

The Potential Use of Calcite Wastes in The Production of Clay Masonry Units

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Abstract

The use of carbonate wastes in ceramic masonry units production might be an environmental friendly way to utilize them. While the presence of coarse-grained calcite in the clay raw material can lead to destruction of the fired product, the controlled amount of fine-grained calcite addition can lead to enhancement of ceramic material properties. Such a fine-grained calcite is present in wastes from limestone aggregates washing and also from Maerz furnace bag filters.

This paper presents laboratory research on the usefulness of carbonate wastes in production of ceramic masonry units. As additives to kaolinite-illite clay, the waste from washing limestone aggregates and the waste from Maerz furnace bag filters were used. As a comparison, ceramic material with the addition of pure calcite to clay also was made.

Selected properties of ceramics materials such as water absorption, porosity, density, frost resistance, and compressive strength were determined. The addition of wastes and calcite to raw material mixtures was at a level of 5%, 10% or 15% by weight. The firing temperature were 950 °C and 1050 °C.

Studies confirmed the possibility of use of the calcite wastes as an additive in production of ceramic masonry units protected and unprotected from external factors (according to PN-EN 771-1).

Keywords: Calcareous waste, Calcite, Building ceramics, Frost resistance

ANALIZA MOŻLIWOŚCI ZASTOSOWANIA ODPADÓW WĘGLANOWYCH W PRODUKCJI CERAMICZNYCH ELEMENTÓW MUROWYCH

Zastosowanie odpadów węglanowych w produkcji ceramicznych elementów murowych może przynieść korzyści ekologiczne. Podczas gdy obecność gruboziarnistego węglanu wapnia w surowcach ilastych jest szkodliwa, to kontrolowana ilość drobnoziarnistego węglanu wapnia, dodana do iłu ceramicznego, może poprawiać właściwości tworzyw. Taki drobnoziarnisty węglan wapnia jest obecny w odpadach z płukania kruszyw wapniennych oraz w pyłach z filtrów workowych zamieszczonych przy piecu Maerza.

Niniejsza praca przedstawia badania laboratoryjne użyteczności odpadów węglanowych w produkcji ceramicznych elementów murowych. Jako dodatki do gliny kaolinitowo-illitowej zastosowano odpad z płukania kruszyw wapniennych i pył z filtrów workowych zamieszczonych przy piecu Maerza. Otrzymane wyniki porównano z wynikami otrzymanymi w przypadku tworzyw wykonanych z mas na bazie iłu z dodatkiem czystego węglanu wapnia. W pracy przedstawiono wybrane właściwości uzyskanych tworzyw, tj. absorpcje wody, porowatość, gęstość i wytrzymałość na ściskanie. Dodatki węglanowe do mieszanin surowcowych wprowadzano na poziomie 5%, 10% lub 15% masowych. Zastosowano temperatury wypalania równe 950°C i 1050°C.

Badania potwierdziły możliwość zastosowania uzyskanych tworzyw jako elementów murowych do zastosowania w murach zabezpieczonych oraz niezabezpieczonych (wg PN-EN 771-1).

Słowa kluczowe: odpady wapienne, kalcyt, ceramiczne materiały budowlane, mrozoodporność

1. Introduction

In the last ten years, studies on the effect of calcium carbonate on properties of building ceramics have become popular [1-15], but their results are inconclusive [16]. In ceramic building materials technology the presence of calcium carbonate admixtures in raw materials is a very important issue. The calcium carbonate has different influence on the properties of ceramic building materials, depending on the particle size and its distribution form in raw materials.

It was found unquestionably that calcium carbonate with a particle size larger than 0.5 mm (commonly called "marl") is a harmful admixture and can cause destruction of building ceramics. Until today in industrial practice, many complex methods of disposal of "marl" are used. These methods primarily rely on its grinding to the silty form. These methods increase the cost of production, but allow using the marly clay resources.

The silty calcium carbonate in raw clay is not a harmful impurity, but in comparison with non-calcareous raw-clay, it significantly changes the course of sintering and properties of the product.

