

The Peculiarities of Hardening of Composite Anhydrite Cement Pozzolana Binding Material with not Burned Natural Anhydrite

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The comparative investigations of gypsum cement pozzolana binding materials (GCPB) and anhydrite cement pozzolana binding materials (ACPB) with not burned natural anhydrite were performed controlling kinetics of hardening, phase composition of new formations generated in the course of hardening, structure, mechanical strength and water resistance. It was established that the component of natural anhydrite with compact crystalline structure provides specific properties to ACPB, i. e. long-term hardening, low porosity of the hardened matrix and good hydraulic properties. At the same plasticity of moulding mix, ACPB density was higher by approximately 25 % than that of GCPB. ACPB early strength is lower than GCPB, however, the gradual hydration of anhydrite over time makes the ACPB hardening structure more compact and stronger. After 28 days ACPB strength was higher by ~11 %, after 4 months ~by 23 %, after 7 months by ~30 % than that of GCPB. During the ACPB hardening, the slower generating new formations of dihydrate gypsum together with new formations of cement hydration make the hardening structure considerably more water resistant. Contrary to GCPB, the hardened ACPB does not loose strength in water, but is developing it further. The process of anhydrite hydration in the hardening ACPB is proceeding for many years and over time its influence on ACPB strength becomes greater than that of cementitious component. It was established that ACPB still contains non- hydrated anhydrite after 15 years of hardening. Basing on the results of investigations the performance characteristics of composite anhydrite binding materials with not burned natural anhydrite were predicted, as well as a possibility to replace cement binding materials by them.

Keywords: natural anhydrite, anhydrite cement pozzolana binding material, gypsum cement pozzolana binding material, hydration kinetics, phase composition, compressive strength, water resistance.

INTRODUCTION

On account of climate change, one of the main tasks set for the building industry is to reduce energy input and CO₂ emission into atmosphere. Since the production of Portland cement, one of mostly used binding materials, distinguishes itself by high energy input and high CO₂ emission (up to 0.9 tons CO₂ per one ton of Portland cement CEM I), it is of utmost importance to cut down its consumption and to use Portland cement only when indispensable. Therefore, many recent researches are carried out into properties of hydraulic composite binding materials or building products with reduced Portland cement content and into possibilities of their application [1–4].

Lithuania has huge underground deposits of anhydrite rock [5, 6]. Anhydrite is a unique raw material. When ground finely, it acquires binding properties. The anhydrite rock of the Pagiriai deposit, which was explored in detail, is extremely pure and the content of main mineral, anhydrite CaSO₄, is 93 %–98 %. The investigations show a possibility to produce anhydrite binding material of high strength (40 MPa and higher) out of ground anhydrite rock without burning or using short-term thermal treatment at not high temperatures. It is established that the optimal grist fineness is about 400 m²/kg [5]. Ground anhydrite also can be used for production of hydraulic anhydrite cement pozzolana binding materials.

The sulphate composite hydraulic binding materials based on gypsum binding materials are long known and largely used [8, 9]. As a sulphate component, hemihydrate gypsum is commonly used, sometimes anhydrite. The hydraulic properties are rendered adding cement, pozzolana materials, granulated blastfurnace slag, fly ashes etc. [8, 10–15]. From them the mostly used are hemihydrate gypsum cement pozzolana binding materials (GCPB). GCPB sets and hardens quickly, however, hemihydrate gypsum obtained by burning of natural gypsum is a friable material and therefore, much water is needed for its mixing. GCPB products are moisture resistant, but do not longterm water action. When used in moist environment at low positive temperatures, they may start disintegrating because of formed destructive mineral thaumasite [16]. Less numerous researches were performed on other composite binding material with slower hardening sulphate component, i. e. anhydrite cement pozzolana binding materials (ACPB). Furthermore, the majority of researches were carried out using burned anhydrite binding material. Usually GCPB and ACPB are regarded as almost identical materials, except for the latter's slower hardening of ACPB and suitability for production of more compact and stronger products. The theory of hardening, prediction of performance in various using conditions and fields of application of these composite binding materials is mainly founded on GCPB investigations. Few are deeper researches to show how and why sulphate composite materials change their properties such as hydraulicity, resistance to environment impact, when the quickly

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hardening component, hemihydrate gypsum, is replaced by slowly hydrating natural anhydrite of considerably more compact crystalline structure.

