Actual Challenges in Materials Science and Processing Technologies II

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Preface

This volume contains peer-reviewed papers prepared as the event of the National Contact Point "Secure, Clean and Efficient Energy" (9-11 November 2020, Dnipro, Ukraine) under the support of the Ministry of Education and Science of Ukraine. Funding was carried out as part of the project "Belt and Road Initiative Institute for Chinese-European studies (BRIICES)" and was funded by the Guangdong University of Petrochemical Technology.

Selected papers cover a wide range of topics regarding solving actual challenges in theoretical and practical research in applied materials science in the context of synthesis, analysis of properties, the technology of materials processing, and their use. A number of effective processes have also been developed for the fabrication of carbonaceous materials.

The book will be interesting and useful for specialists and researchers from various branches of engineering and essential reading for those in the related areas and will inspire future studies and achievement.

A significant issue of this collection is the geography of presented works. The authors who had submitted the research papers for consideration were from China, India, Indonesia, Iraq, Jordan, Kyrgyzstan, Malaysia, Nigeria, Peru, Poland, Russia, South Africa, and Ukraine. More than half of the presented research results obtained by authors in international cooperation and are successful.

Editors acknowledge the contribution of the organization staff, members of program committees, authors, and expert referees who spared their valuable time. Special gratitude to the reviewers for their valuable recommendations has been taken into account to improve the selected papers' quality significantly.

We would like to express the warmest thanks to participants and sponsors for their support. Finally, we express our special heartfelt thanks and gratitude to the Trans Tech Publication team with a dedicated editorial team and rigorous but fair and friendly service.

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Technology of Production of Binder Modifying Nanoadditives

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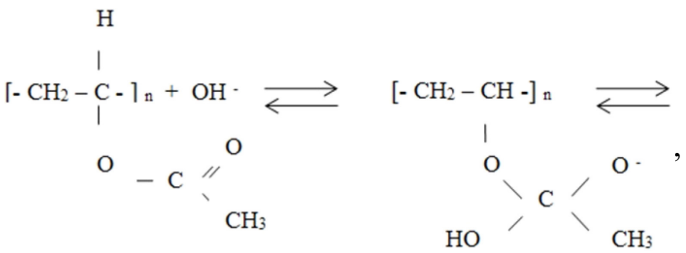
Abstract. The article deals with the issue concerning production of a dry nanoadditive. In order to achieve this goal, an aqueous solution of polyvinyl acetate dispersion (PVAD) and nanotubes, or lime slaking nanoparticles is used. As a result of the hydration process heat is released, the polyvinyl acetate emulsion forms particles with nanotubes in their composition. During the study performed an optimal ratio of all components was established: quicklime + PVAD-CNT – 71-73% and 0.01-0.018 CNT; "Megalith" – 21-25%; ammonium salt – 4-6%, as well as the optimal amount of the complex additive, which is in the range of 1-1.5% by weight of calcium sulfate hemihydrate. Later on the resulting nanoadditive can be used to modify binders or other materials

Introduction

Problem Statement. Development of dry nanoadditives is important for modification of binders, dry mortars and concretes [1-6]. The process of introducing nanosystems (nanoparticles, nanotubes) into the composition of binders is very complex due to their small amounts (from hundredths to thousandths parts of percent), as well as due to their nanometric dimensions [5-15]. The developed method of nanoadditive dispergation requires three-stage mixing in the liquid state. It is used in production as a second component in the form of water dispersion for modification of binders and this complicates the technological process, and in some cases makes it impossible. The authors propose a hypothesis of dry nanoadditive production. The essence of this hypothesis consists in using an aqueous solution of polyvinyl acetate dispersion (PVAD) and nanotubes for lime slaking. As a result of heat release, the polyvinyl acetate emulsion forms particles that contain nanotubes. Later on this nanoadditive can be used to modify binders or other materials.

