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THERMAL REGENERATION OF MINERAL SORBENT USING BURNER UNIT

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This article presents the results of scientific investigations on the thermal regeneration process of a sorbent of mineral origin sorbent using a retort burner. Diesel oil, a petroleum liquid, most often pervades the environment during different catastrophes. The investigated sorbent of mineral origin was used in the standard way that the Fire Service removes such petroleum liquids from the environment during disasters. For research purposes, a regeneration chamber with a retort burner was constructed. The first phase of the investigation was aimed at defining the physico-chemical features of the sorbent after subsequent cycles of the regeneration process. The second phase involved an analysis of the energy and ecological effects of the regeneration process. The results showed that the first three cycles of the regeneration process occurred under low emission conditions. The proposed regeneration method achieved a positive energetic effect with a functional heat stream with an average value of 12.4 kW (average efficiency of the regeneration chamber was 68 %). The method is very efficient, with regeneration rates between 7.2 kg/h and 8.4 kg/h. It requires only a short amount of time for the start-up and extinction of the regeneration chamber, and it is also flexible to changes in the process conditions.

Keywords: thermal regeneration, mineral origin sorbents, retort burner, removal of harmful substances, utilisation of sorbents

1. INTRODUCTION

During the daily routine work of the Fire Service (FS) in Poland, approximately 80 % of the removed flow waters comprises different types of petroleum liquids, primarily diesel oil, furnace oil and petrol (gasoline), which are the main fuels used in vehicles, machines and devices. In the last decade, there was a significant increase in the number of incidents requiring the intervention of the Fire Service brigades. From the year 2000 to the year 2008, the use of sorbents in those incidents more than doubled, from 8,378 uses to 32,624 uses, respectively. Figure 1 shows a summary of the local threats (natural events other than fires) that occurred in Poland from 2000-2008.

Basic sorbents used by FS during fire brigade operations (i.e., rescue, chemical and ecological services) are based on natural diatomaceous earth. Along with the increase in the number of events, there is also a higher demand for the sorbent, resulting in increased production. Thus, the utilisation and regeneration of the sorbents used to remove harmful substance spills becomes very important. Lowering the costs of chemical and ecological rescue operations while minimising the negative impact of the sorbents on the natural environment could be achieved through usage of the nonconventional sorbents or the reconstruction of adsorption features such that the regenerated sorbents can be reused

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(Karthikeyan et al., 2010; Maheswari et al., 2008; Nduka, 2012). Regeneration methods for used adsorbents (with impurities adsorbed from liquid and gas phases) that are found in the literature (Bhatnagar and Jain, 2005; Chang et al., 2004; Conti-Ramsden et al., 2012; Drage et al., 2009; Kubota et al., 2013; Qu et al., 2009; Salvador and Jimenez, 1996) can be classified into the following types: thermal, chemical and extraction; "wet" (carried out by means of steam); gas; vacuous; thermo-vacuous; electrochemical and electrical; and others, such as biological methods that take advantage of X-rays. Considering the point of application of such methods, the regeneration process should have conditions that can be easily controlled, be energy effective and have a minimal harmful impact on the environment without the need for expensive, highly specialised installations (Irvine et al., 2010). Thus, research on low-emission thermal regeneration of inorganic sorbents of mineral origin in a regeneration chamber equipped with a retort burner that generates heat (i.e., additional positive energy) has emerged. The thermal regeneration heat may then be used to heat up each of the 500 fire fighting rescue brigade premises equipped with chambers with a retort burner. Adsorbent regeneration should be in line with the following conditions (Buczek, 2011):

- reconstruction of an initial porous structure, in which a regenerated medium should have a porous structure similar or even better than the original adsorbent,
- regenerate yields of approximately 80-95 % dry mass after taking into account losses resulting from loading abrasion and partial gasification of the carbon matrix,
- neutralisation of secondary waste by post combustion of desorbed compounds and the elimination of impurities in the waste gas stream; and,
- economic profitability after taking into account the total costs related to the creation of a completely new product, waste storage costs, and the total costs of the regeneration process.