No doubt, that the different hardening kinetics of sulphate component, which dominates in GCPB and ACPB composites, influence not only the hardening rate of its, but also the formation of hardening structure and the mineralogical composition of new formation, and thereby their performance characteristics. During GCPB hardening, the quickly hardening sulphate component, hemihydrate gypsum, forms an initial hardening structure from dihydrate gypsum and ensures initial strength, while further strength increase and hydraulic properties are determined by hardening of cementitious component. When ACPB is hardening, the considerably slower hardening and hydrating anhydrite is unable to form a separate sulphate structure and together with cement takes part both in formation of initial hardening structure and further hardening of material. Hydration and hardening of anhydrite, especially of not burned one, may last some years, even over ten years. In our previous researches it was established that not burned natural anhydrite-bearing ACPB, which was hardened for 3 years in moist environment, still contained a significant amount of non-hydrated anhydrite [17] and that even the 15-year-hardened ACPB had it (see Fig. 3). All the above mentioned and the fact that the compact not disintegrated crystalline structure of not burned natural anhydrite requires less water for mixing of ACPB preconditions specific ACPB properties such as longterm hardening, low porosity of hardened matrix, high water resistance, etc. It is established that hardened ACPB with natural not burned anhydrite is more resistant to formation of destructive minerals (ettringite, thaumasite) than GCPB of analogical composition [18].

In this study the comparative investigations of GCPB and ACPB with not burned natural anhydrite were performed following of hardening kinetics, phase composition of new formations generated during hardening, structure, mechanical strength and water resistance. Basing on the results of investigations, the performance characteristics of composite anhydrite binding

materials with not burned natural anhydrite are predicted, as well as a possibility to replace by them the cement binding materials in some fields of application.

MATERIALS AND METHODS

As a sulphate component, ground natural anhydrite and hemihydrate gypsum were used. As a cementitious component, Portland-slag cement CEM II/A-S 42.5 was used. The mineralogical composition of this cement clinker [in mass%] is as follows: C₃A – 57 %; C₂S – 17 %; C₃A – 9 %; C₄AF – 11 %. The content of granulated blastfurnace slag in Portland cement is ~15 %. As a pozzolanic component, carbonate opoka from the Stoniškiiai area (Lithuania) was used. The content of active SiO₂ in it is approximately 51 %, finely dispersed calcium carbonates – approximately 33 %. The chemical and physical properties of separate components are shown in Table 1.

The comparative investigations were performed between sulphate composite binding materials with anhydrite and with hemihydrate gypsum, which are considered as moisture resistant (the cement content in them being 20 %) [8]. With the aim of highlighting the influence of slower hardening anhydrite on longer hardened ACPB strength, the investigations were also performed with ACPB containing less cement, i.e. 10 % and 5 %. The pozzolanic additive-cement ratio (1:1) was selected according to the standard method where the content of free CaO in the liquid phase of hydrating composites after 5 days should not exceed 1.1 g/l, after 7 days – 0.85 g/l [19]. The compositions of moulding mixes and reference marks of specimens are provided in Table 2.

Table 2. Composition of moulding mix

Reference marks of specimens	Composition, %				Water Solid
	G	A	O	C	
GCPB (60, 20, 20)	60	–	20	20	0.70
ACPB (60, 20, 20)	–	60	20	20	0.50
ACPB (80, 10, 10)	–	80	10	10	0.47
ACPB (90, 5, 5)	–	90	5	5	0.45

Table 1. Chemical and physical properties of materials used

Properties	Anhydrite (A)	Gypsum (G)	Opoka (P)	Portland Cement (C)	
				Clinker	Blastfurnace slag
Chemical composition, mass%					
CaO	40.64	35.84	20.20	63.19	45.95
SO ₃	56.71	53.12	0.50	0.53	3.71
CO ₂	0.80	1.22	14.51	–	–
MgO	0.47	0.68	0.06	3.92	4.88
SiO ₂	0.46	2.20	55.30	20.58	35.25
Al ₂ O ₃	0.16	0.31	1.60	5.60	7.10
Fe ₂ O ₃	0.04	0.38	1.53	3.48	0.84
Loss in mass at 400 °C	0.54	6.21	4.90	–	
Fineness Residue on the sieve, %					
200 µm	0.2	1.2	0.2	–	
80 µm	10.5	–	4.0	6.5	
Specific Surface, m ² /kg	360	720	1436	350	

Specimens (cubes 40×40×40 mm) were formed by moulding out of paste with same plasticity (consistence 18 cm according to Suttard's cylinder). Specimens were held in the mould for one day, after they were cured for 27 days under condition providing relative humidity of not less than 98 % and a temperature of 20 °C. After they were divided into two groups cured as follows:

- under the same conditions (A conditions);
- in water at 4 °C, which was changed weekly (B conditions). Under these conditions, the permanent action of water were simulated, also the resistance of hardened material to formation destructive mineral thaumasit was examined [16].

