Hydration and Hardening of Composite Binder Containing Mechanically Activated Hemihydrate Phosphogypsum

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One of Lithuania´s most abundant technogenic inorganic wastes – extractive hemihydrate phosphogypsum (E-PG) was investigated for use in composite gypsum cement pozzolanic binding materials (GCP). E-PG, in such a state, as it is disposed of to stackpiles, cannot be used as a binding material, due to the acidic impurities present in it. Mechanical activation of E-PG and neutralization of acidic impurities by use of cement not only greatly increases E-PG strength, but also gives hydraulic properties. It is necessary to properly select the amount of pozzolanic component needed to avoid the formation of destructive minerals (ettringite, thaumasite) in the hardened GCP composition, i. e. the CaO concentration in the liquid phase of hydrating composition should not exceed after 5 days 1.1 g/l, after 7 days – 0.85 g/l. It was determined, that not only does the activity and mineral composition of pozzolanic component have an influence on CaO concentration, but also does mechanical activation. The neutralization in mixtures with opoka is preformed not only by Portland cement, but also by the finely dispersed carbonates (30 % – 35 %) present in opoka. While in mixtures with silica fume, the acidic impurities are neutralized only by the Portland cement minerals. It was found that mechanical E-PG activation greatly improves the hardened composition's strength and hydraulic properties.
Keywords: phosphogypsum, cement, pozolana, composite binder, hydration, mechanical activation hardening.

1. INTRODUCTION

The phosphatic and fluoride impurities make the main problem of utilization of phosphogypsum in the production of construction item The phospogypsum binder, due to these impurities, possess unstable properties and its strength is low. Globaly there are many scientific research investigations devoted to removing these impurities or to solving its neutralization problems [1 – 6]. It was found, that washing with water or neutralization using alkaline additives, e. g. $Ca(OH)_2$ frequently is not sufficiently effective, because past of the phosphate ions are included into the gypsum crystal structure, also in crystal defects or structure cappiliaries there are always some acidic solutions left. Ammonium hydroxide was proposed to treat phosphogypsum [1], also aqueous of ammonium sulfate solutions [2] and aqueous citric acid solution [3]. In this case, the impurities of phosphates and fluorides are converted into soluble citrates and acids, which are easily removed with a stream of water. In other investigations [5, 6, 9, 10], it was determined, that the use of thermal treatmen with washing it is possible to remove the phosphates and other acidic admixtures present in crystal structures. A process has been developed at the Central Building Research Institute (India) for the beneficiation of phosphogypsum wherein impurities, particularly undecomposed phosphate rock, quartz, etc. retained over 300 µm sieve are discarded, while the bulk of gypsum passing through the sieve is further washed, centrifuged and dried [7]. Lithuanian scientific researchers developed a technology of production of phosphogypsum binder in which the acidic impurities are not washed, but neutralized with lime in a reactor [8]. According to [9] the impurities can be made inactive by heating the phosphogypsum at high temperatures.

JSC "Lifosa" began to use an intensive extraction technology in which the waste is extractive hemihydrate gypsum in an acidic media (E-PG). That is why most of the Lithuanian scientific investigations are devoted to fresh waste containing about 160 kWh/t of accumulated energy [10 – 15]. A mechanical activation technology together with neutralizing alkaline additives, e. g. cement and slag was offered to stabilize E-PG properties and improve strength characteristics [12 – 15]. The unhydrated E-PG particles are uncovered, E-PG crystal accumulations are destroyed and the acidic impurities present in cappilaries and pores are liberated, thus the neutralization process is intensified. It is very effective to use cement as a neutralization additive because it adds hydraulic properties to the hardened material. To avoid the formation of destructive minerals – eteringite, thaumasite; it is necessary to add pozzolanic additives, which in the liquid phase of harden composite react with the available CaO and decrease its concentration, thus stoping the formation of ettringite [16]. Compositions are regarded to be resistant to sulfate corrosion if the available CaO concentration in the liquid phase after 5 days is not more than 1.1 g/l and 0.85 g/l after 7 days. Howewer a very high amount of pozzoulanic material is harmful because it decreases the strength of composite binding materials, increases porosity and water absorbtion, also lowers its frost resistance.

