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PROPERTIES OF MODIFIED PHOSPHOGYPSUM BINDER

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Abstract

Phosphogypsum (PG) is common by-product of chemical fertilizers plants. However, it has limited use in local construction industry. At the same time the deposits of natural gypsum will depleted in several decades and alternative waste by-product gypsum will be required. The main disadvantage of phosphogypsum binder is the need in neutralization of harmful admixtures, aggregation of PG particles during grinding and high water demand. Therefore, there is need in modifying admixtures to facilitate the manufacturing process and achieve sufficient performance characteristics of binder. The paper reports on an investigation of the influence of composite modifying admixture, consisted of slacked lime and superplastisizer, on water-binder ratio, strength properties and peculiarities of structure forming of the binder. Compressive strength of specimens made of modified binders varied from 20 to 24 MPa and bending strength varied from 10 to 12 MPa at the age of 28 days. Per scanning electron microscope (SEM) data, the morphology of $CaSO_4 \cdot 2H_2O$ was not related to the type and portion of admixtures. However, at the application of optimal values of superplasticizer and slaked lime denser disposition of crystals is observed.

Keywords:

Gypsum, phoshogypsum, superplasticizer polycarboxylate, lime, composite admixture.

1 INTRODUCTION

β-hemihydrate calcium sulfate binder is one of the most environmentally friendly binders [Karni 1995]. The main disadvantages, eliminating its application area, are low water resistance and high water consumption leading to low mechanical properties. At the same time, there is limited deposits of natural gypsum whereas by-products of chemical plants are common alternative resource for manufacturing of gypsum binders [Tayibi 2009]. Due to the high content of calcium sulphate (in the range of 80…98%) [Lushnikova 2016] they can substitute natural gypsum in construction products.

Among different types of synthetic gypsum phosphogypsum (PG) [Dvorkin 2008], fluorgypsum [Khatib 2013], borogypsum are most common [Erdogan 1992]. Apart of calcium sulphate, synthetic gypsum may contain silica, acids and other components depending on the kind of chemicals and type of reactions occurred. One of the peculiarities of synthetic gypsum application is need in either

removing or neutralizing impurities. At present energy-consuming methods for preparation of PG to calcination are applied: washing out with water, washing with simultaneous neutralization of the impurities, adding neutralizing, mineralizing and other admixtures [Dvorkin 2008]. Another disadvantage is need in drying out as if PG is obtained in the form of water sludges of fine-grained particles in most of manufacturing processes [Lushnikova 2016]. PG can be radioactive due to the presence of naturally occurring uranium and radium in the phosphate ore. About 5 tons of PG are generated per ton of phosphoric acid production. Annual world generation of PG is around 100-280 Mt [Tayibi 2009].

However, there is limited application of it in many countries. Traditional technologies of β-hemihydrate production of PG have higher water-binder ratio (0.8 to 1) and low compressive strength (1 to 3 MPa) comparing to natural gypsum based binders. Regardless the availability of different technologies

for manufacturing PG based binders there is a problem in reduction of energy consumption for binders.

A series of different admixtures are applied to improve performance characteristics of gypsum binders. The application of the water reducing admixtures is one of the most common ways to reduce water consumption of the binders. There are applied superplasticizers developed for cement-based systems, but most of them have minor water-reducing effect in gypsum. The researches prove the effectiveness of polyacrylate (PA) and polycarboxylate (PC) ethers in neutral environment of gypsum binder [Dvorkin 2009, Fu 2011, Marschetzky 2013]. As for naphthalene-formaldehyde superplasticizer, the electrostatic effect is dominant. ξ-potential increases with increasing alkalinity which yields the maximum electrostatic effect. In the case of polycarboxylate, the steric effect dominates over electrostatic, which is more evident in neutral environments such as gypsum paste. Therefore, the effect of plasticizers in gypsum binder significantly differs due to the differences in the action mechanism [Lee 2008, Müller 2011]. As there is no process of substitution of Na^+ ions at Ca^{2+} ions [Hampel 2009, Ferrari 2010] as in alkaline environment of cement we do not use completely water reducing potential of an admixture.

Formation of alkaline environment by introduction of slaked lime provides more intensive water reducing effect of superplasticizer due to combination of steric and electrostatic effect of molecules of modified polycarboxylate ether [Dvorkin 2009, Marschetzky 2013]. It was observed, that stability of gypsum plaster under the influence of steric effect is better than that caused by electrostatic repulsive force [Peng 2005, Dvorkin 2013].

