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Production of Magnesium Binder Composites Using Local Raw Materials and Technogenic Products

Elvija Namsone
Riga Technical University
Faculty of Civil Engineering Institute of Materials and Structures
Riga, Latvia
elvija.namsone@inbox.lv

Genadijs Sahmenko
Riga Technical University
Faculty of Civil Engineering Institute of Materials and Structures
Riga, Latvia
genadijs.sahmenko@rtu.lv

Aleksandrs Korjakins
Riga Technical University
Faculty of Civil Engineering Institute of Materials and Structures
Riga, Latvia
aleks@latnet.lv

***Abstract* - Building sector is known as one of the biggest polluters, causing environmental pollution and carbon dioxide emissions, most of which are generated during the production process of building materials. Therefore, researchers and manufacturers have become increasingly interested in environmentally friendly materials with low energy consumption. Magnesium based cements are being studied as an alternative to a widespread material as Portland cement, thus reducing the temperature required for calcination. During this research, magnesium binder-based composites using two types of magnesium (local dolomite waste material and caustic magnesia) were produced. Within the framework of this study, several regimes of thermal treatment were used to produce low carbon dioxide and environmentally friendly magnesium binder composites. Physical, mechanical and thermal properties of obtained specimens were tested.**

Keywords - magnesium binder composites, magnesium-based cements, dolomite waste material, magnesium oxychloride cements

I. INTRODUCTION

Portland cement is currently one of the most produced and consumed materials in the world, with an average annual amount of production of 4.6 billion metric tons [1] – [3]. Building industry has significant impact on environment. About 8 % of the world's anthropogenic carbon dioxide (CO_2) emissions are related to the cement and concrete industries; cement is responsible for 95 % of the emissions during the production of concrete [1], [4].

Growing concerns excessive CO_2 emissions led to proposals for low-CO_2 alternative binders [1], [5], [6]. Such binders include magnesium oxide cements which, in combination with other materials, may be used as magnesium oxychloride cements, magnesium phosphate cements, magnesium silicate hydrate cements, etc. [1], [7]

Magnesite ($MgCO_3$) calcination is mainly used for the production of magnesium oxide to be used as raw materials of magnesium oxide-based cements [8], [9]. As another source of magnesite serves dolomite ($CaMg(CO_3)_2$) with larger deposits than magnesite [8], [10]. Magnesium oxide (MgO) forms during the calcination process of dolomite ores and dolomite has been already used as raw material to produce MgO-based cement [8], [11], [12]. Currently the most studied magnesium cements are magnesium oxychloride cement (MOC) and magnesium phosphate cement (MPC) [13].

Magnesium phosphate cement is obtained by a chemical reaction between MgO and soluble acid phosphate. These cements possess vital properties as follows: fast setting, high early strength, excellent fluidity, low shrinkage, high bonding strength, good biocompatibility [8], [14] – [17]. Therefore, MPC have been applied in the following areas: rapid repair, hazardous waste stabilization, biological materials, for the preparation process of foamed concrete and others [8], [13].

Magnesium oxychloride cement, also known as Sorel cement, first was invented in 1867 shortly after the invention of Portland cement [18], [19]. MOC is

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TABLE 1 CONTENT OF DOLOMITE SAMPLES

Content	Samples	
	LP	***LS***
$CaMg(CO_3)_2$ [%]	92 - 94	93 - 95
$CaCO_3$ [%]	2.1 – 3.6	1.5 – 2.5
SiO_2 [%]	other	other

obtained by a chemical reaction between MgO and magnesium chloride ($MgCl_2$) solution at ambient temperature, creating ternary system of MgO, $MgCl_2$ and water [23].

Compared to traditional Portland cement, MOC possesses: light weight, high early strength, good abrasion and corrosion resistance properties, low thermal conductivity [13], [18], [20] – [22]. MOC is widely used at: industrial floor production, grinding wheels. MOC is useful for decorative, fire protection, sound and thermal insulation panels production [18], [19].

Compared to the calcination temperature required for the production of Portland cement, it is many times lower for the production of MOC. Consequently, there is some interest in the construction industry for MOC, because these materials are energy efficiency and has been considered as environmentally friendly [23].

II. MATERIALS AND METHODS

A. Used materials

Magnesium binder compositions were prepared in laboratory conditions. Magnesium oxide (MgO) served as the main component and two types of magnesium were added during the experiment.

