

Quantitative phase analysis of modified hardened cement paste

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Abstract. The relevance of this research is stipulated by the opportunity to control the properties of construction materials through introducing nanomodifying additives. The study of structure parameters of the crystalline phase of hardened cement paste modified by microsilica and Ts38 additives is of great scientific and applied importance.

1. Introduction

Practical application of fine-grained siliceous additives is caused by their ability to provide binding agents with new properties. The articles [1-3] set out the research findings concerning the influence of siliceous additives with different specific surfaces on the hardened cement paste properties [4-6]. Moreover, the regularity of hardened cement paste strength enhancement with complex microsilica and Ts38 additives was analyzed. It was identified that the strength of hardened cement paste modified by complex additives increases by 30 % due to synergetic effect of siliceous additive agents which possess various dispersion degrees. X-ray diffraction analysis was applied to study the features of the hardened cement paste structural condition and the phase composition with additive agents. It is identified that nanodispersed additive agents influence the formation of the cement stone phase composition and structure due to additional volume of low basis hydrated calcium silicate (HCS). The separate introduction of microsilica and Ts38 additives, according to the data of the X-ray diffraction analysis, has different influence on Portlandite ($\text{Ca}(\text{OH})_2$) composition. The introduction of microsilica results in the considerable decrease of Portlandite diffraction line intensity in the test sample caused by high pozzolanic activity of microsilica, while the introduction of Ts38 leads to the increase of the line intensity. The latter can be explained by the insignificant content of the Ts38 additive. By combined introduction of both additive agents the intensity of $\text{Ca}(\text{OH})_2$ lines decreases again. The separate introduction of siliceous additives with different dispersion stimulates the formation of additional hydrated newgrowths, like $\text{C}_2\text{S}_2\text{H}$, CSH(B), $\text{C}_3\text{S}_2\text{H}_3$, $\text{C}_3\text{S}_3\text{H}_3$, but synergistic action of two siliceous additives with different dispersion leads to the increase of the content and number of newgrowths in the hardened cement paste. This explains the strength enhancement of the hardened cement paste [1].

The aim of the further research was a more profound study of structure formation characteristics of the modified hardened cement paste with different compositions using quantitative phase analysis based on the Rietveld method.



2. Materials and methods

The following materials were used to conduct this research: Portland cement of Cem I class, State Standard 31108-2003, microsilica as the byproduct of ferrosilicon treatment produced by Bratsk aluminium production plant, nano- SiO_2 (Ts38), nanodispersed silicon dioxide developed and obtained at the Institute of Theoretical and Applied Mechanics of the Russian Academy of Sciences and the Institute of Nuclear Physics of the Russian Academy of Sciences (Novosibirsk), distilled water prepared in accordance with State Standard 6709-72. The values of specific surface of the materials used in the experiment are presented in Table 1.

Table 1. Specific surface of components

Indicator	Cement	Microsilica	Ts38
Specific surface, m^2/kg	280	2000	38000

The quantitative phase analysis was performed using the modified Rietveld method subject to the power of phase crystal lattice. To carry out the quantitative phase analysis, the authors consider grinded powder particles, which size does not exceed 1-5 micrometers. DRON 4 – 07 used to perform the above mentioned analysis was modified to perform digital signal processing. To run a survey and to take pictures, the authors used copper radiation (K_α) according to the Bragg Brentano scheme with the pace of 0.020, exposure time of 1 sec. in the point and angular range of $17^\circ - 92^\circ$. The voltage on the X-ray tube was 30 kW and the beam current was equal to 25 mA. To carry out the quantitative phase analysis based on the Rietveld method, the authors used reference phases (Table 2) compiled on the basis of structural information data COD of cement materials [7]. To do this research, the authors used complete structural information of the standards which included the space group and class, lattice parameters, atom differential coordinates. Besides, the authors obtained more accurate information concerning phase lattice parameters and some profile parameters, like half-width, reflex intensity, background and etc. Sample-cubes were made of the normal concentration cement paste with the size of $20 \times 20 \times 20$ mm. These cubes were kept in some special forms at $t=20-22^\circ\text{C}$, W 90-95%, then without forms in an exsiccator above water over a period of 27 days and nights. To conduct the quantitative phase analysis, the authors used samples with the following composition: 1 – a reference specimen, 2 – the hardened cement paste with a microsilica additive, 3 – the hardened cement paste with the Ts38 additive agent, 4 – the hardened cement paste with microsilica and Ts38 additive agents. The concentration of additives relative to the cement mass was determined from the whole complex of hardened cement paste characteristics and made up 5% for microsilica and 0,03% for Ts38 [1-3].

