Management of mining wastes through their transformation into useful sorbent

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Abstract Every year a few hundred million or so tons of industrial waste are generated all over Europe. A considerable share is attributable to exploratory wastes from the mining sector and combustion byproducts. The process of their reprocessing and utilization fits into the following rules subject to intensive development, viz.: zero waste economy (Zero Waste Europe), effective use of resources (Resource Efficient Europe) as well as closed-circuit economy (Circular Economy). The article shows some research results to corroborate the concept of industrial waste processing of carbonaceous shales into sorbent materials. The applied process of carbonaceous shale calcination led to the obtaining of a material containing metakaolinite, then used in the synthesis of zeolites. The specific surface of the sorbent obtained in the aforesaid way exceeded 100 m²/g.

1. Introduction

Substances, until recently called waste, are more and more often used as raw materials for new technologies. Limiting natural deposits of mineral resources leads to the search for alternative solutions, especially in the construction and transport sectors [1]. The term “future mineral resources” begins to replace the term "waste", and the term "secondary raw materials" is increasingly used in their nomenclature [2]. This reflects not only their advantages, but also the possible benefits of their future use [3, 4].

23 January 2018 r. The Council of Ministers adopted the document "PROGRAM for the hard coal mining sector in Poland". The Program specified, inter alia, that "The main objective is to create conditions conducive to the construction of a profitable, effective and modern hard coal mining sector, based on cooperation, knowledge and innovation, which, operating in a friendly and predictable program and legal environment, allows for effective use of resource, social and economic capital to ensure the high energy independence of Poland and support the competitiveness of the national economy" [5]. Fulfillment of this concept requires the definition of specific objectives, which also include "Reducing the impact of the hard coal mining sector on the environment and increasing the use of mining waste and accompanying minerals" [5]. It is therefore necessary measures, including the implementation of innovative technologies in order to develop the accompanying minerals and other waste generated at the first processing, extraction and enrichment of deposits. The use of secondary raw materials by enterprises or research centers will not only use their energy and processing potential, but also allow to reduce the use of natural resources [6]. In Polish terminology, mining waste is defined as: "waste generated during the search, extraction, chemical and physical processing of ores and other
minerals” [7]. Minister of Environment of 27 September 2001 (updated in 2020) categorizes the extractive waste to a group of 01. This group is divided into subgroups:

- Subgroups 01 01 – waste from mineral extractions,
- Subgroups 01 03 – wastes from physical and chemical processing of metal ores.
- Subgroups 01 04 - wastes from physical and chemical processing of minerals other than metal ores.
- Subgroups 01 05 - drilling muds and other drilling wastes [7].

The management of mining by-materials, mining waste and the development of clean coal technologies is dealt with, among others, by “TAURON Wydobycie” group, which processes these materials and then allocates them in a usable form to: road and construction aggregate, as fillings and fire prevention materials, scaling material, energy granulate [8].

Such activities reduce the negative impact on the environment and reduce the amount of landfilled waste [9]. According to the data of the Central Statistical Office for 2016-2020, the main source of waste was mining and quarrying, approx. 54% of total waste generated. During this period, every year, the processes of washing and cleaning minerals generated an average of over 30 million tons of waste [10]. This was a consequence of the specific nature of the exploited deposits, the deposit management policy, technologies used to extract raw materials, and ultimately increased customer requirements [11]. 94% waste masses constitute processing waste, which is segregated in the process of mineral enrichment. These can be coarse grain waste (200 - 20 mm), fine grain (20 - 0.5 mm) sludge and flotation waste <1 mm [12, 13]. Both the large amount and the significant fragmentation of the coal fraction justify the need to change the current practices. Their increased use is required, for example, as: basic and supplementary fuel for indicated energy facilities, mastering the production of high-quality coal concentrates or alternative fuel blends [14]. In many cases, fine-grained fractions can be enriched with physical and physicochemical methods leading to high-energy coal concentrates [15]. Such solutions allow the full use of even low-energy, fine-grained coal fractions [16]. Estimates show that only 55.2% of the generated coal combustion residues are reused, largely by the cement and mining industries, however, these solutions do not use all of the waste generated, therefore there is still a need for solutions favoring the removal of coal combustion residues, also friendly to the environment [17].

For years, sorbents have played an important role in the processes of retaining, collecting and absorbing various liquids, which are difficult, toxic and environmentally hazardous substances [18]. These are porous materials that can be of organic (straw, leaves), inorganic (mineral wool, zeolite, sand) or chemical origin [19]. An alternative to the enrichment of sludge and coal shale waste may be their use as a raw material in the sorbent production process. [20]. Due to the correct level of silicon and aluminum, such waste materials are more and more often used in the process of zeolite synthesis [21]. For this purpose, the materials must first be subjected to heat treatment. The calcination process of coal shale transforms kaolinite into metakaolin [22]. In turn, metakaolin is an extremely attractive raw material for the synthesis of sorbents. The advantage of the solution using metakaolin from waste for the production of sorbents is that neither the natural mineral resources nor the areas of their extraction are degraded or destroyed [23].