The estimated strength of ACPB proportional to density of GCPB was calculated according to:

$$f_{\text{estimated}}^{\text{ACPB}} = f_{\text{actual}}^{\text{ACPB}} \frac{\rho_{\text{GCPB}}^2}{\rho_{\text{ACPB}}^2}, \quad (1)$$

where $f_{\text{actual}}^{\text{ACPB}}$ is the actual strength of ACPB, ρ_{GCPB} , ρ_{ACPB} is the density of GCPB and of ACPB accordingly.

The compressive strength of dried specimens was determined by using testing machine H200KU Tensile Test Machine (Tinius Olsen Ltd), the rate of load increase was (2400 ± 200) N/s. The content of hydration water was determined by heating the dried materials at 500 °C temperature. The microstructure of hardened specimens was investigated by using scanning electronic microscope Stereoscan S4-10 (Cambridge Scientific Instruments Ltd, England). A diffractometer DRON-1, Fe-filtered Co K α ($\lambda = 0.17902$ nm) radiation was used for X-ray diffraction analysis.

RESULTS AND DISCUSSIONS

Figure 1 shows the results of investigations of compressive strength in samples of ACPB (60, 20, 20) and GCPB (60, 20, 20), which hardened under the conditions A and B.

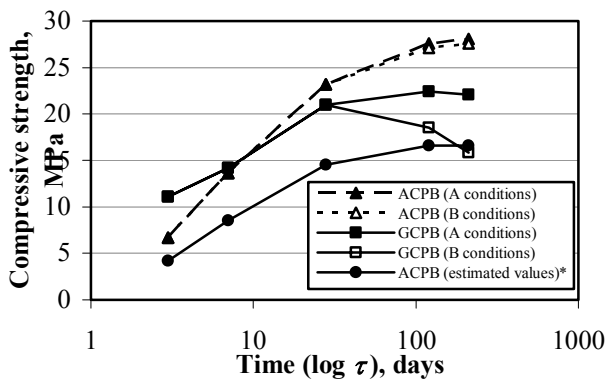


Fig. 1. The variation of compressive strength of GCPB (20, 20, 60) and ACPB (20, 20, 60) in various conditions (the values are determined after 3, 7, 28, 120 and 210 days). *Estimated value of ACPB is calculated from equation 1

From the data given in Fig.1 one can see the difference not only in hardening kinetics and obtained strength of ACPB and GCPB, but also in variation of strength in those specimens, which hardened under permanent action of water. In moist environment the

character of variation in strength of both ACPB and GCPB specimens are similar, except for hardening kinetics. The early strength of ACPB is remarkably lower; however, it increase more rapidly and after 28 days already exceeds the strength of GCPB specimens. Nevertheless, the water action on strength of these composites differs greatly. The strength of GCPB specimens, which were transferred into water after 28 days of hardening, started decrease and after 3 months it decreased by ~12 %, after 6 months by ~25 %. This fact shows that the new formations of cement hardening cannot fully protect the gypous hardening structure of high porosity from water effect and that it starts gradually dissolving and softening. Meanwhile the ACPB specimens further strengthened in water and, as seen from Fig. 1, their strength was close to that of specimens, which hardened under moist conditions. Having in mind that the influence of type of sulphate component on the hydration and hardening of cementitious component is not very significant [20, 21], i.e. in both compositions it hardens in a similar way, one can consider that the different behavior of ACPB and GCPB in water is determined only by peculiarities in properties of sulphate component and hardening. Though cement accelerates the hydration of anhydrite, nonetheless, the hydration of it proceeds considerably slower than that of hemihydrate gypsum. Therefore, for a certain period of time, the influence of new formations of sulphate component on properties of hardening ACPB is less significant than in case of GCPB. The XRD analysis show that the content of anhydrite in the hardening ACPB is gradually decreasing (Fig. 2), but the anhydrite diffraction peaks are still very intense even in the 28 day-hardened samples. They also can be seen in XRD patterns of 15 year-hardened ACPB specimens of analogical composition (Fig. 3).

