



Characterisation of post-production raw material from the *Raciszyn II* deposit as a material suitable for the production of alkaline-activated materials

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Abstract

The clay is the basic raw material used in the production of a wide range of ceramic products. However, global guidelines encourage limiting the consumption of natural resources in the production process. For this reason, research is being conducted in developing technologies that enable the production of full-value products by using post-process materials. The article presents the properties of post-production clay sourced from the Jurassic limestone *Raciszyn II* deposit. In this study, the results of mineralogical (X-ray diffraction) and chemical (X-ray fluorescence) analysis of post-production raw material will be presented. In addition, the leachability in water and the natural radioactivity of the material were established, which determines the possibility of using the raw material in building applications. It was found that, because of the presence of minerals from the kaolinite group in the post-production raw material from *Raciszyn II* deposit, it is suitable for the production of alkaline-activated materials. However, it was necessary to determine the temperature range of its thermal treatment. The processes occurring in the post-production raw material during its heating were characterised by means of thermogravimetry, differential thermal analysis and mass spectroscopy thermal analysis-coupled techniques. The compressive strength properties of alkali-activated materials, produced from the post-process material from *Raciszyn*, analysed after 14 and 28 days of curing, were also presented.

Keywords Waste management · TG/DTA/MS · Compressing test · Alkali-activated materials

Introduction

The *Raciszyn* is one of the locations in Poland, from which Jurassic and Quaternary limestones are extracted. Two deposits, namely *Raciszyn* and *Raciszyn II*, are located there, both belonging to the WKG company. These resources include two main types of limestone: chalky and travertine. Their documented total resources are estimated at approximately 20 million tonnes. This enables the effective exploitation of limestone, amounting to a period

of several decades. Currently, the exploitation of these deposits is related to the processing of quarried natural stone, which is subsequently used in various industrial sectors. For example, in the power industry, it is utilised as a sorbent for flue gas desulphurisation, in agriculture as a mineral fertiliser and in construction chemicals as a filler for mortars and plasters.

The *Raciszyn II* deposit is mined in four levels, each one several metres in height. Several hundred thousand tons of aggregate is extracted annually by means of the blasting method. In turn, the deposit at *Raciszyn II* is characterised by excellent chemical purity. Thanks to this, the products which are sold in the form of aggregates or powder are characterised by low humidity and possess a high degree of reactivity. They are also recognised on the market as decorative and finishing materials (e.g. as travertine). The company dealing in the exploitation of the aforementioned

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deposits is currently introducing a zero-waste production system.

The laboratory tests of the chemical and the physical composition of the by-product, resulting from the processing of lime aggregate, showed that the material usually contains about 60% fully valuable aggregates of various fractions and about 40% clay. This is the reason why a processing plant for the post-production of raw materials, which recovers three main products, has been started. The first is pure limestone with the following fractions: 90–60 mm, 60–30 mm and 30–2 mm. (The smallest fraction is an excellent starting material for the grinding in roller mill for the production of high-quality limestone powder.) The following is lime–quartz sand, which after drying and fractionation, is usually utilised as light filler for mortars and plasters. The third recovered product is clay. Because of it containing reactive aluminosilicates, among other uses, it is an attractive material for the production of alkali-activated materials (AAM) [1–4]. By using the alkaline activation process, it is also possible to obtain, for example, sorbents or synthetic zeolites [5–9]. Moreover, the clays containing high amounts of calcium carbonates can also be used for the production of binders [10] or for the immobilisation of mercury in remediation processes [11]. It is also known to use clay for wastewater treatment containing dyes [12].

The article presents the results of research on the physical and chemical properties of post-process raw material from the *Raciszyn II* deposit, and the possibility of its practical use for the production of alkaline-activated materials (AAM).

Materials and methods

The post-production raw material was sourced from 15 random areas of the Jurassic limestone *Raciszyn II* deposit (Fig. 1), the total area of which consists of 31.43 hectares. The materials to the amount of 50 kg were collected from each location.

The moisture of the materials was determined by means of an analytical method by drying the samples in the MAX50/1/WH moisture analyser at a temperature of 105 °C, until a constant mass was obtained.

The X-ray diffraction analysis (XRD) was performed, using the RIGAKU X-ray diffractometer. The $\text{Cu}_{K\alpha}$ radiation was used, with an angle range of 3° – 70° 2θ , and 0.05° measuring step.

The thermal analysis was carried out using the Netzsch STA449 F3 Jupiter device. The measurements were made in ceramic crucibles at an air atmosphere, with a flow of 40 mL min^{-1} . The shredded and homogenised sample, with the mass of approximately 50 mg, was heated from

the ambient temperature to 1000 °C, with a constant rate of $10 \text{ }^\circ\text{C min}^{-1}$.