Caustic MgO CCM RKMH-F, produced by Austrian company "RHI AG Ltd" with 76 % MgO purity, calcined at 750^{o}C and size distribution 90 % < 30μm was used in the first experimental part.

Magnesium, produced from locally available dolomite waste material, obtained from Pļaviņu and Sīļukalns quarries in Latvia, was added in the second part of the research (compositions LP and LS).

TABLE 2 CAUSTIC MAGNESIUM BINDER COMPOSITIONS

Components [weight proportions]	Magnesium binder compositions					
	T1	***T2***	***T3***	***T4***	***T5***	***T6***
Sand	2.25	2.25	2.25	2.25	2.25	2.25
MgO	1	1	1	1	1	1
$MgCl_2$	0.75	0.63	0.50	0.75	0.63	0.50
H_2O	0	0.25	0.38	0	0.25	0.38
SF	0	0	0	0.13	0.13	0.13

TABLE 3 LIGHTWEIGHT MAGNEISUM BINDER COMPOSITIONS

Components [weight proportions]	Magnesium binder compositions	
	λ1	***λ2***
MgO	1	1
$MgCl_2$	0	0.87
H_2O	0.82	0.64
KP	0.92	0.60
PB-LUX	0.92	0.92

To determine CaMg $(CO_3)_2$ and $CaCO_3$ content in the samples with dolomite waste material, mineralogical analysis (XRD or X-ray diffraction analysis) was performed; the results are presented in Table 1. Performing literature review and differential thermal (DTA) and thermogravimetric (TGA) analyses, three regimes of calcination temperature (730^{o}C, 760^{o}C and 790^{O}C) were used.

Magnesium chloride hexahydrate $MgCl_2{\cdot}6H_2O$ (known as bischofite) containing 47 % $MgCl_2$ served as brine solution and was used at a ratio of 1:1 of mass to water.

Natural, washed sand with fraction size 0-1 mm, supplied by local company "Sakret", Latvia was added as a filler.

Microsilica or silica fume (SF) has fine particle size in a range from 1 µm to 15 nm. SF is pozzolanic additive with complementary cementing properties that helps to improve water resistance and durability of material [1], [24].

B. Magnesium binder compositions

In the first part of experimental study, magnesium binder compositions using technogenic product - caustic MgO were obtained. Six compositions (T1, T2, T3, T4, T5 and T6) with MgO/sand ratio 0.44 and containing variable amount of $MgCl_2$, SF and water were produced, see data in Table 2.

Two compositions (λ1 and λ2) of lightweight magnesium concrete were made. Monopotassium phosphate KH_2PO_4 fertiliser (KP) 0-52-35, supplied by "Prayon S.A." and with P_2O_5 content of at least 51.6 % was used for hardening of magnesia. Synthetic foaming agent "PB-Lux" was added with a ratio of PB-Lux/MgO 0.92 (data summarized in Table 3).

In the second part of the experimental research, compositions using local dolomite waste material were obtained (LP and LS, adding dolomite waste material from

Pļaviņu and Sīļukalna quarries, accordingly, see Table 4.) Magnesium oxychloride cement or Sorel cement mixes with three different calcination regimes and water/binder rations 0.4 and 0.35 were prepared.

TABLE 4 COMPOSITIONS USING DOLOMITE WASTE MATERIAL

Properties	**Magnesium binder compositions**	
	LP	***LS***
Temperature of calcination [^oC]	730	730
	760	760
	790	790
Ratio of water/binder	0.4	0.35

The use of recycled porous glass ceramic aggregates with three particle sizes (0.63-1.25 mm, 1.25-2.5 mm and 2.5-5.0 mm) resulted in lightweight concrete compositions (λP and λS) with water/binder ratio of 0.45, see Table 5.

C. Testing methods

To provide the maximum of MgO phase and the minimum of CaO phase, calcination of dolomite powder using three temperature regimes of 730^{o}C, 760^{o}C and 790^{o}C was performed.

In order to obtain a binder powder with a uniform consistency, the calcined dolomite material was subjected to grinding. The process of grinding was done by using planetary ball mill "Retsch PM 400" 220-230 V; 50/60 Hz and rotation speed 300 rpm. Fig.1 presents the obtained material before and after grinding. Dolomite material from Pļaviņu quarry (LP) was grinded 3.5 min and grinding time of dolomite from Sīļukalns quarry (LS) was 5.5 min. The results of grinding fineness are 75.6 % and 76 % (for LP and LS dolomites, respectively).

