

Prospects for Effective Use of Dolomite in Concrete Compositions

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Abstract – The article discusses possibilities for creating sustainable concrete compositions from local dolomite raw materials. In the first part of the article, practical examples of the use of dolomite quarry by-products (siftings) as a component of concrete mixes are summarized. The second part of article presents experimental study on obtaining caustic dolomite. This method allows obtaining the product with higher added value. Local dolomite raw materials are used and appropriate regimes of thermal treatment have been tested.

Keywords – Dolomite, magnesia cement, sustainable binding material, X-ray test.

I. INTRODUCTION

Dolomite is a widespread sedimentary rock in the flatland part of Europe. It is commonly used in road and building construction for foundation bases and as an aggregate for cement and asphalt concrete. It is considered that dolomite has reduced mechanical properties and reduced resistance against freeze-thaw cycles, comparing to magmatic rock. Therefore, building regulations considerably restrict the use of dolomite rock for concrete exposed to freezing and thawing cycles. At the same time, dolomite aggregate has some benefits. A lot of studies confirm the formation of better contact zone cement paste – aggregate in the case of carbonate aggregate.

Monteiro and Mehta concluded that a hydrated calcium carbonate-calcium hydroxide compound is formed at the interface and formation of smaller calcium hydroxide crystals appears to be responsible for the strengthening of the transition zone [1].

The authors [2] studied the contact zone between cement paste and major concrete minerals (field spar, calcite, quartz, opal and chalcedony). It was found that all the mentioned minerals, except for quartz, begin interacting chemically with the cement paste, which causes weakening of the contact zone of cement paste.

Kayyali [3] confirmed formation of good contact zone between cement paste and carbonate rock.

The benefits of the use of magmatic rocks as concrete aggregate are arguable. The main problem of magmatic rock is alkali-silica reactions between silica aggregate and alkalines presented in cement [4].

Dolomite is a cheap and locally available material in the regions where magmatic rocks are unavailable. A lot of experimental and practical results confirm possibilities to produce excellent concrete compositions from locally available dolomite.

Other perspective application of dolomite rock is obtaining dolomite lime and magnesium binder (caustic dolomite) as binding materials for mortar and concrete. Magnesium binder has a lot of advantages, specifically it provides good contact zone with organic natural fiber aggregate.

The first part of this article presents a review of the works devoted to the use of local dolomite resources as filler in different concrete mixtures as well as to the application of dolomite lime in natural fiber composites. The second part of the article discusses application potential of dolomite lime and some experimental results on technology of producing magnesium cement from local dolomite rocks. Thereby, the objectives of this research are to find the most effective and appropriate ways for utilizing local dolomite.

II. REVIEW OF USE OF LOCAL DOLOMITE AS COMPONENT OF CONCRETE MIXTURES

There is a significant amount of small dolomite fractions remaining as the secondary product of dolomite quarries. The problem of its rational utilisation has not been solved yet. The secondary product of dolomite quarries is a multi-fractional mix (particle size range from 0.1 mm up to 8 mm) – see Fig. 1. It may contain up to 30 % of fine and ultra-fine particles (<100 µm), which may be used as a micro-filler. It should be noted that micro-filler is an important component of modern concrete mixtures. The first function of micro filler is preventing segregation in highly workable mixes [5]. The second function is filling micro voids creating more dense microstructure and increasing impermeability [6].



Fig. 1. Unfractionated dolomite by-product (left) and fractions after sieve size analysis (right).

There have been a lot of efforts to incorporate secondary dolomite raw materials in the self-compacting concrete (SCC) as a micro-filler. Positive results were obtained by researchers Rudžionis et al. [7]. Previous studies done by authors [8] show that replacing traditional quartz sand by dolomite sand slightly increases water absorption, but in spite of this fact, resistance against freeze-thaw cycles up to F150 is achieved in all cases.

Also dolomite by-product has been tested in the lightweight aggregate concrete (LWAC) compositions. This type of LWAC

consists of cement, silica sand and expanded clay (exclay aggregate), the most popular lightweight aggregate. In these experiments natural sand has been replaced by dolomite sand containing fractions smaller than 8 mm and ultra-fine particles <0.1 mm. LWAC based on dolomite sand insures the same mechanical properties and water impermeability as LWAC prepared with natural sand. Compressive strength close to 25 MPa is achieved for both compositions. Furthermore, the incorporation of dolomite by-products improved the workability and stability of the produced mixes [9].