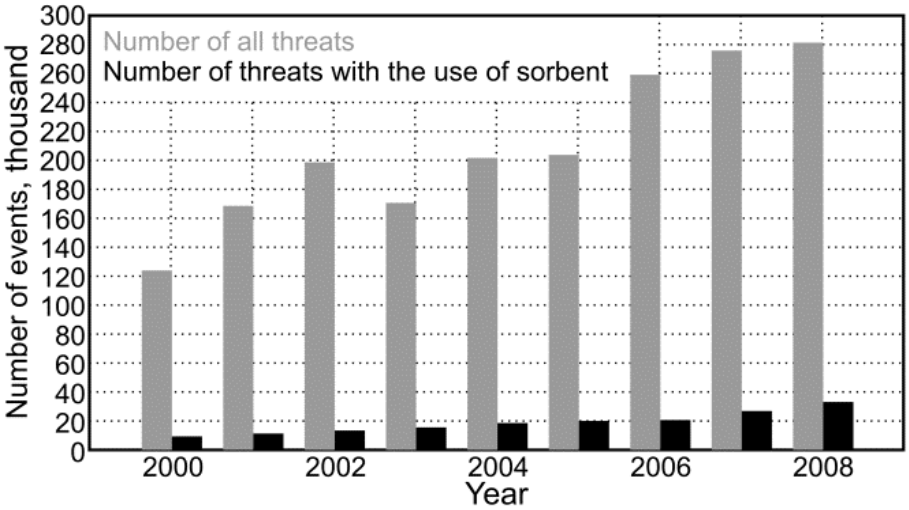

Fig. 1. Summary of local threats from 2000-2008

2. EXPERIMENTAL

All scientific experiments related to the regeneration process were performed in a specially designed and built research stand. A diagram of the stand is shown in Figure 2. The basic element was a regeneration chamber equipped with a retort burner. The sorbent was delivered from a storage container by means of a feeding screw. The air needed for the regeneration process was transported through a ventilator and nozzle system with simultaneous measurement of the air stream volume using a rotameter. Above the retort burner was a waste gas deflector; it extended the time of the waste gas in close proximity of the burner. To control the temperature of the regeneration process and to sample for

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gas impurities, special ports were incorporated, as shown in Figure 2. There were four objectives for the current investigation:

1. Determination of the sorption features of the investigated sorbent before and after thermal regeneration using the retort burner.
2. Quantification of the gas and solid impurities produced during the thermal regeneration of the non-organic sorbent.
3. Determination of the energy effect of the thermal regeneration of the sorbent.
4. Optimisation of the conditions for the low-emission thermal regeneration of the mineral sorbent in the combustion chamber equipped with the retort burner.

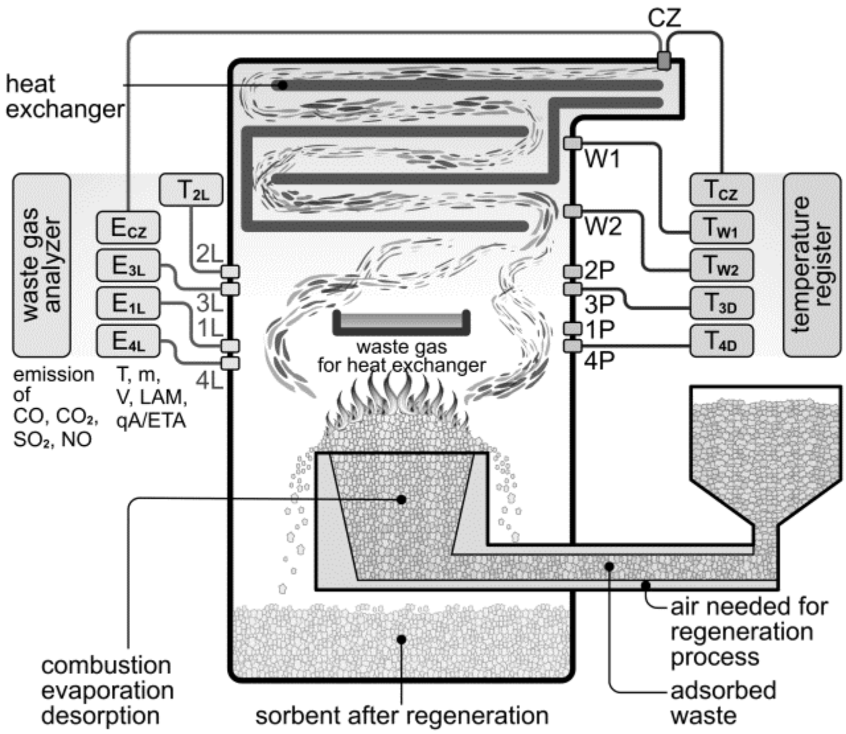

Fig. 2. Research stand – the regeneration chamber with the retorted burner and the measurement ports

The range of the performed experiments is presented in Figure 3. The entire investigation comprised two main phases. The first phase was devoted to the determination of the physico-chemical features of the sorbent, whereas the second phase included an energy and ecological analysis of the thermal regeneration process. Five regeneration cycles were carried out during the study.

