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Preliminary Study of the Pozzolanic Activity of Dumped Mine Wastes Obtained from the North Bohemian Basin in the Czech Republic

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Three dumped raw materials, a tuff and two bentonites, obtained from two mining sites at the North Bohemian basin in the Czech Republic, have been studied in order to evaluate them as pozzolanic admixtures in lime mortars for employment in restoration of cultural heritage objects. After thermal activation (800 °C; 5 h), their pozzolanic properties were compared with those of commercial metakaolin. Quantitative phase analysis with the Rietveld method from X-ray powder diffraction patterns, morphological observations, as well as the Frattini and the modified Chapelle tests were performed. In addition, lime mortars, incorporating the fired materials, were prepared and subjected to simultaneous thermal analysis after a 28-day initial curing (20 ± 1 °C; 60 ± 5 % RH). The results showed that all three materials possess pozzolanic activity. However, when employed in lime mortars they did not result in formation of pozzolanic reaction products. Two methods were proposed to improve their reactivity; grinding to obtain finer particle size and removal of quartz content where necessary.

Keywords: pozzolanic activity, dumped mine wastes, lime mortars, thermal analysis.

1. INTRODUCTION

Pozzolanic mineral admixtures, also known as supplementary cementitious materials (SCMs), are used as main constituents or additives in the production of various building materials. The European standard EN 197-1 [1] identifies several types of cement, which contain mineral admixtures of natural or artificial origin in percentages ranging from 6 % to 55 % by mass of cement. Besides cement production, SCMs are used in concrete technology by adding them separately in the concrete mixture [2] when certain properties are required for special civil engineering works. Mixing slaked lime with pozzolanic additives to obtain hydraulic lime [3, 4] is also a well-known technique used since the ancient times [5 – 7].

ASTM C595/C595-16 [8] defines as pozzolan „a siliceous and aluminous material which in itself possesses little or no cementitious value but in presence of moisture chemically reacts with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties", namely calcium-silicate hydrates, calcium-aluminate hydrates and calcium-alumino-silicate hydrates [9]. In general, the chemistry of SCMs is characterized by lower calcium content than Portland cement [2], thus, pozzolanic reaction results in the formation of silicon-rich silicate hydrates [10]. However, when SCMs contain a notable amount of calcium oxide, then hydraulic properties also appear, as in the case of Class C fly ash and blast-furnace slag [9]. Mineral admixtures affect also physically the development of structure and properties of the final material. This is due to their fineness, which contributes to the refinement of pore structure and reduction of permeability of the final product [11].

A large number of materials possess pozzolanic properties. Natural pozzolans, derived from natural mineral deposits, are either employed directly or subjected to activation processes (e.g. thermal activation of kaolinite clays to form metakaolin) [9]. They are usually of volcanic origin and rich in zeolitic minerals. Volcanic ash, crushed pumice, diatomaceous earth, chert and shale are typically referred as natural pozzolans [12]. Artificial pozzolanic mineral admixtures are usually by-products of industrial processes. Examples include fly ash derived from the combustion of coal, blastfurnace slag obtained from pig iron production, rice husk ash, sugar cane bagasse ash, silica fume, recycled glass, biomass combustion ash, and coal fly ash [2, 12]. Paris et al. [12] have published an extensive review of waste products employed as SCMs in concrete production.

The excavation of kaolin and bentonite is an important mining activity in the Czech Republic. Most of the exploitable reserves are situated in the North Bohemian basin. In 2013, Czech Republic was ranked 5th and 13th in the world, concerning kaolin and bentonite exploitation, respectively, accounting for 8.53 % (3.108 kt) of the world's kaolin production (36.437 kt) and for 1.37 % (226 kt) of the world's bentonite production (16.505 kt) [13].

During cultivation of mining sites, several layers have to be removed before reaching the targeted mineral. These mine wastes are usually stockpiled in large amounts. Their exploitation as secondary raw materials may mitigate the environmental impact and bring economic advantages. The main aim of this paper is to evaluate the pozzolanic

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potential of dumped materials, collected from two mining sites (Rokle and Černý vrch) in the Czech Republic. The ultimate purpose is to use them as additives for the preparation of hydraulic lime mortars, supposed to be employed in restoration works. Comparison with a commercial product (metakaolin) available on market was also performed.

2. GEOLOGICAL ASPECTS

The raw materials were obtained from two bentonite deposits located in the Ústí nad Labem Region of the Czech Republic. The geological description of the two areas is summarised below, according to literature data [14].

