# THERMAL ANALYSIS OF PHYSICAL AND CHEMICAL CHANGES OCCURING DURING REGENERATION OF ACTIVATED CARBON

by

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*High-temperature thermal process is a commercial way of regeneration of spent granular activated carbon. The paper presents results of thermal analysis conducted in order to examine high-temperature regeneration of spent activated carbon, produced from coconut shells, previously used in drinking water treatment. Results of performed thermogravimetric analysis, derivative thermogravimetric analysis, and differential thermal analysis, enabled a number of hypotheses to be made about different phases of activated carbon regeneration, values of characteristic parameters during particular process phases, as well as catalytic impact of inorganic materials on development of regeneration process. Samples of activated carbon were heated up to 1000 °C in thermogravimetric analyser while maintaining adequate oxidizing or reducing conditions. Based on diagrams of thermal analysis for samples of spent activated carbon, temperature intervals of the first intense mass change phase (180-215 °C), maximum of exothermic processes (400-450 °C), beginning of the second intense mass change phase (635-700 °C), and maximum endothermic processes (800-815 °C) were determined. Analysing and comparing the diagrams of thermal analysis for new, previously regenerated and spent activated carbon, hypothesis about physical and chemical transformations of organic and inorganic adsorbate in spent activated carbon are given. Transformation of an organic adsorbate in the pores of activated carbon, results in loss of mass and an exothermic reaction with oxygen in the vapour phase. The reactions of inorganic adsorbate also result the loss of mass of activated carbon during its heating and endothermic reactions of their degradation at high temperatures.*

Key words: *thermal analysis, activated carbon, thermogravimetric analysis, regeneration, differential thermal analysis*

## Introduction

High temperature regeneration of activated carbon exhausted in water treatment process is characterized by complex physical and chemical processes that depend on a large number of parameters. The processes directly affect carbon regeneration efficiency, thereby also affecting ability of activated carbon to regain its *adsorbing* capacity and be reused. Numerous chemical compounds adsorbed from fresh water and their mutual reactions during thermal treatment, as well as different conditions associated with production and origin of activated carbon, make difficult to predict behavior of activated carbon during high temperature

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regeneration. Regeneration is carried out in reducing atmosphere of flue gasses. Most commonly used gasification agents in process of high temperature regeneration of spent activated carbon are CO and hydrogen supported with $CO_2$ and steam. The CO and hydrogen are products of incomplete combustion of fuel (usually gaseous). For the reason, experimental investigations addressing regeneration of activated carbon are of great interests to researchers and industrial users worldwide. Kinetics of the different phases occurring during thermal regeneration process were analysed by the means of *derivatographs*. Derivatographs are devices used for conducting comparative thermogravimetric analysis (TGA), where TGA curve displays mass loss of a sample as a function of temperature and time, derivative thermogravimetric analysis (DTG), where DTG curve displays the rate of mass loss as a function of temperature and time, and differential thermal analysis (DTA), where DTA curve displays presence of exothermic or endothermic processes occurring in a sample during heating.

Based on TGA and DTG curves obtained by derivatographic analysis of spent carbon sample heated in nitrogen atmosphere at a rate of 20 °C per minute, it can be concluded that in spite of the fact that mass of the sample is reduced gradually, DTG curve indicates development of several processes: moisture desorption, thermal desorption of organic and inorganic matters adsorbed by activated carbon, and finally carbonization of solid pyrolysis residue [1].

Results of particular interest have been reported in [2]. These refer to investigation of high temperature regeneration of activated carbon exhausted with different substituted phenols. Phenol and phenolic compounds are often used as adsorbate in experiments addressing regeneration of granular activated carbon (GAC) [2-10] exhausted with organic compounds from *aqueous* solutions. All DTG curves obtained as a result of thermal treatment experiments conducted for spent activated carbon samples were observed to display several peaks indicative of maximum mass loss rates. Since activated carbon was exhausted with only one organic compound, it is clear that different compounds were extracted during different extraction phases and at different temperatures. This means that phenolic compounds reacted with the surface of activated carbon and that physical and chemical adsorption of phenolic compounds had occurred. Therefore, the first peak observed on DTG curve corresponded to thermal desorption of organic molecules adsorbed through the process of physical adsorption. Separation of phenol adsorbed through physical adsorption occurred at temperatures of 300-425 K, separation of aminophenols at 300-450 K, while separation of nitrophenols occurred at 350-450 K. The first, previously mentioned peak was not noticed on DTG curves obtained for cresol. Since there is no reason for cresol to not be physically adsorbed on activated carbon, this suggests that physically adsorbed cresol had been transformed into chemically adsorbed compound during the thermal treatment applied. This phenomenon, clearly manifested in the case addressed, points out the transformation of physically adsorbed matter into chemically adsorbed matter [2]. The presence of two maximum mass loss peaks on DTG curve obtained for regeneration of activated carbon exhausted with phenol is explained in the following manner [2]: the first peak is attributed to physical desorption of phenol, while the second peak denotes desorption of chemically bound phenol. These peaks on DTG curves are also observed in experiments [4] of thermal regeneration of spent activated carbon exhausted with phenol. However, thermal analysis performed for regeneration of the same activated carbon sample but in the presence of strong oxidizing agent (ozone) has revealed the absence of the second peak on DTG curve. This means that the oxidizing agent did not affect physical adsorption of phenol, but has partially prevented its chemical adsorption. Such phenomenon may be explained by formation of oxygen complexes on the surface of activated carbon under

oxidizing conditions [4]. Oxygen complexes have been claimed to prevent chemical adsorption of phenol molecules. Experimental investigation, presented in [5], suggested that regeneration performed under non-oxidizing conditions degraded the adsorption capacity of activated carbon which was rapidly depleted after several successive regeneration cycles. It was concluded that gasification phase at enough high temperatures, is necessary to achieve an efficient regeneration. Gasification enables elimination of carbonized residue from the surface of activated carbon, thereby facilitating restoration of its adsorption capacity.