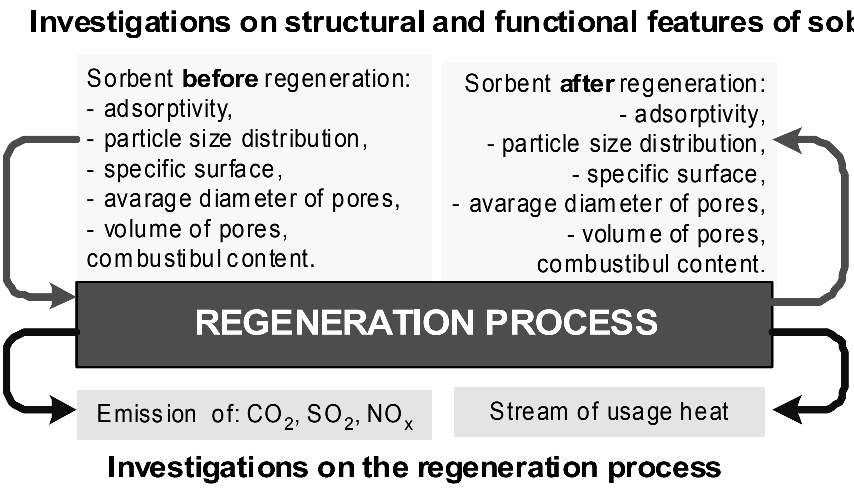

Fig. 3. Concept diagram of the range of experiments for the regeneration process

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The sorbent was impregnated again after each thermal regeneration cycle. A typical non-organic sorbent of mineral origin most often used by FS brigades during ecological rescue actions was used in the investigations. The chemical content of the sorbent is presented in Table 1.

Table 1. Sorbent chemical content before thermal regeneration

Sorbent chemical content	
Content of SiO_2	74 %
Content of Al_2O_3	11 %
Content of Fe_2O_3 / FeO	7 %
Content of MgO	2 %
Content of CaO	1 %
Other	5 %

According to the legal regulations in Poland, sorbents that are acceptable for use by the Fire Service should have the following features: no less than 80 % of active carbon's (granulation between 4-8 mm) ability to absorb light oil and 95 % of the sorbent's mass should not have a granulation smaller than 0,3 mm. The diesel oil was the adsorbate, which can be found under different commercial names, such as Ekodiesel Plus 50 B,D,F, Ekodiesel ULTRA B,D,F, Standard Urban Diesel Oil 25, Super Urban Diesel Oil 05 and VERVA ON. Initial investigations determined the specific conditions for the regeneration process, namely, the sorbent mass and air volume. The air volumetric flow rate was 2.3 m^3/min, while the fuel mass flow rate ranged from 0.12-0.14 kg/min. The combustible content in the regenerated sorbent was no higher than 5%, compared to the initial value of 2.5 %. The temperature of the walls of the combustion chamber was above 500 °C; the temperature inside the chamber, measured using a thermo-vision camera aimed directly inside the chamber, was 1000 °C. Figure 4 presents the variability of the combustible content in the regenerated sorbent and the average temperature registered in the combustion chamber during optimisation of sorbent mass stream. A sorbent flow below 0.12 kg/min during the thermal regeneration process resulted in an insufficient level of regeneration, as exhibited by a significant combustible content in the sorbent at the end of the entire process. An incomplete regeneration process was observed when the combustible content in the sorbent was greater than 10 % of the sorbent's mass. Additionally, simultaneous measurements of the average temperatures in the combustion chamber during the regeneration process showed than an incomplete process can be caused by cooler thermal conditions.

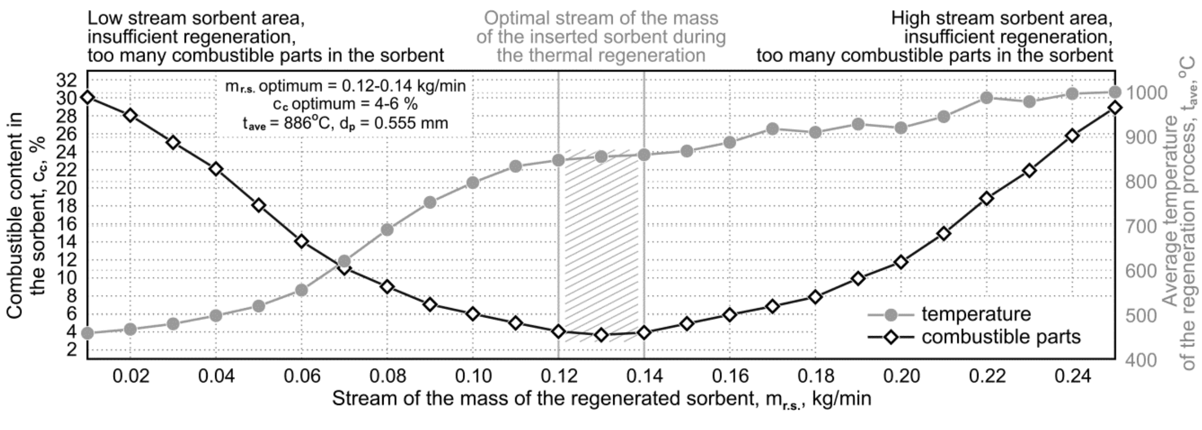

Fig. 4. Optimisation of the sorbent mass flow conditions of the regeneration process