Although calcareous raw clays are used in the building ceramics technology, up till now, the addition of fine calcium carbonate to the building ceramic masses has not been used on a large scale [1], and the opinion about its effect on sintering and properties of the products are divided. Despite the relatively large literature resources in this theme, there is no comprehensive and universal development, which could be used in the technology of building ceramics. Until now the use of carbonate raw materials as additives in the manufacture of fired ceramics is known, comprising glazed ceramic tiles, stove tiles, earthenware, stoneware, and majolica [17]. These products differ from the fired ceramic building materials in the manufacturing technique (with respect to the process of shaping and firing temperatures) and the type of major raw materials (they are mainly lightfiring kaolinite clays). Illite-kaolinite and kaolinite-illite clays are most commonly used in ceramic building technology. These clays sinter at much lower temperatures than the kaolinite clays. Diversity of technological processes and clay raw materials used produce difficulties in the application of carbonate additives in building ceramics.

Continuous development of the construction industry and regulations imposed by the European Union make the producers of building ceramics to improve the production technology and the quality of products. The improvement of production technology is understood as the use of modern methods of mass production, forming, drying and firing, which increase the production capacity and quality of products, while reducing the energy consumption. The latter one is also achieved by applying the low-sintered additives to raw mixtures, which allow reducing the firing temperature. Another challenge for manufacturers of building ceramics is to reduce production costs. It may be achieved by using waste materials as a substitute for the major raw material or additives modifying the properties of the product.

The aim of this study is a detailed analysis of the impact of fine calcium carbonate wastes on the sintering of ceramic masses made of domestic triassic raw clay with the addition of a various amount of calcite wastes. The effect of wastes on properties of the building ceramics is also studied.

2. Methodology

Based on the previously obtained results [16], Triassic clay from Patoka deposits was selected to prepare masses for sintering. Waste from washing limestone aggregates (marked as N) and waste from Maerz furnace bag filters (marked as L) were used as additives to the masses. An additive of pure calcite (marked as CC) was also applied for comparison purposes. The calcite additive to raw materials mixtures was 5%, 10% and 15% by weight, and the wastes were incorporated to masses to match the same resultant CaO contents. Test samples were formed from plastic masses by extrusion. The firing temperatures were selected to be 950 °C and 1050 °C. The study was divided into three stages: (i) characteristics of raw materials, (ii) determination of application properties of fired bodies, (iii) studies of the phase composition and microstructure of final materials.

The raw materials were subjected to analysis of chemical composition by X-ray fluorescence, using a PANalytical Axios^{mAX}-Advanced sequential WD-XRF spectrometer equipped with 4 kW Rh operating power. Particle size of the additives was determined using a laser Malvern Master-Sizer 2000 analyser. Apparent and real densities, open and closed porosity, water absorption, bending and compressive strengths, and frost resistance were examined for final materials, according to methods described in Ref. [16].

A detailed analysis of the phase composition of final materials was carried out by the XRD method (a Phillips PW-1040 analyser) in the 20 measuring range 5-60°. The microstructure of materials was observed using a scanning electron microscope FEI Nova NanoSEM 200 with an EDS attachment.

3. Results and discussion

3.1. Raw materials analysis

The chemical compositions of the mass components was shown in Table 1. The clay was of the red deposit type; it had high content of Fe_2O_3 , which may act as a fluxing agent [1]. Moreover, it was of the non-calcareous clay type. The waste from washing limestone aggregates (N) had the smallest content of CaO among all additives. It is due to the presence of clay minerals, which constitute about 20 wt.%, according to

Table 1. Chemical composition ([wt.%], semi-quantitative analysis) and loss on ignition of mass components. Tabela 1. Skład chemiczny ([% mas.], analiza półilościowa) i straty prażenia surowców.

Oxide	Clay	CC	N	L
SiO ₂	56.44	0.10	10.94	1.11
Al ₂ O ₃	20.51	0.10	4.69	0.55
Fe ₂ O ₃	9.08	-	1.67	0.18
TiO ₂	0.94	-	-	0.03
CaO	0.25	54.55	44.26	54.78
MgO	1.04	0.10	0.45	0.19
K ₂ O	1.89	-	0.63	0.15
Na₂O	0.07	-	0.06	0.05
SO ₃	0.05	0.01	0.06	0.11
P ₂ O ₅	0.08	-	0.09	0.01
CI	0.01	0.00	0.01	0.16
Sum	99.75	99.99	99.17	99.99
LOI [%]	9.40	45.12	36.14	42.64

Description of symbols: CC - pure calcium carbonate, N - waste from washing limestone aggregates, <math>L - waste from Maerz furnace bag filters, LOI - loss on ignition.