Investigations examining catalytic effects of metals and their impact on high temperature regeneration processes are oriented in two directions. The first group of investigations focuses on the analysis of catalytic mechanisms attributed to accumulated metal particles, whose presence in activated carbon can not be avoided [1, 12-15]. The second group of investigations focuses on the use of catalytic process to enhance regeneration of activated carbon and obtain improved characteristics. In these experiments, metals or metal oxides in activated carbon act as catalyzer in process of high temperature regeneration. For these experiments optimal parameters of process were investigated. The main goal of these investigations is to obtain satisfactory level of regeneration under milder conditions (lower temperatures, shorter residence time, and similar) so as to increase cost-effectiveness of the process [6, 7, 11, 16]. For example, it is well known that calcium considerably increases the rate of gasification process, enabling even 3-25 times higher rates of reactions than the rates recorded during non-catalytic processes [12]. Catalytic effects of calcium accumulated in activated carbon were examined in detail in [1], where experiments were conducted on pyrolysed, unused and spent carbon samples. Experiments, presented in [1], were performed with $CO_2$ as gasification agent, under non-oxidizing conditions. The DTG curves showed sample reactivity in gasification phase at temperatures between 680-1200 °C for all samples.

## Experimental investigation

The paper addresses thermal analysis of unused, spent and regenerated activated carbon samples obtained from the Water Treatment Plant "Makiš" in Belgrade, Serbia. The analysis was performed in order to identify phenomena occurring during heating of the samples examined. Activated carbon was produced by Trayal Corporation (Krusevac, Serbia) from carbonized coconut shells subjected to gasification and steam activation processes.

Experimental investigation was conducted using five different activated carbon samples.

The first two samples (sample no. 1 and no. 2) were samples of previously regenerated activated carbon in multiple-hearth furnace capacity of 220 kg/h of regenerated carbon. Regeneration of samples in multiple-hearth furnace was performed in the atmosphere of flue gasses produced by incomplete combustion of gaseous fuel. In addition, sample no. 1, relative to sample no. 2, had longer residence time in the regeneration furnace during regeneration process but was regenerated without the use of steam. Sample no. 2 had shorter residence time in the furnace, but its regeneration included addition of steam during activation phase of regeneration process. According to properties of activated carbon samples shown in tab. 1, samples of regenerated activated carbon have approximately the same characteristics as new (unused) activated carbon. The higher values of the methylene blue index, lower iodine number and BET surface area of regenerated activated carbon in relation to the new (unused) points to the fact that regeneration leads to the partial disruption of porosity of primal material. As a result, due to reduction of micro-pores (which reduces iodine number and BET surface area), meso- and macro-pores are formed (indicator of meso- and macro-porosity

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**Table 1. Experimentally determined properties of activated carbon samples**

| Properties | Unit | GAC samples | | | | |
|---|---|---|---|---|---|---|
| | | Unused GAC | No. 1 | No. 2 | No. 3 | No. 4 |
| Ash content | % m/m | 5.05 | 9.36 | 8.94 | 7.96 | 19.78 |
| Iodine number | mg/g | 1050 | 962 | 935 | 539 | 241 |
| Methylene blue index | ml | 18-19 | 21.5 | 20.5 | 18 | 6.8 |
| The BET surface area | $m^2$/kg | 1152.6 | 984.8 | 814.4 | 561.3 | 33.8 |
| Abrasion number | % | 90 | 83.5 | 76.7 | 72.4 | 94.7 |
| Apparent (bulk) density | kg/$m^3$ | 430-470 | 474.2 | 484.7 | 535.0 | 641.8 |
| The GAC particle density | kg/$m^3$ | 771.7 | 929.2 | 892.8 | 1018.2 | – |
| True density | kg/$m^3$ | 1500.3 | 1770.5 | 1885.1 | 1817.5 | – |

is methylene blue index). In addition, higher ash content in samples of regenerated activated carbon is the result of adsorption of inorganic matter that can not be removed by regeneration.

Third sample was a new (unused) activated carbon sample. Fourth and fifth samples (samples no. 3 and no. 4) were samples of spent (exhausted) activated carbon. Samples no. 3 and no. 4 of spent (exhausted) activated carbon are significantly different. Sample no. 3 was used in the treatment of drinking water for 9 months, and the sample no. 4 even 36 months. Due to the long period of exploitation, iodine number and methylene blue index for sample no. 4 are lower than for the sample no. 3. On the other hand, high ash content in sample no. 4 is confirmation that inorganic matter was adsorbed in this sample.

Low values of iodine number and methylene blue index are indicators of activated carbon saturation. New, unused granular activated carbon (GAC) and regenerated activated carbon (sample no. 1 and no. 2) have the expected high values of these parameters in relation to samples of saturated (exhausted) activated carbon (sample no. 3 and no. 4).

These differences in the samples of activated carbon will have a significant impact on the resulting diagrams of samples thermal analysis (TG, DTG, and DTA curves).

Ash content in samples were determined according to ASTM D 2866-94, iodine number according to ASTM D 4607-94, methylene blue index according to NORIT company method, abrasion number according to ASTM D3802-79, and density according to ASTM D 2854-96. The BET surface area was determined by gas chromatograph method of nitrogen adsorption on Perkin-Elmer-Shell model 212D Sorptometer.

All five samples were examined under the oxidizing conditions (air atmosphere) and under reducing conditions (nitrogen atmosphere, representing a mixture of nitrogen and residual air). None of the samples was subjected to any pre-treatment, apart samples of spent carbon which were preliminary air-dried at ambient conditions. All samples were heated starting from the ambient temperature up to the temperature of 1000 °C, with pre-set heating rate of 10 °C per minute. Thermal analysis of activated carbon samples was performed by the means of derivatographs which were used for conducting comparative TGA, DTG, and DTA of the samples.