When the sorbent's mass flow rate was greater than 0.14 kg/min, it caused the combustible content in the sorbent to increase again after the regeneration process; the temperature in that case was slightly

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higher. High sorbent mass flow rates resulted in short thermal regeneration times and, consequently, insufficient burning of the adsorbed combustible liquid and insertion of air into the regeneration chamber. Additionally, unfavourable effects such as the agglomeration of particles occurred. Sinters in the sorbent excluded it from use in rescue activities. Figure 5 presents a photograph of the particle agglomeration phenomenon in the regenerated sorbent.

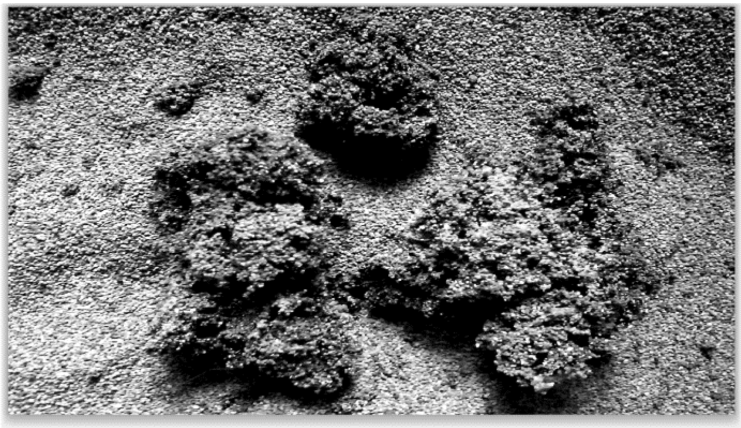

Fig. 5. Photograph of sinters formed under high sorbent flow rates and temperature conditions

3. RESULTS AND DISCUSSION

3.1. Physico-chemical features of the investigated sorbent in the regeneration process

At the first the particle size distribution was used to the description of the regeneration process. The particle size determination was carried out by sieve analysis (with sieve shakers - mechanical sieving). A sieve analysis of the sorbent's particles was performed after each cycle of the regeneration process; significant changes in the size distribution of the investigated sorbent's samples were not observed. Subsequent cycles of the regeneration resulted in changes in the colour of the sorbent, which were related to soot remaining on its surface. A distribution of the average diameter of the particles for the sorbent samples subjected to regeneration as a function of their mass content in different fractions is shown in Figure 6.

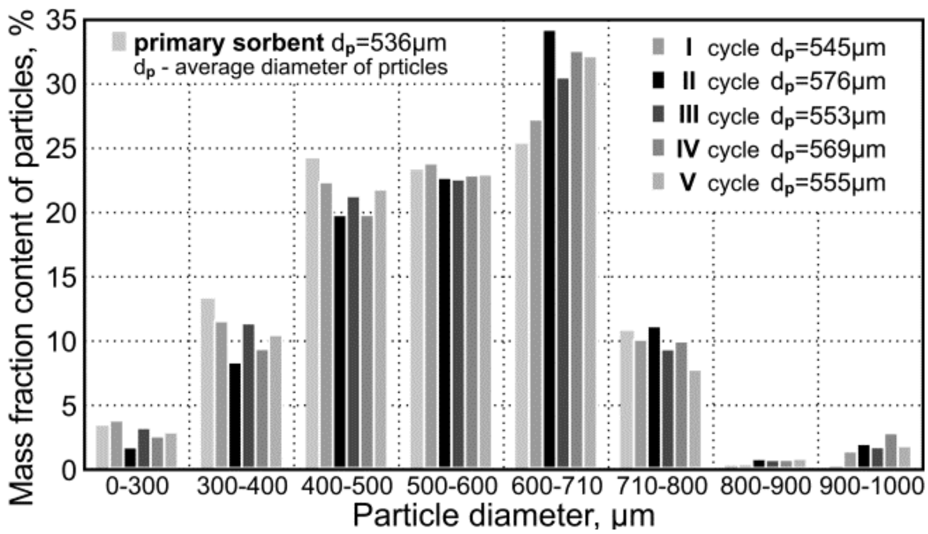

Fig. 6. Distribution of the average diameter of particles for sorbent samples subjected to regeneration as a function of their mass content in different fractions

