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Influence of Granulated Milled Slag Glass Additive on Hemihydrate Phosphogypsum Hardening

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A mechanical activation method for saving the accumulated waste energy (about 160 kWh/t) found in phosphogypsum was investigated and developed. The state of phosphogypsum in which it is disposed to stackpiles can not be used for production of construction materials due to the acidic admixtures present in it, which block its hydration and hardening processes, so new methods for neutralizing this negative effect were investigated.

In earlier investigation, various energy consuming additives like Portland cement and lime were used, so the construction material products integral energy expenditures were high. Slag glass could be used for neutralization, hydration and hardening kinetic regulation of phosphogypsum acidic admixtures. The aim of this investigation was to determine the interaction of slag glass with the acidic admixtures present in phosphogypsum.

It was found, that slag glass is an effective neutralizing additive for acidic admixtures present in phosphogypsum, which allows to regulate the phosphogypsum hydration and hardening duration and also to replace the energy consuming additives like Portland cement and lime proposed earlier.

Keywords: phosphogypsum, gypsum, gypsum cement, hydration, hardening, mechanical activation.

INTRODUCTION

Extractive hemihydrate phosphogypsum (E-PG) is the most abundant mineral waste material in Lithuania, stackpiles of which are rapidly increasing, while its use remains unsolved up till now. A sharp increase in technogenic gypsum output is being observed worldwide [1]. JSC "Lifosa" disposes of more than 1 million tons of E-PG each year, thus losing about 160 kWh of accumulated waste energy with every ton. So it is absolutely necessary to search for effective means of reprocessing it, thus saving the energy in the waste. Various acidic admixtures are present in E-PG – soluble mineral acidic compounds have the largest influence on gypsum binding material properties [2]. These are unreacted apatite, H_3PO_4 and H_2SO_4, CaS, iron, aluminium as well as other trace chemical element salts [3]. E-PG can also contain radioactive admixtures, however the radioactivity of JSC "Lifosa" waste E-PG does not exceed the maximum admissible norms (determined according to [4]).

A mechanical activation method was proposed and tested for reprocessing E-PG which allows to save the accumulated energy in it [5 – 7] in place of well-known repulpation [8 – 10]. However, the problem associated with regulation of the activated mass'es hydration and hardening processes remain unsolved. This problem was tried to be solved by adding various acid neutralizing additive, e. g. Portland cement and lime to the activated E-PG binder. However, due to the high-energy requirement for these additive (Portland cement ~1000 kWh/t, lime ~1200 kWh/t), the E-PG binder ecobalance structure worsens, while the hydration and hardening processes encounter new hardly solvable problems (ettringite, taumasite formation and its influence on structure stability) [11]. Granulated metallurgical slag (further on in the text – slag glass) can be used as a E-PG hydration and hardening kinetics regulating additive. This is one of the most abundant metallurgical industry's waste products arising where minerals are melted [12]. It is widely used waste material in the construction industry as a secondary (reusable) raw material. Every ton of granulated slag glass contains over 1000 kWh of chemical energy which can not be used until it is excited by additive's initiating hydrolysis.

The choice of E-PG neutralizing and modifying, hydration and hardening process regulating additives requires the evaluation of the amount of energy used for its fabrication and also the amounts of pollutant emissions into the environment. The integral energy expenditures for production of various binding materials and CO_2 emission into the environment were calculated using the material ecobalance method [11] and are given in Table 1.

The influence of mechanical activation on technogenic E-PG properties has not been investigated sufficiently. It is well known [11 – 13], that E-PG possesses a porous structure, its synthesis takes place in an acidic media (phosphoric acid extraction from apatite process), where crystals form differently, than those during the production of gypsum from natural raw materials. Here, acidic solutions are left in the crystal's defects and voids, also the structure's capillaries contain the remains of acids, the neutralization of which is still a complex and not entirely explained process.

Our investigation, differently from many others, where calcium sulphate is used only as a slag glass activating additive, uses E-PG as the main binding material in the mass. The aim of this work was to determine the slag glass'es interaction kinetics intensity phenomena in E-PG

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Table 1. Energy consumption for production of various construction materials, taking in to account raw material extraction

No/ No	Material	Integral energy consumption, (kwh/t)	Integral gaseous pollutant (CO_2) emissions, (kg/t)
1	Construction gypsum	200 – 250	88.0 – 110.0
2	E-$CaSO_4 \cdot 0,5H_2O$*	10.0 / 20.0	2.0 / 4.0
3	Portland cement	1000	500
4	Lime	1200	600

*data given here is when accumulated energy in E-PG is not lost.