XRD and DTA results not presented in this article. $Ca(OH)_2$, free CaO and SiO₂ were also present in the waste from Maerz furnace bag filters (L). During compiling the raw materials mixtures, the composition was calculated, so that the amount of CaO in each sample added with the waste corresponded to the CaO amount in the respective mixture contaning 5%, 10% and 15% by weight of calcite (CC).

Grain size distributions of the additives with marked modes are shown in Fig. 1. The median value of the CC, N and L additive is 44.906 μ m, 23.467 μ m, and 6.0201 μ m, respectively. Hence, the most fine-grained additive is the waste from Maerz furnace bag filters, and the most coarse-grained additive is the pure calcium carbonate. Despite the content of clay particles in the waste from washing limestone aggregates, it has the intermediate grain composition.

3.2. Materials properties

The properties of materials fired at 950°C and 1050°C are shown in Table 2 and Table 3, respectively. For both of the firing temperatures only the smallest N additive (5% sample) caused a small increase in apparent density. In other cases



Fig. 1. Grain size distributions of additives. Rys. 1. Składy granulometryczne dodatków.

Table 2. Properties of materials fired at 950 °C. Tabela 2. Właściwości tworzyw wypalonych w 950 °C.

all types and amounts of the additives caused a decrease in apparent density which was the greater the larger was the addition amount.

The real density is a function of all crystalline and amorphous components of material. Therefore, the results must be commented in relation to the actual phase composition of the studied materials, which is presented in detail further, indicating the presence of quartz, mullite, hematite, gehlenite, anorthite, calcium sulfate and gypsum. According to the mineral data base [18], the real density of the mentioned phases is 2.62 g/cm³, 3.05 g/cm³, 5.30 g/cm³, 2.98 g/cm³, 2.73 g/cm³, 2.97 g/cm³, and 2.30 g/cm³, respectively. The real density and content of amorphous component are not known, so assuming the constancy of the amorphous phase it is possible to conclude only that the real density can decrease with decreasing the amount of hematite, mullite, gehlenite and calcium sulfate.

Open porosity and water absorption are the properties connected together. Therefore, both of them increased proportionally with the increasing amount of the CC addition for materials fired at 950°C (Table 2), and did not change significantly for materials fired at 1050°C (Table 3) in comparison with the material with no additives. The open porosity and water absorption increased proportionally with the increasing amount of the L addition for materials fired at 950 °C and 1050 °C in comparison to the material with no additives. For both temperatures only the materials with the smallest L amount (5% sample) had smaller open porosity and water absorption than materials without additives. The usage of the N additive caused a decrease in open porosity and water absorption for materials fired at both temperatures. Only the materials originated from the masses with the largest L addition (15% sample) had higher open porosity than the materials without additives. This behaviour was related to the type of additive (especially L-waste, which contained clay minerals), grain size, kinetics of decarbonation CaCO₃ and kinetics of reactions between CaO and the clay matrix.