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The average diameter increased slightly in the first and second regeneration cycles; it increased from an initial average diameter d_p of 536 µm to 545 µm and 576 µm in the first and the second cycles, respectively. Subsequent regeneration cycles did not cause any further increase in the average diameter of the particles; after the fifth cycle, it was 555 µm. Differences in the values of that parameter ranged from 9-40 µm in particular cycles of the regeneration process. The largest increase in the particles' diameter occurred in the 600-700 µm fractions; an increase was also observed for the last fraction (800-1,000 µm). Other investigated ranges exhibited a decrease in diameter or remained constant (and in the same proportions). Visual changes in the investigated samples are shown in Figure 7. All of the described changes in the particle size distribution of the sorbent due to the thermal regeneration process do not prevent its use in the operational activities of the Fire Service. During the thermal regeneration process, none of the five cycles caused significant granulometric changes in the investigated sorbent samples. Next for characteristics of the sorbent at each regeneration cycle the specific surface area and the pore volume were determined. Measurements were carried on Physisorption Analyzer ASAP 2010 of Micromeritics Corporate Company. The specific surface area was calculated with BET method, and the pore volume was estimated with BJH method.

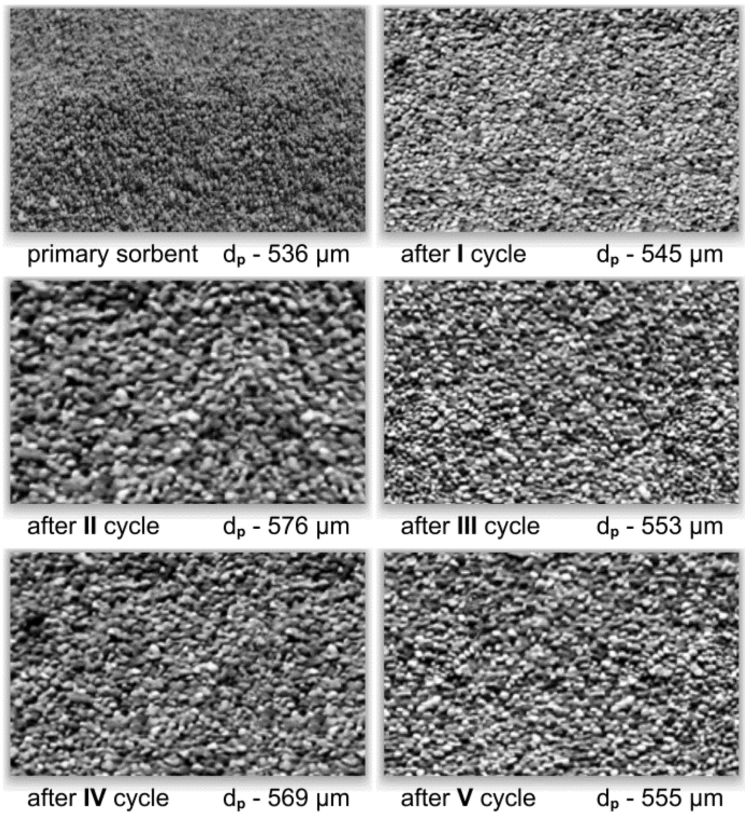

Fig. 7. Visual changes in the sorbent samples subjected to regeneration

The specific surface area of the adsorbent particles in low-porous adsorbents ranges from a few to more than ten m^2/g, whereas for high-porous adsorbents, it is in the range of 900 – 1,800 m^2/g. The investigated sorbents belong to the low-porous group; their specific surface areas ranged from 17 to 29 m^2/g. A decrease in the maximum value of the specific surface area was observed in the sorbent samples after the fourth cycle of regeneration, as shown in Figure 8. It can be assumed that such a decrease in the surface area of low-porous sorbents does not indicate a significant loss of its adsorptive features. Figure 9 shows a decrease in the pore volume of the samples of the investigated sorbent. The decrease in pore volume was not observed in the first regeneration cycle; the initial value was 0.10 cm^3/g. The next two cycles of regeneration led to a 10 % decrease in pore volume to a value of 0.09 cm^3/g, and the final two cycles decreased the volume to 0.07 cm^3/g. Figure 10 presents the average pore diameter of the sorbent samples throughout the thermal regeneration process. It can be concluded that

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the thermal regeneration process caused an increase in the average diameter of the pores ranging from 1 to 3 nm. Such an effect may be caused by the thermal impact on the structure of the particles of the investigated sorbent. The decrease in pore volume with a simultaneous increase in the average diameter of the pores indicates that the thermal effect of regeneration results in connecting the pores in the particles of the investigated sorbent. The observed increase in the average diameter of the pores is not sufficiently significant to impact the operational features of the sorbent after regeneration.