The degree of leachability of easily mobile elements was determined after a 24-h extraction period of samples, which were placed in distilled water, in accordance with the PN-EN 12457-4:2006 standard. The analysis of the chemical composition of the solution was carried out by means of emission and mass spectrometry with inductively excited plasma (inductively coupled plasma–optical emission spectrometry ICP-OES and inductively coupled plasma–mass spectrometry ICP-MS) on PerkinElmer Plasm 40 and ELAN 6100 spectrometers. The analyses were performed in an accredited hydro-geochemical laboratory (AB 1050). The content of SO_4 sulphate was determined by turbidimetry, in accordance with PN-C-04566-10:1979. The content of chlorides was determined by means of an argentometric titration, in accordance with the PN–ISO 9297:1994 standard. The content of HCO_3^- bicarbonates was determined by alkalimetric titration.

The radioactivity tests were performed using the high-resolution gamma spectrometry method by means of the HPGe detector, on a device equipped with a well-type germanium detector, with an active anti-incense *Annulus* shield. In accordance with applicable law, i.e. the regulation of the Council of Ministers, in the case of “requirements regarding the content of natural radioactive isotopes in raw materials and materials used in buildings for human and livestock habitation, as well as in industrial waste used in construction, and the control of the content of these isotopes”, building materials are qualified on the basis of two activity indicators, defined according to the following relationships:

$$f_1 = \frac{C_K}{3000 \text{ Bq kg}^{-1}} + \frac{C_{\text{Ra}}}{300 \text{ Bq kg}^{-1}} + \frac{C_{\text{Th}}}{200 \text{ Bq kg}^{-1}}$$

$$f_2 = C_{\text{Ra}}$$

where C_K , C_{Ra} and C_{Th} are the isotope concentrations of potassium ^{40}K , radium ^{226}Ra and thorium ^{228}Th , expressed in Bq kg^{-1} .

Before preparing the AAM, the post-production raw material was dried for 48 h at 105 °C. Next, it was ground, calcined and mixed with general construction sand with a particle size below 50 μm , which constituted 50 mass%. The alkaline solution consisted of a 12 M solution of NaOH and sodium silicate in a ratio of 1:3.

The compressive strength tests, according to EN 12390-3, using the Matest 3000 kN, were carried out on $150 \times 150 \times 150 \text{ mm}$ cubic samples, at room temperature after 14 and 28 days of curing.