Lightweight aggregate concrete blocks find wide application in modern building construction, mainly as a wall material. The most popular material is exclay blocks, which are characterized by highly porous structure and are produced using vibro-pressing technology. In accordance with [10], silica sand may be replaced by secondary dolomite sand in vibro-pressed LWAC blocks. The obtained blocks with dolomite sand are characterized by the same compressive strength; density reduction effect up to 45 kg/m³ was achieved.

Summarizing the above mentioned research, it may be noted that angular shape and porous surface of secondary dolomite aggregate particles is a limiting factor regarding mix flowability. It may be compensated by the use of appropriate plasticizers and silica fume admixtures. Another serious drawback of the secondary dolomite aggregate is heterogeneity of the mix and particle agglomeration during exposed storing. It may be compensated using intensive mixing technology. Other method of dolomite deep treatment included its thermal processing and further grinding.

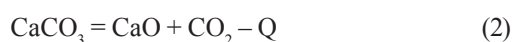
III. DOLOMITE LIME AND MAGNESIA AS BINDING AGENTS (REVIEW)

Producing a binding agent is an alternative way for rational use of dolomite resources. This method envisions thermal treatment of dolomite raw materials. Depending on the temperature of thermal treatment, different kinds of binding agents may be obtained.

Thermal decomposition of dolomite takes place in the temperature range of 700 – 900 °C, and thermograms show two peaks of endothermic effects, consequently, the process takes place in two stages. In the first stage of dissociation MgO and CaCO₃ are formed:



and CaO in the second stage:



Moreover, contradictory data on dolomite calcining reported in the literature appears to refer mainly to different compositions of raw materials and modes of calcining. According to [11], endothermic effect corresponding to decomposition of magnesia component appears within the temperature range 720 – 760 °C, and of calcium one – within the range 895 – 910 °C. Based on [12], the main peaks of dolomite decomposition endoeffects are

observed at 810 °C and 900 °C, in addition, partial overlapping of dissociation processes was recorded.

Dolomite lime production process takes place at the temperature close to 1000 °C, providing full decomposition and formation of calcium and magnesium oxides. Dolomite lime hardening is based mainly on carbonation of calcium hydroxide, like in the natural lime. Magnum oxide in this case is over-burned and non-reactive (so called “dead” magnum oxide). At the same time, some kinds of dolomite lime show much better strength properties comparing to lime. This effect may be explained by the presence of hydraulic admixtures when coal fuel is used.

In the previous experiments, compressive strength of dolomite lime mortar samples has been compared to various types of air lime [13], summarized in Table I. To enhance the compressive strength and to make the limes more hydraulic a pozzolanic additive metakaolin was added. Experiments were carried out on mortar samples when sufficient amount of amorphous SiO₂ material was added to hydrated lime. In presence of water it creates calcium silicate hydrate or C-S-H:



TABLE I
LIME USED IN SAMPLE PREPARATION

Name	CaO+ MgO content, %	Active lime, %	Bulk density, kg/m ³	Color	Producer
Hydrated lime CL90	>90	>80	627	white	Lhoist Bukowa. PL
Hydrated lime CL80	>80	>65	417	white	Krasnosolsk- strojmateriالي
Quicklime DL60	>60	X	807	grey	Saulkalne. LV

Mix compositions of lime with metakaolin are summarized in Table II. For each type of lime, four different proportions of metakaolin were added – 0 %, 5 %, 10 % and 20 %. and ratio is 1 : 2.