Due to the structure of the skeleton in combination with the ion exchange and sorption properties, the sorbents obtained as a result of synthesis are used in engineering and environmental protection, and in most cases are used as: molecular sieves, gas cleaning materials (e.g. in carbon capture processes for CCS - carbon capture and storage) or materials for removing heavy metals Zn, Cd, Ni, Pb, Cr from sewage. Reacted sorbents containing i.a. heavy metals can be utilized by various methods, namely: solidification in concrete as additives to the blast furnace charge or it can be leached from them, e.g. with a NaCl solution, on average 30 million tons of waste [23, 24], materials for removing methylene blue [25]. Fly ash based geopolymers are used as lead adsorbents [26], copper ions [27] and cobalt [28] from aqueous solutions.
2. Materials and methods

The carbonaceous shales subject to study were collected from the coal mines, respectively, Piast (KWK Piast) and Rydułtowy (Ruch Rydułtowy). The material was disintegrated on a jaw crusher and then ground in a Retsch ZM200 ultra-centrifugal mill on a 0.040 mm sieve. The material thus prepared was subject to calcination in chamotte furnaces at a temperature of 750°C. Afterwards, a synthesis of zeolites was performed in 100 ml cylindrical polypropylene vessels. For this purpose, 1 g of sample was mixed with 20 ml of 2.75 M NaOH solution. Then, the remaining NaOH solution was removed; the samples were washed in distilled water so as to reach a pH close to 9. The final stage was the drying of samples at 105°C for 24 hrs [29]. Table 1 shows the description of samples of materials used in the tests.

Table 1. Description of samples according to the deposit from which the raw material was collected and the processing stages

| Symbol | Description                                              |
|--------|-----------------------------------------------------------|
| N1     | Carbonaceous shale from the KWK Piast Coal Mine           |
| N2     | Carbonaceous shale from the Rydułtowy Coal Mine (Ruch Rydułtowy) |
| K1     | Material from the KWK Piast Coal Mine after calcination at 750°C |
| K2     | Material from the Rydułtowy Coal Mine (Ruch Rydułtowy) after calcination at 750°C |
| S1     | Material from the KWK Piast Coal Mine after synthesis     |
| S2     | Material from the Rydułtowy Coal Mine (Ruch Rydułtowy) after synthesis |

XRD analyses were performed with a Rigaku SmartLab X-ray diffractometer with the following parameters: CuKα radiation, reflective graphite monochromator, lamp voltage 45 kV, lamp current 200 A, step: 0.05°2θ, counting time per step = 1 s. The values of lattice parameters obtained have been used for the phase identification of samples under analysis. For this purpose, the data from the ICDD (International Centre for Diffraction Data 2016) catalogue and XRAYAN computer program were utilized.

The topography of the particle surfaces and the chemical microanalysis were performed with a JEOL JSM-820 scanning electron microscope equipped with an EDS system. Before SEM examination, the samples were covered by a thin gold layer by sputter coater JEOL JEE-4X.

The measurements of porosity and of the size of specific surface were carried out using an ASAP 2020 sorptomat. Degassing of the samples was carried out at 100°C for 24 hrs. In order to determine the distribution function or the volume of pores in the materials under investigation, the recorded low temperature (-196 °C) nitrogen adsorption isotherms were applied. In order to determine the volume of mesopores the Barrett, Joyner and Halenda (BJH) method was used. After the synthesis, Brunauer-Emmett-Taller (BET) analysis was used for determining the specific surface of the samples of raw materials and materials under investigations.

3. Results

Figures 1a and 1c show the results of XRD analyses for carbonaceous shales collected, respectively, from the deposit of coal mines KWK Piast and Ruch Rydułtowy. The diffraction patterns recorded for the sorbents obtained are presented in figures 1b and 1d. On the basis of the obtained results it was found that irrespective of where the raw material was collected, the predominant mineral components in the carbonaceous shales (N1 and N2) are quartz, kaolinite and illite accompanied by some phase derived from dolomite, chlorite and potassium feldspars.
Figure 1. Diffraction patterns of the samples: N1 (a), S1 (b), N2 (c) and S2 (d).