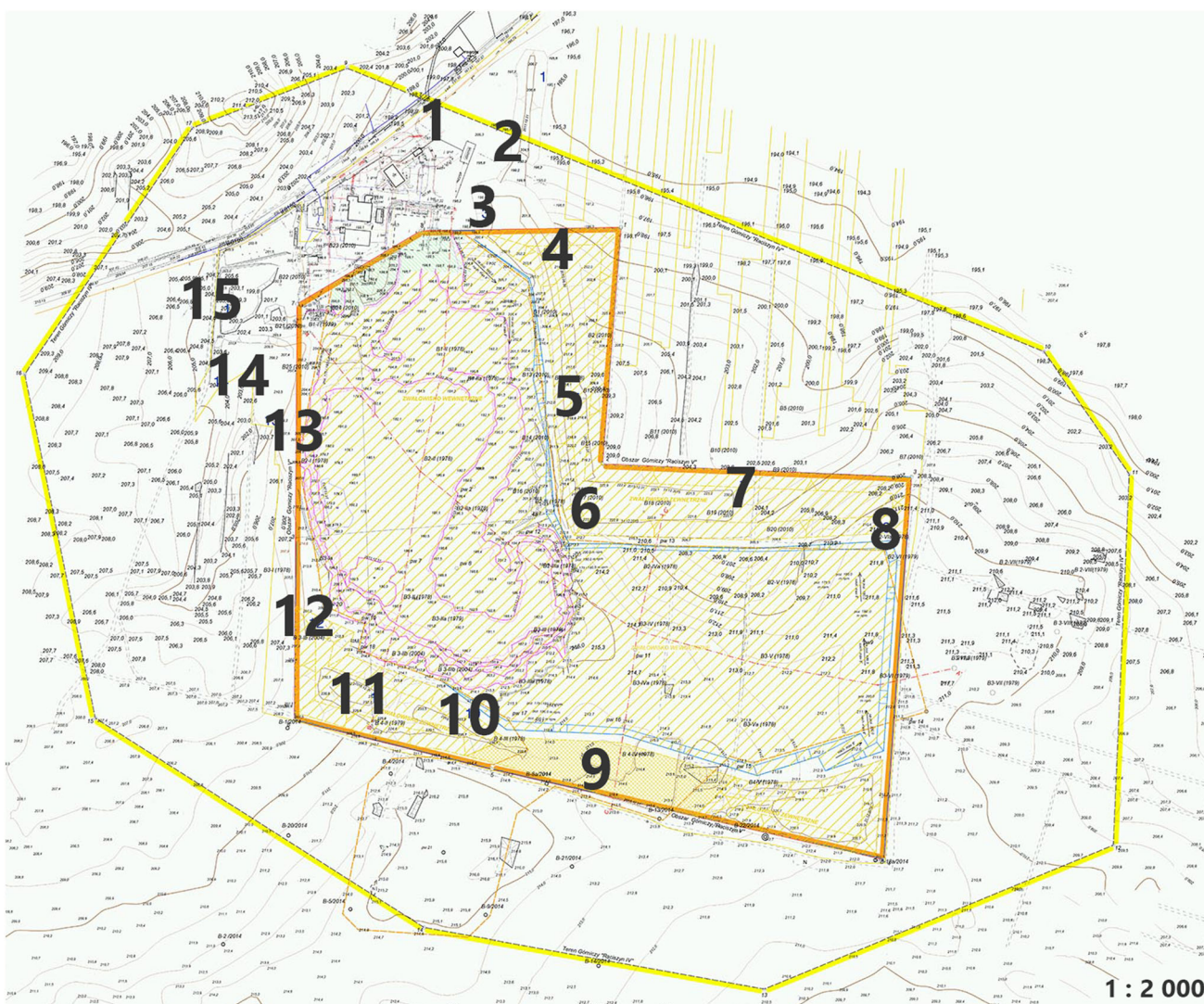


Fig. 1 Map of the Raciszyn II deposit with 15 locations from which the post-production raw material for analysis was collected

Table 1 Results of XRF analysis of post-production raw material taken from the 15 deposit locations shown in Fig. 1

Component %	No of samples														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
SiO ₂	25.5	29.2	25.7	26.0	25.4	28.7	27.9	27.6	30.2	26.0	27.5	25.7	25.2	25.5	25.9
Al ₂ O ₃	11.3	11.9	11.2	11.5	10.9	11.3	13.5	12.9	13.4	11.7	12.7	12.5	11.8	12.0	12.0
CaO	56.1	52.2	56.7	56.1	56.9	53.1	51.6	52.5	49.4	55.2	53.1	54.8	56.7	56.7	55.9
Na ₂ O	0.5	0.2	0.2	0.3	0.3	0.3	0.2	0.3	0.2	0.7	0.1	0.1	0.1	0.1	0.1
K ₂ O	0.5	0.6	0.5	0.5	0.5	0.6	0.5	0.5	0.6	0.6	0.5	0.5	0.4	0.5	0.4
SO ₃	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Fe ₂ O ₃	3.9	3.8	3.9	3.7	4.0	3.9	4.2	4.2	4.3	3.9	4.1	4.3	3.9	3.8	3.7
MgO	0.6	0.7	0.6	0.6	0.6	0.7	0.7	0.7	0.7	0.7	0.6	0.7	0.6	0.6	0.6

Results and discussion

Table 1 presents the elemental composition, as determined by the X-ray fluorescence (XRF) method, of all 15 analysed samples. The table includes only those elements whose concentration exceeded 0.5%. Based on the obtained results, it was observed that, regardless of the location of the samples taken for testing, the chemical composition of the post-production raw material was similar. This proves the high homogeneity of the entire area of the Jurassic limestone *Raciszyn II* deposit. In addition to oxygen, silicon and aluminium, the post-production raw material has high amounts of calcium, which, as is well known, has a large effect on the properties of the alkaline-activated products [10]. The analyses showed that the moisture content of the material in its delivery condition, regardless of the place of its collection, was about 25%.

Because of these repetitive and very consistent results of XRF and humidity analyses, for each of the post-production raw material taken from various locations at the Raciszyn deposits, the XRD tests were carried out only for sample no. 7. Based on the registered XRD pattern (Fig. 2), it was concluded that the dominant phases in calcium clay mineral composition are calcite (01-083-4611) and quartz (01-075-8320). They are accompanied by clay minerals from the kaolinite group. The least numerous components are the hard to define calcium silicates.