Theoretical Substantiation. Chemistry of interaction of complex additive components (PVAD-lime) can be presented as follows [16]:



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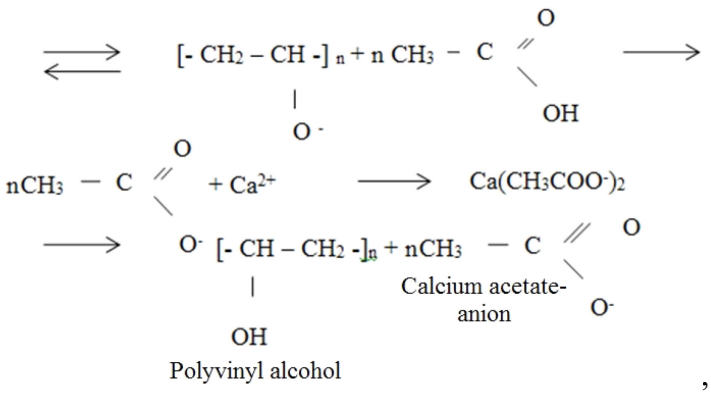

, (2)

The structural peculiarity of polyvinyl alcohol molecules consists in presence of hydrophilic groups – OH related to ionic and polar structures. The hydrocarbon radical is nonpolar and is a hydrophobic component of molecules. Thus, the hydrophilic part of the polyvinyl alcohol molecule is ionic and is adsorbed on the surface of gypsum binder particles, forming a monomolecular film with its hydrophobic part oriented from the gypsum particles. In the result of hydrolysis reactions calcium acetate is formed; it provides an increased concentration of calcium ions in the solution, which leads to a slower formation of crystallization centers ($CaSO_4 \cdot 2H_2O$) resulting in a slower gypsum binder solidification [16].

Research Results

First, the matter concerning influence caused by polyvinyl acetate dispersion and quicklime on the calcium sulfate hemihydrate hydration processes, formation of a dry additive based on these processes and production technology development for the developed additive was considered.

As a result of the studies performed it was determined that introduction of polyvinyl acetate dispersion (from 0.5 to 1%) increases the solidification period of calcium sulfate hemihydrate (Fig. 1), at 0.5%, there is a slight decrease in the water-gypsum ratio. PVAD contents of over 0.8% lead to an increase in the water-gypsum ratio and reduce the strength by 5-8%. With the content of polyvinyl acetate dispersion up to 1% the period of gypsum solidification is increased (Fig. 1). The period of setting initiation (start of hardening) is insufficient for using it in the sphere of production.

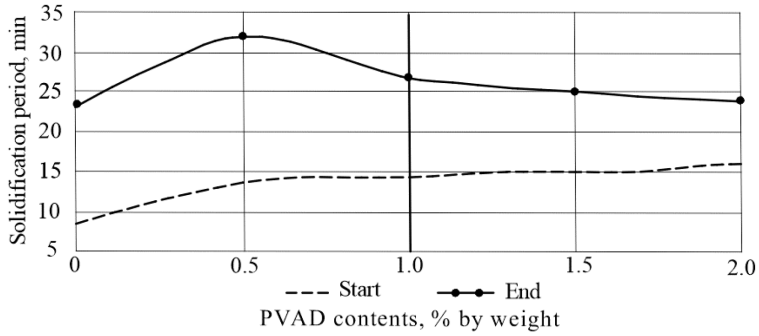

Fig. 1. The curve of influence caused by PWAD on the gypsum plaster solidification period

Studies of heat release during hydration of gypsum with PVAD added (0.5%) showed that the temperature peak (41°C) is reached in 33 minutes after addition of water, or 7-10 minutes after the end of solidification (Fig. 2). Introduction of PVAD in the amount of 0.8% of the gypsum mass increases the interval of reaching temperature peak to 45 minutes after mixing with water.

Redispersed polymer powder was developed using the method of dispergation of polyvinyl acetate dispersion and mixing with a highly exothermic agent – air-hardening lime. Due to the heat released during the process of lime slaking with an aqueous solution of PVAD concentrated from 0

to 3%, redispersed polymer powders (RPP) were obtained. Studies of influence caused by RPP showed a highly effective impact on the solidification period (Fig. 3).

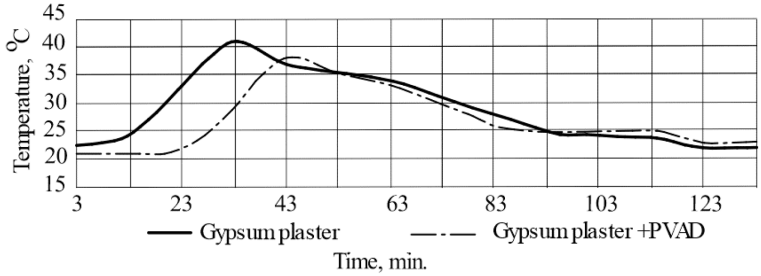

Fig. 2. Curve of temperature changes during hydration of calcium sulfate hemihydrate and gypsum with PVAD added.