3. Results and discussion

The results of the quantitative phase analysis of the test samples are illustrated in Tables 2 – 5 and in Figures 1-4.

The Rietveld method was used to assess the contribution of phase intensity of a particular lattice in the integral intensity through nonlinear least square of the difference method of X-rays integral and experimental intensities, depending on the variation of the phase lattice profile and structure parameters [9-11]. The X-ray diffraction pattern depicts experimental and integral intensities, their differences, as well as calculating intensities of particular phases after a full-profile more precise definition of their structure parameters. Tables 2-5 illustrate the improved values of phase lattice parameters under the investigated conditions. The intensity of residual radiation in the X-ray diffraction patterns was approximated by the twentieth degree of polynomial. The quantitative phase analysis demonstrates a satisfactory degree of convergence of calculating integral intensities relative to experimental ones. The degree of convergence criteria is identified as being equal to $R_{wp}=9.38, 8.6, 9.69$ and 8.26 %. Figures 1-5 show experimental, integral intensities of some particular phases after a full-profile more accurate definition of their structure parameters. There is a weak reflection

overlapping and contributions of the fraction of amorphous phase components in the presented X-ray diffraction patterns. It should be also mentioned that the bases of some reflexes are extended. There are considerable differences in X-ray diffraction patterns of the hardened cement paste check sample and its modified sample. Nano and microsilica additive agents have influence on the hardened cement paste phase formation and vary its lattice structural condition, volume, phase energy while hardening.

The results of the quantitative phase analysis of the hardened cement paste presented in Table 2 shows that the reference sample consists of the following phases: $\text{Ca}_5\text{Si}_6(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, $\text{Ca}_3(\text{SiO}_3\text{OH})_2 \cdot 2\text{H}_2\text{O}$, $\text{Ca}_6\text{Si}_3\text{O}_{11}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, $\text{Ca}_5(\text{SiO}_4)_2(\text{OH})_2$, $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$, $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{OH})_4$, $\text{Ca}_7(\text{SiO}_5)_4$. The total integral phase intensity is more than 98.391 %, where $\text{Ca}_5\text{Si}_6(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, $\text{Ca}_3(\text{SiO}_3\text{OH})_2 \cdot 2\text{H}_2\text{O}$, $\text{Ca}_6\text{Si}_3\text{O}_{11}(\text{OH})_2$ play the key role. The convergence criterion is as follows: $R_{\text{wp}}=9.38$.

Thus, the introduction of microsilica resulted in considerable redistribution of phase fractions (Table 3): $\text{Ca}_5\text{Si}_6(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ - from 27.607% to 35.953%; $\text{Ca}_3(\text{SiO}_3\text{OH})_2 \cdot 2\text{H}_2\text{O}$ - from 19.661% to 4.052%; $\text{Ca}_6\text{Si}_3\text{O}_{11}(\text{OH})_2$ - from 14.680% to 15.947%; $\text{Ca}(\text{OH})_2$ - from 13.196% to 9.705%; $\text{Ca}_5(\text{SiO}_4)_2(\text{OH})_2$ - from 10.282% to 16.122%; $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ - from 6.531% to $1.39 \cdot 10^{-5}\%$; $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{OH})_4$ - from 5.297% to $4.09 \cdot 10^{-4}\%$; $\text{Ca}_7(\text{SiO}_5)_4$ - from 1.137% to 16.400%, relative to the test sample. The total intensity of the above mentioned phases constitutes 98,744%, the convergence criterion and is equal to $R_{\text{wp}}= 8.6$ %. There is a considerable change in the lattice volume of some certain phases: Tobermorite - from $774,637 \text{ \AA}^3$ to 750.986 \AA^3 ; Deliate - from 598.348 \AA^3 to 596.017 \AA^3 ; Reinhardbraunsite - from 467.772 \AA^3 to 454.638 \AA^3 ; Reinhardbraunsite - from 496.430 \AA^3 to 459.83 \AA^3 .