Based on the recorded thermogravimetry, differential thermal analysis and mass spectroscopy (TG/DTA/MS) curves (Fig. 3), it was found that, during the heating up of the post-production raw material, a several-stage process of

decomposition of its constituents takes place [13, 14]. The first phenomenon occurring at temperatures of around 220 °C is dehydration, during which the sample loses 1.34% mass. This effect is mainly related to the presence of water adsorbed on the surface of the sample. Subsequently, at a temperature range of 220–350 °C, the effects associated with the dehydroxylation process are observed. This is evidenced by the increase in water vapour content (m/z 18), in the mentioned temperature range, and a weak endotherm effect reaching a minimum at approximately 287 °C [15, 16]. This effect is characteristic of goethite iron hydroxides. On the other hand, on the XRD pattern of a non-calcined sample (Fig. 2), no peaks originating from goethite were registered, indicating that its content in the sample was minor. However, the light cream colour of the sample confirms the presence of the hydrated iron compound. The recorded change in mass, at the temperature range from 220 to 350 °C, amounted to 0.59%. In the temperature range from 350 °C to approximately 550 °C, the process of dehydroxylation occurred again. This is evidenced by the recorded intensive growth of gaseous products of m/z 18 and 17, released as a result of the decomposition of the sample. In addition, this effect is accompanied by a clear endotherm effect recorded on the DTA curve, reaching a minimum at 480 °C. This phenomenon is caused by the dehydroxylation of kaolinite present in the sample. The recorded change in mass, at the temperature range from 350 °C to approximately 550 °C, was 2%. The low intense endotherm effect which reached a minimum, recorded at 573 °C, is related to the transition of the low-temperature variety of β -quartz to the high-

Fig. 2 The XRD pattern of post-production raw material taken from the location marked in Fig. 1 as number 7

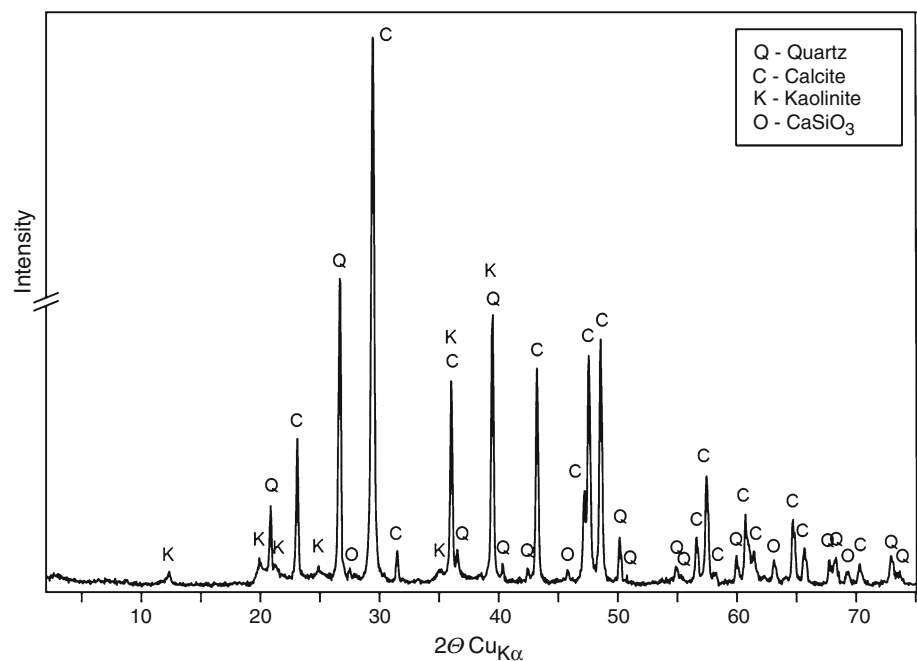
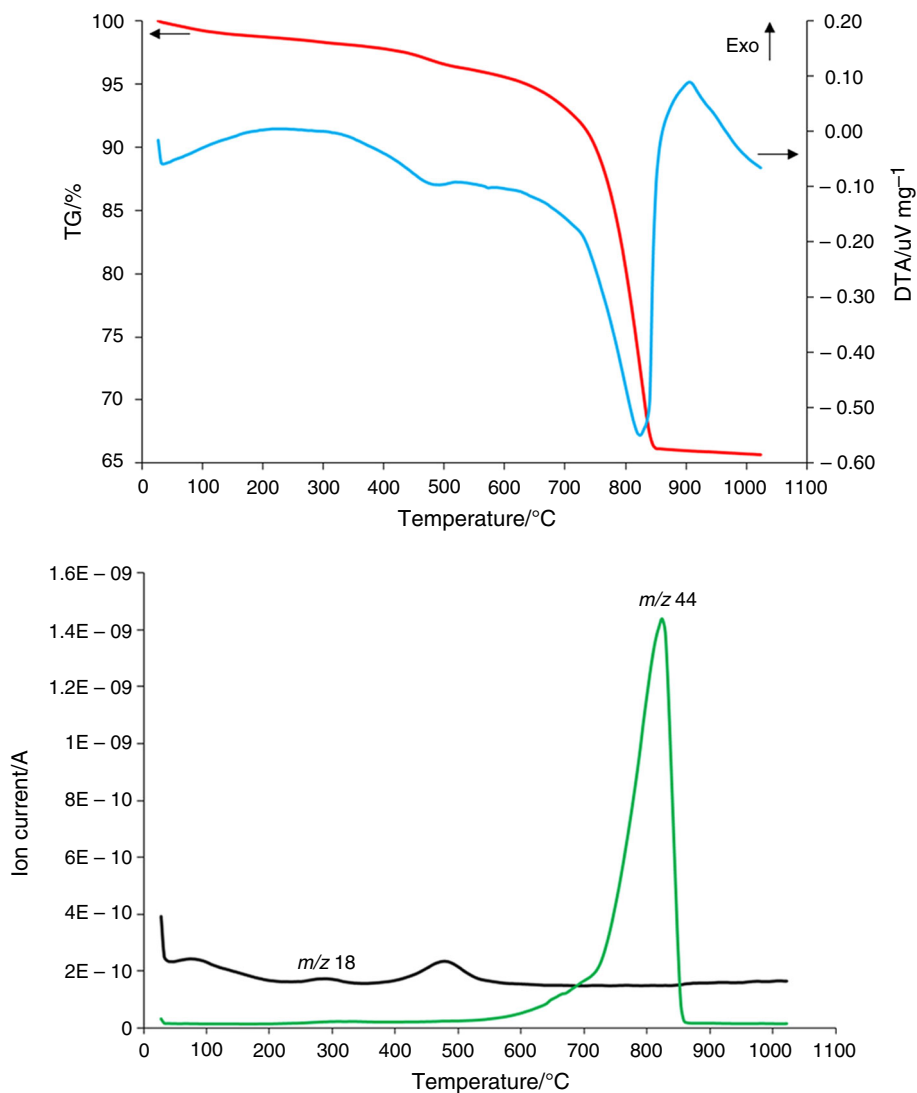