The aim of this investigation was to investigate the E-PG mechanical activation influence on available CaO concentration in harden E-PG, cement and pozzolana compositions (E-PGCP) as well as its physicomechanical

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Table 1. Chemical composition of materials

Material	Content, %											
	SO$_3$	CaO	Al$_2$O$_3$	Fe$_2$O$_3$	P$_2$O$_{5b}$	P$_2$O$_{5v.t}$	F	MgO	SiO$_2$	K$_2$O	Na$_2$O	LOIs
E-PG	56.7	40.1	0.22	0.13	1.72	0.56	0.53	trace	–	–	–	6.8
O	0.37	16.3	1.83	0.74	–	–	–	0.12	66.1	0.23	–	14.3
MS	0.35	0.25	0.2	0.05	–	–	–	0.4	96.66	1.2	0.1	0.6

properties and to ascertain the consistent pattern of the selection of optimal pozzolana and cement ratio (P/C).

2. MATERIALS AND METHODS

E-PG obtained from Kovdor apatite was used in the investigation:

– E-PG(K) – freshly removed from the conveyer, not refreshed and unhydrated E-PG. Its moisture content – 33 %, temperature 67 °C, pH – 2.65;

– E-PG(N) – immediately dried after removal from the convyer to constant mass at 55 °C temperature E-PG. Amount of hydrated water – 8.8 %;

– E-PG(M) – immediately dried and mechanically activated E-PG. Amount of hydrated water – 6.7 %.

Portland cement CEM II 42.5 N according to EN 197-1(C) was used as the neutralizing addtive. Specific surface area was 357 m²/kg, clinker mineral composition was: C$_3$S – 64 %, C$_2$S – 18 %, C$_3$A – 9.5 %, C$_4$AF – 10.5 %. Its amount in E-PGP compositions was 10 %.

Stoniškių quarry carbonate opoka (o) and microsilica (MS) was used as pozzolanic addtitives. The specific surface area of opoka milled in disintegrator was 1400 m²/kg, the amount of finely dispersed carbonates ~33 %, amount of active SiO$_2$ ~52 %. The microsilica specific surface area was 2000 m²/kg, amount of active SiO$_2$ ~96 %.

The chemical composition of the used materials is given in Table 1.

The mechanical activation of E-PG was conducted in a disintegrator DIA-01 (3000 rpm).

The influence of various factors on the available CaO concentration in hydrating E-PGCP compositions was investigated by using the standart method [17]. E-PGCP suspensions with various P/C ratios were conducted at 20 °C temperature and once at day were shaked, the CaO concentration in the liquid phase was determined after 5 and 7 days. According to these investigation results the P/C ratio for E-PGCP strength property investigations was chosen.

Table 2. Composition of E-PGCP specimens

Serial No	E-PG type	P/C ratio	Composition, %			
			E-PG	C	O	MS
1	E-PG (N)	0.9	81	10	9	–
2	E-PG (N)	0.4	86	10	–	4
3	E-PG (M)	0.9	81	10	9	–
4	E-PG (M)	0.4	86	10	–	4
5	E-PG (K)	0.9	81	10	9	–
6	E-PG (K)	0.4	86	10	–	4

Strength properties were investigated using the paste of uniform plasticity (consistence 120 mm according to Suttard's cylinder). Specimen cubes (40×40×40) cm were casted from E-PGCP paste. The formation of specimens from dried E-PG was carried out by mixing all the components in water, while the formation of specimens with freshly removed from the convyer E-PG(K), cement and pozzolanic additives was preformed by directing them to the disintegrator with moist E-PG and them adding the required amount of water. The compositions of formation mass mixture are given in Table 2.

The specimens were hardened in the conditions of 100 % relative humidity and at 20 °C. Resistance to water (softeness coeficient) was determined by immersing the dried specimens into 20 °C water for 4 h. The setting time was determined by Vicat apparatus. The amount of hydrated water (H) was determined by heating the dried material at 400 °C temperature.

X-ray diffraction patterns of mineral composition investigations were recorded by using diffractometer DRON-1, Fe-filtered Co K$_\alpha$ ($\lambda = 0.17902$ nm) radiation.

3. RESULTS AND DISCUSSIONS

The variation of available CaO content in hydrating E-PGCP compositions. To avoid the formation of destructive minerals in the hardened composition it is need to know the P/C ratio which depends not only on the pozzolanic additives activity, but also on other factors such as sulfate component type and as well as the dispersity of this components [18, 19]. In the case when phosphogypsum is used, the acidic impurities could also have an influence on the available CaO concentration. The results of investigations of available CaO concentration in hydrating E-PG compositions are give in Table 3.