2 AIM AND SCOPE OF RESEARCH

The main aim of research was developing the effective modifier for gypsum binder based on phosphogypsum to eliminate the disadvantages of the binder by decreasing water/binder ratio, regulation of hardening rate and increasing mechanical properties of hardened gypsum.

The scope of the current research is determination the technological parameters of PG based binder production and influence of composite admixture consisted of SP and slaked lime on the setting time, water consumption, mechanical properties of the gypsum binder and definition the optimum content of the admixtures from the point of maximum values of mechanical properties.

3 MATERIALS AND METHODS

3.1 Materials

Dump phoshorgypsum accumulated at the local fertilizing plant was used in this investigation (Rivne, Ukraine) (see Tab.1).

As time of storage of PG increases the amount of the coarse fractions (above 0.4 mm) gradually increased. Particle size distribution of dump PG, show multidispersity of the material with prevalent grains of size ranges 0.1 to 0.4 mm, 0.05 to 0.1 mm and less.

Furthermore, we have observed that the content of water-soluble acidic admixtures in dump PG reduces

significantly with time. The content of water soluble P_2O_5 at the age of 20 years is at least 10 times lower compared to the fresh one [Dvorkin 2008]. Humidity of PG is within the range (15±3) %. Dump PG requires grinding with subsequent neutralization of acid admixtures.

Tab. 1: Chemical composition of phosphogypsum (% by mass).

Component, %	Phosphogypsum
SiO_2	-
Al_2O_3	0.34
Fe_2O_3	0.16
CaO	38.30
MgO	0.004
SO_3	59.1
P_2O_5 total	0.69
P_2O_5 water soluble	0.04
F^-	0.14
Cl^-	0.01
L.O.I.	–

Tab. 2: Properties of superplasticizers.

Name (trade name)	Dynamon SP3	Melflux 1641F	Melflux 2651F
Manufacturer	Mapei	BASF Construction Polymers, Trostberg, Germany	
Chemical base	acrylic polymer	modified polycarboxylic ether	
Average water reduction (for cement based concrete), %	up to 40%	up to 50%	
Average strength increasing at water-to-binder ratio decreasing (for cement based concrete), %	up to 50%	up to 60%	
Dosage recommendation, % by cement weight	0.5…1.5	0.05…1.5 (for alumina cement) 0.05…0.5 (for ordinary PC)	
Physical shape	liquid	powder	powder
Density, g/cm³	1.06 ± 0.02	-	-
Dry content, %	22	-	-
Bulk density, kg/m³	-	400…600	300…600
Color	amber	yellowish	yellowish to brownish
pH value (solution)	5.5…7.5	6.5…8.5	6.5…8.5

The dump PG was subjected to natural purification by rains thawed snow in dumps. Thus, radioactivity of PG is within the required limits and didn't exceed 370 Bq/kg.

The PG can be used in the manufacture of binders, and possible creation of commercial products, as it meets the following Ukrainian standard specifications:

- calcium sulphate content is less than 90 %;

- total amount of phosphates content (in terms of P_2O_5) is less than 1.5 %;

- water soluble phosphates content (in terms of P_2O_5) is less than 0.15 %;

- fluorides content (in terms of F) is less than 0.4 %.

As an alkaline admixture slake lime with 87% activity (CaO+MgO content) was used.

The properties of superplasticizers used are shown in Tab. 2.

3.2 Methods

At the first stage of the research there have been selected manufacturing parameters of non-modified PG binder (neutralization, thermal treatment, grinding). At the second stage, there have been investigated the influence of modifying admixtures and optimal proportion of modified binder was determined. There were tested paraments of gypsum paste (water-gypsum ratio, normal consistency, setting time) and hardened gypsum (bending and compressive strength).

PG was tested as normal consistency of gypsum pastes by Suttard cylinder, setting time and mechanical properties were conducted per standard

methods ASTM C472 - 99(2014). Bending at compressive strength was tested at the specimens 4x4x16 cm. For each composition 3 specimens were tested.