Fig. 3 The TG and DTA curves as well as the changes in intensity of H₂O (*m/z* 17 and 18) and CO₂ (*m/z* 44), recorded during post-production raw material heating from an ambient temperature up to 1000 °C



temperature version of α -quartz. The last stage of sample transformation, recorded on the curve during heating, is the process of calcite thermal dissociation. The maximum endotherm effect was recorded at a temperature of 825 °C. This process starts at a temperature of around 520 °C and ends at 860 °C. The confirmation of this effect is an intense increase in the course of the curve, presenting the change in CO₂ content (*m/z* 44) in released gaseous products during calcite dissociation. The maximum peak of *m/z* 44 mass was recorded at a temperature of 830 °C. The loss in mass associated with this process amounted to 30.2%.

The analysis of TG/DTA/MS curves led to the conclusion that the most intense thermal changes during heating the post-production raw material occurred at the temperature range between 700 and 900 °C. To optimise the thermal processing of the post-production raw material for an XRD analysis, the samples were calcined at 700 °C, 750 °C, 820 °C and 900 °C, respectively. It was observed

that the mineral composition of the calcined sample at 700 °C (Fig. 4) has not significantly changed, compared to the non-calcined post-production raw material composition (Fig. 2). The calcite (01-083-4611) and quartz (01-075-8320) were still the dominant components. The calcium silicates are also present in trace amounts. The only observed difference in the sample, after the calcination process, relative to the non-calcined sample is the lack of kaolinite, which has been dehydroxylated as a result of the high temperature (Fig. 3).

Figure 5 shows the results of a XRD analysis of post-production raw material calcined at 750 °C. Constantly, the dominant components in the mineral samples were calcite (01-083-4611) and quartz (01-075-8320). In addition, there were also transformation products from the primary components of the sample. Mainly they belong to the calcium silicates: Ca₂SiO₄ (04-017-5841) and Ca₂Si₂O₇.