As it can be seen, the available CaO concentration in the liquid phase depends not only on the pozzoulanic addtitives activity but also on other factors, i. e. drying of E-PG as well as mechanical activation. Comparison of CaO concentrations in compositions with mechanically unactivated dried E-PG(N) and not dried E-PG(K) showed, that E-PG drying increases the CaO concentration. This is most probably determined by macrostructural changes in the dried material, due to which the reactivity of E-PG and acidic impurities decreases. On the other hand the influence of mechanical activation is the opposite, i. e. compositions with mechanically activated E-PG(M) showed a lower available CaO concentration. This is determined by a finer material dispersivity, also during mechanical activation acidic solutions are removed from the cappiliares and pores, various passive impurities films are grinded away from crystal surfaces, the reactivity of E-PG increases and changes in compositions hydration products interactivity occur. The lower available CaO amount in compositions with mechanically activated E-PG(K) can be

explained by the fact that in freshly removed from the convyer E-PG, the acidic impurities reactivity is higher, it reacts intensively with the cement hydration product – available CaO and lowers its concentration. When corbonate opoka is used as the pozzolanic additive, part of the acidic impurities react with it and also with finelydispersed carbonates, so the CaO concentration decrease is not so sharply defined, while in E-PGCP(K) compositions with microsilica which contains almost only active SiO_2, the amount of available CaO is some what lower, than in analogical E-PGCP(M) compositions. It is clear, that in this case, the available CaO concentration is primarily determined by its and acidic impurities reaction, so the selection of P/C ratio according to the previously given method is not reliable and the P/C ratio absolutely needs to be corrected.

Table 3. Available CaO content in E-PGCP liquide phase

Composition	P/C	CaO content, g/l	
		5 day	7 day
E-PG(N) + C + O	0.5	1.52	1.18
	1.0	1.06	0.81
	1.5	0.87	0.71
E-PG(N) + C + MS	0.5	0.80	0.67
	1.0	0.35	0.30
	1.5	0.15	0.12
E-PG(M) + C + O	0.5	1.23	1.02
	1.0	0.95	0.62
	1.5	0.61	0.34
E-PG(M) + C + MS	0.5	0.67	0.40
	1.0	0.28	0.12
	1.5	0.20	0.06
E-PG(K) + C + O	0.5	1.29	1.15
	1.0	0.96	0.77
	1.5	0.68	0.43
E-PG(K) + C + MS	0.5	0.61	0.12
	1.0	0.28	0.10
	1.5	0.11	0.01

The XRD analysis showed (Fig. 1), that the smaller primary ettringite amounts form in compositions with mechanically activated E-PG (diffractional maximum 0.980, 0.561 nm). As we know, the formation rate and amount of primary ettringite in hardening GCP compositions depends directly on the available CaO concentration in the liquid phase. Primary entringite arises in yet unhardened compositions and does not posses any destructive influence, however at certain exploitation conditions (low positive temperature, high humidity, high CO_3^- ion concentration), it influences the formation of another destructive mineral – thaumasite [20]. Thaumasite formation is more dangerous than ettringite, because it can be formed also in GCP compositions with a sufficient amount of pozzolanic addtitive. So, E-PGCP compositions with mechanically activated E-PG should be more resistant to environment influence.