Table 2. Raw material chemical composition

Raw material	Chemical compound, %										
	SO_3	CaO	Al_2O_3	Fe_2O_3	P_2O_{5g}	P_2O_{5ws}	F	MgO	SiO_2	K_2O	Ignition losses
E-PG	55.75	39.04	0.22	0.13	1.74	0.56	0.53	–	–	–	2.59
Slag glass	–	48.94	6.83	1.41	–	–	–	3.52	34.1	–	5.2
Opoka	0.37	16.3	1.83	0.74	–	–	–	0.12	66.15	0.23	14.26

Note: g – general, ws – water soluble.

containing acidic admixtures, also to select neutralizers and to determine the amounts which could allow to regulate the formation mixtures hardening durations.

MATERIALS AND METHODS

Materials

Unhydrated E-PG obtained from Kovdor apatite was used, which is a waste material and disposed to stackpiles (moisture content – 32 %, temperature – 65 °C, pH – 2.65).

Granulated, milled slag glass was used as a setting time regulator and acidic medium neutralizing additive with a specific surface area – 264 m^2/kg, pH – 11.5.

The efficiency of the process was determined by using other mineral additives: high-strength Portland cement CEM I 42.5 R; LST EN 197-1:2001 (Cem) with a specific surface area of 357.4 m^2/kg. The clinker composition used for Portland cement production was: C_3S – 61 %, C_2S – 19 %, C_3A – 7 %, C_4AF – 13 %. An additive from Stoniškių quarry-carbonate opoka milled by using a disintegrator was used with Portland cement. This amorphous active ingredient had a specific surface area – 1441.6 m^2/kg. The opoka and Portland cement ratio was 1 : 1.

The chemical composition of raw materials are given in Table 2.

Monoethanolamine was also used as a setting time regulating additire.

Investigation method

The materials' chemical composition was determined by using conventional methods.

X-ray diffraction analysis of mineral compositions was conducted by using difractometer DRON-1.

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

Unactivated and mechanically activated E-PG mixture pH control was conducted by using a portable pHmeter (model pH-330i), the solid mixture and distilled water ratio was 1 : 10. Measurements were made with 0.01 accuracy.

Six series of specimens (Table 3) were formed with each material. Formation mixture water/solids (w/s) ratio was 0.43.

Table 3. Specimen series formation mixture composition

No/ No	Formation mixture composition
1	Unactivated E-PG (100 %)
2	Activated E-PG (100 %)
3	97 % E-PG (activated) + 3 % slag glass
4	95 % E-PG (activated) + 5 % slag glass
5	90 % E-PG (activated) + 10 % slag glass
6	80 % E-PG (activated) + 10 % Portland cement + + 10 % opoka

The end of the setting (hardening) process was determind by using a Viko instrument. The physical and mechanical properties were determined by forming the binder mass (spreading <7 cm) in forms (4 cm × 4 cm × 6 cm) and vibrating them.

Specimens were harden at ambient conditions and at 60 °C temperature and were tested after 7 and 28 day curing period.

The mechanical properties were determined by using an universal testing machine UMM-10.

The formation mixture's w/s ratio was regulated by adding additional amounts of boiling water.

RESULTS AND DISCUSSIONS

The E-PG as taken from the phosphoric acid production convyer has a moist sand consistency and is a friable material. It remains in such a condition for approximately 1 hour after removal from the convyer. After that period, it begins to hydrate and hard crumps appear, this hampers the material's dosage and feeding into the disintegrator. After 1 ½ hour, the E-PG becomes a creep mass which is unsuitable for further reprocessing. That is why we used E-PG in such amounts, that could be used up not later than in 1 h time after removal from the convyer. Various formation mass pH values and setting times were obtained depending on neutralization agent's nature and amount used (Table 4).

Data obtained by investigating specimens with slag glass were compared with those obtained by using other neutralization agents – Portland cement and opoka mixture and with monoethanolamine. The results are given in Fig. 1.