## Results and discussion

*Characteristic thermal analysis curves obtained*
*for regenerated, unused, and spent GAC samples*

Results of thermal analysis (TGA, DTG, and DTA) are presented in figs. 1 and 2, both for experiments performed under oxidizing conditions (air atmosphere) and inert conditions (nitrogen atmosphere).

*Analysis and discussion*

The TGA curve displays gradual mass loss during thermal investigation of the samples examined. However, these diagrams enable only a small number of changes to be observed. Majority of relevant data is obtained through analysis of DTG curves since they enable different mass loss phases to be identified and correlated to specific processes occurring during activated carbon heating. For the said reason, during analysis performed and presented in this paper particular attention has been paid to DTG data processing. In addition, phenomena identified in TGA and DTG curves were additionally checked and confirmed by DTA phase diagrams.

Before analysing the results obtained for activated carbon samples, it is possible to draw some general trends from the shape of TGA, DTG, and DTA curves.

Curves obtained for all examined samples are characterised by a distinctive peak that starts at 50-60 °C and reaches maximum value at 110-120 °C. This peak on DTG curve indicates a sudden mass loss, while its presence on DTA curve signifies endothermic process reactions. The indicated peak on the curves occurs due to desorption of residual moisture from the activated carbon samples.

The TG curves obtained for regenerated activated carbon samples heated under oxidizing and reducing conditions (figs. 1 and 2) are quite similar in shape, indicating that similar processes have developed in the samples. At the same time, it is obvious that the steepness of TG curve obtained for spent activated carbon is bigger than the steepness of TG curve obtained for unused and regenerated carbon samples. This indicates that mass loss is more significant in case of spent carbon samples.

The DTG curve obtained for regenerated carbon samples heated in oxidizing atmosphere, figs. 1(a) and 1(b), exhibits several characteristic process phases after the moisture separation phase, as follows.
–  In the first phase occurring after the moisture separation phase (period between temperatures $t_p$ and $t_{p,1}$), DTG curve is almost horizontal, meaning that mass reduction occurs at a constant rate (TG curve is a sloping straight line). Low mass loss rate and small slope of the TG curve indicate slowly developing process.
–  In the second phase (period between temperatures $t_{p,1}$ and $t_m$), mass loss rate increases significantly, reaching approximately the same value in case of each regenerated carbon sample. As seen from the related DTA curves, this phase is characterised by extremely exothermic process reactions.
–  In the third phase (period between temperatures $t_m$ and $t_{p,2}$), mass is again reduced at approximately constant rate, which continues all the way until very high temperatures are reached (700-750 °C).
–  In the last, fourth phase (period between temperatures $t_{p,2}$ and $t_e$), when the highest process temperatures are reached (above 750-800 °C), mass of activated carbon samples again starts to reduce rapidly, but now the processes are no longer exothermic, but are mainly endothermic.