Statistical modeling methods have been applied for planning the experiments and description the results [Montgomery 2000, Sonebi 2004, Dvorkin 2012]. For solving technological problems, second order polynomial regression equations were applied as follows:

$$y = b_0 + \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k} b_{ij} x_i x_j + \sum_{i=1}^{k} b_{ii} x_i^2 \qquad (1)$$

where
y is the output parameter value;
b_0, b_i, b_{ij}, b_{ii} are the regression coefficients;
x_i, x_j, are the investigated factors;
k is the number of factors.

4 RESULTS AND DISCUSSION

4.1 Parameters of manufacturing of phoshorgypsum binder

For selection of technological parameters of PG manufacturing, three-level three-factors plan B_3 [Montgomery 2000, Dvorkin 2012] was used in the experiment. The equation (1) has following form:

$y=b_o+b_1x_1+b_2x_2+ b_3x_3+b_{11}x_{11}^2+b_{22}x_{22}^2+ b_{33}x_{33}^2+$

$+b_{12}x_1x_2+ b_{13}x_1x_3+ b_{23}x_2x_3 \qquad (2)$

Tab. 3. Terms of experiment planning (1st stage)

Factors designation		Variation levels			Range of variation
Symbolic	Natural	Bottom (-1)	Mean (0)	Upper (+1)	
x_1	Temperature of thermal treatment, ^0C	120	150	180	30
x_2	Percentage of the lime, %(by PG weight)	1	2	3	1
x_3	Maximum sieve residue №02, %	5	15	25	10

Tab. 4. Matrix of planned experiment for k=3 (1st stage)

Test no. U		Factors (symbolic)			Factors (natural)			Output parameter	
		x_1	x_2	x_3	X_1	X_2	X_3	f_c^{2h}, MPa	f_c^d, MPa
N_1	1	+1	+1	+1	180	3	25	2.8	5.4
	2	+1	+1	-1	180	3	5	3.2	6.3
	3	+1	-1	+1	180	1	25	1.7	4.6
	4	+1	-1	-1	180	1	5	2.5	5.2
	5	-1	+1	+1	120	3	25	1.6	4.6
	6	-1	+1	-1	120	3	5	2.2	5.6
	7	-1	-1	+1	120	1	25	0.8	4.1
	8	-1	-1	-1	120	1	5	1.7	4.7
N_α	9	+1	0	0	180	2	15	3.0	5.8
	10	-1	0	0	120	2	15	2.0	5.2
	11	0	+1	0	150	3	15	3.1	6.0
	12	0	-1	0	150	1	15	2.3	5.2
	13	0	0	+1	150	2	25	2.7	5.4
	14	0	0	-1	150	2	5	3.4	6.2
	15	0	0	0	150	2	15	3.2	5.9
N_0	16	0	0	0	150	2	15	3.1	5.7
	17	0	0	0	150	2	15	3.3	5.8

Tab. 3 presents a range of variation of the factors. Matrix of planned experiment and results of testing compressive strength of the specimens at the age of 2h (f_c^{2h}) and in dried state (f_c^d) are shown in Tab. 4.

Phosphogypsum neutralization with lime milk was made for all mixes. For complete neutralization of phosphogypsum and providing sufficient homogeneity, PG was kept for 1-3 days (subjected to ageing). Before calcination phosphogypsum was dried to a residual humidity - 1-2%, drying temperature was up to 100 ^{0}C. The duration of the calcination was 2 h. Binder was grounded in the laboratory ball mill.

Regression equations of compressive strength of PG binder after 2 hours (3) and after drying (4) were obtained:

$$f_c^{2h} = 3.1 + 0.5x_1 + 0.4x_2 - 0.3x_3 - 0.6x_1^2 -$$
$$- 0.4x_2^2 - 0.04x_3^2$$

(3)

$$f_c^d = 5.9 + 0.3x_1 + 0.4x_2 - 0.4x_3 - 0.4x_1^2 -$$
$$- 0.3x_2^2 - 0.09x_3^2$$