TABLE II
COMPOSITION TO TEST REACTIVITY OF LIMES

Sample name	Lime type	Lime, g	Meta, g	Sand, g	Water, g	Hydr. Add, %
C0	CL90	300	0	600	266	0 %
C1	CL90	285	15	600	266	5.0 %
C2	CL90	270	30	600	266	10.0 %
C3	CL90	240	60	600	266	20.0 %
C4	CL80	300	0	600	300	0 %
C5	CL80	285	15	600	300	5.0 %
C6	CL80	270	30	600	300	10.0 %
C7	CL80	240	60	600	300	20.0 %
C8	DL60	300	0	600	200	0 %
C9	DL60	285	15	600	200	5.0 %
C10	DL60	270	30	600	200	10.0 %
C11	DL60	240	60	600	200	20.0 %

The results seen in Fig. 2 show that addition of metakaolin significantly increases compressive strength of all types of lime. For CL90 20 % of metakaolin increased the strength by 3.37 MPa, for CL80 – by 1.72 MPa and for DL60 – by 4.27 MPa. Initial strength is also higher for DL60, which is explained by the admixtures from the coal fuel used.

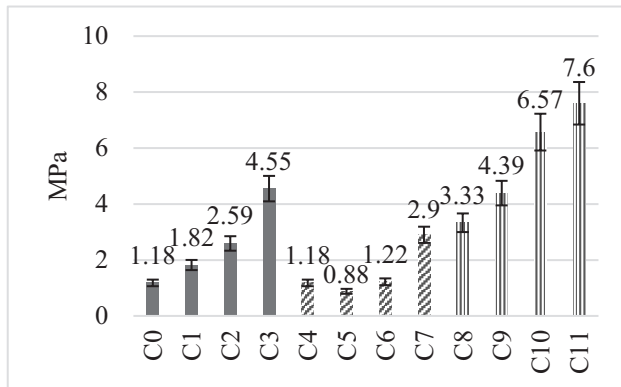


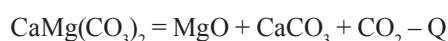
Fig. 2. Strength results of various air limes with metakaolin.

In modern construction, such limes with enhanced strength are used as binders for natural fiber composites, mainly for lime-hemp concrete (LHC). These materials are made from hemp shives that are by-products of hemp-fibre production; they act as a filler and hydraulic lime as a binder. They are used as self bearing wall insulation materials that are used together with load-bearing timber frame. They have good thermal insulation capabilities (around 0.07 W/m·K) [14], high water vapour permeability, good acoustical and fire resistance properties [15].

LHC materials also have negative CO₂ balance [16], which means that these materials sequester more CO₂ than is released in its production. There are two main contributors to this CO₂ absorption – hemp stalks sequester carbon dioxide through photosynthesis and hydrated lime in the binder hardens by carbonisation [17]. This is one of the reasons why lime and dolomitic lime are used in these materials. Lime also contributes to water vapour permeability, fire resistance properties and improves the resistance to bio-degradation.

IV. PRODUCTION OF MAGNESIA BINDER FROM DOLOMITE

It is known that dolomite decomposition takes place within the temperature range of 700 – 900 °C, where thermograms normally show two peaks of endothermic effects, consequently the process takes place in two stages. In the first stage of dissociation MgO and CaCO₃ are formed:



and CaO in the second stage:



Moreover, contradictory data on dolomite calcining reported in the literature appears to refer mainly to different compositions

of raw materials and modes of calcining. According to [11], endothermic effect corresponding to decomposition of magnesia component appears within the temperature range 720 – 760 °C, and of calcium one – within the range 895 – 910 °C. Based on [12], the main peaks of dolomite decomposition endoeffects are observed at 810 °C and 900 °C, in addition, partial overlapping of dissociation processes was recorded.

Multiple subsequent studies [18], [19], [20], [21] report that the main problem of binder production from dolomite is absence of sharp boundary between decomposition of CaCO₃ and MgCO₃. All authors agree upon negative effect of calcium oxide, leading to decrease of strength and water resistance of the forming rock. Thus, to obtain caustic dolomite, calcining should be performed so that the product would contain as much MgO as possible and not more than 1 – 2 % CaO, which is highly complicated.

Existing literature data analysis allows concluding that:

- it is possible to produce a high-strength binder from dolomite rocks. At the same time, widespread occurrence of dolomite rocks that allows avoiding significant transportation costs and comparatively low temperature of calcining make production of binder from dolomite a promising solution for construction industry;
- it is necessary to search for opportunities to control calcining processes to ensure that minimal decomposition of calcium component occurs at most complete decarbonization of magnesia component. Analysis of literature shows that depending on rock deposits, due to differences in chemical composition, original rock impurities, dolomite crystallization, calcined rock size distribution and other factors, both calcining temperature range and the needed isothermal exposure times vary.