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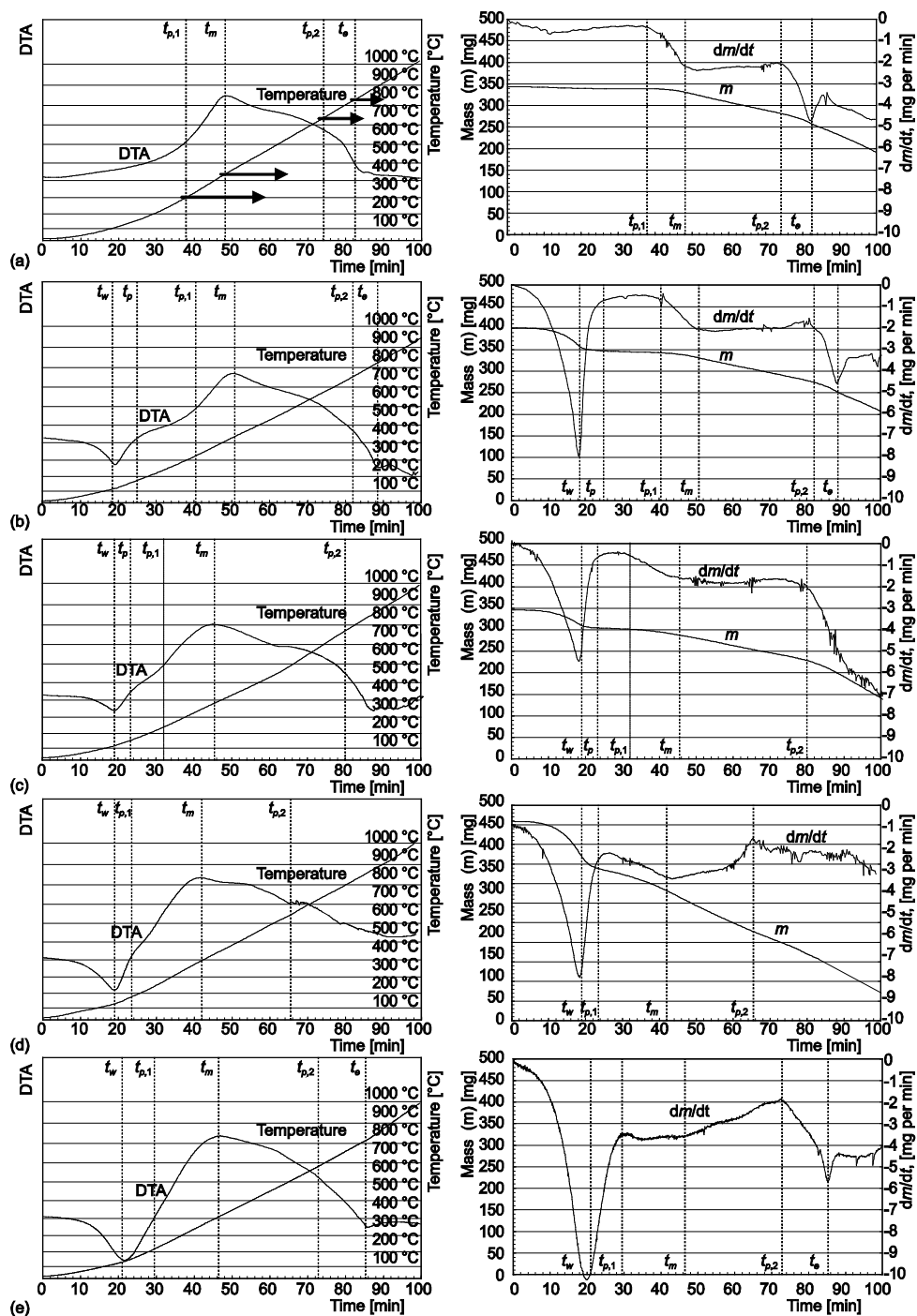
**Figure 1. The TG, DTG, and DTA curves for heating of activated carbon under oxidizing conditions; (a) sample no. 1, (b) sample no. 2, (c) unused GAC, (d) sample no. 3 (spent GAC), and (e) sample no. 4 (spent GAC)**
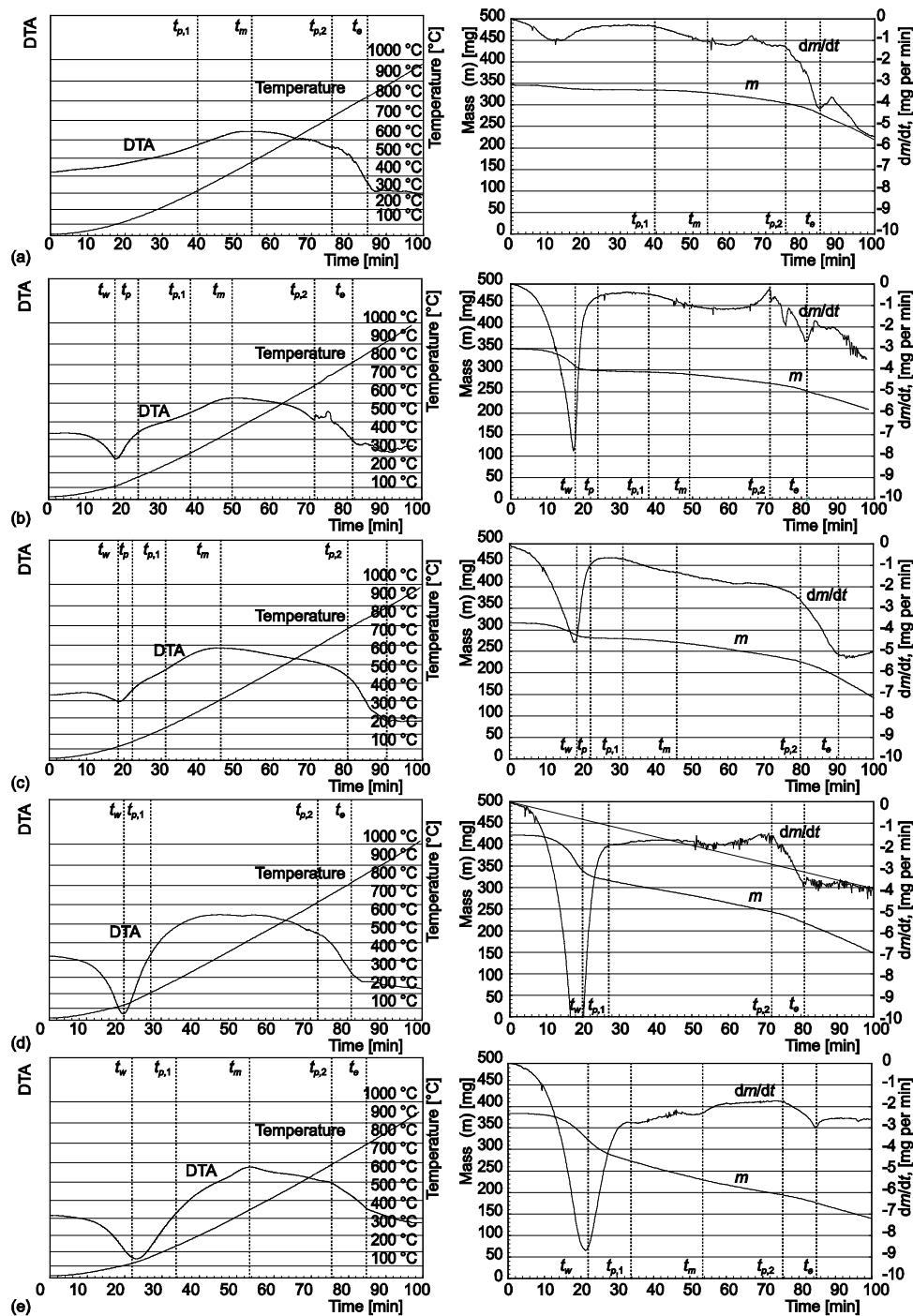
Figure 2. The TG, DTG, and DTA curves for heating of activated carbon under reducing
conditions (nitrogen): (a) sample no. 1, (b) sample no. 2, (c) unused GAC, (d) sample no. 3
(spent GAC), and (e) sample no. 4 (spent GAC)