The deposit in Rokle (Chomutov district) is located on the border of the cadastral areas of the villages Rokle, Krásný Dvoreček and Vinaře, about 10 km south-west of the town of Kadaň. From this deposit kaolin and bentonite are mined. The kaolin deposit is related to the “Ohárce” crystalline gneiss weathering zone. The bentonite deposit is situated in the north-western part of this area. The occurrence of bentonite is related to the pyroclastic rocks of the volcanic district of Doupov Mountains (Doupovské hory). Quaternary colluvial deposits, loams and, exceptionally, loess loams, ranging from 0.5 to 3 m in thickness, are on top of the stratigraphic sequence. The upper Tertiary layer consists of several basalt bodies (from 2 m to 22 m thick), ranging from compact olivine basalts to completely weathered basalts and tuffs. The underlying bentonite raw material, with a thickness ranging from 40 m to 60 m, is occurring within pyroclastic rocks consisting of fine-grained tuffs with large content of montmorillonite. The colour of these rocks is grey, brown, blue, red and violet. Small concretions of calcite, sandstone and coal clay can be also found. At the base of the bentonite deposit are Oligocene sediments – kaolin and sand (thickness of about 3 m). Partially weathered crystalline gneiss is situated below these sediments.

The geological and topographical characteristics of the bentonite deposit in Černý vrch (Most district) are quite different. The deposit is located on the border of the cadastral areas of the villages Střimice, Braňany and Želenice. The locality belongs to the Tertiary volcanic area of the Bohemian Central Uplands (České středohoří). The occurrence of bentonite deposits is related to the presence of pyroclastic rocks of the Tertiary volcanic complex. The stratigraphic sequence is characterised on top by about 2 m of Quaternary loess, clay and terrace gravels of the Bílina river. The first bentonite layer occurs under these deposits. It consists of reddish, brown and green bentonites, which are employed in foundry and building industry. An about 11 m thick layer of partially weathered olivine basalts, black, grey-black and green-black in colour, is lying under the bentonite. Limonite, dolomite and calcite are filling the frequent dislocations present in the basalts. They are followed by the second bentonite layer, about 10 m thick, consisting of high quality blue, green and green-blue bentonite, which finds application as raw material for the production of pet litter. The base of the deposit consists of compact olivine basalts in the western and northern part of the area, as well as of Cretaceous marls, clays and sands.

3. EXPERIMENTAL INVESTIGATION

3.1. Materials

Three dumped raw materials, obtained from the two different sites described above, were investigated. Two of them were obtained from the deposit in Rokle; a tuff (tR) derived from the Tertiary layer and the underlying bentonite (bR). The third raw material was also a bentonite (bCV) obtained from the upper bentonite layer of the deposit in Černý vrch. About 10 kg of each raw material were dried at 110 °C for 12 h and then passed through a hammer crusher, in order to reduce particle size to < 5 mm.

Preliminary tests were performed in order to determine the optimal firing conditions to obtain a product with high amorphous content at a conveniently low temperature. The raw materials were subjected to firing at 700 °C, collecting samples every hour for up to 5 h. The same procedure was performed at 800 °C. According to the results, which will be discussed in section 4, firing at 800 °C for 5 h, applying a heating rate of 5 °C/min, was selected as the most suitable regime.

After thermal treatment, each material passed through a jaw crusher, resulting in a particle size reduction to < 1 mm, and then it was milled for 1 min using a vibrating mill. Particle size distribution and chemical composition were determined. For comparison, a commercial metakaolin (M) produced by ČLUZ a.s. (Mefisto K_{05}) was used.

A pure lime mortar and three lime mortars with partial replacement (40 %) of lime with bR, bCV and M were produced (binder to sand ratio of 3:1; water to binder ratio of 0.2). For this purpose, commercial standard lime CL90 (Vápenka Čertovy schody a.s.) and quartz sand with a maximum grain size of 2 mm were used. Mortar specimens (prisms of 40 × 40 × 160 mm) were prepared. The specimens left in the moulds for 48 h and then demoulded and aged into climate chamber for 26 days (20 ± 1 °C; 60 ± 5 % RH).

3.2. Test methods

Particle size distribution of the studied materials was determined with a CILAS 1090 particle size analyser. Their chemical composition was determined with a PANalytical Axios FAST WDXRF spectrometer with Rh anode and a flow proportional detector.