V. MATERIALS AND METHODS

The mineralogical composition was determined by X ray diffraction methods using “D8 Advance” diffractometer (Bruker AXS, Germany) under the following survey conditions: an X-ray tube – copper (CuKα-radiation), with a nickel filter. The X-ray tube voltage is 40 kV, current – 40 mA, exposure – 1.1 hour, sample diameter – 10 mm; goniometer rotation rate – 4 deg/min; time constant – 1.0 sec; impulse counting rate – 1·10⁴ imp./sec.

The scope of this research included comparative analysis of specifics of magnesia binder production from dolomite residues of two quarries in the Vladimir Region – Andreyevsky (the Sudogodsk Region) and Melehovsky (The Kovrov Region) further referred to as (A) and (K) respectively.

The mineralogical composition of the raw material of two quarries is given in Table III.

Technical magnesia chloride (bishofite MgCl₂·6H₂O) was used as the grouting fluid.

To obtain magnesia binder and to determine optimal calcining temperatures that provide a maximum yield of MgO phase, at the minimum yield of CaO phase, dolomite powder was calcined during 1 hour in the kiln at the temperature of 600 °C – 900 °C. Also the effect of calcining duration was investigated at the temperatures 780 °C, 820 °C and 840 °C. An example of phase composition of the calcined dolomite is presented in Fig. 3.

TABLE III
MINERALOGICAL COMPOSITION OF USED DOLOMITE SAMPLES

Compound name	Chemical formula	Space group		Y-Scale (%)		S-Q (%)	
		A	K	A	K	A	K
Dolomite	$\text{CaMg}(\text{CO}_3)_2$	R-3 (148)	R-3 (148)	89.83	89.04	98.51	95.10
Quartz	SiO_2	P3221 (154)	P3221 (154)	4.64	1.86	1.49	0.99
Calcite	CaCO_3	R-3c (167)	R-3c (167)	—	3.66		3.91

The summarized X-ray test results for calcined samples at various temperatures and exposure times are presented in Table IV.

Based on the data presented in Table IV, the following conclusions can be made:

- the maximum possible yield of MgO phase that forms during calcining of the dolomite taken directly from different quarries (crushing residues) does not exceed 30–35 %.
- the calcining temperature range letting MgO form most actively lies in the range 800 – 900 °C for the tested materials;
- the maximum amount of CaO phase is formed in the same temperature range, the maximum yield is recorded in the range around 900 °C;
- fineness of pre-ground dolomite does not have significant influence on the temperature range producing the maximum MgO yields.

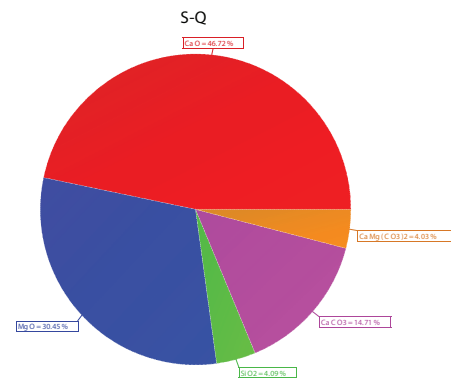
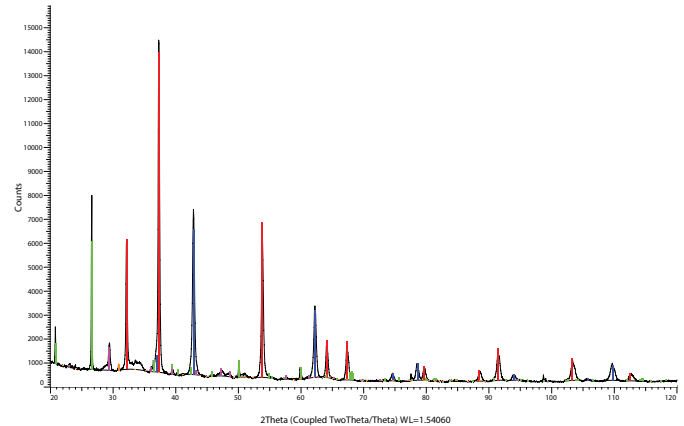


Fig. 3. Results of X-Ray analysis of dolomite sample (No. A) calcined at 800 °C during 60 minutes.