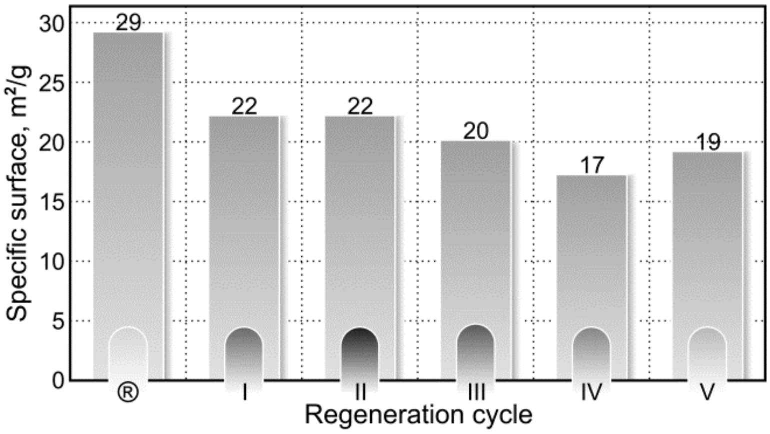

Fig. 8. Changes in the specific surface area of the sorbent at each regeneration cycle

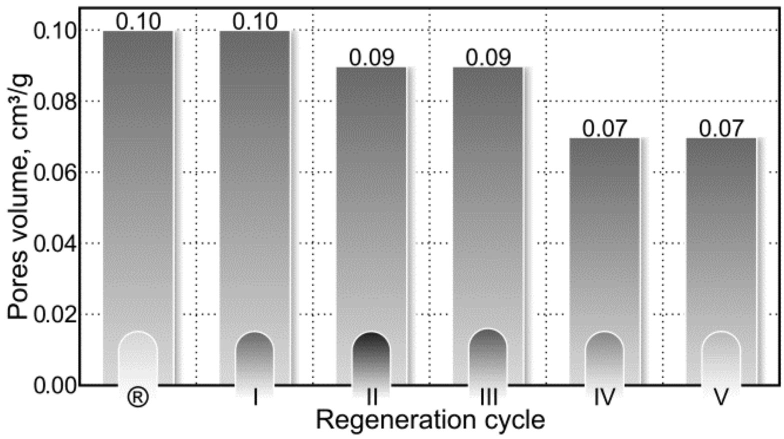

Fig. 9. Changes in the pore volume of the sorbent at each regeneration cycle

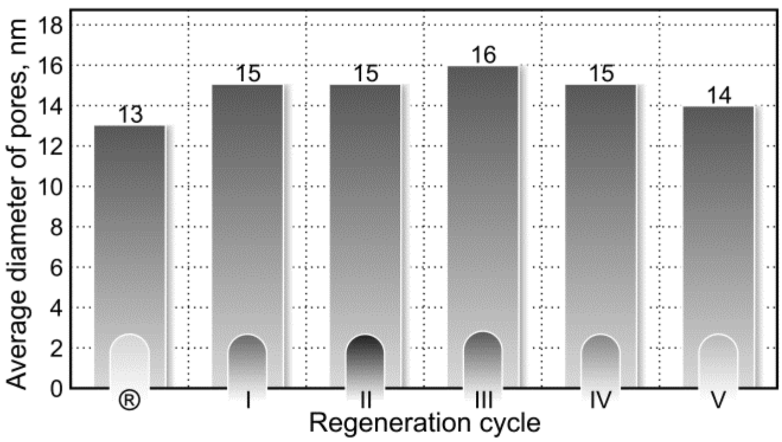

Fig. 10. Changes in the average diameter of the sorbent's pores at each regeneration cycle

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Changes in the level of the adsorbed liquid in the sorbent samples after each cycle of regeneration are presented in Figure 11. The initial adsorptivity of oil by the sorbent (measured using the Westinghouse method) was 95 %. After the first cycle of regeneration, the adsorptivity decreased to 92 %. The following three cycles of regeneration further decreased the adsorptivity of the oil to 83 %, and the final fifth cycle subsequently increased the adsorptivity to 89 %. The greatest decrease in the adsorptivity of the sorbent occurred after the fourth cycle of the regeneration. However, the levels attained in all cycles of the process were within the requirements for use during rescue actions. None of the changes in the sorbent's adsorptivity affect its adsorption features. The required sorbent adsorptivity, even during re-use, is 80 %. The results show that each regeneration cycle achieves this minimum level of adsorptivity. The analysis of the physico-chemical characteristics of the investigated samples confirmed that the thermal regeneration process did not worsen the basic structural features of the sorbent. Thus, after all of the cycles of the regeneration process, we maintained a product that is acceptable for use in its intended application.