Fig. 4 The XRD pattern of clay calcined at 700 °C

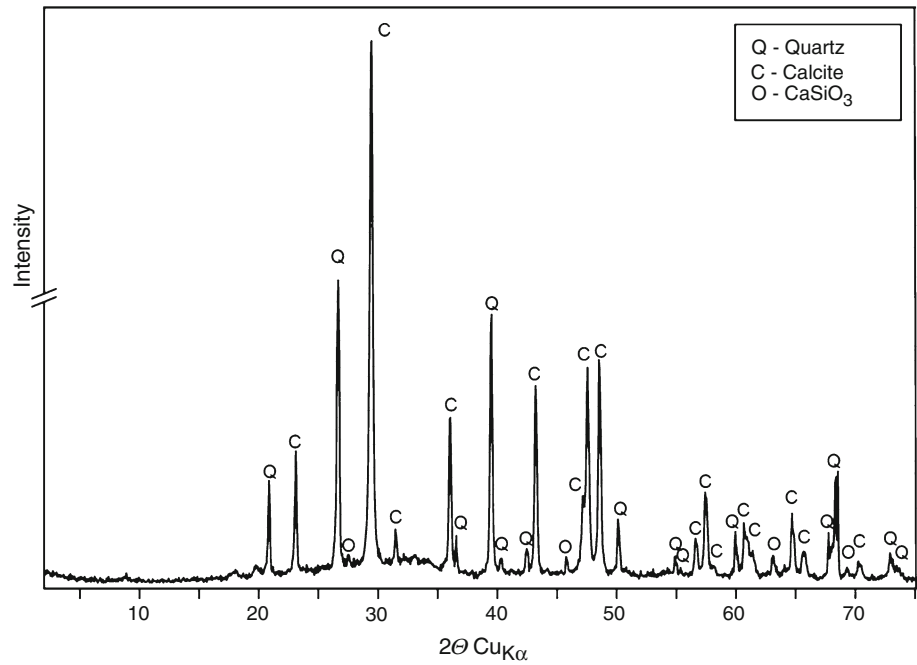
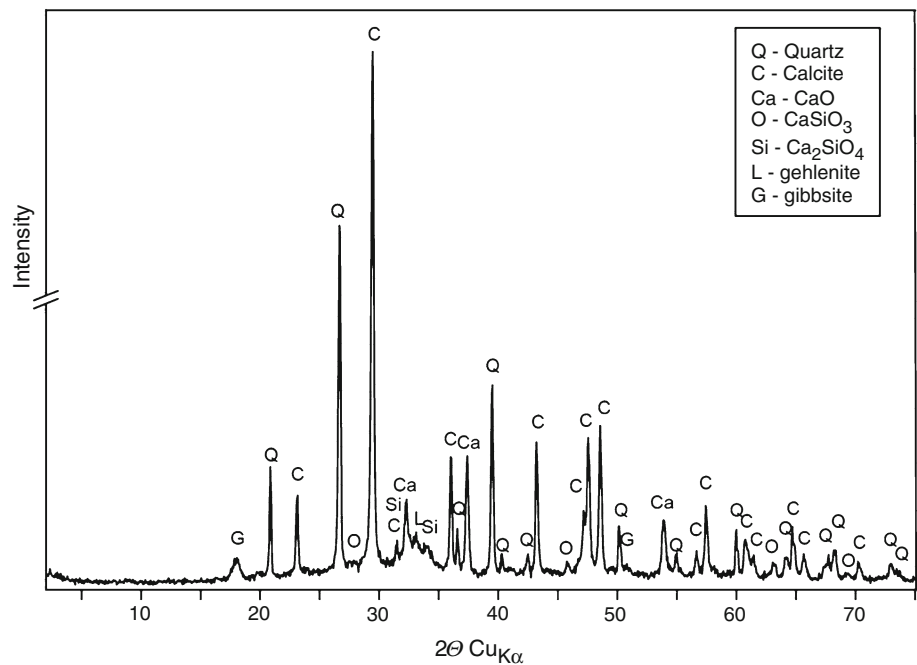


Fig. 5 The XRD pattern of clay calcined at 750 °C



The results of XRD post-production raw material calcined at 820 °C once again confirmed that, after such heat treatment, its composition is dominated by calcite (01-083-4611) and quartz (01-075-8320). In addition, there is only a small amount of primary calcium silicates. The products from the thermal transformation of the sample are also visible. This is confirmed by the presence of: (1) calcium oxide, which is a product of thermal dissociation of calcite and (2) a small amount of gehlenite $\text{Ca}_2\text{Si}_2\text{O}_7$, which

appears as a result of the Si and Ca reactions released from the structure of kaolinite and calcite, respectively.

In the mineral composition of the sample calcined at 900 °C (Fig. 7), in addition to quartz (01-075-8320) and primary calcium silicates, the presence of products from the thermal transformation of the initial components of the sample was also observed. The calcium oxide is dominant, which is a product of thermal calcite dissociation. In addition, there is gehlenite $\text{Ca}_2\text{Si}_2\text{O}_7$ and wollastonite