TABLE IV
INFLUENCE OF CALCINING REGIME ON BINDER CHEMICAL COMPOSITION (SUMMARY)

(A)											
		MgO		CaO		CaCO ₃		SiO ₂		CaMg(CO ₃) ₂	
600 °C 1 hour	coarse					0.74		1.16		98.10	
	midle					0.37		2.35		97.28	
	fine	0.33				0.46		1.76		97.45	
700 °C	coarse	3.6				5.7		1.13		89.57	
	fine	3.29				5.26		3.41		88.04	
800 °C	coarse	30.02		39.77		19.07		3.69		7.45	
	fine	30.45		46.72		4.03		4.09			
900 °C	coarse	33.89		64.21				1.9			
	fine	33.74		59.06		5.3		1.89			
750 °C											
10 min.		0.61				4.16		2.66		92.56	
20 min.		1.22				5.31		2.22		91.24	
30 min.		1.19				5.85		2.21		90.75	
		A	K	A	K	A	K	A	K	A	K
Initial							3.91	1.49	0.99	98.51	96.10
780 °C	30 min.	15.26	4.16	10.60	1.99	44.72	28.17	3.52	1.58	25.89	64.09
	60 min.	8.34	11.05	1.43	9.61	9.0	59.56	1.07	1.32	80.17	18.46
	80 min.	25.52	25.89	28.76	49.14	39.71	21.81	3.76	2.14	3.49	
820 °C	10 min.				0.96		7.46	1.77	0.76	98.23	90.83
	30 min.	15.63	22.67	14.56	35.3	63.24	40.76	3.19	1.28	3.38	
	60 min.	33.78	29.03	64.57	68.6			1.65	1.51	0.86	
840 °C	30 min.	29.79	28.1	64.77	62.34	3.85	8.33	1.60	1.32		

To determine calcining temperature intervals more accurately, thermal tests with use of thermal analysis techniques were conducted: thermogravimetric analysis, differential scanning calorimetry and differential thermal analysis.

Fig. 4 and Fig. 5 show thermal analysis data for dolomite samples from two quarries, which demonstrate that decomposition temperatures of magnesium and calcium components are found to be located close (811 and 841 °C for the Kovrov quarry and coincide to those of the Andreyev quarry (810 °C).

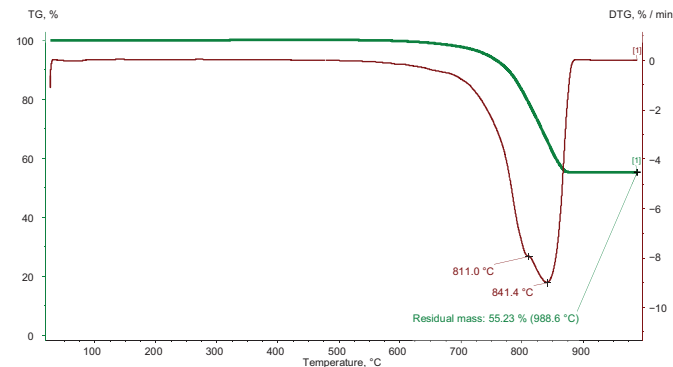


Fig. 4. K Sample TGA. Green curve – TG. Brown curve – DTG. Residual mass 55.2 % masses.

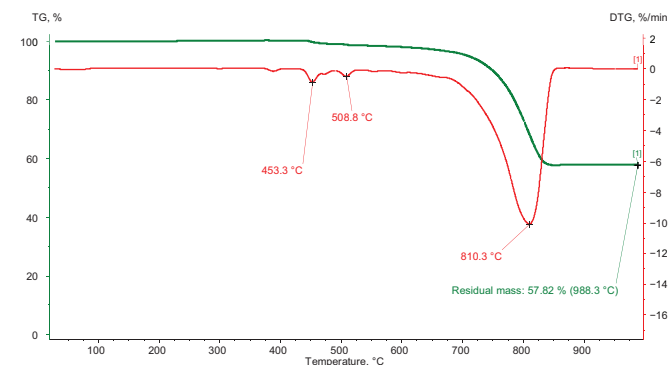


Fig. 5. A Sample TGA. Green curve – TG. Red curve – DTG. Residual mass 57.8 % masses.