The content of hydrated anhydrite in the hardening ACPB can be approximately calculated basing on the investigations of hydration of ACPB and cement (Fig. 4). It is assumed for calculation that the variations of cement hydration kinetic in ACPB are not significant, i.e. the anhydrite component neither accelerates, nor slows down cement hydration. Then the water content in ACPB (60, 20, 20) composite received due to hydration of anhydrite component, H_A^{ACPB} in %, is calculated according to:

$$H_A^{\text{ACPB}} = H_A^{\text{ACPB}} - 0.2 \times 4.9 - 0.2 \times H_C, \quad (2)$$

where H_{ACPB} is the content of hydration water in hardening ACPB in %; 4.9 is the content of hydration water in opoka in % (see Table 1); H_C is the content of hydration water in hydrating cement in %.

The content of hydrated anhydrite, A_H , in % of all anhydrite present in the composite is calculated according to:

$$A_H = \left(\frac{H_A^{\text{ACPB}}}{0.6 \times 20.3} \right) \times 100, \quad (3)$$

where 20.3 is the amount of hydration water when natural anhydrite hydrates fully, in %.

The calculations show that after 3 days about 45 % anhydrite hydrated, after 7 days ~56 %, after 28 days ~63 %, after 4 months ~70 %, after 7 months ~74 % anhydrite.

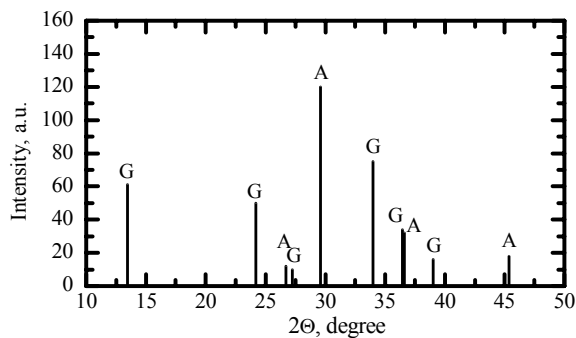
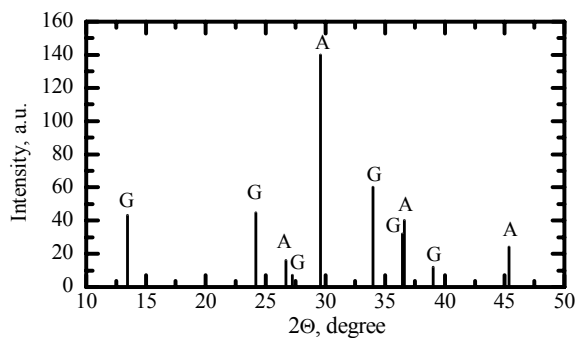


Fig. 2. X-ray diffraction patterns of ACPB (60, 20, 20) samples, which hardened under the conditions A: a – after 3 days, b – after 28 days

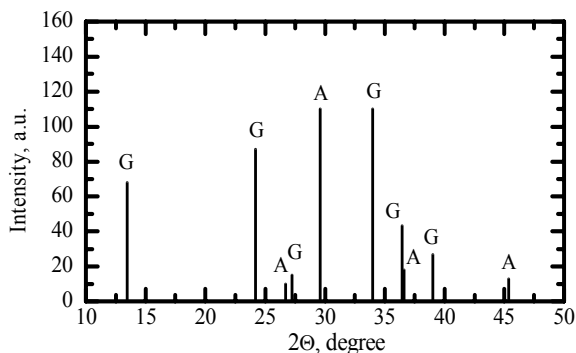


Fig. 3. X-ray diffraction pattern of ACPB (60, 20, 20) samples, which hardened for 15 years under the conditions A

Along with growth of hydration degree, the influence of sulphate component on strength and other properties of hardened material is increasing. However, as can be seen, ACPB, which was kept in water, did not weaken (Fig. 1). This fact shows that the hardening structure, which generated out of new formations of dihydrate gypsum in the consequence of gradual anhydrite hydration, is more resistant to water action than the structure generated during hardening of hemihydrate gypsum. Perhaps the most important factor, which preconditions high water resistance of ACPB, is a very compact structure of hardened material. Owing to compact structure of particles of natural anhydrite, for mixing of ACPB much less water is needed than for GCPB (see Table 2). Moreover, along with gradual anhydrite hydration, the ACPB microstructure is

compacting further. The values of density of the hardened GCPB and ACPB specimens and its variation over time are given in Table 3.