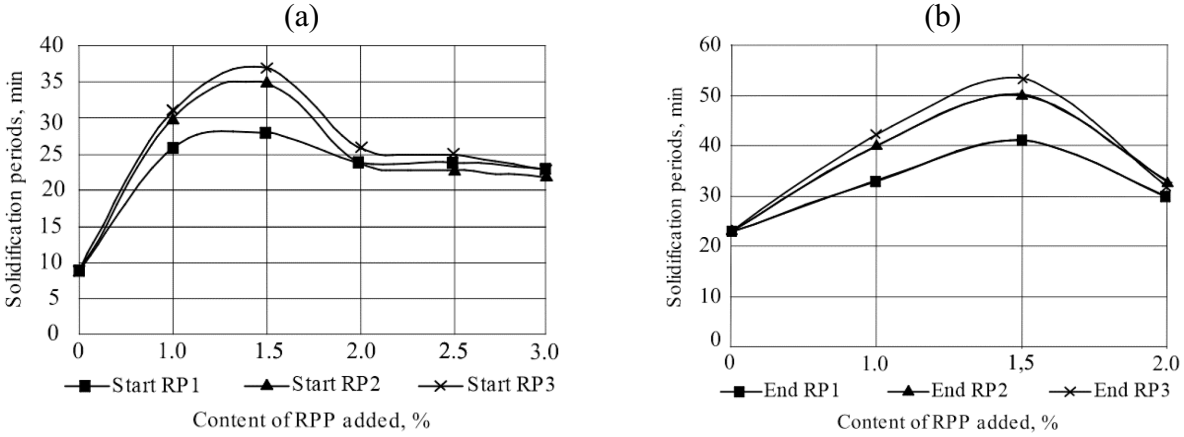

Fig. 3. Curves of influence caused by PVAD on the solidification period of calcium sulfate hemihydrate: (a) start of solidification; (b) end of solidification

Addition of PVAD with a content of 1-1.5% (by weight) gives an opportunity to increase the time of solidification start to 30-35 min, and in case of PVAD content of 3.5 and 41% the time is increased up to 1-1.5 hours. At the same time, there is also an increase of strength both at compression, and at bending.

Components of the developed RPP Calcium hydroxide, polyvinyl alcohol, salts of calcium acetate can be observed on the X-ray pattern (Fig. 4).

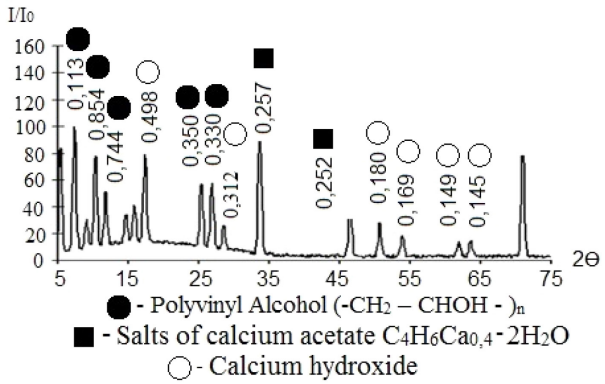

Fig. 4. X-ray diffraction pattern of the RPP additive

Microstructure of the additive (Fig. 5) represented as round-shaped crystals. Analysis of thermodynamic curves shows a significant difference between heat release during hydration of gypsum plaster with RPP additives and heat release in case with calcium sulfate hemihydrate (Fig. 6). The temperature peak of the thermodynamic process of gypsum plaster hydration with RPP

additives is 40-38°C, which is 3-5°C lower. The period of temperature rise corresponds to the difference in time between the start and end of solidification.