(4)
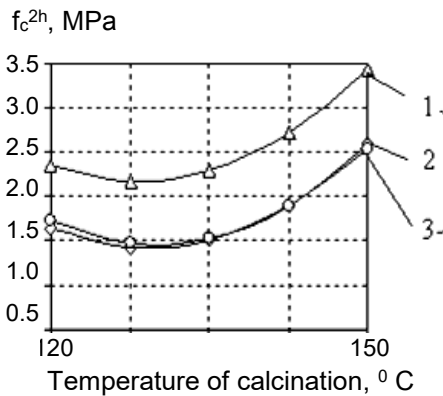
Fig. 1. Dependence of compressive strength of PG binder at 2h on calcination temperature and lime content: 1 – 3%; 2 – 2%; 3 – 1%; sieve 02 residue - 15%
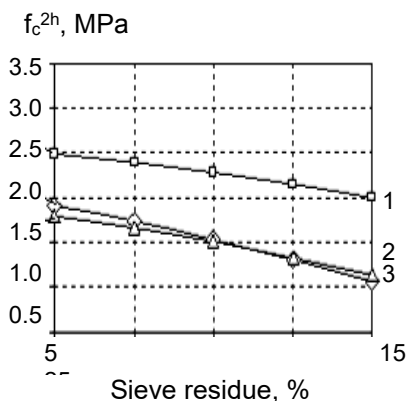

Fig. 2. Dependence of compressive strength of PG binder at 2h on sieve residue and lime content: 1 – 3%; 2 – 2%; 3 – 1%; calcination temperature -150 ^{0}C

The variations of compressive strength at the age of 2h are shown on Fig. 1 and Fig. 2. As shown in Fig. 1, the optimal temperature for calcination of PG binder is within the range 150-160^{0}C. The optimum lime content in terms of active CaO is about 2-2.5%. With increasing the fineness of grinding strength

increases linearly with a slight increase of water consumption (Fig. 2).

During PG grinding in ball mills there was intensive aggregation of binder particles and their sticking to grinding balls. Therefore, it is desirable to use apparatus in which the process of grinding conducts without substantial accumulation of electrostatic charges: roller mills, disintegrators and others.

There was determined the influence of water-gypsum ratio on the compressive strength of PG binder (Fig.3). The reduction of W/G from 0.7 to 0.5 led to ab significant increasing the strength of PG. Based on research data, we came to conclusion that compressive strength can be described by the formula similar to that for cement based composites like T.Powers formula f=AX^n, where X is water-binder ratio, and A and n – coefficients, n is equal 2-3. Dependence of compressive strength on W/G ratio can be approximated by the formula:

$f = A(W/G)^n$ (5)

According to experimental data, the coefficients were determined: *A ≈ 0,63, k ≈ -1,25.*
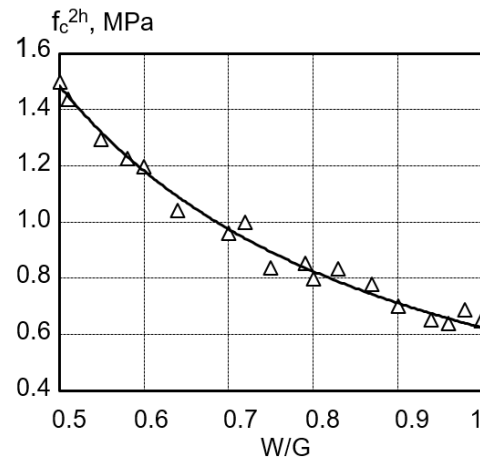

Fig. 3. Compressive strength at 2 h depending on water-gypsum ratio (calcination temperature 150^{0}C, lime content – 2%, sieve 02 residue – 15%)

Therefore, this study has shown that for PG neutralization 2-2.5% of lime can be used, the optimum temperature calcination of phosphogypsum is 150-160^{0}C, grinding fineness should meet the requirements of a sieve residue No.02 within 5 to 0%.

Thermographic analysis was performed for justification of optimum temperature of PG dehydration under heating of PG phosphogypsum samples for 23 h at temperatures between 20 and 750^{0}C (Fig. 4). and by measuring changes in electric resistance at heating (Fig. 5).