Ts38 influence was taken into account in works [1-3, 8, 12, 13].

Compared to the test sample, the introduction of Ts38 additive also leads to considerable redistribution of phase fractions (Table 4): $\text{Ca}_5\text{Si}_6(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ - from 27.607% to 27.049%; $\text{Ca}_3(\text{SiO}_3\text{OH})_2 \cdot 2\text{H}_2\text{O}$ - from 19.661% to 54.402%; $\text{Ca}_6\text{Si}_3\text{O}_{11}(\text{OH})_2$ - from 14.680% to $1.37 \cdot 10^{-6}\%$; $\text{Ca}(\text{OH})_2$ - from 13.196% to 16.09%; $\text{Ca}_5(\text{SiO}_4)_2(\text{OH})_2$ - from 10.282% to 0.235%; $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ - from 6.531% to $3.16 \cdot 10^{-5}\%$; $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{OH})_4$ - from 5.297% to 0.0018%; $\text{Ca}_7(\text{SiO}_5)_4$ - from 1.137% to $5.16 \cdot 10^{-6}\%$. The total intensity of the above mentioned phases constitutes 98,774%, the convergence criterion is equal to $R_{\text{wp}}= 9.69$ %. There is a considerable variation in the lattice volume of some certain phases: Tobermorite - from $774,637 \text{ \AA}^3$ to 743.925 \AA^3 ; Afwillite - from 871.256 \AA^3 to 941.720 \AA^3 ; Deliate - from 598.348 \AA^3 to 571.199 \AA^3 ; Reinhardbraunsite - from 467.772 \AA^3 to 583.013 \AA^3 ; Katoit - from 1986.353 \AA^3 to 1883.927 \AA^3 ; Reinhardbraunsite - from 496.430 \AA^3 to 460.243 \AA^3 .

Compared to the test sample, the introduction of complex additives resulted in redistribution, reduction and disappearance of the phase fraction in the modified hardened cement paste (Table 5): $\text{Ca}_5\text{Si}_6(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ - from 27.607% to 25.51%; $\text{Ca}_3(\text{SiO}_3\text{OH})_2 \cdot 2\text{H}_2\text{O}$ - from 19.661% to 23.24%; $\text{Ca}_6\text{Si}_3\text{O}_{11}(\text{OH})_2$ - from 14.680% to 0%; $\text{Ca}(\text{OH})_2$ - from 13.196% to 6.68%; $\text{Ca}_5(\text{SiO}_4)_2(\text{OH})_2$ - from 10.282% to 0.004%; $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ - from 6.531% to 0.01%; $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{OH})_4$ - from 5.297% to 8.55%; $\text{Ca}_7(\text{SiO}_5)_4$ - from 1.137% to 36.76%. There is a considerable variation in the lattice volume of some certain phases: Tobermorite - from $774,637$ to 754.012 ; Afwillite - from 871.256 \AA^3 to 808.729 \AA^3 ; Deliate - from 598.348 \AA^3 to 570.358 \AA^3 ; Portlandite - from 54.951 \AA^3 to 55.102 \AA^3 ; Reinhardbraunsite - from 467.772 to 529.141 ; Hydrogarnet - from 1986.353 \AA^3 to 2255.46 \AA^3 ; Reinhardbraunsite - from 496.430 \AA^3 to 455.448 \AA^3 . The total intensity of the above mentioned phases constitutes 98,74%, the convergence criterion is equal to $R_{\text{wp}}= 8.26$ %.