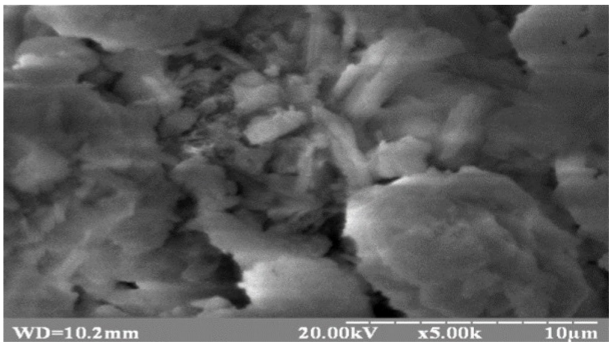

Fig. 5. Photomicrograph of the RPP powder

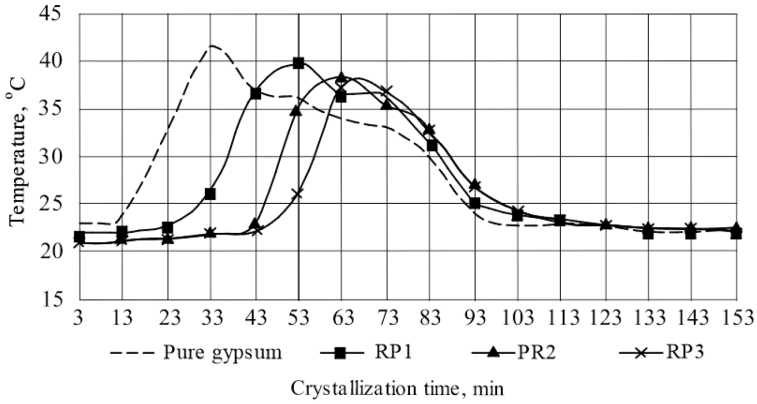

Fig. 6. Curves of temperature change during process of calcium sulfate hemihydrate hydration in the presence of additives

The beginning of temperature reduction is 1.0-1.2 hours, and corresponds to the end of the binder hydration processes. This corresponds to the presented mechanism of hydration in the presence of the obtained additive. The RPP additive should be quick-soluble within 0.5-1.5 minutes. In order to achieve the desired efficiency during development of RPP ammonium salts were used; these salts significantly increase the dissolution rate of the additive.

The additive production technology was developed (Fig. 7). Quicklime is ground to a fraction of 1-2 mm, dozed into the mixer-hydrator, and ammonium salts are fed in the amount of 1-6% of the additive (by weight); and all components are mixed until a homogeneous mixture. Then a water-dispersed polyvinyl acetate emulsion with a density of 1.06-1.18 g/cm is added by jet. Content required for lime hydration and obtaining a dry powder is determined from a given concentration of PVAD in the additive.

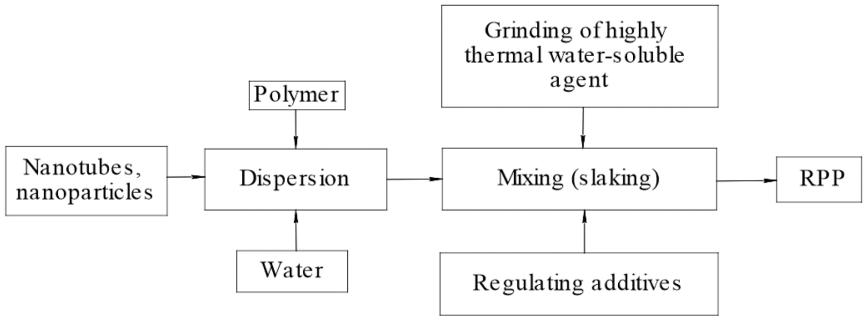

Fig. 7. Technological scheme of dry RPP RPP+CNT additive production

The theoretical and experimental studies performed gave an opportunity to obtain RPP+CNT in the dry state for regulating gypsum solidification time within the range of 45-70 minutes or more.

The advantage of this class of additives consists in an efficient method of their production, which eliminates the drying process and so reduces energy consumption. By means of using these additives in an amount of 1-1.5% of the binder (by weight), you can adjust physical and mechanical properties of dry mixtures.

When researching structure, rheological and mechanical properties, shortcomings reducing the quality of the gypsum mixture structure were determined: water separation, increase of the water-gypsum ratio resulting in a decrease in strength. In order to eliminate these shortcomings, a study was conducted on modification of additives using the simplex-lattice method of planning the experiment. The essence of this method consists in changing factors of influence by introduction of ammonium salts, superplasticizers “Megalit”, “Sika” etc. So, ammonium salts in the additive (Fig. 8) affect the crystal shapes of the additive components: a needle shape is formed providing increase the specific surface area, which leads to an increased solubility of the additive.