Results proved that the loss of moisture occurs within 4h at a maximum temperature of 50^{0}C, at 90^{0}C started the conversion of dihydrate to hemihydrate. The gradual increase in temperature to 120-170^{0}C (Fig. 4) didn't resulted in further loss of crystallization water. Binding properties reveal significantly only after calcination at least 140^{0}C ($f_c \geq$ 0.2-0.3 MPa). It can be explained by a change in morphology of hemihydrate calcium sulfate and phosphate compounds. At a temperature 200 ^{0}C there is observed further dehydration of phosphogypsum with a gradual transition into anhydrite. Interval of

hemihydrate is limited to temperatures 90- 170^{0}C. There is a correlation between maximum strength of binder and maximum mass loss due to dehydration and maximum β-hemihydrate content. Thermogravimetric studies were partly confirmed by measuring changes in electric resistance of PG at heating (Fig. 5).
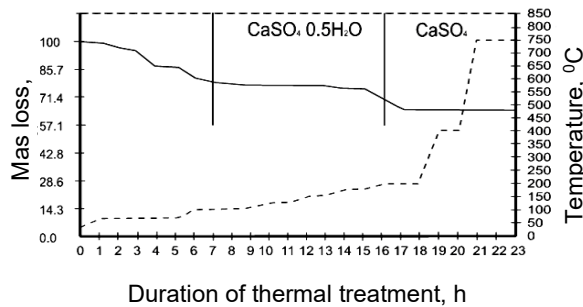

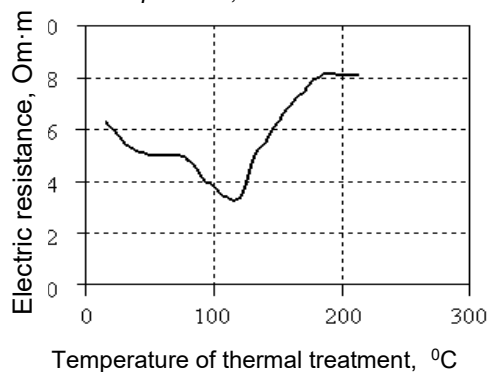*Fig 4. TGA diagram of phosphogypsum (full line: temperature; dotted line: mass loss*

Fig .5. Electric resistance change in the process of thermal treatment of dump phosphogypsum

According to the data, there was a decline in the electric resistance, which can be explained by increased evaporation of moisture in heated phosphogypsum. Subsequent stabilization of electric resistance at a temperature 75 ^{0}C (while physically bound water is present), and then a sharp drop up to 115^{0C}. Electric resistance stabilizes at minimum value at 115 to 130^{0}C. At that temperature, apparently dihydrate dehydration and formation of β-CaSO$_4$·0.5H$_2$O finish. Within the temperature range 130 to 180^{0}C starts transition β-CaSO$_4$·0.5H$_2$O into dehydrated form of β-hemihydrate, as it is shown in Fig.5 as the sharp increase in electric resistance. After that electric resistance value stabilized at maximum level.

We can conclude that thermogravimetric results and measuring changes in electric resistance at heating confirmed that the optimum temperature range for PG calcination is close to 150-160^{0}C.

4.2 Influence of modifying admixtures on phogogypsum binder

Based on the results of previous stage, PG calcined at 160^{0}C and with sieve residue less than 5% was used for the second stage of research.

At the second stage of research three-level two-factors plan B$_2$ for experiment was applied [Montgomery 2000, Dvorkin 2012]. The aim of the experiment was definition of optimal content of superplasticizer Melflux 1641F and lime.

The binders mixed with water according to standard methods. Consistency of the binder achieved was 200mm±10 mm (flow spread by Suttard cylinder). Terms of planning of the experiment are shown in Tab. 5, matrix of planning in Tab. 6.

Tab. 5. Terms of experiment planning (2st stage)

Factors designation		Variation levels			Range of variation
Symbolic	**Natural**	**Bottom (-1)**	**Mean (0)**	**Upper (+1)**	
x$_1$	Ratio SP/lime (by weight)	0.19	0.25	0.31	0.06
x$_2$	Total percentage of SP + lime, %(by PG weight)	2.1	2.9	3.7	0.8

Tab. 6. Matrix of planned experiment for k=2 and output parameters (2st stage)