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Figure 3 gives the DTG curves for all five samples of activated carbon. It is important to mention that for the sake of brevity, all data obtained for one set of experimental conditions are presented in the same diagram.
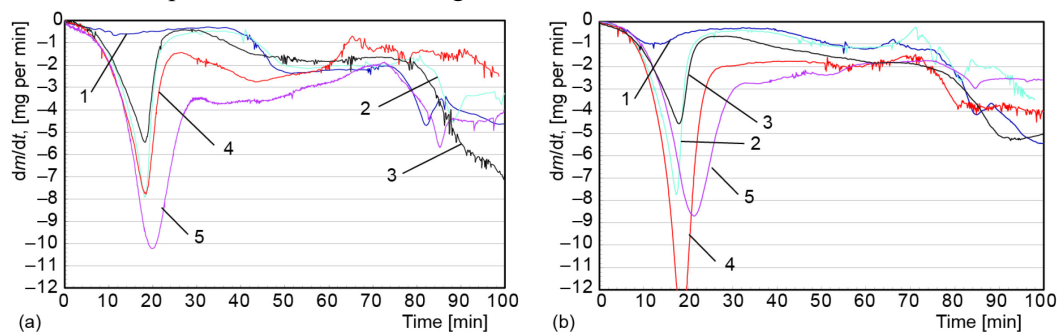


**Figure 3. The DTG curve for heating of activated carbon under (a) oxidizing conditions (air), and (b) reducing conditions (nitrogen);** *1 – sample no. 1, 2 – sample no. 2, 3 – unused GAC, 4 – sample no. 3 (spent GAC), 5 – sample no. 4 (spent GAC)*

The DTG curves obtained for regenerated carbon samples heated in reduced atmosphere, figs. 2(a) and 2(b), display the presence of all of the aforementioned phases, but with less pronounced changes between different process phases.

The DTG curves obtained for unused activated carbon sample which was heated either in oxidizing or reduced atmosphere, figs. 1(c) and 2(c), exhibit certain differences when compared to the previously mentioned regenerated carbon samples:

– although present, the first two phases are less pronounced, meaning that mass loss in these phases is smaller,
– the third phase, characterized by constant mass loss rate, ends at approximately the same temperature as in case of regenerated carbon samples, and
– in the last, fourth phase, when mass of the sample starts again to reduce rapidly, changes are much more pronounced.

The DTG curve obtained for spent activated carbon sample no. 3, which was heated in oxidizing atmosphere, fig. 1(d), exhibit considerable differences when compared to other samples as follows.

– The first phase, characterized by constant mass loss rate, is practically non-existent. Mass loss rate increases practically immediately, indicating that the mass of carbon sample is changing more rapidly. This additional mass loss in oxidizing atmosphere results from decomposition of adsorbate which is not found in regenerated and unused carbon samples.
– In the following phases of the process, the sample's mass loss rate continuously decreases and the period characterized by constant mass loss rate is not observed. During further heating, this constant decrease in mass loss rate probably results from deposition of carbonized materials from adsorbate during thermal treatment of activated carbon.
– After reaching minimum value, the mass loss rate starts to increase again. It is important to mention that this phenomenon occurs earlier *i. e.* at lower temperatures (about 630-640 °C) and develops considerably slower than in case of previously analysed samples. These facts indicate that a mechanism leading to repeated increase in mass loss rate is different. The increasing mass loss rate now results primarily from gasification of carbonised materials present in the pores of activated carbon, with gasification starting at aforementioned temperatures of 630-640 °C and continuing until the end of the analysed process.

The DTG curve obtained for spent carbon sample no. 4, figs. 1(e) and 2(e), which is characterised by much higher saturation level than the sample no. 3, exhibits a constant decrease in mass loss rate after the moisture evaporation phase. This continues all the way until high temperatures are reached (680 °C), when mass loss rate starts to increase again. Similarly as in the case of spent carbon sample no. 3 and unlike in regenerated and unused activated carbon samples, the period characterised by constant mass loss rate is not clearly distinguished. A constant decrease in mass loss rate is seemingly a phenomenon that is quite opposite from what would be the expected sample behavior, primarily since the analysed spent carbon sample contains the highest concentration of adsorbed substances that would lead one to expect constant increase in mass loss rate. However, DTG curve clearly indicates that processes occurring in the analysed carbon sample in the phases following initial moisture evaporation develop at the fastest possible rate. This means that the shape of DTG curve (indicating decrease in the mass loss rate) does not suggest that thermal desorption of the adsorbate is not present, but rather that the said process has begun much earlier, even during the moisture evaporation phase. Later on, thermal desorption is accompanied by intense carbonization of materials contained in the pores of activated carbon, causing the mass loss rate to be decreased. Still, as expected, the absolute values of mass loss rates obtained for the analysed carbon sample remain higher than the values obtained for other examined samples, all the way until thermal desorption of adsorbed material is fully completed.

Based on the previous observations, there are two noticeable key differences in behavior of saturated activated carbons compared to samples of new (unused) and previously regenerated activated carbons in the industrial multiple-hearth furnace, when heated in derivatograph. Samples of the new (unused) and previously regenerated active carbon are characterised by the existence of the first phase (period between temperatures $t_p$ and $t_{p,1}$) without or with very low mass loss rate, while this stage does not exist for the samples of spent activated carbon. Obviously, a sudden change in mass that occurs in samples of spent activated carbon at low temperatures, immediately after the evaporation of moisture, is the result of desorption and decomposition of organic adsorbate in spent activated carbon. Also in DTG diagrams for samples of spent activated carbon noticeable is the period of decrease of mass loss rate at the end of the temperature interval $t_m$ to $t_{p,2}$. This reduction of the mass loss rate is a consequence of formation a secondary carbon (carbon residue) in the pores of activated carbon which is a process that takes place during the thermal decomposition of adsorbate at higher temperatures.

Tables 2, 3, and 4 present characteristic temperatures indicative for all observed thermal processes.