X-ray powder diffraction (XRPD) was performed on the materials before and after the thermal treatment. Prior to testing, all samples were ground and homogenized by hand in agate mortar. Data were collected in the angular range 4 – 82° 2θ using a Bragg–Brentano θ-θ diffractometer (Bruker D8 Advance), Cu Kα radiation ($\lambda = 1.5418$ Å), equipped with a LynxEye 1-D silicon strip detector, at 40 kV and 40 mA. Divergence 0.6 mm slit and 2.5° Soller slits were mounted on the incident beam pathway. The pathway of the diffracted beam included a Ni filter and Soller slits (2.5°). A virtual step scan of 0.0102° 2θ with 0.4 s/step counting time was employed. The side loading technique was used in order to minimize a priori preferred orientation of crystallites. The samples were allowed to spin at 15 rpm to improve particle statistics.

Quantitative phase analysis (QPA) with the Rietveld method was performed on the measured XRPD patterns. Amorphous fractions were quantified only in fired samples by adding 10 wt.% of internal standard α-Al_2O_3 (NIST SRM 676a) [15] to the powders. Refinements were performed with the TOPAS 4.2 software (Bruker AXS).

Scanning electron microscopy (SEM) was used to observe the morphology of the raw materials before and after firing. For this purpose, a FEI QUANTA FEG 450 instrument equipped with an energy dispersive (EDS) detector was used. The samples were mounted on aluminum stubs, coated with 5 nm thick gold film prior to analysis and observed at 20 kV accelerating voltage.

The "Frattini test" (EN 196-5 [16]) and the "modified Chapelle test" (NF P 18-513 [17]) were performed to determine the pozzolanic activity of each raw material. Prior to these tests, each material passed through a 125 μm sieve, as recommended in the standard procedure.

Simultaneous thermal analysis was used to investigate the formation of pozzolanic reaction products in lime mortars. Measurements were performed with a BÄHR Thermoanalyse STA 504 instrument, using alumina crucible, N_2 gas flow, heating rate of 20 °C/min and temperature range 20 – 1100 °C.

4. RESULTS AND DISCUSSION

As previously mentioned, the raw materials were subjected to preliminary firing prior to the selection of the optimal firing conditions for the subsequent tests. As an example, the XRD patterns of bCV, after firing at 700 °C and 800 °C for 1 h and 5 h, are presented in Fig. 1. No notable mineralogical changes were observed at 700 °C, independently of the firing duration. This has to be expected, because 700 °C is a temperature too low to result in complete decomposition of phyllosilicates, and longer dwell times did not help. Firing at 800 °C for 1 h was also not effective in decomposing phyllosilicates. However, after 5 h of heating at this temperature the characteristic XRD peaks of phyllosilicates were reduced. Similar trends were also observed for the raw materials tR and bR. Firing at 800 °C for 5 h was selected as the optimal regime for thermal activation of the studied raw materials. Other authors have determined the optimal firing temperature, using thermogravimetric analysis [18 – 22]. In this paper, such an approach was not adopted, because the effect of dwell time is not reproduced by this analytical method.

The results from the QPA with the Rietveld method, before and after firing, applying the selected firing regime, are presented in Table 1. The agreement factor of the refinements, as defined in TOPAS software [23], ranged between 4.0 and 9.6. As expected, the mineralogy of the materials differs significantly before and after thermal treatment. Before firing, tR was dominated by quartz and phyllosilicates (43.3 %); minor amount of hematite was also found. The samples bR and bCV were comprised mostly of phyllosilicates (87.6 % and 85.2 %, respectively); other minor minerals include quartz, hematite and anatase. Heat treatment at 800 °C led to partial decomposition of phyllosilicates in bCV sample, whereas, in samples tR and bR, montmorillonite and kaolinite also disappeared, leaving small amounts of residual muscovite.

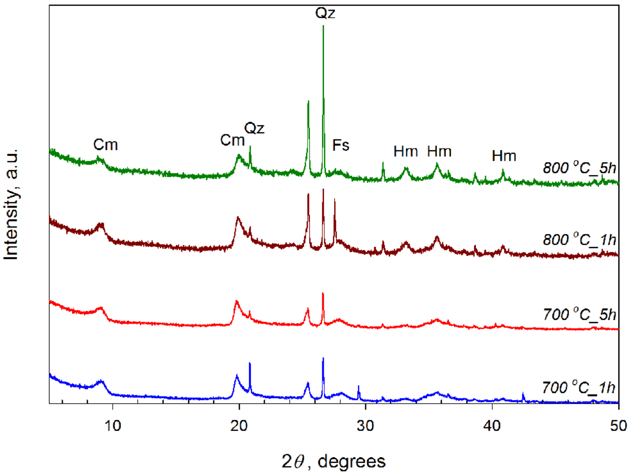

Fig. 1. XRD patterns of bCV raw material after firing at 700 °C and 800 °C for 1 h and 5 h (Cm: clay minerals; Qz: quartz; Fs: feldspar; Hm: hematite)