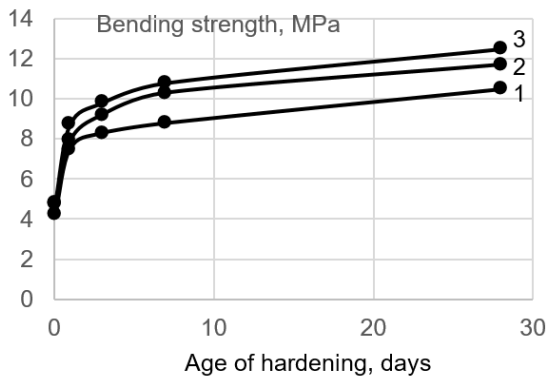| Test no. U		Factors (symbolic) x$_1$	x$_2$	Factors (natural) X$_1$	X$_2$	W/G	Flow spread (Suttard cylinder), mm	Setting time, min initial	final	f$_c^{2h}$ MPa
N$_1$	1	+1	+1	0.31	3.7	0.37	220	20	26	5.50
	2	+1	-1	0.31	2.1	0.42	210	17	21	5.40
	3	-1	+1	0.19	3.7	0.42	210	16	20	5.20
	4	-1	-1	0.19	2.1	0.50	195	14	19	4.04
N$_α$	5	+1	0	0.31	2.9	0.40	210	18	21	4.84
	6	-1	0	0.19	2.9	0.48	210	15	19	4.50
	7	0	+1	0.25	3.7	0.39	220	17	22	5.45
	8	0	-1	0.25	2.1	0.47	195	15	19	4.85
	9	0	0	0.25	2.9	0.42	220	16	21	4.55
N$_0$	10	0	0	0.25	2.9	0.42	220	16	22	4.58
	11	0	0	0.25	2.9	0.42	220	15	21	4.56

Fig. 6: Kinetics of bending strength of modified PG binder depending on the type of SP

Based on experimental data in given range of SP and lime content, regression equation (6) of compressive strength modified PG binder at 2 h (f_c^{2h}, MPa) was obtained:

$$f_c^{2h} = 4.61 + 0.33x_1 + 0.31x_2 - 0.1x_1^2 + 0.47x_2^2 \quad (6)$$

There was determined that the optimum content of multifunctional modifier for PG, containing lime + SP, is within the range 3 -3.7%, with ratio SP/lime = 0.28-0.31. When total consumption of admixtures reduces, the optimum ratio of the admixtures slightly increases. The strength of the hardened binder mixed with a standard hand mixer with three loops during 30 secs does not exceed 6 MPa after 2 h of hardening at W/G ≈ 0.45-0.55.
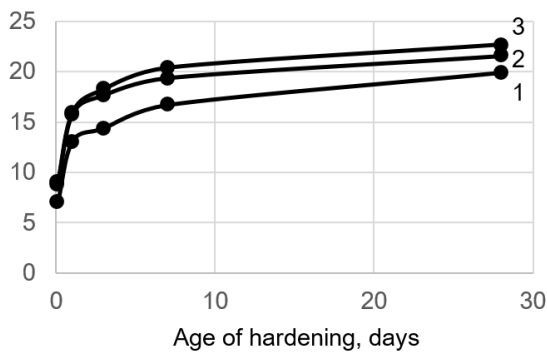

Fig. 7: Kinetics of compressive strength of modified PG binder depending on the type of SP

Further research proved that to achieve high strength of PG and low values of W/G for the same consistency of paste, method of preparation (mixing) test binder and duration of hardening make significant influence.

It was observed that at application of "forced" mixing at adding modifier SP+lime at the optimum ratio higher strength parameters at W/G ≤ 0.35 can be achieved (Fig. 6). Such intensive mixing can be made in muller mixers during 2-3 min. Small portions of binder for laboratory research can be mixed by hand for 3 to 6 min. Gypsum paste has flow spread 180 to 220 mm and initial setting time 18 to 25 min. Consumption of lime as a part of multifunctional modifier is about 3% (2% of CaO) can be explained by the need in completion of PG neutralization at achieving lower W/G and higher strength (Tab. 6).

Composite admixture lime + Melflux affected not only the strength and water demand of PG binder, but also setting time.
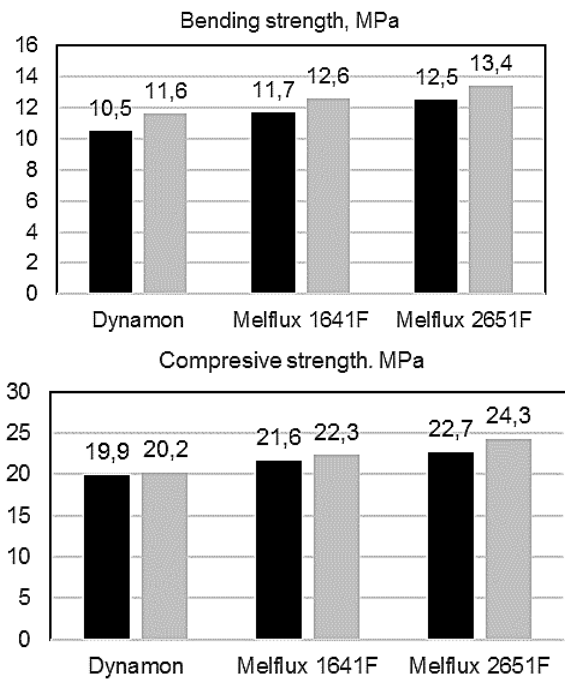