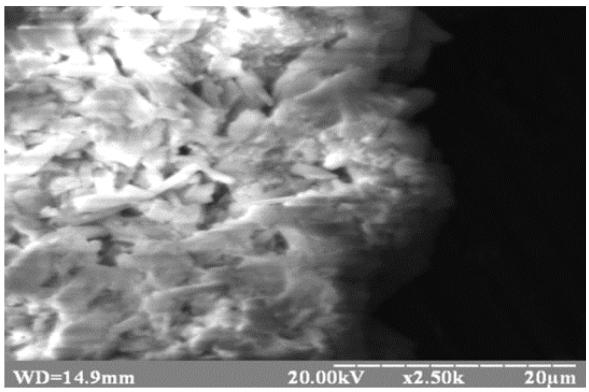

Fig. 8. Photomicrograph of the modified additive powder

The optimal amount (1.0-1.5% calcium sulfate hemihydrate by weight) was determined for increasing gypsum solidification period.

In order to determine optimal compositions of a complex additive modification based on quicklime and PVAD-CNT, a step-by-step method of experiment planning and PFE-2n is used. In order to increase the dissolution rate of dispersion additives ammonium salts were added in the amount of 1-6% of the additive (by weight) (or 0.01-0.09% of the binder weight). Results of the PFE 22 planning method (Tables 1-3) are presented in Fig. 8. The following variables were accepted in the matrix of the PFE-22 full-factor experiment: X_1 – content of PPP2, %; X_2 – content of NH4CI, %. Results of processing experimental studies conducted according to the experiment plan are presented in Fig. 9.

Table 1. Interval of component changes

Variation levels	X_1	X_2
Upper level	1	0.01
Zero level	1.25	0.05
Lower level	1.5	0.09

Table 2. Planning matrix

Experiment No	X_1	X_2	X_1 CONTENT RPP2, % + 0.01% CNT	X_2 content NH_4CI, %	Solidification periods, min		R_{compr}, MPa
					start	end	
1	+1	-1	1.5	0.01	45	66	6.64
2	-1	+1	1	0.09	47	56	6.12
3	-1	-1	1	0.01	38	47	6.48
4	+1	+1	1.5	0.09	54	72	6.52

Table 3. Experiment plan

No	Plan*			Composition in % by weight			W/G	Solidification periods, min		R_{compr}, MPa
	X_1	X_2	X_3	Additive, (PVAD+ NH_4CI) %	Plasticizer, %	Gypsum %		Start	End	
1	1	0	0	1.5	0.5	98	0.48	75	101	7.36
2	0.5	0.5	0	0.75	1.25	98	0.46	60	81	7.4
3	0	1	0	0	2	98	0.45	39	58	6.5
4	0	0.5	0.5	0	1.25	98.75	0.47	33	55	6.1
5	0	0	1	0	0.5	99.5	0.48	25	55	6.2
6	0.5	0	0.5	0.75	0.5	98.75	0.48	40	72	7.25
7	0.334	0.333	0.333	0.5	1	98.5	0.46	45	75	7.1