As seen in the phase diagrams obtained by thermal analysis of samples no. 1 and no. 2, the two carbon samples exhibit quite similar behavior. The goal of the investigation performed was to examine whether regenerated carbon sample whose treatment included the use of steam (sample no. 2) and the carbon sample regenerated without the use of steam (sample no. 1) exhibited some differences in behavior when heated up to 1000 °C. In addition, phenomena observed for these regenerated samples were to be compared with processes occurring during heating of unused and spent carbon samples. Based on the termogravimetric curves obtained for each of the two regenerated carbon samples, heated in oxidizing, figs. 1(a) and 1(b) as well as in reducing atmosphere, figs. 2(a) and 2(b), it is concluded that at lower temperatures (below 300 °C), mass of the examined samples changes only slightly, without taking into account moisture evaporation. However, this mass loss, although slow, still exists. This is also confirmed by DTG curve which indicates that mass loss rate is not zero, as well as by DTA curve which suggests the presence of exothermic processes. Still, more

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**Table 2. Parameters obtained by thermal analysis of regenerated activated carbon samples**

| | | $t_w$ [°C] | $t_p$ [°C] | $t_{p,1}$ [°C] | $t_m$ [°C] | $t_{p,2}$ [°C] | $t_e$ [°C] |
|---|---|---|---|---|---|---|---|
| Sample no. 1 | Air | – | – | 300 | 440 | 730 | 800 |
| | Nitrogen | – | – | 310 | 480 | 720 | 825 |
| Sample no. 2 | Air | 110 | 180 | 330 | 430 | 740 | 815 |
| | Nitrogen | 110 | 170 | 320 | 440 | 690 | 810 |
| | | d$m$/d$t$ [mgmin$^{-1}$] | d$m$/d$t$ [mgmin$^{-1}$] | d$m$/d$t$ [mgmin$^{-1}$] | d$m$/d$t$ [mgmin$^{-1}$] | d$m$/d$t$ [mgmin$^{-1}$] | d$m$/d$t$ [mgmin$^{-1}$] |
| Sample no. 1 | Air | – | – | 0.40 | 2.20 | 2.05 | 4.70 |
| | Nitrogen | – | – | 0.40 | 1.05 | 1.40 | 4.20 |
| Sample no. 2 | Air | 7.95 | 0.75 | 0.70 | 2.05 | 1.80 | 4.60 |
| | Nitrogen | 7.75 | 0.60 | 0.45 | 1.00 | 0.25 | 2.65 |

**Table 3. Parameters obtained by thermal analysis of unused activated carbon samples**

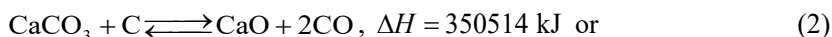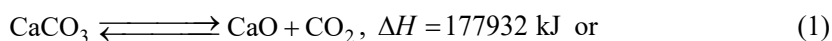| | | $t_w$ [°C] | $t_p$ [°C] | $t_{p,1}$ [°C] | $t_m$ [°C] | $t_{p,2}$ [°C] | $t_e$ [°C] |
|---|---|---|---|---|---|---|---|
| Unused GAC | Air | 110 | 150 | 230 | 380 | 770 | – |
| | Nitrogen | 110 | 150 | 230 | 400 | 785 | 880 |
| | | d$m$/d$t$ [mgmin$^{-1}$] | d$m$/d$t$ [mgmin$^{-1}$] | d$m$/d$t$ [mgmin$^{-1}$] | d$m$/d$t$ [mgmin$^{-1}$] | d$m$/d$t$ [mgmin$^{-1}$] | d$m$/d$t$ [mgmin$^{-1}$] |
| Unused GAC | Air | 5.45 | 0.70 | 0.50 | 1.60 | 2.05 | – |
| | Nitrogen | 4.60 | 0.90 | 0.75 | 1.35 | 2.65 | 5.20 |

**Table 4. Parameters obtained by thermal analysis of spent activated carbon samples**

| | | $t_w$ [°C] | $t_{p,1}$ [°C] | $t_m$ [°C] | $t_{p,2}$ [°C] | $t_e$ [°C] |
|---|---|---|---|---|---|---|
| Sample no. 3 | Air | 115 | 180 | 400 | 635 | – |
| | Nitrogen | 115 | 205 | – | 700 | 815 |
| Sample no. 4 | Air | 120 | 210 | 405 | 680 | 810 |
| | Nitrogen | 120 | 215 | 450 | 690 | 800 |
| | | d$m$/d$t$ [mgmin$^{-1}$] | d$m$/d$t$ [mgmin$^{-1}$] | d$m$/d$t$ [mgmin$^{-1}$] | d$m$/d$t$ [mgmin$^{-1}$] | d$m$/d$t$ [mgmin$^{-1}$] |
| Sample no. 3 | Air | 7.80 | 1.80 | 2.70 | 0.90 | – |
| | Nitrogen | 13.40 | 2.05 | – | 1.60 | 3.85 |
| Sample no. 4 | Air | 10.25 | 3.55 | 3.60 | 1.90 | 5.65 |
| | Nitrogen | 8.70 | 2.75 | 2.25 | 1.80 | 3.00 |

significant mass loss may be considered to be practically non-existent until reaching temperatures of 300-330 °C. This indicates that the adsorbate, which usually decomposes below indi-

cated temperatures, was removed during carbon regeneration process, but also that oxidation of initial carbon configuration is weak.