Sample	D	ρ _p [g/cm ³]	ρ _r [g/cm³]	A [%]	P _° [%]	P _z [%]	R _{zg} [MPa]	<i>R</i> _{sc} [MPa]	M [cycle]
0%	-	2.07±0.01	2.78±0.01	11.7±0.1	24.0±0.2	1.4	16±1	65±1	15
5%	сс	2.01±0.01	2.82±0.01	12.0±0.2	24.1±0.3	4.7	22±1	94±4	20
10%		1.95±0.01	3.05±0.03	12.8±0.2	24.7±0.3	11.6	23±2	69±2	20
15%		1.89±0.01	2.98±0,02	13.7±0.1	25.7±0.2	11.0	20.9±0.7	47±4	20
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5%	N	2.08±0.01	2.83±0.02	9.8±0.2	20.2±0.3	6.3	22±2	73±2	20
10%		2.00±0.01	2.93±0.01	9.9±0.1	19.6±0.2	12.3	24.2±0.9	66±2	20
15%		1.91±0.01	2.95±0.01	10.2±0.2	19.94±0.07	15.7	24.6±0.8	40±3	20
5%		2.01±0.01	2.97±0.03	11.2±0.2	22.4±0.3	9.9	28±2	73±2	35
10%	L	1.90±0.01	2.86±0.01	12.6±0,3	23.9±0.5	9.4	28.3±0.6	71±1	35
15%		1.82±0.01	3.01±0.03	13.9±0.1	25.2±0.2	14.5	24±2	36±2	20

Description of symbols: D – type of additive, ρ_r – apparent density, A – water absorption, P_o – open porosity, P_z – closed porosity, R_{zg} – bending strength, R_{sc} – compressive strength, M – frost resistance.

Table 3. Properties of materials fired at 1050°C. Tabela 3. Właściwości tworzyw wypalonych w 1050°C.

Sample	D	ρ _p [g/cm³]	ρ _r [g/cm³]	A [%]	P _. [%]	P _z [%]	<i>R</i> _{zg} [MPa]	R _{sc} [MPa]	M [cycle]
0%	-	2.30± 0.01	2.87±0.01	5.6± 0.1	13.2± 0,1	6.9	38± 1	79± 1	30
					-				
5%		2.22± 0.01	2,.84± 0.01	5.4± 0.1	11.9± 0.3	10.1	35± 1	102± 3	*
10%	СС	2.09± 0.01	2,73± 0,03	5,5± 0.2	11.7± 0,1	11.6	33± 2	82± 1	*
15%		1.99± 0.01	2.70± 0.01	5.4± 0.1	11.6± 0.4	14.8	30± 3	43± 1	*
5%		2.32± 0.01	2.71± 0.01	0.54± 0.04	1.3± 0.1	13.1	44± 1	117± 9	*
10%	N	2.11± 0.02	2,77± 0.03	2.7± 0.1	5.7± 0.1	18.0	38± 2	99± 2	*
15%	1	1.96± 0.01	2.83± 0.01	6.4± 0.2	12.5± 0.1	18.3	33± 1	64± 3	*
5%		2.22± 0.01	2.67± 0.03	2.1± 0.2	4.5± 0.2	12.5	40± 3	113± 1	*
10%	L	1.95± 0.01	3.09± 0.01	9.8± 0.5	18.9± 0.4	18.0	28± 1	84± 3	*
15%		1.84± 0.01	3.13± 0.03	12.0± 0.3	22.1± 0.2	19.1	25± 2	44± 1	50

Description of symbols: D - type of additive, $\rho - apparent density$, A - water absorption, $P_o - open porosity$, $P_z - closed porosity$, $R_{zg} - bend-ing strength$, $R_{sc} - compressive strength$, M - frost resistance, * – material showed no damage after 150 freeze-thaw cycles.



Fig. 2. XRD patterns of materials without additives fired at 950 °C and 1050 °C; Q – β -quartz (PDF 86-1560), H – hematite (PDF 79-0007), As – aluminium silicate (PDF 89-0889); highlighted peaks correspond to 100% of theoretical intensity.

Rys. 2. Dyfraktogramy rentgenowskie tworzyw bez dodatków wypalonych w 950 °C i 1050 °C; Q – β -kwarc (PDF 86-1560), H – hematyt (PDF 79-0007), As – glinokrzemian (PDF 89-0889); podkreślonym pikom odpowiada 100% teoretycznej intensywności.

In all cases an increase in bending strength is observed for the materials fired at 950°C. For the materials fired at 1050°C only the matrix with the smallest addition of N and L wastes (5% samples) had higher bending strength by 16% and 5%, respectively, when compared to the material without additives. The 10% samples of materials in case of the N addition had the same bending strength as the reference material.

For all materials and temperatures the additives on the level of 5% and 10% caused an increase in compressive strength. The best results were obtained for 5% of CC added to the masses fired at 950°C and the equivalent amounts of N and L added to the masses fired at 1050°C.