After the process of calcination and activation in alkali conditions (S1 and S2), the predominant phase in the materials produced is Zeolite – A. Such a result as obtained irrespective of the type of raw material used. In the structure of the sorbents also illite, quartz, calcite and potassium feldspars was determined. The occurrence of these minerals shows an incomplete reaction of the substrates during the synthesis held at 80°C for 24 hrs. It is commonly known that the efficiency of synthesis of sorbents and zeolites does not reach 100% [30, 31], since the material subject to reaction is not entirely able to be transformed into zeolite phases. There will always be some unreacted phases left, referred to as non-reactive. The use of an appropriate modification of the process parameters may increase the tendency of the raw material to produce sorbents. The presented results are of a research nature. The conducted analysis proves the presence of zeolite A, it can be used to conduct a more in-depth review and characterization of phases such as sodalite octahydrate or zeolite Na-P1.

Table 2 shows the results illustrating the shares of pores for a specific surface as recorded for the materials after calcination and alkali synthesis. An analysis of the results obtained confirmed that the modification made to the hydrothermal conditions had not only allowed the phase composition to be changed, but also the micromorphology of the materials. After the process of synthesis, the specific surface of the sample S\(_{\text{BET}}\) from the KWK Piast coal mine increased from 18 m\(^2\)/g to 103 m\(^2\)/g. Meanwhile, in the case of the KWK Rydultowy coal mine, the increase in the said parameter was better, viz from 12 m\(^2\)/g to 126 m\(^2\)/g. The total volume of pores in the sample from the KWK Piast coal mine was doubled, viz from 0.031 cm\(^3\)/g to a value of 0.061 cm\(^3\)/g; yet, in the case of the sample from the coal mine KWK Rydultowy, the total volume of pores increased by 37% from 0.035 cm\(^3\)/g to 0.048 cm\(^3\)/g. For both the samples, the volumes of micropores increased by several times. Such considerable changes were not recorded for the volumes of macro- and mesopores.
Table 2. Porosity and specific surface of samples according to the deposit of origin of the raw material as well as the their processing stage

| Symbol | $S_{\text{BET}}$ [m$^2$/g] | $V_{\text{tot}}^{0.99}$ [cm$^3$/g] | $V_{\text{mik}}^{\text{BR}}$ [cm$^3$/g] | $V_{\text{mez}}^{\text{BJH}}$ [cm$^3$/g] | $V_{\text{mak}}$ [cm$^3$/g] |
|--------|----------------|----------------|----------------|----------------|----------------|
| K1     | 18             | 0.031          | 0.005          | 0.019          | 0.007          |
| S1     | 103            | 0.061          | 0.039          | 0.014          | 0.008          |
| K2     | 12             | 0.035          | 0.005          | 0.020          | 0.010          |
| S2     | 126            | 0.048          | 0.048          | 0.036          | 0.027          |

$S_{\text{BET}}$ [m$^2$/g] – specific surface acc. to Brunauer – Emmett – Teller (BET) theory,
$V_{\text{tot}}^{0.99}$ [cm$^3$/g] – total specific volume of pores for a relative pressure $p/p_0 = 0.99$,
$V_{\text{mik}}^{\text{BR}}$ [cm$^3$/g] – volume of micropores (pores with widths under 2 nm) according to Dubinin – Radushkevich method,
$V_{\text{mez}}^{\text{BJH}}$ [cm$^3$/g] – volume of mesopores (pores with a width greater than 2 nm and less than 50 nm) according to the Barrett method - Joyner - Halve (BJH),
$V_{\text{mak}}$ [cm$^3$/g] – volume of macropores (pores wider than 50 nm).

Figure 2 shows the morphology of products from the synthesis of calcinated exploratory wastes from the coal mines, respectively, KWK Piast – photograph a and KWK Rydultowy – picture b. The average size of the resulting grains is approximately 5 micrometers.

Figure 2. SEM images of samples S1 (a), and S2 (b).

4. Conclusions

Based on the tests carried out, it was shown that the application of low temperature hydrothermal synthesis allowed a transformation of carbonaceous shales into a sorbent. The calcination process mainly influences the phase composition of the raw material, while during the synthesis the topography of the material additionally changes - the increase of the specific surface area and porosity. After calcination, zeolite A phases were noticed in the material tested, the structure is coagulated, particles having a cubic solid shape are clearly distinguishable. A-type zeolite was obtained irrespective of the deposit from which the raw material had been drawn. Specific surface areas $S_{\text{BET}}$ exceeding 100 m$^2$/g obtained show that such materials may be utilized in the industrial applications. The appropriate selection of hydrothermal conditions for waste materials from the mining sector allows to obtain a structure that can be successfully used for the production of sorbents. Extending research to other modifications and processes may help to obtain the structure type with ion exchange and sorption properties.

Finally, the studies have shown that it is possible to obtain synthetic sorbents from waste products, and that the parameters of such sorbents are comparable to those of synthesis products made from raw materials extracted from natural resources.
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