*Note: X1 – additive; X2 – plasticizer; X3 – gypsum

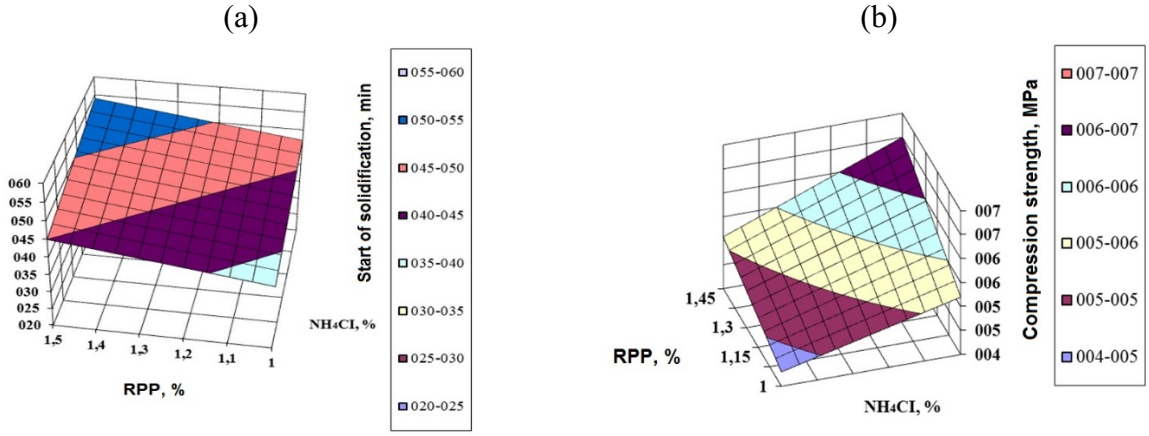

Fig. 9. Results of processing experimental studies: (a) – periods of gypsum mixture solidification (start); (b) – compression strength

Comparative analysis of the curves describing solidification start and end shows that increase of RPP2 additive (in amount of 1.25-1.5%) and NH_4CI (in amount of 0.074-0.09%) in the mixture leads to a later end of solidification – 65-70 minutes.

When studying the influence of RPP2 additives with CNTs and NH_4CI on strength characteristics it is found that the maximum strength is typical for compositions with NH_4CI content of 0.074-0.09% and RPP2 content of 1.46-1.5% with CNTs of 0.001%. Further increases of NH_4CI content in compositions with equal content of RPP2 result in increased strength.

The reason for improved physical and technical properties of gypsum with the introduction of ammonium salt to the additive is presented as changes in crystal shapes and crystal structure of the additive components (Fig. 7, 10). Crystals of forming compounds have less rounded, elongated form resulting in an increased dispersion of the additive and denser packaging.

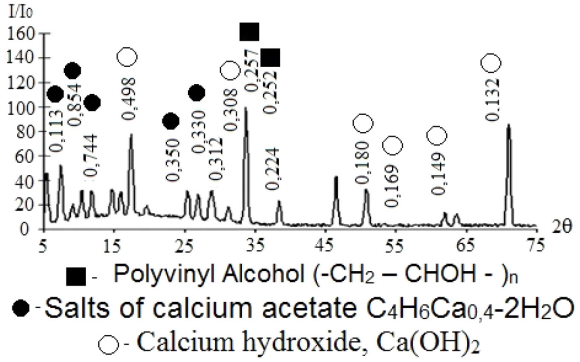

Fig. 10. X-ray diffraction pattern of the modified additive

Calculation of properties by regression equations was performed on a PC by means of "SIBES" program (USUCT – the Ukrainian State University of Chemical Technology). Results of studies performed are presented in Fig. 11.