Fig. 6 The XRD pattern of clay calcined at 820 °C

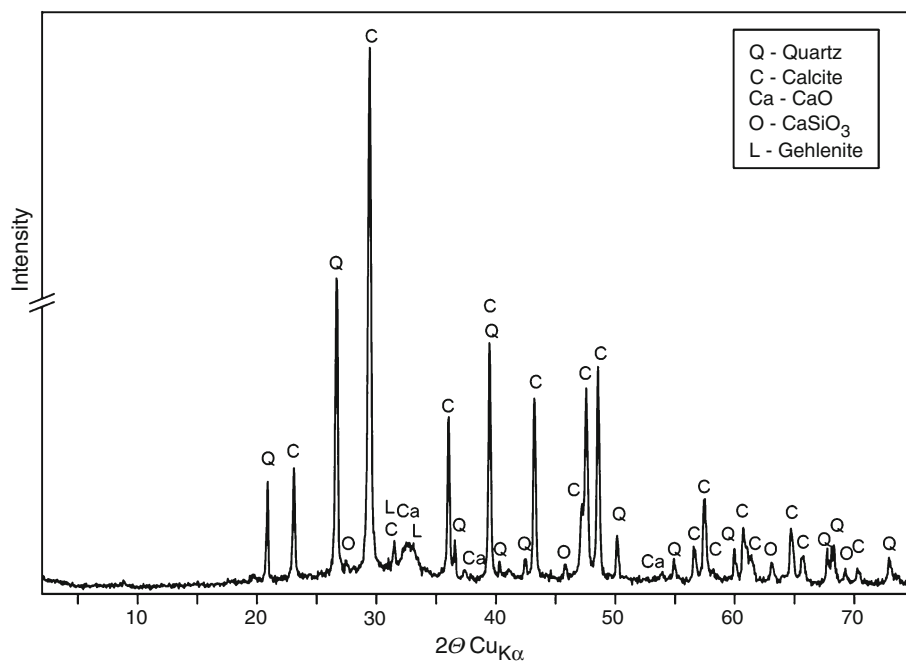
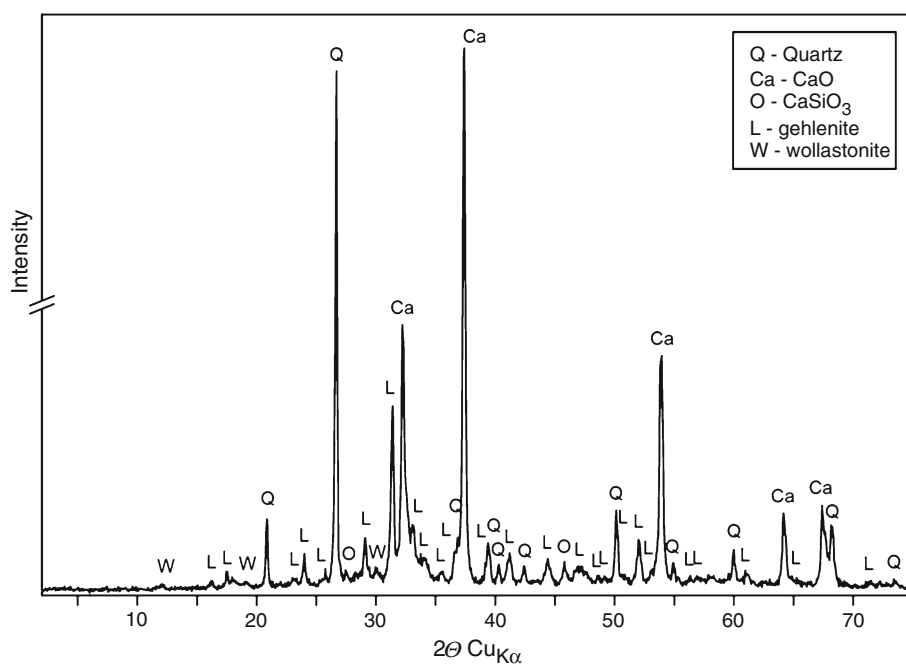


Fig. 7 The XRD pattern of clay calcined at 900 °C



CaSiO_3 , both of which appear as a result of Ca and Si reactions occurring in the calcite and kaolinite.

Table 2 presents the results of leachability in water of elements from post-production raw material collected from the Raciszyn II deposit. Of all the analysed ions present in aqueous extracts, aluminium was found to be the only one exceeding the limit value. In accordance with the applicable legal regulations, i.e. the ordinance of the Minister of the Environment, regarding the conditions to be met when

introducing sewage into waters or to the ground and on substances particularly harmful to the aquatic environment, the acceptable concentration of aluminium is 0.3 mg dm^{-3} , while the measured concentration in the extraction solutions was 0.651 mg dm^{-3} .

The pH of the aqueous solution, after the 24-h extraction process, proved to be alkaline and it was 10.9. This value exceeds the acceptable pH range, which should be in the range from 6.5 to 9.