Universal testing machine "Zwick Z100" with the maximal test force of 100 kN was used to conduct the compressive strength test. The pressure was applied with 0.0005-600 mm/min speed. The samples were exposed under relative humidity conditions (~90-95 %) and temperature 15-20^{o}C; the dimensions of the test samples 50x50x50mm.

TABLE 5 LIGHTWEIGHT MAGNEISUM BINDER COMPOSITIONS

Properties	**Magnesium binder compositions**					
	λP			***λS***		
Particle fraction size [mm]	0.63-1.25	1.25-2.5	2.5-5.0	0.63-1.25	1.25-2.5	2.5-5.0
The amount of particles [wt%]	-	-	100	-	-	100
	20	40	40	20	40	40
Bulk density [kg/m^3]	225	186	170	225	186	170
Ratio of water/binder	0.45			0.45		

Fig. 1. Dolomite material before and after grinding.

Testing of thermal conductivity was carried out according to guidelines of the LVS EN 12667 standard. It was recorded by equipment for measuring the thermal flow "Laser Comp's FOX 600" with thermal conductivity range 0.01-0.2 W/mK. Testing parameters were determined at 0^{o}C for the upper and at 20^{o}C for the lower panel.

Specimens-plates were tested in a hardened and dried condition with the following geometry: 300x300x48 mm, 300x300x40 mm, 300x300x50 mm and 300x300x47 mm (for λ1, λ2 – compositions being prepared using caustic MgO and for λP and λS – compositions being made adding local dolomite waste material).

III. RESULTS AND DISCUSSION

A. Density and compressive strength

Samples obtained by adding both caustic MgO (compositions T1-T6) and dolomite powder from local quarries (compositions LP and LS) were subjected to a 7-day compressive test.

Analysing the results of caustic magnesia compositions, it can be seen that as the amount of $MgCl_2$ decreases, so do the strength values (data presented in Fig.2). For example, reducing the amount of $MgCl_2$ in the compositions T1-T3 by 66%, the compressive strength decreases in the range from 29.5 MPa to 9.2 MPa.

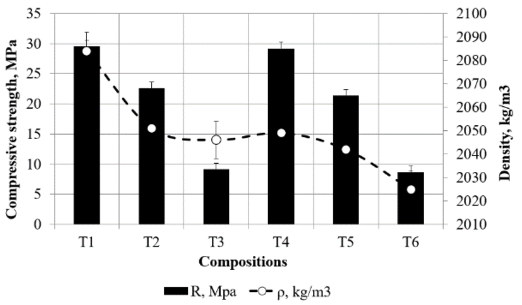

Fig. 2. Results of compressive strength test (using caustic magnesia).

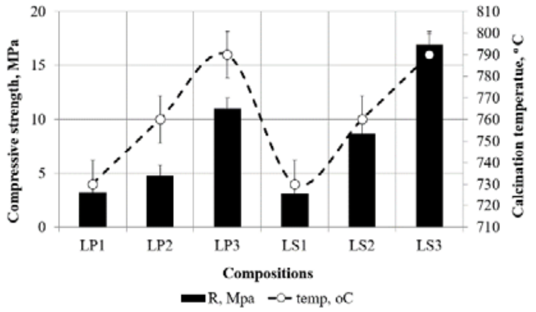

Fig. 3. Results of compressive strength test (using local dolomite waste material)

Summarizing the obtained data from the compositions in the production of which local dolomite powder was added, it can be concluded that the strength values depend on the calcination temperature (data presented in Fig.3). As the calcination temperature increases, the compressive strength also increases.

Maximal compressive strength values of the tested samples were obtained when more magnesium oxide was released during the calcination process. For both series (LP and LS), when dolomite powder from Pļaviņu (LP) and Sīļukalns (LS) quarries was added during production, the maximal strength was observed at a temperature of 790°C and was 7.73 MPa and 13.82 MPa higher than at 730°C calcination.

B. Water/binder ratio – compressive strength

A following relationship was observed between the water/binder ratio and the compressive strength (the corelation of water/binder ratio and compressive strength is presented in Fig.4): a higher water/binder ratio resulted in lower strength values.

The water/binder ratio increased from 0.25 to 0.45 and the values of compressive strength decreased from 29.5 MPa to 8.7 MPa when testing the specimens produced using technogenic product (caustic magnesia).

Compositions from local raw material (dolomite powder) included two water/binder ratios 0.4 (LP mixes) and 0.35 (LS mixes); the maximal strength value between LP series samples was 11.0 MPa while it was 17.0 MPa when LS series samples were tested.