The frost resistance test showed that the usage of the studied additives in masses can improve material's resistance for freeze-thaw cycles. The best results were obtained for the calcite and the waste from washing limestone aggregates.



Fig. 3. XRD patterns of materials with additives at 10% level after firing at 950 °C and 1050 °C; Q – β -quartz (PDF 86-1560), H – hematite (PDF 79-0007), An – anorthite (PDF 02-0523), G – gehlenite (PDF 89-5917), W – wollastonite (PDF 42-0550), Cs – calcium sulfate (PDF 26-0328); highlighted peaks correspond to 100% theoretical intensity.

Rys. 3. Dyfraktogramy rentgenowskie tworzyw z dodatkami na poziomie 15% po wypaleniu w 950 °C i 1050 °C; Q – β -kwarc (PDF 86-1560), H – hematyt (PDF 79-0007), An – anortyt (PDF 02-0523), G – gehlenit (PDF 89-5917), W – wollastonit (PDF 42-0550), Cs – gips (PDF 26-0328); podkreślonym pikom odpowiada 100% teoretycznej intensywności.

In conclusion, it can be stated that the materials manufactured with calcite waste additions can be used in ceramic building industry [19]:

 for production of ceramic masonry units protected from external factors: all types of materials fired at 950 °C, excluding the material without additives due to the frost resistance smaller than 20 cycles,

- for production of ceramic masonry units unprotected from external factors: all types of materials fired at 1050°C, excluding the following materials: without additives (due to the frost resistance smaller than 25 cycles) with the N additive on the 15% level (due to the absorption higher than 6%) and with the L additive on the 15% level (due to unsatisfied absorption).



Fig. 4. Microstructure of materials fired at 950 °C (a, b, c, d) and 1050 °C (e, f, g, h) originated from masses with no additive (a, e) and with additives of CC (b, f), N (c, g), and L (d, h) each at 10 wt.% level.

Rys. 4. Mikrostruktura tworzyw ceramicznych wypalonych w 950 °C (a, b, c, d) i 1050 °C (e, f, g, h) uzyskanych z mas bez dodatku (a, e) i z dodatkami CC (b, f), N (c, g) i L (d, h) na poziomie 10% mas.

According to the detailed results and standard requirements [19-20] the first and second type of materials can be produced minimally at the class 30 and the class 35, respectively.

3.3. Phase composition and microstructure

The phase composition of fired materials is shown in Figs. 2 and 3. In the material without additives fired at 950 °C the main phase components are β -quartz, hematite and aluminosilicate. A very small quantity of mullite is present in the material fired at 1050 °C.

In materials with the additives new phase components are observed: gehlenite (for both materials), anorthite (in the materials fired at 1050 °C), wollastonite (in the materials fired at 1050 °C), and calcium sulfate (in the materials added by the N and L wastes fired at 950 °C). The highest anorthite amount was detected for the materials with the L waste additive fired at 1050 °C. This is the evidence for the best kinetics of the reaction between CaO and clay matrix, which is most probably due to the smallest grain size of the additive.

Microstructures of fired materials are shown in Fig. 4. New closed porosity is observed in all materials with the additives. For materials with the calcite (CC) and N waste addition, around big pores some envelopes are observed. As indicated in Ref. [18] the envelopes are composed of a glassy-phase. In materials with the L additive only a small amount of envelopes is observed in places of large grains. Small closed pores with no clear envelopes dominated the microstructure which proves that thanks to the smallest grain size this material had the best reaction rate between CaO and the clay matrix.

4. Summary

In this paper the usefulness of calcite wastes in production of ceramic masonry units was analysed. Wastes from washing limestone aggregates and Maerz furnace bag filters were used as additives to kaolinite-illite clay. As a comparison, ceramic materials with additions of pure calcite to clay were also prepared. Studies confirmed the possibility of usage of the calcite wastes as an additive in production of ceramic masonry units:

- protected from external factors: all types of materials fired at 950 $^{\circ}\mathrm{C},$

- unprotected from external factors: all types of materials with the N and L wastes at 5% and 10% levels fired at 1050°C.