Table 2 The leachability in water of post-production raw material elements taken from the *Raciszyn II* deposit

Element	Leachability/mg dm ⁻³	Limit value/mg dm ⁻³
Ag	0.011	0.1
Al	0.651	0.3
As	< 0.001	0.1
B	< 0.001	1
Ba	0.004	2
Ca	8.111	–
Cl	5.530	1 000
Co	0.002	1
Cr	0.016	0.5
Cu	0.015	0.5
Fe	0.205	10
HCO ₃	12.570	–
K	1.564	80
Mo	0.013	1
Na	2.119	800
Ni	0.001	0.5
P	0.704	3
Pb	0.004	0.5
SO ₄	15.760	500
Sb	0.003	0.3
Se	< 0.001	1
Si	17.198	–
Sn	0.004	2
Ti	0.017	1
Tl	0.001	1
V	0.014	2
Zn	0.011	2

Table 3 The results of the post-production raw material radioactivity test taken from the *Raciszyn II* deposit

Radioisotope	Concentration measured in post-production clay from the <i>Raciszyn II</i> deposit/Bq kg ⁻¹	Lowest and highest median values occurring naturally in the soil, according to the UNSCEAR 2000 report/Bq kg ⁻¹
²²⁶ Ra	10.1 ± 0.8	17/60
²²⁸ Ra	20.6 ± 1.1	11/64
²²⁸ Th	19.2 ± 1.2	11/64
²¹⁰ Pb	10.6 ± 1.1	17/60
⁴⁰ K	84.5 ± 5.5	140/850
¹³⁷ Cs	0.10 ± 0.05	–

The results of the post-production radioactivity study measured by gamma spectrometry are presented in Table 3. The table also presents the lowest and the highest median values occurring naturally in the soil, consistent

Table 4 Compressive strength of alkaline-activated materials dependent on the curing time and the calcination temperature of the post-production raw material

The temperature of clay calcination/°C	Compressive strength MPa after	
	14 days of curing	28 days of curing
700	15.3 ± 0.8	16.4 ± 0.6
750	17.1 ± 0.7	16.0 ± 0.4

with the UNSCEAR (United Nations Scientific Committee on the Effects of Atomic Radiation) 2000 report [17]. It was observed that the values of radioactive nuclides, ²²⁶Ra, ²¹⁰Pb and ⁴⁰K, in post-production raw material are smaller than the median of the lowest values for soil, whereas nuclides, ²²⁸Ra and ²²⁸Th, are contained in the lower limit of the lowest soil concentrations. On the basis of the radioactivity test results for post-production raw material, the activity indicators f_1 and f_2 were also determined as 0.16 ± 0.01 and 10.1 ± 0.8 , respectively. It is well known that the activity indicator f_1 determines the content of natural radioactive isotopes in the tested material, while the index f_2 indicates the content of the radium isotope ²²⁶Ra. For raw materials and building materials, which will be used in buildings intended for human or livestock habitation, according to the legal provisions in force and mentioned in the methodology, the most restrictive requirements regarding these activity indicators are applied. They may not exceed by more than 20% the value of $f_1 = 1 \text{ Bq kg}^{-1}$ and $f_2 = 200 \text{ Bq kg}^{-1}$, respectively. The determined values of activity indicators, for post-production raw material, from the *Raciszyn II* deposit clearly indicate that this material fulfils the legal requirements regarding the possibility of its use in building applications.

Based on the results of the coupled thermal analysis (Fig. 3) and XRD (Figs. 4–7), it was found that the calcination temperature range of post-production raw material, collected from the *Raciszyn II* deposits, should be in the 700–750 °C range. Therefore, for the production of AAM, the post-production raw material was used after the calcination process performed at 700 °C and 750 °C, respectively. The calcination process at these temperatures was carried out for 240 min. The compressive strength of materials prepared in this way was tested after 14 and 28 days of curing, respectively. The results obtained are presented in Table 4. It was observed that the extreme temperatures used, from the optimal range of calcination, had no significant effect on the obtained compressive strength results. In addition, it was also observed that after just 14 days of curing, the material obtained stable strength properties. The recorded compressive strength values for alkali-activated materials, based on post-production raw

material, are comparable to the results obtained for geopolymers produced from metakaolin [11].

Conclusions

For the first time, results regarding the characteristics of the properties and the possibilities of practical management of post-production raw material from the Jurassic limestone *Raciszyn II* deposit have been presented. The mineralogical and chemical analyses, carried out at 15 locations from the *Raciszyn II* deposit, confirmed its homogeneity and the existence of minerals from the kaolinite group present in the post-production raw material. The chemical composition of this post-production material allowed it to be used as a raw material for the production of alkaline-activated materials. However, the calcination process of the raw material at the set temperature range was initially required. The results of the coupled thermal analysis of TG/DTA/MS allowed for the interpretation and determination of temperature ranges of processes occurring during the heating of the post-production raw material, i.e. dehydration, dehydroxylation, allotropic conversion of quartz and thermal dissociation of calcite. Both the results of water leaching of elements from the post-production raw material and the results of research on its radioactivity clearly indicate that this material fulfils legal requirements regarding the possibility of its use in building applications. The alkaline-activated materials based on post-production raw material from the *Raciszyn II* deposit obtain stable compressive strength values after 14 days of curing.

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