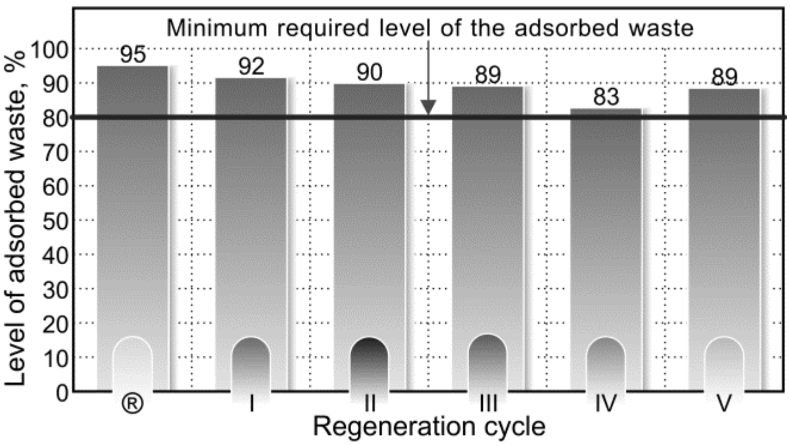

Fig. 11. Level of adsorbed liquid in the sorbent samples at each regeneration cycle

An analysis of the physico-chemical features of the investigated sorbent in the regeneration process presented herein allowed us to conclude the following: the proposed method of sorbent regeneration does not destroy the porous structure nor weaken the mechanical strength of the sorbent, all five cycles of thermal regeneration maintained the level of adsorptivity required for this type of sorbent and the sorbent particles' slight tendency for agglomeration does not change their functional features, allowing the possibility for them to be used several times.

3.2. Energy and ecological effect of the regeneration process

Measurement of the combustible content in the sorbent samples after its thermal regeneration process indicated a level of burning of the adsorbed combustible liquid. In Figure 12, the combustible content in samples of the investigated sorbent are presented. The initial sorbent combustible content was 2.5%. The combustible content after the first cycle of the regeneration process was 4.2 %, showing an increase of 1.7 % with respect to the initial content.

The second cycle increased the combustible content by 0.5 %, and in the third cycle, the level was much higher. In the fourth and fifth cycles of regeneration, the combustible content was 6.1 % and 5.9 %, respectively. Such changes indicated a decrease in the level of regeneration of the sorbent after the third cycle and worsening sorption features. Subsequent regeneration cycles of the sorbent could lead to significant worsening of the sorbent with respect to its structural features as well as its technical and operational features. In all five cycles of regeneration, the combustible content in the samples indicated that the level of thermal regeneration was sufficient. The research and control of the regeneration

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process were also carried by gas analyzer. To this aim was used FT-IR (Fourier Transform Infrared) multiparameter portable gas analyzer GASMET DX-4000 of Gasmet Technologies Company. Changes in the concentration of gas impurities for all five regeneration cycles are presented in Figure 13.