Hydrations kinetics. The amount of hydrated water (H) in hardening E-PGCP compositions investigation
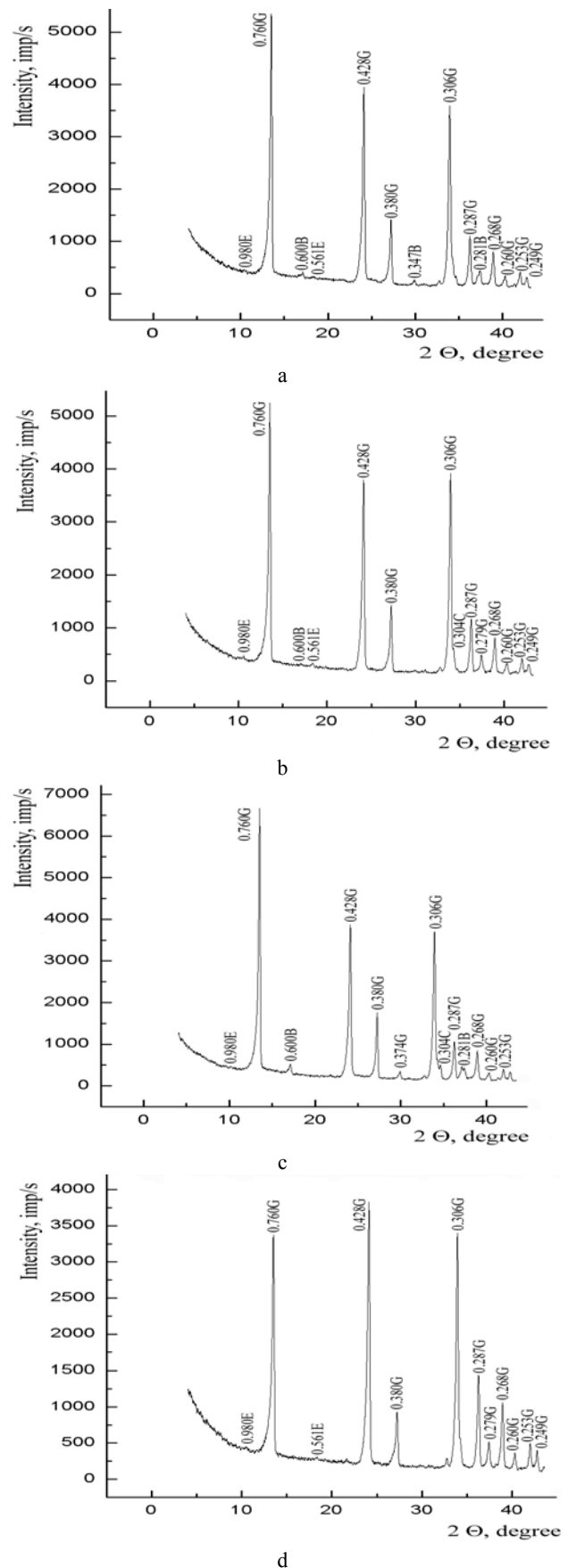
Fig. 1. X-ray diffraction patterns of hardened E-PGCP with opoka. a, b – E-PGCP(N) after 1 day and 7 days respectively; c, d – E-PGCP(M) after 1 day and 7 days respectyvely. E – ettringite; B – basanite; G – dihydrate gypsum; C – calcite

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results show, that mechanical E-PG activation does not have practically any influence on E-PGCP composition hydration rate (Fig. 2). An higher amount of H in E-PGCP(N) compositions after 1 h and 3 h reflect only a higher H amount in the initial E-PG(N) component (see Clause 2). After 1 day the amount of H in all the compositions was almost even and according to this, it can determine that a larger amount of E-PG has been hydrated. The XRD patterns of these specimens yet showed low intensity basanite diffractional maximum (0.600, 0.347) (Fig. 1, a, c). After 7 days, these peaks were observed only in XRD patterns of compositions with mechanically unactivated E-PG (Fig. 1, b). This demonstrates, that a small amount of unactivated E-PG can exist unhydrated for a longer time.
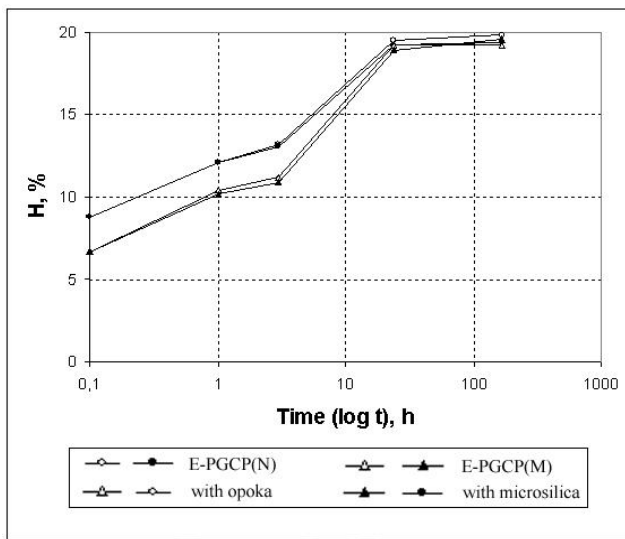
the hydration rates of E-PG(N) and E-PG(M) are similar (Fig. 2) it is absolutely clear that the faster setting is determined by the hardening structures formation features, i. e. in the compositions with activated phospogypsum newformations adhere better between themselves and setting times decreases. Mechanical activation has a especially large influence on the compositions strength properties (Fig. 3). Mechanically unactivated E-PG particles are porous, contain voids and if they are not destructed then acidic impurities films are left on the crystal's surfaces which block the formation of hardening structures. E-PG activation increases the strength of compositions several times, enables the formation of a more dense structure and increases the water resistance (Fig. 3).