Table 4. Formation mixture properties

Series No	pH	Initial setting time, min.	Final setting time, min.
1	2.44	35	60
2	2.65	0.5	1,0
3	6.41	58	110
4	8.84	71	118
5	10.45	90	180
6	11.58	26	86

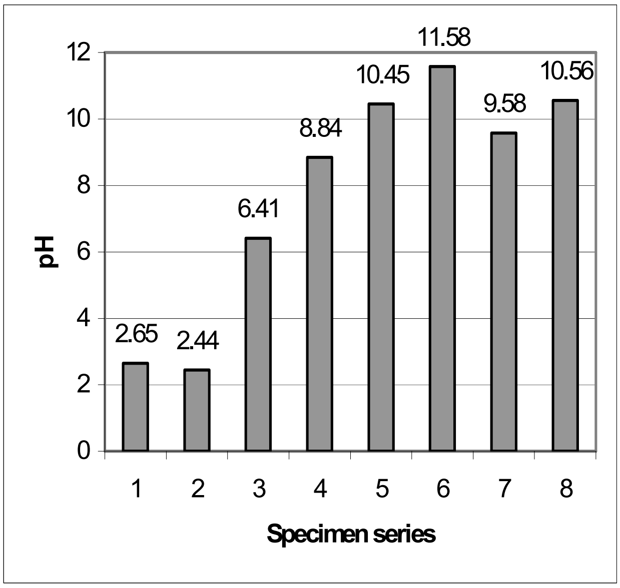

Fig. 1. Dependency of pH value on additive amount and nature. 1 – unactivated E-PG (100 %); 2 – activated E-PG (100 %); 3 – E-PG with 3 % slag glass; 4 – E-PG with 5 % slag glass; 5 – E-PG with 10 % slag glass; 6 – E-PG with 10 % Portland cement and opoka; 7 – activated E-PG with 1 % monoethanolamine; 8 – activated E-PG with 5 % monoethanolamine

As it can be seen from Fig. 1, small amounts of slag glass can significantly increase the value formations mixtures pH – e. g. addition of only 3 % increases the pH value to 6.45, while 10 % – up to 10.45. The highest pH value increase (11.58) was found for specimens containing a 10 % Portland cement and opoka additive, while the monoethanol requirement is the lowest – to neutralize the acidic E-PG media we need to add not more than 1 %.

The obtained data demonstrated, that the destruction of the initial E-PG porous structure increases the acidity of the media (pH value before disintegration was 2.65, after disintegration – 2.45). This can be explained by the fact that during mechanical activation, the acidic solutes in the crystal defects, pores and capillaries are leacht out.

The use of the intensive impact centrifugal mechanical activation method allows the acidic solutes present in the porous E-PG crystal structures to take part in the neutralization process.

It was found, that E-PG in the ready for disposal condition, can not be used due to the acidic admixtures present in it, which hamper the hardening process and destabilizes one of the most important E-PG binding materials' property like vitality (setting time). The addition of carefully selected addtitives during mechanical activation of E-PG allows to obtain a binder with stable properties. Changes in the system's pH values allows for changes in the amphoteric metal ions state in the liquid hardening system's medium. Therefore changes are observed in the kinetic process and harden rock properties.

The initial and final hardening kinetics dependency on neutralizing agent amounts and nature are given in Fig. 2.