Two peaks at 453 and 509 °C possibly refer to sample dehydration. Furthermore, there is a chance of the main TG curve drift due to structural heterogeneity of the sample. The sample is represented by a set of hard fine particles (not powder) and that is why primary decomposition of these particles is accompanied by mechanic destruction and mass loss curve drift.

The study of the microstructure of the forming cement paste during hydration was done with help of raster electron microscopy equipped with local chemical analysis add-on.

Fig. 6 (a) shows typical structure, resulting from hydration of magnesia binder, consisting of individual micro-sized particles of $Mg(OH)_2$ that form dense conglomerates, their zoomed image (arrow-marked) is shown in Fig. 6 (b). Furthermore, in certain areas that make 30–40 % of the total amount acicular crystals of magnesia oxichlorides have been identified.

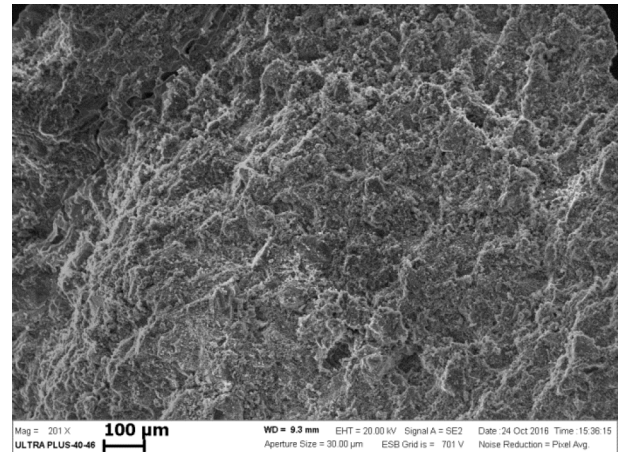


Fig. 6 (a). Typical micro structure of hydrated magnesia cement.

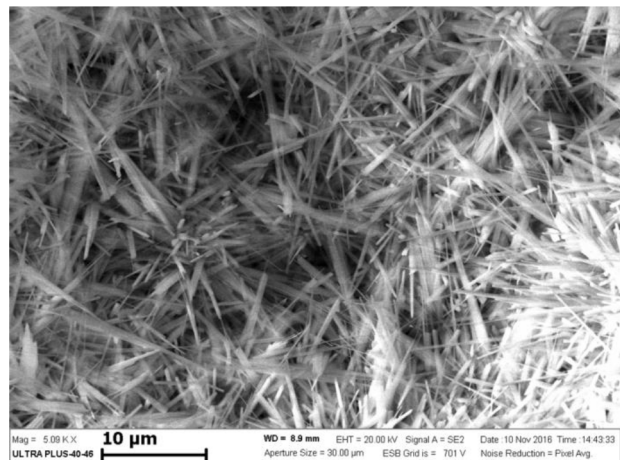


Fig. 6 (b). Acicular crystals of magnesia oxichlorides have been identified.

VI. CONCLUSION

Sedimentary rock dolomite nowadays is the basic source of coarse aggregate in building construction. Complex approach to rational use of dolomite resources provides for complete use of by-products of dolomite quarries. The first observed direction is the use of dolomite fines as a fine component in modern concrete, it is confirmed that by-products of dolomite quarry (fine fractions) may be successfully used as micro-filler in self-compacted concrete, allowing to achieve high (up to S3 flow class) workable mix. They can be also used as effective micro filler in lightweight aggregate concrete and exclay concrete wall blocks.

The second observed direction is obtaining caustic dolomite for binding agent in magnesium binders. It has been concluded that calcining duration and temperature are important factors of dolomite preparation.

Rational use of dolomite resources very closely corresponds to the conception of sustainability and life cycle of building materials.

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