Phyllosilicates usually disappear at 700 – 900 °C, however, owing to kinetic factors, relicts can survive [24, 25]. As a consequence of thermal decomposition of phyllosilicates, amorphous was formed (41.7 % in tR, 84.5 % in bR and 88.7 % in bCV). In all samples, quartz content remained substantially the same after heat treatment at 800 °C. This is because higher temperatures (~1200 °C) are required for the partial decomposition of quartz by reaction with the product of decomposition of clay minerals [26]. Hematite content increased in bR sample after firing, while no significant difference was observed in tR and bCV samples. Minor amounts of spinel and ilmenite formed in bCV sample.

SEM micrographs of bR and bCV samples, before and after firing at 800 °C for 5 h, are indicatively presented in Fig. 2. The layered structure, typical of phyllosilicates, before firing is clearly visible (Fig. 2 a and b), whereas after firing this feature is less apparent (Fig. 2 c and d).

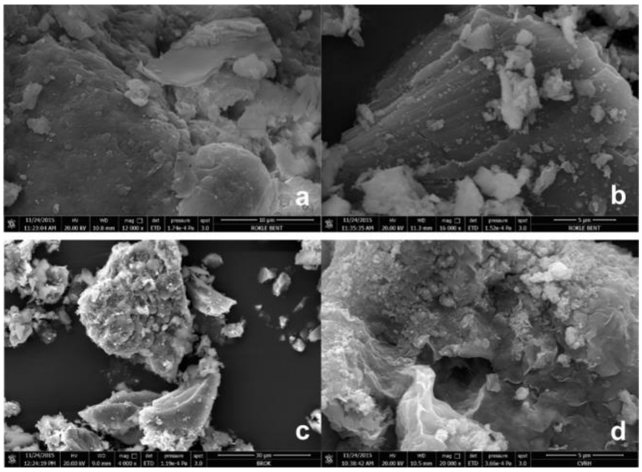

Fig. 2. SEM micrographs of: before firing a – bR; b – bCV; after firing c – bR; d – bCV

A comparison of the chemical composition (Table 2) and mineralogical composition (Table 1) before and after firing of the raw materials indicates that almost all the silicon and aluminium oxides, except of those contained in quartz and in the residual muscovite, were included in the amorphous formed.

Table 1. Quantitative phase analysis (wt.%) of the studied raw materials before and after firing at 800 °C, as determined by XRD and Rietveld refinement

Phase	Before thermal treatment			After thermal treatment at 800 °C		
	tR	bR	bCV	tR	bR	bCV
Quartz	55.4 (4)	5.1 (1)	2.2 (1)	50.1 (2)	5.2 (1)	1.3 (1)
Muscovite	12.0 (3)	16.2 (4)	18.4 (6)	6.7 (1)	2.8 (2)	-
Montmorillonite	1.5 (2)	61.3 (7)	42.4 (1)	-	-	-
Kaolinite	29.8 (4)	10.1 (4)	24.4 (8)	-	-	-
Hematite	1.3 (1)	1.3 (2)	5.5 (3)	1.1 (1)	6.2 (1)	4.7 (1)
Anatase	-	6.0 (2)	7.1 (3)	0.4 (1)	1.3 (1)	0.5 (1)
Spinel	-	-	-	-	-	4.0 (1)
Ilmenite	-	-	-	-	-	0.7 (1)
Amorphous	-	-	-	41.7 (7)	84.5 (3)	88.7 (3)

Concerning iron oxide, in case of tR and bCV samples, it was mostly included in amorphous since the amount of hematite remained substantially the same after firing. A fraction of iron, along with magnesium, contributed in spinel formation in bCV sample. In sample bR, the increase of hematite after firing is due to the iron derived from decomposition of phyllosilicates; the rest was included in amorphous. The higher amount of titanium oxide in bR and bCV samples is reflected in the anatase content of the raw materials. After firing, titanium dioxide was included mainly into amorphous, since anatase content significantly decreased in both samples. The presence of ilmenite in sample bCV indicates that part of titanium dioxide was combined with iron to form this mineral. It should be noted that the high level of iron oxide in samples bR and bCV is responsible for their red colour.