Slightly more intense reactions occur at temperatures above 300 °C or 330 °C in cases when samples no. 1 and no. 2 were heating in oxidizing (air) atmosphere, figs. 1(a) and 1(b). Similar, but slightly less pronounced intensification of process reactions was also recorded when samples no. 1 and no. 2 were heated in reducing atmosphere (nitrogen and air mixture), figs. 2(a) and 2(b). It is reasonable to assume that temperatures above 300-330 °C cause more intense volatilization and oxidation, primarily with respect to the basic structure of the activated carbon. A peak observed on DTA curve indicates that thermal maximum of exothermic oxidation processes is reached in case of all four experimental regimes (in oxidation and reducing atmospheres). This peak coincides quite well with a moment identified on DTG curve as the end of increasing mass loss rate phase. Further on, mass continues to change at a constant rate, whereby the rate of processes occurring in reducing atmosphere is approximately two times lower than the one recorded for experiments performed in oxidizing atmosphere, tab. 2. This observation goes for both sample no. 1 and no. 2. The indicated behavior continues all the way until temperatures of 730 °C and 720 °C are reached for sample no. 1, figs. 1(a) and 2(a), tab. 2, when heated in oxidizing and reducing atmosphere, respectively, *i. e.* temperatures of 740 °C and 690 °C for sample no. 2, figs. 1(b) and 2(b), tab. 2, when heated in oxidizing and reducing atmosphere, respectively. However, a slight difference in the behavior of sample no. 1 and no. 2 was noticed. This difference is best observed during thermal treatment of sample no. 2 in reducing atmosphere, when process intensity is found to be considerably reduced at temperatures of 630-640 °C, fig. 2(b). During further heating of samples no. 1 and no. 2, mass loss rate starts again to increase, reaching maximum value at 800-825 °C for both samples considered (tab. 2 presents the values acquired during the experiments performed). In the same time, the processes observed to develop at these high temperatures are characterised by endothermic reactions. This is probably due to decomposition of inorganic admixtures which could not have been removed by carbon regeneration processes nor could they have been thermally decomposed, since the indicated temperatures represent maximum operating temperatures for regeneration furnaces. For example, it is most likely that, at indicated temperatures, endothermic reactions describing degradation of calcium compounds adsorbed from treated water occur:

$$CaCO_3 \rightleftharpoons CaO + CO_2, \quad \Delta H = 177932 \text{ kJ} \text{ or} \tag{1}$$

$$CaCO_3 + C \rightleftharpoons CaO + 2CO, \quad \Delta H = 350514 \text{ kJ} \text{ or} \tag{2}$$

$$Ca(OH)_2 \rightleftharpoons CaO + H_2O, \quad \Delta H = 64595 \text{ kJ} \tag{3}$$

Compared to previously described processes developing in regenerated carbon samples, unused carbon sample behaves somewhere differently when heated. Firstly, the increase in mass loss rate is observed earlier, at temperatures of 230 °C, irrespective of whether the sample was heated in oxidizing or reducing atmosphere, figs. 1(c) and 2(c), tab. 3. This suggests that the content of volatile matters in unused activated carbon is higher and that, having in mind that the carbon was not used and that these matters could not have originated from adsorbed matters, volatile matters represents the main component of unused carbon sample. Thermal maximum of exothermic reactions, tab. 3, is reached at slightly lower temperatures (380-400 °C) compared to regenerated carbon samples. During further heating, a sudden mass

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loss starts to occur only when temperatures of 770-785 °C are reached, tab. 3, with not recorded decrease in mass loss rate prior to reaching the indicated temperatures. Absence of mass loss rate decrease phase and higher temperatures of the beginning of the intense mass loss decrease is most probably result from the fact that there is no adsorbate in the pores of unused activated carbon sample. Adsorbate in the pores of activated carbon was carbonized. Carbonization and formation of coke residue would initially lead to mass loss rate decrease for samples no. 1 and no. 2, figs. 1(a), 1(b), 2(a), and 2(b). Later on, oxidation of secondary carbon leads to increased mass loss rate. Since samples of regenerated activated carbon (samples no. 1 and no. 2) contain residual adsorbate from the process of high temperature regeneration, phase of intense increase in mass loss rate takes place at lower temperatures compared to the unused sample of activated carbon that does not contain the adsorbate. It is also interesting to note that while heating regenerated carbon samples no. 1 and no. 2 in the air atmosphere, mass loss rate practically remains constant over the temperature range of 450-700 °C, maintaining the value of 2 mg per minute, tab. 2. However, while heating the unused carbon sample over the same temperature range, mass loss rate is recorded to be lower and equalled 1.5-1.6 mg per minute, tab. 3. The fact that there is no organic adsorbate in the pores of regenerated carbon samples, together with earlier observation that the volatile content of unused carbon sample is higher, would cause one to expect higher mass loss rate in case of unused carbon sample. It is therefore concluded that oxidation reactions are probably catalysed by inorganic matters (metals) that have remained present in the regenerated activated carbon. These matters cause the rates of related oxidation reactions developing in the regenerated carbon to be higher, in the same time increasing the mass loss rate.

The last phase, occurring at temperatures above 770-785 °C, is characterized by significant mass loss in the unused carbon sample, with mass loss rate at temperatures above 1000 °C exceeding 7 mg per minute, fig. 1(c), a value not recorded in either one of the investigated samples, not even in case of spent activated carbon samples. The fact that such phenomenon was not observed in case of previously regenerated samples probably results from the fact that carbon samples which were subjected to several regeneration cycles do not contain remains of heavily volatile matters which are, in case of unused carbon sample, not fully carbonized after the primary thermal treatment applied during production of activated carbon. It is possible that these remaining matters have been disintegrated during carbon regeneration, which basically represents the second cycle of the heating process. In the same time, this means that it is possible for the overall carbon mass loss recorded during high temperature regeneration to be higher than what would be expected based on the quantity of adsorbate in the spent carbon.

In case of spent carbon sample no. 3 thermal desorption phase starts to develop intensively at 180 °C, tab. 4. This is indicated on DTG curve obtained for spent carbon sample heated in oxidizing atmosphere, fig. 1(d), where mass loss rate starts to increase from the mentioned temperature. Since this phenomenon is not detected this early either in case of unused or regenerated activated carbon, it is clear that the recorded mass loss results from thermal desorption of the adsorbate. Bearing in mind that thermal analysis was performed in the presence of free oxygen, combustion of light volatile matters enables the process to be exothermic, in spite of the fact that thermal desorption is by definition an endothermic process. Thermal maximum of exothermic reactions is recorded at approximately 400 °C, fig. 1(d), tab. 4, similarly as in the case of unused and regenerated carbon samples. Thermal maximum of exothermic reaction fully coincide with maximum mass loss rate of the sample. At that moment, mass loss rate is higher than the values recorded for unused and regenerated activat-

ed carbon, which is quite expected due to separation of adsorbed compounds. Similarly, spent carbon sample heated in reduced atmosphere exhibits mass loss rate, recorded in the adsorbate thermal desorption phase, which is 2-4 times higher than in case of regenerated and unused activated carbon. However, related indicative peaks are not observed either in DTG or DTA curves. The absence of indicative peak in DTA curve obtained for samples heated in reduced atmosphere, which would be expected to occur at 400-450 °C and would suggests competition of exothermic processes, probably results from intense adsorbate volatilization, which is an endothermic process.