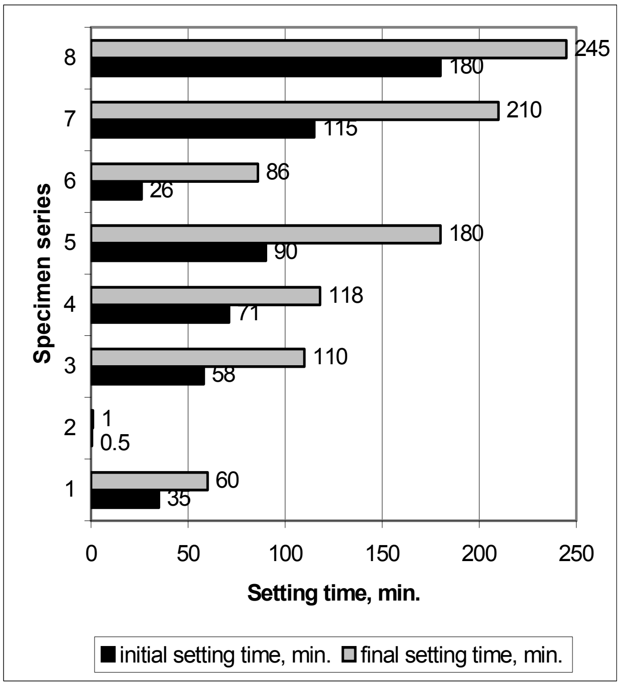

Fig. 2. The dependency of setting time on additive nature and amount. 1 – unactivated E-PG (100 %); 2 – activated E-PG (100 %); 3 – E-PG with 3 % slag glass; 4 – E-PG with 5 % slag glass; 5 – E-PG with 10 % slag glass; 6 – E-PG with 10 % Portland cement and opoka; 7 – activated E-PG with 1 % monoethanolamine; 8 – activated E-PG with 5 % monoethanolamine

A characteristic feature is that activated E-PG without additives begins to set already after 0.5 min., so we need to slow down the binding, because in the opposite case, the E-PG would set and harden in the disintegrator – leaving no time for further technological operations. Very small amounts of slag glass can significantly slow down the E-PG binding and increase the vitality duration in comparision with cement and opoka additive: the addition of 10 % of slag glass causes initial setting after 90 min., while in formation mixtures containing 10 % Portland cement and opoka mixture setting begins after 26 min. the comparison of this data with monoethanolamine, shows that the later is the most effective initial and final time retarder – only a 1 %, admixture retards the formation mixtures initial setting time by almost 2 hours.

The specimen's physical and strength properties are presented in Table 5.

Table 5. Specimen physical and strength properties

No/ No	Physical properties (after 28 days)			Strength, MPa			
				Undried specimens		Dried specimens	
	Density, kg/m^3	Specimen moisture content, %	Water absorbtion, %	R_{RC}/R_{RF} after 7 days	R_{RC}/R_{RF} after 28 days	R_{RC}/R_{RF} after 7 days	R_{RC}/R_{RF} after 28 days
1	1070	4.83	23.4	1.23 / 0.95	1.27 / 1.03	1.32 / 1.01	1.31 / 1.07
2	1740	6.11	12.6	12.3 / 5.75	13.6 / 5.83	13.1 / 6.12	14.7 / 7.11
3	1750	9.81	12.7	12.5 / 5.23	14.3 / 5.69	13.6 / 5.61	16.8 / 6.25
4	1760	7.54	11.6	13.7 / 5.53	14.6 / 5.88	14.4 / 6.04	18.2 / 7.00
5	1790	6.91	10.2	14.4 / 5.89	15.3 / 6.34	15.0 / 6.44	18.4 / 6.59
6	1830	7.20	8.80	11.8 / 5.51	17.4 / 9.61	17.5 / 6.75	19.7 / 10.4

Note: RC/RF – compressive and lexural strengths.

It was also determined, that unactivated E-PG specimens posess a low density and strength. Specimens made with mechanically activated E-PG showed significantly increased strength and density values. As it can be seen, the increase in the amount of slag glass additive, has a positive effect on the specimens properties – its strength and density increases, while the water absorbtion decreases. Specimens made using formation mixtures containing 10 % slag glass showed a compressive strength on the average 9 % higher, than for specimens with 3 % slag glass and 4 % higher than for specimens with 5 % slag glass; the flexural strength was correspondingly 10 % and 3 % higher. A slightly higher density and strength was observed for specimens made with Portland cement and opoka additive. The specimen's strength with slag glass depends very little on the hardening duration (after 28 days it increased on the average by 8 %), while for the specimens formed with a Portland cement and opoka mixture showed a 32 % increase.

The addition of slag glass to E-PG allows to obtain a new type of gypsum cement, which differs from well-known gypsum cement compositions, so in this case the energy consuming Portland cement is replaced by a technogenic waste material and there is no need for an active SiO_2 additive to lower Ca^{2+} ion concentrations in the liquid phase, because no higher alkaline calcium aluminates are formed during the hydrolysis of slag glass, which could initiate the synthesis of etringite in the hardening system.