Table 2. Chemical analysis of the fired raw materials (% w/w).

Oxide	tR	bR	bCV	M
SiO_2	64.43	50.20	44.64	55.98
Al_2O_3	28.69	16.15	18.70	39.18
Fe_2O_3	3.02	18.88	22.41	0.86
CaO	1.01	3.74	4.82	1.18
MgO	0.70	3.61	3.09	0.83
MnO	0.01	0.24	0.06	0.01
K_2O	1.22	1.36	0.30	0.65
Na_2O	0.03	0.14	0.23	0.00
P_2O_5	0.07	0.68	0.43	0.01
TiO_2	0.51	4.67	4.01	0.38
SrO	n.d.	0.03	0.02	n.d.
LOI	0.30	0.29	1.29	0.92

ASTM C618-15 [27] specifies the chemical requirements for a raw material to be considered as a Class N (raw or calcined natural pozzolans) material: $SiO_2 + Al_2O_3 + Fe_2O_3 \geq 70$ %, $SO_3 \leq 4$ %, moisture content ≤ 4 % and LOI ≤ 10 %. According to Table 2, the sum of silicon oxide, aluminium oxide and iron oxide for tR, bR and bCV is 96.1 %, 85.2 % and 85.8 %, respectively, while for all three of them LOI ≤ 1.3 %. SO_2 was not detected by XRF analysis. In the case of tR raw material, its total content of basic oxides is rather similar to that of the commercial product M (96.0 %). It is worth noting that this does not ensure that tR is the raw material with the highest pozzolanic activity, since its high SiO_2 content is mainly due to the presence of quartz, which does not contribute effectively to the pozzolanic activity [19]. In this respect, Chackchouk et al. [19] claim that chemical analysis is an indicator of reactivity rather than a single factor to predict pozzolanic activity.

The results of Frattini test are summarized in Fig. 3. The points corresponding to each studied material fall below the curve of calcium oxide in the saturated solution, indicating that all of them could be considered as pozzolanic materials [16]. The results of the modified Chapelle test (Table 3) confirmed those of Frattini test, showing that all three raw materials could react as pozzolanic ones. However, their pozzolanic activity is 33 % (tR), 66 % (bR) and 46 % (bCV) lower than that of M. One important aspect to be considered in the evaluation of these results is the particle size distribution (Table 3).

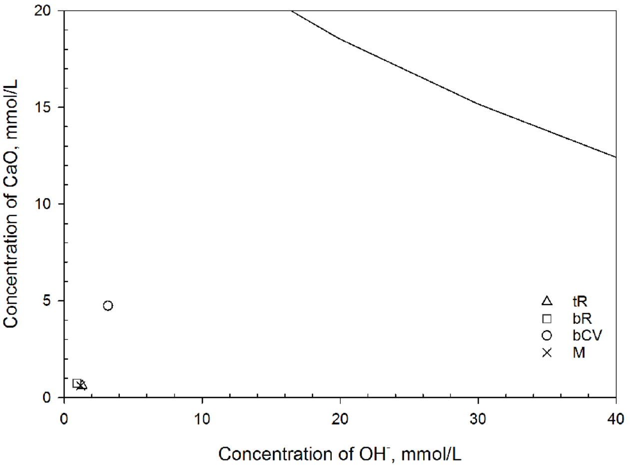

Fig. 3. Results of the Frattini test (EN 196-5). Points fall below the curve, denoting the pozzolanic activity of the studied materials

Table 3. Particle size distribution data (d_{10}, d_{50}, d_{90}) and pozzolanic activity (modified Chapelle test) of the studied materials.

Sample	d_{10}, μm	d_{50}, μm	d_{90}, μm	$Ca(OH)_2$, mg/g material
tR	7.3	39.8	136.9	829.5 ± 65.1
bR	8.3	58.7	189.8	421.2 ± 18.1
bCV	6.3	49.6	161.6	668.8 ± 37.5
M	1.5	5.2	12.5	1226.2 ± 15.4

The commercial product M is much finer than the three samples presented here. The pozzolanic activity of tR sample is quite satisfactory compared to bR and bCV ones, despite its high quartz content. The reason for this good result is the sieving below 125 μm prior to Frattini and

Chapelle tests. In this way, quartz was probably removed from tR sample, increasing the fraction of the phases able to provide pozzolanic activity. This is not the case in bR and bCV samples, because of their low quartz content.