The minimum class of materials protected and unprotected from external factors is 30th and 35th, respectively.

Literature

- Skripnikowa, N. *et al.*: Carbonate Waste and Wall Ceramic Produced Therefrom, *Vestnik TGASU*, 3, (2013), 214-218 (in Russian).
- [2] Ekonomakou, A., Geralis, A., Stournaras, C. J.: The utilization of water industry wastes in ceramic products, *Key Eng. Mater.*, 206-213, (2002), 843-846.
- [3] Turgut, P.: Limestone dust and glass powder wastes as new brick, *Mater. Struct.*, 41, (2008), 805-813.
- [4] Raupp-Pereira F., Hotza, D., Segadães, A. M., Labrincha, J. A.: Ceramic formulations prepared with industrial wastes, *Ceram. Int.*, 32, (2006), 173-179.
- [5] Algin, H. M., Turgut, P.: Cotton and limestone powder wastes as brick material, *Constr. Build. Mater.*, 22, (2008), 1074-1080.
- [6] Raupp-Pereira F., Ribeiro, J. M., Segadães, A. M., Labrincha, J. A.: Extrusion and property characterisation of waste-based ceramic formulations, *J. Eur. Ceram. Soc.*, 27, (2007), 2333-2340.
- [7] Bilgin N., Aygül Yeprem H., Arslan, S., Marşoglu, M.: Use of waste marble powder in brick industry, *Constr. Build. Mater.*, 29, (2012), 449-457.
- [8] Dhanapandian, S., Balasubramani, G., Thirunavukkarasu, R.: Utilization of granite and marble sawing powder wastes as brick materials, *Carp. J. Earth Environ. Sci.*, 2, (2009), 147-160.

- [9] Eliche-Quesada D., Martínez-García, C., Martínez-Cartas, M. L., Cotes-Palomino, M. T., Pérez-Villarejo, L., Cruz-Pérez, N., Corpas-Iglesias, F. A.: The use of different forms of waste in the manufacture of ceramic bricks, *App. Clay Sci.*, 52, (2011), 270-276.
- [10] Pappu, A., Saxena, M., Asolekar, S. R.: Solid wastes generation in India and their recycling potential in building materials, *Build. Environ.*, 42, (2007), 2311-2320.
- [11] Martirena, J. F., Da, R. L., Betancourt, D.: Improvement of engineering properties of fired clay bricks through the addition of calcite, in conference materials: 7th IMC, London, (2006).
- [12] Diaz Y., Betancourt D., Martirena J. F.: Influence of grinding fineness of calcium carbonate on physic-chemical properties and durability on red ceramic bricks, *Revista ingeniería de construcción*, (2011), 269-283.
- [13] Xavier, G. C., Alexandre, J., Saboja Jr, F.: The use of powder marble by-product to enhance the properties of brick ceramic, *Constr. Build. Mater.*, 21, (2007), 1950-1960.
- [14] Sokólar R., Vodová, L., Grygorová, S., Śtubňa, I., Śin, P.: Mechanical properties of ceramic based on calcite waste, *Ceram. Int.*, 8, (2012), 6607-6612.
- [15] European Commission: LIFE NanoCeramiCO2 Climate Change Prevention by the inclusion of nanoparticles in clays for the reduction of Ceramic Industry CO₂ emissions, (LIFE13 ENV/ES/00037), (2015).
- [16] Kłosek-Wawrzyn, E.: The effect of calcium carbonate on the sintering proces of ceramic masses and the properties of ceramic building materials, PhD Thesis, Supervisor: Małolepszy, J., Akademia Górniczo-Hutnicza im. St. Staszica w Krakowie, Kraków (2016), (in Polish).
- [17] Duggal, S. K.: *Building Materials*, Third Edition, New Age International, New Delhi, (2008).
- [18] Mineral Data Base WebMineral: http://webmineral.com
- [19] PN-EN 771-1+A1:2015-10: Specification for masonry units Part 1: Clay masonry units.
- [20] PN-EN 772-1+A1:2015-10: Methods of test for masonry units – Part 1: Determination of compressive strength.

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