The hydrolysis and hardening of slag glass begins with sulphate activation. The solvable SiO_2 enters the solution during slag glass hydrolysis and reacts with the Ca^{2+} surplus, thus lowering its concentration and blocking etringite formation. There is enough of Ca^{2+} ions formed in the liquid solution during slag glass hydrolysis to neutralize the acidic solutes, water solvable P_2O_5 and F admixtures, so they could form various insolvable compounds.

The X-ray diffraction (XRD) analysis of specimens showed the following results (Fig. 3).

The degree of hydration was determined by XRD analysis according to changes in basanite and gypsum dihydrate peak intensivities. As we can see from the obtained results no unharden gypsum (dihydrate) is found in specimens formed using pure activated E-PG after 28 days, while in specimen formed using Portland cement and opoka mixture, we can clearly see hemihydrate gypsum peaks. A similar picture was observed for specimens containing slag glass additive.

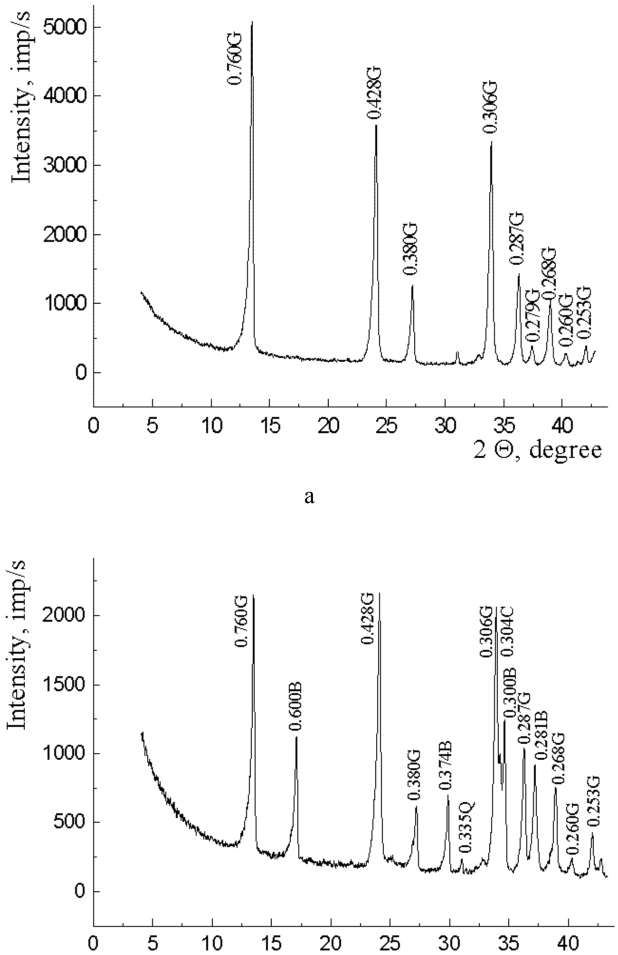

Fig. 3. X-ray diffraction patterns of specimens hardened for 28 days. a – pure activated E-PG, b – activated E-PG with 10 % Portland cement and 10 % opoka. G – gypsum; B – basanite; Q – quartz; C – calcite

The silicic acid, aluminum and iron hydroxide compound formation during pH changes can cause the kinetic process control to be substituted by diffusion control, due to which another type of (modified) hardened gypsum cement structure is formed. This case is especially probable when a hydrosilicate gel forms in the hardening system with Portland cement and slag glass additive.

CONCLUSIONS

1. It was determined that granulated and milled slag glass (specific surface area up to 250 m^2/kg) is an effective additive for neutralizing the acidic phosphogypsum medium, it does not only neutralize the acidic admixtures, but also allows to regulate the E-PG hydration and setting time duration.
2. We found that it is expedient to use granulated or milled slag glass after the evaluation of various different neutralizing additive from the energy consumption point of view. Its use would allow to replace energy consuming additives (like Portland cement, lime), while the specimen's mechanical properties with these additives and milled slag glass are similar.
3. It was found that slag glass is a more effective retarder than Portland cement and opoka mixture, when the initial and final setting times are compared. Monoethanolamine (up to 1 %) retards the E-PG setting time most effectively and increases the prepared mixtures vitality up to 2 hours.

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