Fig 8. Bending and compressive strength of modified PG binder specimens at the age of 28 days (black bars) and after drying (grey bars)

There have been determined the effect of other polyacrylate and polycarboxylate based superplasticizers on setting time of PG binder (Tab. 7). For complex additive Melflux 1641F+lime the optimal setting time is within 18 to 25 min, for Melflux 2651F +lime – 50 to 70 min, for lime + Dynamon SP3 setting time is 15 to 20 min. Therefore, modified binders based on PG can be rated as slow-hardening gypsum binders.

Tab. 7: Compositions of modified PG binder with different SP (flow spread – 180-220 mm)

#	Type of SP	SP content, % by PG weight	Lime content, % by PG weight	W/G
1	Dynamon SP3	0.66	3	0.34
2	Melfulx 1641 F	0.60	3	0.32
3	Melfulx 2651 F	0.60	3	0.31

As strength parameters at the age of 2 h are not representative for such binders there were determined the strength at the age of 1,3, 7, 28 days and upon drying (Fig. 6-8). The results of strength tests of a binder at the age of 1 day are significantly higher than in 2 h of hardening. The important feature of such binders is clear trend in strength growing over time up to 7 days at 80 to 100%. For dried specimens, compressive strength reaches 20 to 24 MPa, and bending strength 10 to12 MPa.

Specimens of modified phosphogypsum binder in 2 h reached 7 to 9 MPa, and after 1 day it was 16 MPa. To our opinion it is appropriate to define the grade of modified PG and binder at the age of 1 day (24 hours).

The data of Fig. 6-8 prove that mechanical properties of PG binder containing polyacrilate SP Dynamon are close to the strength of specimens containing polycarboxylate SP. The effectiveness of Melflux 2651 F is higher than Melflux 1641 F due to the longer side chains of the molecules and higher steric effect.
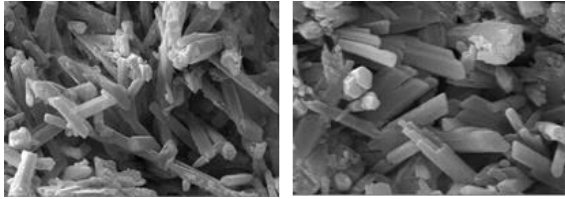

Fig 9. Micrographs of non-modified PG binder (W/G=0.9, left) and modified PG binder specimens (0.6% Melflux 1641F+ 3% lime, W/G=0.32, right)

As it can be seen from SEM micrographs (Fig. 9), the morphology of $CaSO_4 \cdot 2H_2O$ was not related to the type and portion of admixtures comparing to the PG binder specimens.

However, at the application of optimal values of superplasticizer and slaked lime denser disposition of crystals is observed.

5 CONCLUSIONS

The optimum technological parameters for PG binder production are calcination temperature from 150 to 160^0C, grinding fineness up to 5% residue on 02 sieve and lime as neutralizing admixture content 2 to 2.5%.For reduction W/G ratio and increasing mechanical properties of PG binder PA and PC superplasticizers are recommended to add due to the dominance of steric effect. To create alkaline environment and involve electrostatic effect of SP the enough lime is about 2 to 2.5% by gypsum mass comparing to 0.5 to 0.6% of SP is required. Modified PG based binder has compressive strength of specimens from 20 to 24 MPa and bending strength varied 10 to 12 MPa at 28 days. Per SEM data, the morphology of $CaSO_4 \cdot 2H_2O$ was not related to the type and portion of admixtures. However, at the application of optimal values of superplasticizer and slaked lime denser disposition of crystals is observed.

6 REFERENCES

[Dvorkin 2008] Dvorkin, L.Y., Myronenko, A.V, and Polishchuk-Gerasimchuk, T.O. *New technologies of phosphogypsum binder made of dump phosphogypsum.* Resourses saving materials, elements, structures and buildings, 2008, 16 (1), 27-34 (In Ukrainian).