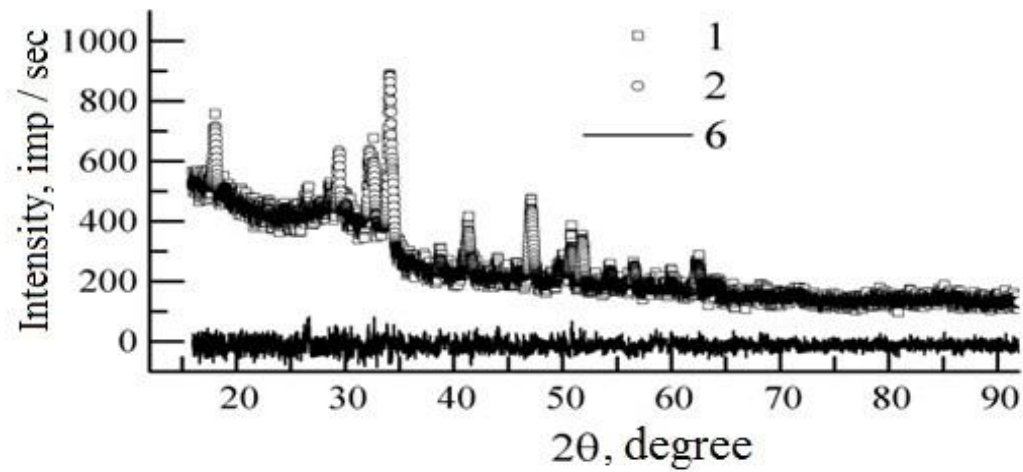


Figure 1. Quantitative phase analysis of the reference composition: 1 – experimental diffraction pattern, 2 – theoretical diffraction pattern; $R_{wp}= 11.237\%$.

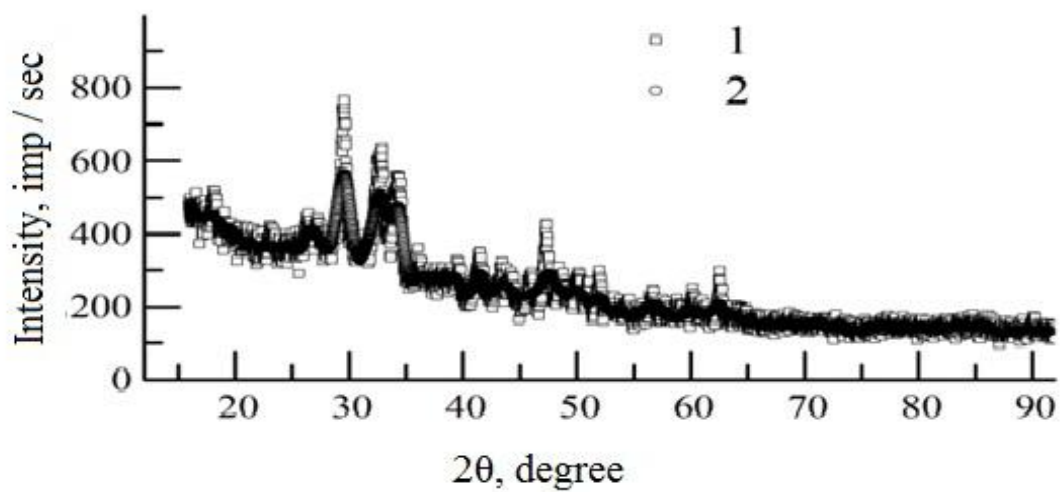


Figure 2. Quantitative phase analysis of hardened cement paste with microsilica additive agent: 1 – experimental diffraction pattern; 2 – theoretical diffraction pattern; $R_{wp}= 9.329\%$.