Reduced mass loss rate occurring at temperatures above 400 °C is most probably caused by completion of thermal desorption phase and adsorbate degradation, as well as separation of secondary carbon which has remained present in the pores of activated carbon during carbonization phase. Minimum mass loss rate occurs at 635 °C for sample heated in oxidizing atmosphere, fig. 1(d), tab. 4, and at 700 °C for sample heated in reducing atmosphere, fig. 2(d), tab. 4. Following these temperatures, mass loss rate starts to increase again.

In the same time, spent carbon sample no. 4 is sample with the highest adsorbate content. Thermal disintegration of this sample also starts pretty early *i. e.* at 210-220 °C, tab. 4, as indicated in thermoanalytical curves obtained. As a matter of fact, it is probable that thermal desorption processes start even earlier, but are not easily observed from thermal diagrams due to high moisture quantities that are being desorbed in the early stages of the heating process. Therefore, when comparing both spent carbon samples with regenerated and unused carbon sample, it is evident that in case of spent carbon there is no phase characterized by small or insignificant mass change at temperatures above the moisture separation temperature.

In case of sample no. 4, mass loss rate recorded at temperatures of 200-500 °C is the highest when compared to the values obtained for other examined samples, tab. 4. This is fully in accordance with the fact that this sample contains the highest content of volatile adsorbates which are thermally desorbed and combusted in the gas phase. In addition, inorganic matters present in the sample probably act catalytically, thereby intensifying process reactions. Sample no. 4 most certainly contains considerably more inorganic matters than spent carbon sample no. 3, since sample no. 4 was used in water treatment processes for longer period of time. Data presented in tab. 1 clearly show that ash content in this sample is absolutely the highest. Mass loss rate for sample no. 4 reaches 3.6 mg per minute, tab. 4, and it is considerably higher than maximum mass loss rate recorded for spent carbon sample no. 3 (2.7 mg per minute, tab. 4). To the contrary of spent carbon sample no. 3, mass loss rate of sample no. 4 following this point still continues to increase, while DTA curve in this phase of the process does not exhibit characteristic point of inflection. Up to the temperatures corresponding to the thermal maximum of exothermic reactions *i. e.* up to 405 °C in case of heating in oxidizing atmosphere, mass loss rate remains approximately constant. Later on, when exothermic oxidation is deemed fully completed, mass loss rate decrease down to the minimum value of 1.9 mg per minute, recorded at 680 °C, fig. 1(e), tab. 4. This results from the fact that adsorbates desorption and separation of secondary carbon is completed. In reducing atmosphere, a period characterized by decreasing mass loss rate ends at approximately the same temperature (690 °C). From this temperature on, mass loss rate starts to increase, similarly to phenomena observed in other examined samples, reaching maximum value at temperatures similar to those obtained for regenerated carbon samples (800-810 °C). This process is characterized by endothermic peak value which most probably indicates decomposition of inorganic compounds. Once again, it is necessary to stress out that this maximum mass loss rate was not observed in case of unused carbon free of inorganic admixtures.

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## Conclusions

Thermal analysis was used to examine efficiency of activated carbon regeneration processes and behavior of various activated carbon samples. Data obtained from TG, DTG, and DTA analysis were used to examine different phases of thermal treatment process. It has been concluded that the highest differences between the percentage mass loss recorded for spent carbon sample, on one side and regenerated and unused carbon samples on the other, are found at temperatures below 400 °C. The observed differences continue to be considerable all the way until temperatures of 500-600 °C are reached. The temperature of 400 °C in the same time represents a temperature when thermal peak of exothermic reactions occurs. Therefore, the indicated temperature range is characterised by intense thermal desorption and adsorbate degradation. Bearing in mind that thermal analysis was performed in the presence of free oxygen, combustion of desorbed matters resulted in peak rate of exothermic reactions, as indicated on DTA curve. Thermal desorption processes start to develop at temperatures as low as 180-210 °C in case of oxidizing atmosphere. Mass loss rate of spent carbon sample (2.7 mg per minute for sample no. 3 and 3.6 mg per minute for sample no. 4) in this phase is found to be 2-4 times higher than the rates recorded for unused and regenerated carbon, as a result of adsorbate separation process. On the other hand, at temperatures between 600 and 800 °C, when thermal desorption of organic adsorbate is definitely over, higher mass loss rate recorded for regenerated carbons in comparison to lower values obtained for unused activated carbon most probably results from catalytic activity of metals present in inorganic adsorbate. Therefore, catalytic activity of metals becomes quite pronounced over the considered range of temperatures and may lead to process reactions with carbon which comprises initial activated carbon configuration. The negative effect of these reactions may be reflected in increased mass loss of activated carbon during the regeneration process.

## Nomenclature

$t_e$ – temperature corresponding to the maximum mass loss rate during endothermic processes, [°C]

$t_m$ – temperature corresponding to the thermal maximum of exothermic processes, [°C]

$t_p$ – temperature corresponding to the beginning of the phase characterized by very small or null sample mass change, [°C]

$t_{p,1}$ – temperature corresponding to the beginning of the first intense mass change phase, [°C]

$t_{p,2}$ – temperature corresponding to the beginning of the second intense mass change phase (minimum mass loss rate peak), [°C]

$t_w$ – temperature corresponding to the maximum moisture separation rate, [°C]

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