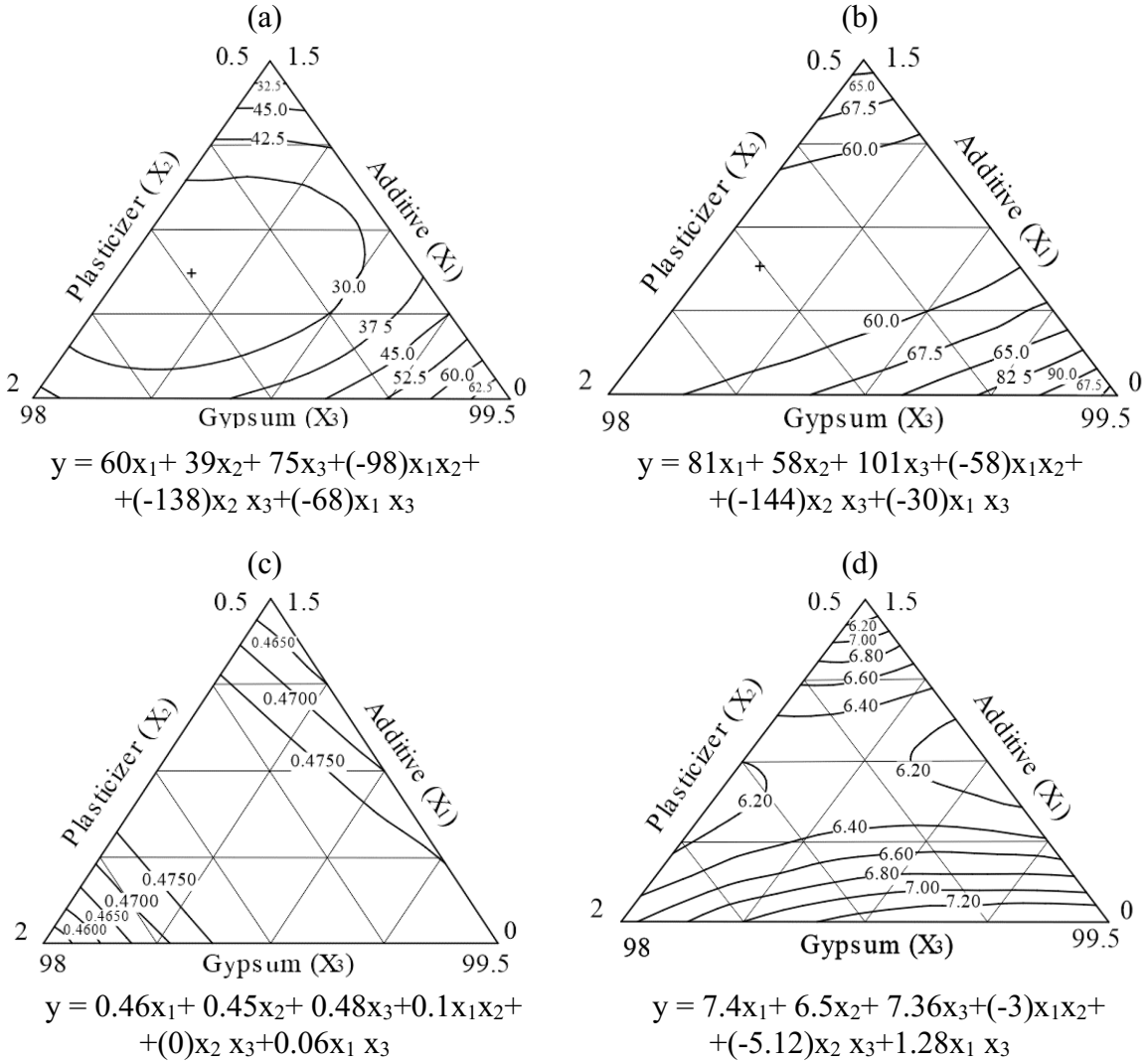

Fig. 11. Characteristics of gypsum mixtures: (a) – start of solidification; (b) – end of solidification; (c) – water-gypsum ratio; (d) – compression strength

Analysis shows that typical areas of change in water-gypsum ratio (W/G ratio) are located perpendicular to the axis of the main component – gypsum binder and mainly depend on the content of "Megalith" and addition of RPP2CNT. Thus, increase of the RPP2 additive (0.75-1.5% by weight) leads to an increased W/G ratio B/G (up to 0.48).

Influence caused by "Megalit" plasticizer is also ambiguous, the highest plasticizing ability is observed at introduction of "Megalit" in the amount of 0.5-2% (by weight). Thus, it can be assumed that the optimal content of components ("Megalit" and additives) is 1-1.5% by weight.

Conclusions

The results of studies obtained during RPP modification by means of NH_4CI electrolyte and "Megalit" surfactant are qualitatively different depending on concentrations of these substances. Introduction of an optimal amount of electrolyte and superplasticizer to the mixture of RPP and gypsum binder significantly reduces the dissolution rate of the binder. This can be explained by the fact that on the one hand introduction of ammonium salts accelerates the process of calcium hydroxide dissolution in the redispersed powder resulting in increased concentration of calcium ions

in solution as well as in slower formation of crystallization centers $SSO_4 \cdot 2H_2O$. On the other hand, due to the exchange reaction between the electrolyte and the binder a loose and porous calcium chloride film can be formed.

Under these conditions the superplasticizer obstructs the processes of film formation by means of reducing metabolic reaction intensity. In addition to that, the plasticizer increases diffusion resistance and reduces permeability of the film if it is formed (by means of closing pores). Studies conducted according to the full-factor plan established an optimum ratio of all components: Quicklime +PVAD-CNT – 71-73%; "Megalith" – 21-25%; ammonium salt 46%, as well as the optimal amount of the complex additive, which is in the range of 1-1.5% by weight of calcium sulfate hemihydrate.

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