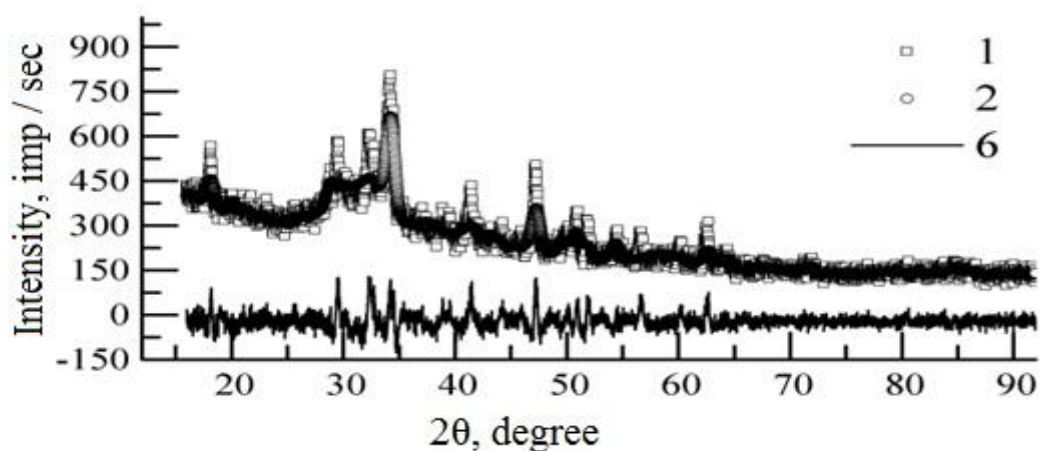


Figure 3. Quantitative phase analysis of hardened cement paste with Ts38 additive agent: 1 – experimental diffraction pattern; 2 – theoretical diffraction pattern, $R_{wp}=9.69\%$.

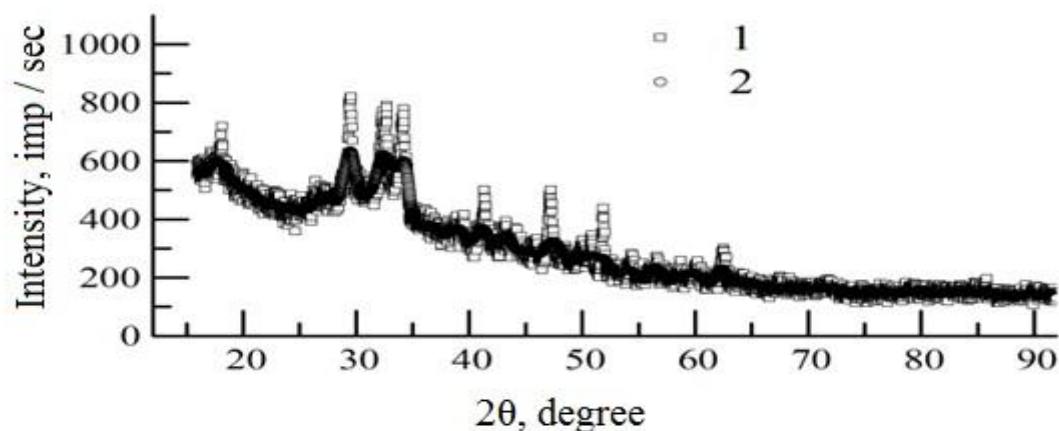


Figure 4. Quantitative phase analysis of hardened cement paste with microsilica and Ts38 additive agents: 1 – experimental diffraction pattern; 2 – theoretical diffraction pattern, $R_{wp}=8.765\%$.

Table 2. Phase composition of hardened cement paste without additives

N	Number of the card	Chemical formula	Chemical name	Number of atoms	Crystal system and class	Percentage, %
1	96-900-2246	$\text{Ca}_5\text{Si}_6(\text{OH})_2 \cdot 4\text{H}_2\text{O}$	Tobermorite	30	P1, Triclinic	27.607
2	96-901-3985	$\text{Ca}_3(\text{SiO}_3\text{OH})_2 \cdot 2\text{H}_2\text{O}$	Afwillite	84	P1, Triclinic	19.661
3	96-900-9534	$\text{Ca}_6\text{Si}_3\text{O}_{11}(\text{OH})_2$	Deliate	44	P1, Triclinic	14.680

4	96-100-1769	Ca(OH) ₂	Portlandite	12	P-3m1, trigonal	13.196
5	96-152-9965	Ca ₅ (SiO ₄) ₂ (OH) ₂	Reinhardbraunsite	40	2/m, monoclinic	10.282
6	96-900-1777	Ca ₃ Al ₂ (OH) ₁₂	Katoit	263	m-3m, Cubic	6.531
7	96-900-5159	Ca ₃ Al ₂ (SiO ₄) ₂ (OH) ₄ *	Hydrogarnet	203	m-3m, Cubic	5.297
8	96-901-1877	Ca ₇ (SiO ₅) ₄	Reinhardbraunsite*	40	2/m, monoclinic	1.137
Total intensity of initial concrete is 98.391						