C. Thermal conductivity

Thermal properties were tested on samples with caustic magnesia and synthetic foaming agent (λ1, λ2 compositions) and on samples with dolomite waste material and granulated aggregate (porous ceramics) (λP, λS compositions), see the results of thermal conductivity test in Fig.5.

Density values of 348 kg/m^3 and 305 kg/m^3 were obtained using synthetic foaming agent (λ1, λ2), but for compositions with porous glass ceramics (λP, λS) it was about two times higher. With the increase of density values, the coefficient of thermal conductivity also increased. The coefficient was 0.088 W/mK and 0.07 W/mK for the compositions with technogenic product used (caustic magnesia), and it was 0.115 W/mK and

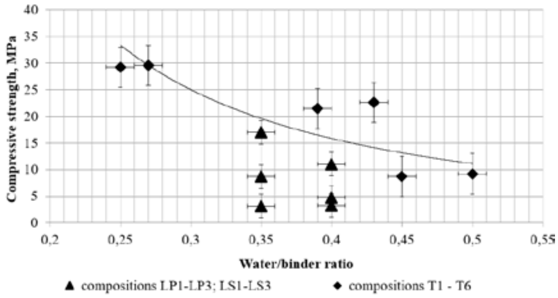

Fig. 4. Corelation of water/binder ratio and compressive strength

0.097 W/mK for the compositions with local raw material (dolomite powder).

Comparing to the results from similar mixes, it can be concluded that the values of coefficient of thermal conductivity decrease with the increase of the amount of $MgCl_2$ (caustic magnesia compositions). When comparing to the data obtained using the porous ceramics of three fractions, it can be seen the results are quite similar: density of λP – 613 kg/m^3 and of λS – 600 kg/m^3.

IV. Conclusions

In the experimental part of the research, two series of magnesium binder compositions were prepared by using technogenic product (caustic magnesia, produced by “RHI AG”, Austria) with an average density value 2050 kg/m^3 and 7-day compressive strength value 20.1 MPa (values were in the range of 8.7-29.5 MPa); and by using local raw material (dolomite powder from Pļaviņu and Sīļukalna quarries in Latvia) with the values of 7-day compressive strength 3.27-17.0 MPa.

The results of the research allow to conclude that calcination temperature affects the strength values. Analysing local dolomite powder compositions, it was observed that with the increase of the calcination temperature, when more magnesium oxide is released, the maximal strength values of these samples were obtained. Specimens produced using dolomite from Pļaviņu quarry at calcination temperature 790°C showed average strength value 11.0 MPa, but samples using Sīļukalns dolomite material at the same temperature had 7-day compressive strength of 17.0 MPa. While testing the prepared specimens with a calcination temperature of 730ºC, about 70 % and 81 % lower compressive strength values were obtained.

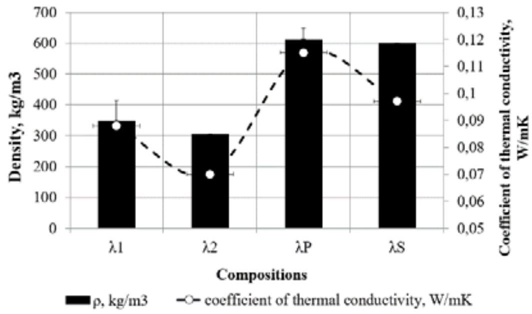

Fig. 5. Results of thermal conductivity test

It was also observed that the amount of magnesium chloride also affects the strength values – as the magnesium chloride content of the mixtures decreased, the compressive strength values also decreased. Addition of 66 % less magnesium chloride to the compositions resulted in a 70 % reduction in strength values (for the T4-T6 compositions from 29.2 MPa to 8.7 MPa).

The results of the study show that a higher water/binder ratio resulted in lower 7-day compressive strength values. Using caustic magnesia, the tested specimens showed about 70.1 % lower values when increasing water/binder ratio from 0.25 to 0.45. Using dolomite waste material and increasing the ratio by 13%, an average compressive strength values decreased in a range from 9.6 MPa to 6.3 MPa.

The use of synthetic foaming agent in the production of lightweight magnesium binder compositions resulted in 43.2 % and 49.2 % lower density values, and in 23.5 % and 28 % lower values of coefficient of thermal conductivity, comparing to the results of the specimens being prepared by adding porous glass ceramics aggregate.

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