[Dvorkin 2009] Dvorkin L.Y., Lushnikova N.V. *Properties of Gypsum Binders Modified with Complex Admixtures*. Ibausil, Internationale Baustofftagung, Tagunsbericht Weimar, Institut fűr Baustoffkunde, 2009; Band I: 1-0701 – 1-0707.

[Dvorkin 2012] Dvorkin L., Dvorkin O. and Ribakov Y. *Mathematical Experiments Planning in Concrete Technology*. New York: Nova Science Publishers, Inc., (2012).

[Dvorkin 2013] Dvorkin, L., Myronenko, A., Dvorkin, O., Lushnikova N. *Effect of Low-Alumina Blast Furnace Slags and Phosphogypsum Dihydrate on Properties of Supersulfated Cements*. Journal "Scientific Israel- Technological Advantages", 2013 , Vol.15, # 2, 16-29.

[Erdogan 1992] Erdogan Y., Genç H., Demirbas A. *Utilization of borogypsum for cement*. Cement and Concrete Research. Sept 1992, 22(5), 841–844.

[Hampel 2009] Hampel Ch., Zimmermann J., Sulser U. *Einfluss der Structur von PCE-Verflűssigern auf das Abbinden von beta-Halbhydrat*. Ibausil, Internationale Baustofftagung, Tagunsbericht Weimar, Institut fűr Baustoffkunde, 2009. Band I: 1-0381- 1 - 0386. (in German)

[Ferrari 2010] Ferrari L., Kaufmann J., Winnefeld F. and Plank J. *Interaction of cement model systems with superplasticizers investigated by atomic force microscopy, zeta potential, and adsorption measurements*. Journal of Colloid and Interface Science. 2010, 347:15–24.

[Fu 2011] Fu L.-F.,Deng Z., Zang Y., Zheng B. et al. *Effect of molecular structure of polycarboxylate superplasticizers on gypsum dispersion*. Acta Polymerica Sinica, 2011, (3): 294-301.

[Karni 1995] Karni J., Karni E. *Gypsum in construction: origin and properties*. Materials and Structures. 1995, 28(2): 92-100.

[Khatib 2013] Khatib, J.M., Mangat, P.S., Wright, L., 2013. Early age porosity and pore size distribution of cement paste with flue gas desulphurisation (FGD) waste. J. Civ. Eng. Manag. 19 (5), 622–627

[Lee 2008] Lee S.J., Liotta F.J, Schwartz S.A. *A new generation of gypsum dispersing agents*. Global Gypsum Magazine, 2004. June: 12-20.

[Lushnikova 2016] Lushnikova N. and Dvorkin L. *The sustainability of lightweight aggregates manufactured from clay wastes for reducing the carbon footprint of structural and foundation concrete.* In book: Sustainability of Construction Materials. Ed. by. J. Khatib. Cambridge: Woodhead Publishing, 2016, 643-681.

[Marschetzky 2013] Marschetzky M., Fischer H.-B., Ludwig H.-M. Superplasticizers in the calcium sulfate system – plasticizing action and influence on hydration. ZKG International. January 2013, 66(2):42-54.

[Montgomery 2000] Montgomery D.C. *Design and analysis of experiments*. 5th ed. New Jersey: Wiley, 2000.

[Műller 2011] Műller M., Hampel C. (2011) *Influence of gypsum raw material on performance of polycarboxylate-ether high-range water-reducing additives*. Global Gypsum Magazine May:14-21.

[Peng 2005] Peng J., Qu J., Zhang J., Chen M., Wan T. Adsorption characteristics of water reducing agents on gypsum surface and its effect on the rheology of gypsum plaster. Cement and Concrete Research. 2005, 35(3): 527–531.

[Sonebi 2004] Sonebi, M., *Applications of Statistical Models in Proportioning Medium Strength Self-Compacting Concrete*, ACI Materials Journal, Vol. 101, No. 5, 2004, pp. 339-346

[Tayibi 2009] Tayibi, H., Choura M., López F.A., Alguacil, F.J. and Delgado, A. L. Environmental impact and management of phosphogypsum (Review). Journal of Environmental Management 90(8):2377-86 · May 2009.