Table 3. Phase composition of hardened cement paste with microsilica additive

Chemical formula	Composition	Lattice parameters							Percent age, %
		a, Å	b, Å	c, Å	α, deg.	β, deg.	γ, deg.	V, Å ³	
Ca ₅ Si ₆ (OH) ₂ * 4H ₂ O	Reference	11.124	7.3281	9.5885	97.6	89.31	89.40	774.63	27.607
	Test	10.827	7.2991	9.5855	97.3	89.85	88.27	750.98	35.953
Ca ₃ (SiO ₃ OH) ₂ *2H ₂ O	Reference	16.347	5.8012	11.269	95.4	124.8	124.8	871.25	19.661
	Test	16.347	5.8151	11.271	93.6	124.9	83.20	872.18	4.052
Ca ₆ Si ₃ O ₁₁ * (OH) ₂	Reference	6.8516	6.9622	12.900	89.9	98.15	100.7	598.34	14.680
	Test	6.8620	6.9602	12.896	89.9	98.97	101.4	596.01	15.947
Ca(OH) ₂	Reference	3.595	3.5955	4.9080	90.0	90.00	120.0	54.951	13.196
	Test	3.5990	3.5990	4.8742	90.0	90.00	120.0	54.676	9.705
Ca ₅ (SiO ₄) ₂ * (OH) ₂	Reference	11.410	4.9129	8.9167	90.0	110.6	90.00	467.77	10.282
	Test	10.943	5.1124	8.7393	90.0	110.6	90.00	454.63	16.122
Ca ₃ Al ₂ (OH) ₁₂	Reference	12.418	12.418	12.418	90.0	111.5	90.00	1914.9	6.531
	Test	12.418	12.418	12.418	90.0	90.00	90.00	1914.9	1.39* 10 ⁻⁵
Ca ₃ Al ₂ (SiO ₄) ₂ * (OH) ₄	Reference	12.570	12.570	12.570	90.0	90.00	90.00	1986.3	5.297
	Test	12.570	12.570	12.570	90.0	90.00	90.00	1986.35 8	4.09* 10 ⁻⁴
Ca ₇ (SiO ₅) ₄	Reference	8.9148	11.453	5.0721	90.0	90.00	106.5	496.43	1.137
	Test	9.4370	11.724	4.2851	90.0	90.00	104.0	459.83	16.400
Total intensity with silica additive is equal to 98.744									

Table 4. Phase composition of hardened cement paste with Ts38 additive agent

Chemical formula	Composition	Lattice parameters							Percent age, %
		a, Å	b, Å	c, Å	α, deg.	β, deg.	γ, deg.	V, Å ³	
Ca ₅ Si ₆ (OH) ₂ * 4H ₂ O	Reference	11.124	7.328	9.588	97.64	89.31	89.40	774.637	27.607
	Test	10.901	7.152	9.635	97.82	88.12	90.46	743.925	27.049
Ca ₃ (SiO ₃ OH) ₂ * 2H ₂ O	Reference	16.347	5.801	11.269	95.40	124.85	83.88	871.256	19.661
	Test	16.419	6.342	11.468	101.56	125.02	74.74	941.720	54.402
Ca ₆ Si ₃ O ₁₁ (OH) ₂	Reference	6.851	6.962	12.900	89.97	98.15	100.7	598.348	14.680
	Test	6.756	7.233	12.977	86.32	105.44	110.70	571.199	1.37 10 ⁻⁶
Ca(OH) ₂	Reference	3.595	3.595	4.908	90.00	90.00	120.00	54.951	13.196

Ca ₅ (SiO ₄) ₂ (OH) ₂	Test	3.5940	3.594	4.8951	90.00	90.00	90.00	54.759	16.09
	Reference	11.410	4.912	8.9167	90.00	110.63	90.00	467.772	10.282
	Test	11.910	5.269	9.3321	90.00	84.56	90.00	583.013	0.235
Ca ₃ Al ₂ (OH) ₁₂	Reference	12.418	12.418	12.418	90.00	111.58	90.00	1914.983	6.531
	Test	12.242	12.242	12.242	90.00	90.00	90.00	1834.981	3.16 10 ⁻⁵
Ca ₃ Al ₂ (SiO ₄)* (OH) ₄	Reference	12.570	12.570	12.570	90.00	90.00	90.00	1986.353	5.297
	Test	12.350	12.350	12.350	90.00	90.00	90.00	1883.927	0.0018
Ca ₇ (SiO ₅) ₄	Reference	8.9148	11.453	5.072	90.00	90.00	106.55	496.430	1.137
	Test	8.8018	11.32	4.800	90.00	90.00	105.87	460.243	5.16 10 ⁻⁶
Total intensity with silica and Ts38 additives is equal to 97.774									