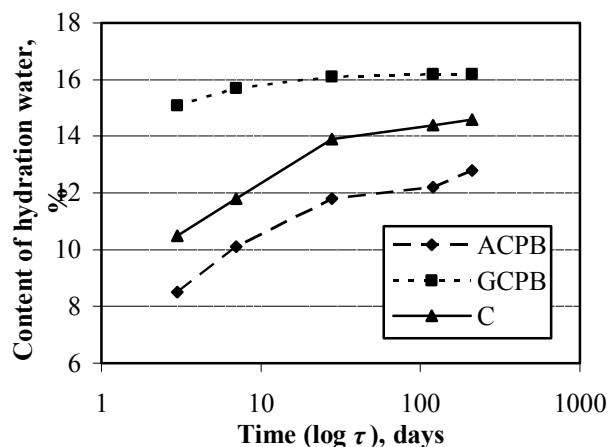


Fig. 4. The hydration kinetics of ACPB (60, 20, 20), GCPB (60, 20, 20) and cement (the values are determined after 3, 7, 28, 120 and 210 days)

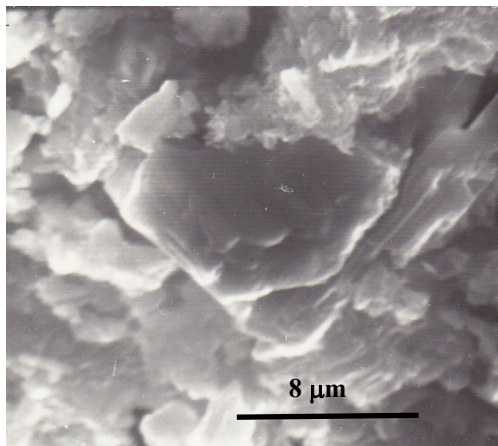
Table 3. The density of hardened GCPB and ACPB, kg/m³

Reference marks of specimens	Hardening time, days				
	3	7	28	120	210
GCPB (60, 20, 20)	1080	1090	1100	1100	1100
ACPB (60, 20, 20)	1360	1380	1400	1420	1440

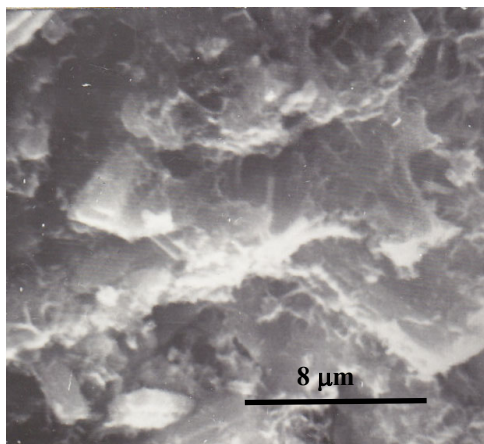
Fig. 5 shows the SEM photos of microstructure in ACPB and GCPB samples, which were hardened for 4 months in the conditions B. One can see that ACPB is considerably compact than GCPB.

Density is one of the most important characteristics determining water resistance of gypsum matrix [22–24]. Extremely compacted gypous products ($\rho \geq (1600–1800)$ kg/m³) are even regarded as suitable for service in field environment [25]. Of importance is also the fact that the liquid phase of hardening ACPB, due to slow anhydrite hydration, is constantly supersaturated by Ca²⁺ and SO₄²⁻ ions in respect to dihydrate gypsum (the solubility of metastable anhydrite being from 2.60 g/l to 3.10 g/l, that of dihydrate gypsum 2.04 g/l), what impedes solution of concretion contacts of dihydrate gypsum and disintegration of hardening structure.