The discussion above showed that tR fulfilled the typical requirements of a pozzolanic material. However, its high quartz content led us to exclude it from the production of lime mortars in this preliminary study. Its amorphous fraction (41.7 %) was considered insufficient to form calcium-silicate and calcium-aluminate hydrates. This material could be employed after the removal of quartz fraction. Such process requires the evaluation of economic and technological aspects that are beyond the scope of the present work.

Thermal analysis was performed on samples of lime mortars, produced with pure lime or with its partial substitution with bR, bCV and M, after 28 days of initial curing. In literature, there is no agreement about the amount of pozzolanic material to be used in replacement of lime. To the best of our knowledge the values range between 25 to 50 % [18, 19, 28, 29]. Considering the previously mentioned economic and environmental aspects, in terms of cost/benefits, the use of thermally activated pozzolanic materials is justified only if added to mortars in relatively high amount. For this reason, in the present study a replacement of 40 wt.% has been chosen. The obtained DTA curves are presented in Fig. 4. In all samples, the characteristic peaks of calcium hydroxide (at ~430 °C) and calcium carbonate (at ~740 °C) are observed. The sample containing metakaolin shows an additional broad peak at ~150 °C attributed to the dehydration of calcium-silicate and/or calcium-aluminate phases [18, 19, 21, 28, 29]. Thus, only metakaolin contributed in the formation of such phases, although bR and bCV had shown pozzolanic potential. This different behaviour could be attributed to the lower pozzolanic activity of the material as a whole (i.e. including the coarse fraction excluded by sieving before the pozzolanic activity tests). However, as noted above, the much coarser particle size of bR and bCV samples, compared to commercial metakaolin (Table 3), undoubtedly had a detrimental effect on the development of the pozzolanic reaction products. In fact, the increase in specific surface area of particles greatly enhances the reaction rate, which is, in general, a sluggish process.

The chemical and mineralogical composition of all three fired materials, their morphology and the pozzolanic activity test results indicate that they are potentially suitable to be used as pozzolanic materials. However, their ineffectiveness to produce pozzolanic reaction products, when incorporated in lime mortars, has to be considered, since the ultimate aim is to employ them in restoration works. The reduction of particle size, applying an effective grinding process, and the removal of quartz fraction from sample tR are the main steps towards the increase of their reactivity. In a next study, both actions will be undertaken. In addition, economic and environmental evaluation of the processes will be performed, which will be related to the material properties, in order to clarify whether or not the exploitation of these dumped materials is beneficial.

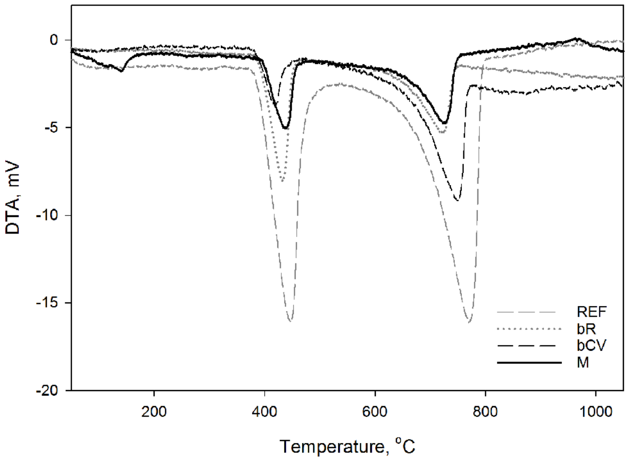

Fig. 4. DTA curves of pure lime mortar (REF) and lime mortars with the addition of bR, bCV and M

5. CONCLUSIONS

The study of the three dumped raw materials, obtained from two mining sites in the Czech Republic, showed that their chemical composition fulfils the requirements for considering them as pozzolanic materials to be employed in lime mortars for restoration of cultural heritage objects. The mineralogical analysis after firing (800 °C; 5 h) has proved the formation of considerable amount of amorphous in two of them (bR and bCV), due to the decomposition of phyllosilicates, indicating pozzolanic reactivity. In case of tR sample, the much higher amount of quartz and the lower amount of phyllosilicates, compared to bR and bCV samples, resulted in less amorphous. According to the Frattini and the modified Chapelle tests results, all three fired materials possess pozzolanic activity, however lower than that of commercial metakaolin. Sample tR was not used in lime mortars preparation, due to its high quartz content. Thermal analysis showed that bR and bCV samples did not contribute in the formation of calcium-silicate and calcium-aluminate hydrates in lime mortars after 28 days. This is likely due to their coarse particle size. Further grinding processing and removal of quartz fraction from tR raw material are suggested for improving materials effectiveness.

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