Table 5. Phase composition of hardened cement paste with complex additive

Chemical formula	Composition	Lattice parameters						V, A ³	Percent age, %
		a, A	b, A	c, A	α, deg.	β, deg.	γ, deg.		
Ca ₅ Si ₆ (OH) ₂ * 4H ₂ O	Reference	11.124	7.3281	9.5885	97.64	89.31	89.40	774.637	27.607
	Test	10.856	7.2908	9.6095	97.27	90.18	88.02	754.012	25.51
Ca ₃ (SiO ₃ OH) ₂ * 2H ₂ O	Reference	16.347	5.8012	11.269	95.40	124.8	83.88	871.256	19.661
	Test	16.423	5.6424	10.810	100.1	124.41	79.189	808.729	23.24
Ca ₆ Si ₃ O ₁₁ (OH) ₂	Reference	6.8516	6.9622	12.900	89.97	98.15	100.70	598.348	14.680
	Test	6.8678	7.0306	12.920	93.17	106.19	105.87	570.358	~ 0
Ca(OH) ₂	Reference	3.595	3.5955	4.9080	90.00	90.00	120.00	54.951	13.196
	Test	3.6062	3.60626	4.8924	90.00	90.00	120.00	55.102	6.68
Ca ₅ (SiO ₄) ₂ * (OH) ₂	Reference	11.410	4.9129	8.9167	90.00	110.63	90.00	467.772	10.282
	Test	10.690	5.80165	9.1390	90.00	111.01	90.00	529.141	0.004
Ca ₃ Al ₂ (OH) ₁₂	Reference	12.418	12.4180	12.418	90.00	111.58	90.00	1914.983	6.531
	Test	12.418	12.4181	12.418	90.00	90.00	90.00	1914.985	0.01
Ca ₃ Al ₂ (SiO ₄)* (OH) ₄	Reference	12.570	12.5704	12.570	90.00	90.00	90.00	1986.353	5.297
	Test	13.114	13.1143	13.114	90.00	90.00	90.00	2255.461	8.55
Ca ₇ (SiO ₅) ₄	Reference	8.914	11.4537	5.072	90.00	90.00	106.55	496.430	1.137
	Test	9.356	10.8893	4.689	90.00	90.00	72.402	455.448	34.76
Total intensity with silica and Ts38 additives is 98.74									

3. Conclusion

The analysis of the research findings of the quantitative phase analysis demonstrates that the introduction of siliceous additives in the cement mix compared with the reference samples leads to reduction, redistribution and disappearance of the phase fraction content in the hardened cement paste.

The introduction of microsilica additives facilitates Portlandite fixation at the stage of final strength formation, leads to the reduction of Afwillite, Katoit, Hydrogarnet phase fraction and the increase of Tobermorite, Deliate, Reinhardbraunsite, Reinhardbraunsite* phase fraction. The fact of extra volume of low basic hydrated calcium silicate in the hardened cement paste results in improving physical-mechanical characteristics.

The introduction of Ts38 leads to the reduction of Tobermorite, Deliate, Reinhardbraunsite, Reinhardbraunsite*, Hydrogarnet, Katoit phases fraction and the increase of Portlandite, Afwillite phase content which explains some hardened cement paste strength retrogression by the introduction of nano SiO₂ without any intermediate constituent on micro silica.

The use of a complex additive agent for hardened cement paste modification ensures the fixation of Deliate, Reinhardbraunsite, Katoit phases and results in the considerable reduction of Portlandite phase fraction and the increase of Afwillite, Hydrogarnet, Reinhardbraunsite* phases fraction. The above-mentioned fact explains the strength enhancement of the samples proceeding from synergetic effect caused by the introduction of complex additive.

Thus, it was established that nano- and microsilica additives have a profound effect on the qualitative and quantitative composition of crystalline phases which largely determine the construction and technical characteristics of the hardened cement paste.

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