The peculiarities of GCPB and ACPB hardening structure and the factors determining their strength may be evaluated by estimating strength at the same density (equation 1). The estimated values of ACPB strength ($f_{estimated}$) at same density as GCPB are given in Fig. 1. One can see that at same density, the ACPB hardening structure would be weaker than that of GCPB. This shows that higher strength of ACPB is subject only to higher density of hardened material. As mentioned above, the cementitious component in both composites is hardening in a similar way, therefore, it is obvious that for a certain period of time, the contribution of slower hydrating anhydrite component to strength of hardening composite remains lower than that of quickly hardened hemihydrate gypsum. By increasing the duration of hardening and the



a



b

Fig. 5. The photos of microstructure in ACPB (60, 20, 20) and GCPB (60, 20, 20) samples, which hardened for 4 months under the conditions B: a – ACPB, b – GCPB

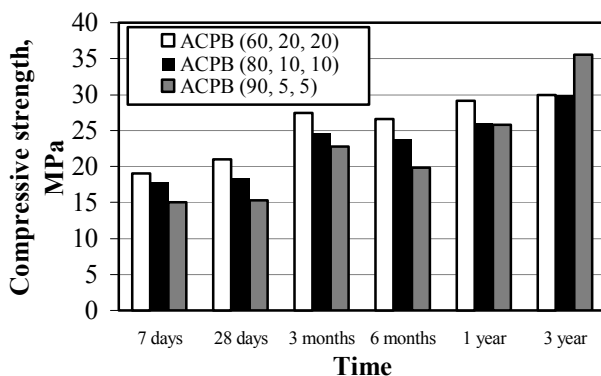


Fig. 6. The compressive strength of ACPB with different content of cement

hydration degree, the difference between GCPB strength and estimated ACPB strength of same density is gradually decreasing. Thus, the ACPB structure is strengthening along with generation and concretion of new formations of further anhydrite hydration. The influence of anhydrite component on longterm reinforcement of ACPB is confirmed also by the researches pursued into strength variations of compositions with lower cement content in moist environment (Fig. 6). One can see that for a certain period of time (up to 1 year), ACPB samples with higher

cement content (20 %) were stronger, however, after 3 years the samples with 10 % cement practically reached the same strength and as to samples with 5 %, they were even stronger.

So, the component of natural anhydrite not only enables to obtain high density of hardened material in a rather simple way, but also ensures longterm reinforcement of ACPB structure and considerably better hydraulic properties than in case of GCPB. By its character of hardening, strength and hydraulic properties, ACPB is close to cementitious binding materials and in some spheres of application can replace them. Since the major part of ACPB is constituted by not burned natural anhydrite powder, its use would allow for cutting down energy input and CO₂ emission and would contribute to realization of the programs related to reduction of greenhouse effect and energy saving.

CONCLUSIONS

The slower hardening component of natural anhydrite of compact crystalline structure provides specific properties to ACPB, such as longterm hardening, low porosity of hardened matrix and good hydraulic properties. At same plasticity of moulding mix, the density of hardened ACPB is approximately higher by 25 %, the strength after 28 days is higher by ~11 %, after 4 months by ~23 %, after 7 months by ~30 % than that of GCPB. Along with ACPB hardening, the slower generating new formations of dihydrate gypsum together with the new formations of cement hydration make the hardening structure considerably more resistant to water action. Contrary to GCPB, ACPB when hardened in water does not loose its strength, but is strengthening further.

The process of anhydrite hydration going on in ACPB, which is hardening in moist environment, lasts many years and over time (in our investigations after 3 years) the influence of hardening of anhydrite component on ACPB strength is already higher than that of cementitious component. It is established that in ACPB, which hardened for 15 years, a certain amount of not hydrated anhydrite still remains. According to character of hardening, strength and hydraulic properties, ACPB with natural anhydrite is close to cementitious binding materials and in some spheres of application can replace them.

REFERENCES

1. **Gailius, A., Kinuthia, J.** Editorial. Modern Building Materials and their Investigation Methods *Journal of Civil Engineering and Management* 15 (2) 2009: pp. 129–130.
2. **Neithalath, N; Persun, J., Hossain, A.** Hydration in High-performance Cementitious Systems Containing Vitreous Calcium Aluminosilicate or Silica Fume *Cement and Concrete Research* 39 (6) 2009: pp. 473–481.
3. **Zhang, J., Gong, C., Guo, Z., Zhang, M.** Engineered Cementitious Composite with Characteristic of Low Drying Shrinkage *Cement and Concrete Research* 39 (4) 2009: pp. 303–312.
4. **Kinuthia, J., Snelson, D., Gailius, A.** Sustainable Medium-Strength Concrete (CS-Concrete) from Coliery Spoil in South Wales UK *Journal of Civil Engineering and Management* 15 (2) 2009: pp. 149–157.