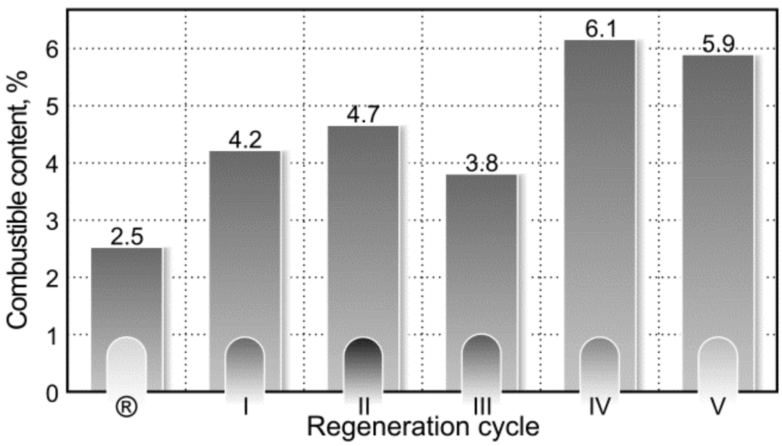

Fig. 12. Combustible content in the sorbent samples at each regeneration cycle

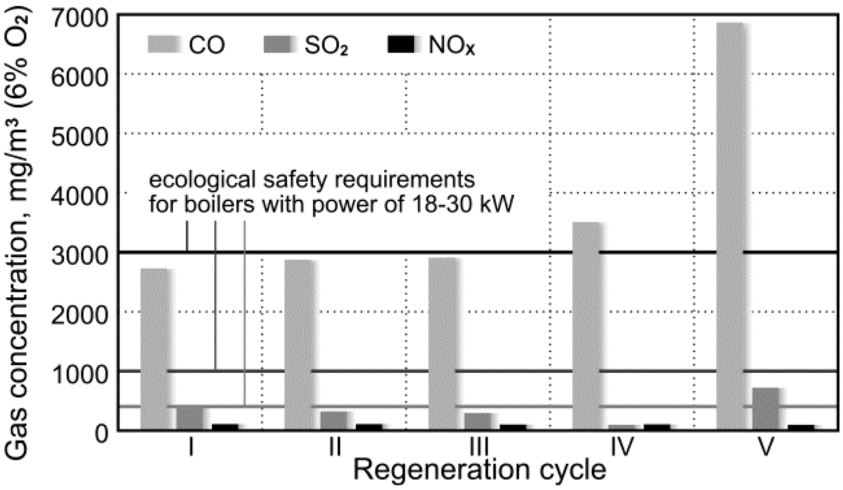

Fig. 13. Changes in the average concentration of gas impurities at each regeneration cycle in relation to the ecological requirement for chambers equipped with a retorted burner

The results of this study were compared to the ecological safety requirements of 25 kW boilers (6 % O_2): CO – 3,000 mg/m^3, SO_2 – 1,000 mg/m^3 and NO_x – 600 mg/m^3. The results clearly show that the concentration levels of CO, SO_2 and NO_x in the first three regeneration cycles were below the permissible ecological requirements. During the two next cycles, a significant increase in the average concentrations of the gas impurities, especially CO, was observed. In the fourth cycle of regeneration, the concentration of CO was 3,477 mg/m^3, which is above the permissible level; the highest increase in CO concentration was obtained in the fifth cycle of the regeneration. The results indicated that after the first cycle of regeneration, CO emission increased in the range of 138-4,128 mg/m^3. The concentration levels of SO_2 and NO_x were substantially below the permissible limits in all five cycles of the regeneration process. During long periods in which the levels of SO_2 and NO_x concentrations were observed, the analyser showed zero or very small concentration values of those gases. It may be concluded that a triple regeneration process results in low-emission burning. An analysis of the concentration levels for the next two cycles shows that the significant increase in CO concentration is an effect of incomplete regeneration of the sorbent during the first three cycles of the process. One advantage of the proposed thermal regeneration is the potential to generate heat from the sorbent

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regeneration process. In Figure 14, the average heat stream produced during all cycles of regeneration is presented, and it can be observed that the values of the heat stream ranged from 11.5-13 kW.

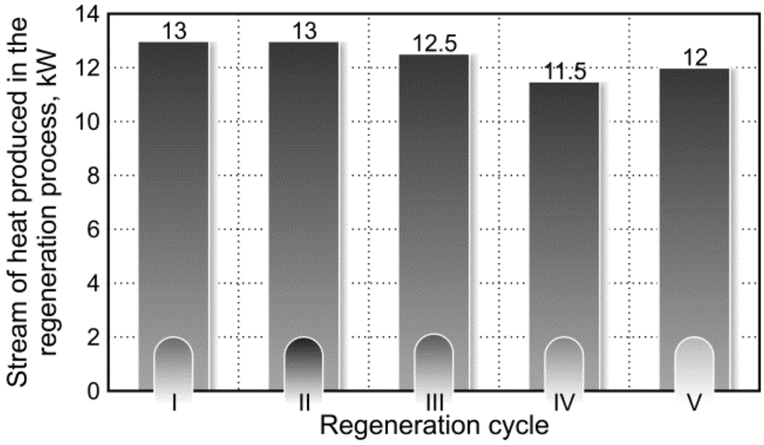

Fig. 14. Average heat stream produced in all cycles of the regeneration process

An analysis of the energy and ecological effect of the regeneration process allowed us to conclude the following: the emission of gas impurities and the increase in the combustible content of the sorbent proves the need for low-emission conditions for the first three cycles of the regeneration process and the thermal stream, with an average value of 12.4 kW, and the average efficiency of the regeneration chamber (68 %) present the possibility of re-using the waste heat from the sorbent regeneration process for heating purposes.

4. CONCLUSIONS

The proposed method of the thermal sorbent regeneration using a regeneration chamber equipped with a retort burner is characterised as highly productivity, ranging from 7.2-8.4 kg/h. It has short regeneration chamber start-up and extinguishing times and is adaptable to changes in process conditions. Practical possibilities and aspects of the regeneration of non-organic sorbents of mineral origin may allow it to be considered for the following technical solutions: classic thermal regeneration (i.e., in connection with the thermal installation), connection of the regeneration process with the retrieval of waste heat and installation of the regeneration system in connection with advanced utilisation technologies for the remaining desorbed gas impurities.

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