Table 4. Setting times of E-PGCP composition

Composition	Setting times, min	
	initial	final
E-PG(N) + C + O	240	345
E-PG(N) + C + MS	225	285
E-PG(M) + C + O	150	225
E-PG(M) +C + MS	90	105
E-PG(K) + C + O	105	125
E-PG(K) + C + MS	90	105

Fig. 2. Hydratios kinetics of E-PGCP(N) and E-PGCP(M)

Setting times, strength, density and water resistance. The mechanical activation of E-PG sharply decreases the setting times of E-PGCP composition (Table 4). Because

As we can see from the investigation results, the mechanical E-PG activation would be one of most effective method for E-PG property improvement and stabilization. Economically and technologically it is rational activate moist E-PG freshly removed from the convyer together with acidic impurities neutralizing and hydraulic property improving components. That will first of all lower the construction product production energy expenditures, simplify the technological process and allow produce the building products of GCP material with high strength and increased water resistant properties.
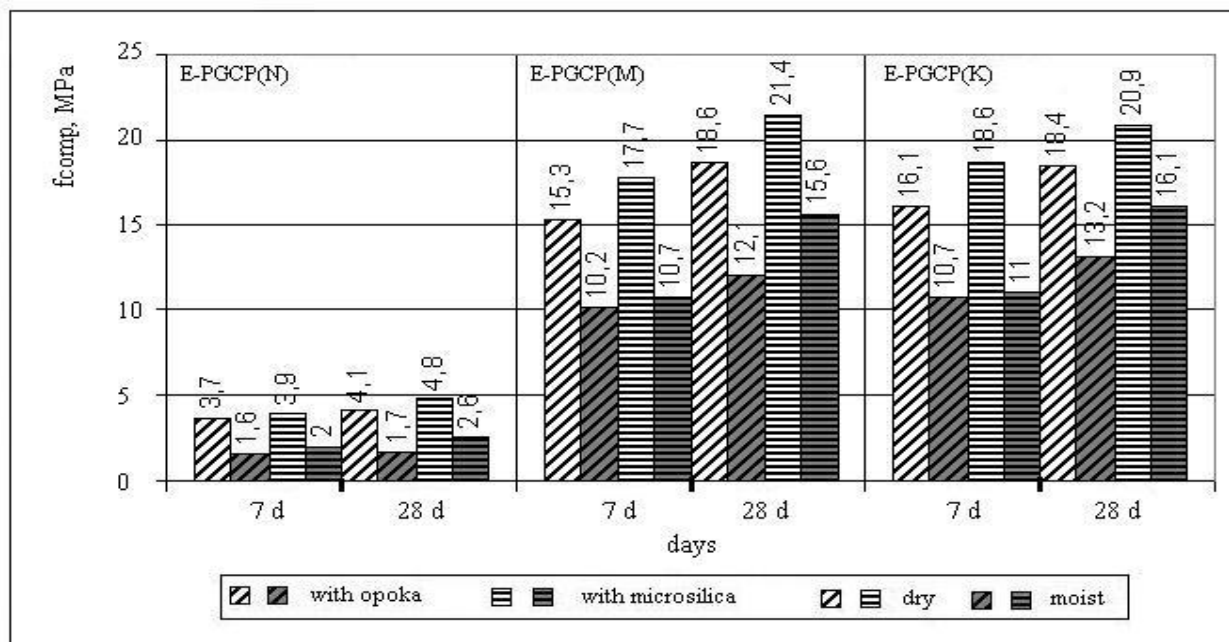

Fig. 3. Compressive strength of E-FGCP composition

4. CONCLUSIONS

Mechanical E-PG activation decreases the available CaO concentration in hardening E-PGCP composition liquid phase, less primary etringite is formed. It is possible to lower the amount of pozzolanic additives in such compositions, while the harden material should be more resistant to thaumasite formation.

E-PGCM compositions with mechanically activated and unactivated E-PG showed similar hydration rates. It is possible to acertain, that the faster setting of compositions with mechanically activated E-PG and substantially higher strength is mostly determined by structure formation pecularities. The destruction of the primary E-PG porous structure and hardening blocking acidic impurities films allows the newformations accrete between themselves and form a compact continuous dense structure of hardening materials. Compositions with mechanically activated E-PG showed an approximately 10 % – 20 % more dense structure, strength increased by 4 – 5 times, while water resistance – up to 30 %.

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