5. **Lasys, A., Kadūnas, V.** Lithuanian Anhydrite and Its Utilization *International Cement Review* 11 1994: pp. 39–41.
6. **Grigelis, A., et al.** Geology of the Lithuania. Monograph. Vilnius, Mokslo ir enciklopedijų leidykla, 1994: pp. 322–325 (in Lithuanian).
7. **Žvironaitė, J.** Anhydrite Rock Grinding Peculiarities and Investigation of Compositions with Anhydrite Aggregates *Chemical Technology (Cheminė technologija)* 2 (36) 2005: pp. 101–108 (in Lithuanian).
8. **Volzenskij, A. B., Feronskaja, A. V.** Gypsum Binder and Products. Moscow, Strojizdat, 1974: 326 p. (in Russian).
9. **Feronskaja, A. V.** The Development of Theory and Practice in the Field of Gypsum Binders *Building Materials (Stroitelnyje materialy)* 2 2000: pp. 26–28 (in Russian).
10. **Colak, A.** The Long-term Durability Performance of Gypsum-Portlandcement-Natural Pozzolan Blends *Cement and Concrete Research* 32 2002: pp. 109–115.
11. **Kovler, K.** Setting and Hardening of Gypsum-Portland Cement-Silica Fume Blends, Part1: Temperature and Setting Expansion *Cement and Concrete Research* 28 (3) 1998: pp. 423–437.
12. **Kovler, K.** Setting and Hardening of Gypsum-Portland Cement-Silica Fume Blends, Part 2: Early Strength, DTA, XRD, and SEM Observation *Cement and Concrete Research* 28 (4) 1998: pp. 523–531.
13. **Kaminskas, A., Pričkaitienė, J., Rimkevičius, M., Špokauskas, A.** Investigations of Water Resistance of Samples Made from Extractive Semi-hydrate Gypsum *Materials Science (Medžiagotyra)* 7 (1) 2001: pp. 44–47.
14. **Kaminskas, A., Gaidučis, S., Mačiulaitis, R.** Influence of Granulated Milled Slag Glass Additive on Extractive Hemihydrate Phosphogypsum Hardening *Materials Science (Medžiagotyra)* 13 (3) 2007: pp. 224–228.
15. **Shen, W., Zhou, M., Zhao, Q.** Study on Lime-fly Ash-phosphogypsum Binder *Construction and Building Materials* 21 2007: pp. 1480–1485.
16. **Alksnis, F. F.** Hardening and Destruction of Gypsum Cement Composite Materials. Leningrad, Strojizdat, 1988: 103 p. (in Russian).
17. **Žvironaitė, J., Gerulis, P., Kerienė, J.** Investigation of Anhydrite Cement Pozzolana Binding Material with Different Aggregates *The 9th International Conference Modern Building Materials, Structures and Techniques, Selected papers, Vol. I, Vilnius Gediminas Technical University, 2007*: pp. 219–223.
18. **Kaminskas, A., Žvironaitė, J.** The Peculiarities of Destructive Mineral Formation in Gypsum Cement Pozzolana Compositions *Technique and Technology of Silicate (Technika i technologija silikatov)* 3–4 2001: pp. 13–20 (in Russian).
19. TU 21 31-62-89 Gypsum Cement Pozzolana Binder (in Russian).
20. **Winnefeld, F., Lothenbach, B., Figi, R., Rytz, G., Plotze, M.** The Influence of Different Calcium Sulfates on the Hydration of Portland Cement – a Practical Study *ZKG International* 3 (58) 2005: pp. 62–70.
21. **Žvironaitė, J., Špokauskas, A.** Natural Anhydrite as Cement Setting Retarder *Chemical Technology (Cheminė technologija)* 1 (47) 2008: pp. 31–35 (in Lithuanian).
22. **Singh, M., Garg, M.,** Relationship between Mechanical Properties and Porosity of Water-resistant Gypsum Binder *Cement and Concrete Research* 3 (26) 1996: pp. 449–456.
23. **Sattler, H.** The Importance of Porosity for the Properties of Hardened Gypsum Plaster Products *ZKG International* 1 (50) 1997: pp. 54–62.
24. **Hernandez, F., Trivino, F., Menendez, I.** Reducing the Porosity of Hardened Hemihydrate Plaster by Impregnation with Salt Solution *ZKG International* 7 (49) 1996: pp. 408–411.
25. **Baranov, I. M.** New Composite Gypsum Products for Facing of Building Facades *Building Materials (Stroitelnyje materialy)* 6 2006: pp. 4–5 (in Russian).