especially with CaO) was detected. This effect can occurs due to higher calcium concentrations in the environment. Significantly lower amounts of free water were discovered in the samples aged in an alkaline environment. Conversely, higher amount of CSH was found in these samples. This phenomenon would correspond to faster hydration reaction course in this environment.

Acknowledgements

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