

## ASSESSMENT OF THE AUTO-OXIDATION TENDENCY AND THE STORAGE EFFECTS ON THE QUALITY OF LIGNITE IN OLTENIA BASIN

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**ABSTRACT.** Coal auto-oxidation is an undesirable chemical phenomenon that occurs due to the interaction of coal with atmospheric oxygen, a phenomenon that takes place during the coal life cycle, from the extraction moment until it is used. Thus, it is imperative to understand this process not only for the prevention of coal autoignition in the mining industry, but also for the optimization of the coal storage. The aim of this work was to assess the chemical behavior such as the oxidation, self-heating, and auto-ignition characteristics of coal in Oltenia Basin, Romania during its storage period. The hydrogen peroxide oxidation testing was used to determine the auto-oxidation tendency of lignite, while for the monitoring of coal quality during the storage process, coal samples were taken from a coal stack after 0, 5, 10, 20 and 30 days of storage and analyzed regarding the moisture (39,71%), ash content (35.21 – 37,11%), calorific value (1940 – 1875 kcal/kg), and volatile compounds (36.71 – 37,27%). A good correlation between the autoxidation and the content of volatile matter was observed. Compared to the initial values measured in initial coal samples (day 0), the carbon content and the superior calorific value decreased, while the ash content increased after a period of 30 days of storage. Thus, it can be concluded that knowing the self-ignition characteristic of lignites is important both for managing coal stocks and for evaluating the impact that coal storage can have on the environment.

**Keywords:** coal oxidation, lignite auto-oxidation, coal oxygen absorption, coal quality degradation, Oltenia basin

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## INTRODUCTION

Coal oxidation is an undesirable phenomenon occurs due to the interaction of coal with atmospheric oxygen [1,2]. From an economic point of view, the oxidation of coal causes significant losses of qualitative and quantitative nature, both in the production and in the consumption units, because of the degradation of the initial parameters existing in the deposit [3,4]. In addition, the oxidation of coal results in emissions of toxic gases, such as carbon monoxide [5]. The behavior of the oxidation process for diverse types of coal samples can be observed by simultaneous monitoring of several parameters: the loss of the content of CO<sub>2</sub>, CO, and H<sub>2</sub>O [5]. It was reported that even after 20 years of oxidation, coal still produces carbon oxides. The release of CO<sub>2</sub> during these experiments was estimated to be 88% of the absorbed oxygen. In the same time, under normal conditions, the production of CO is between 1 and 4% of the absorbed oxygen [6].

Among the existing coals, lignite has several main characteristics that explain its auto-oxidation and auto-ignition tendency, such as: the high oxidation rate, high friability, and the presence of finely divided pyrites in the coal mass [7,8]. The alteration of coal properties results in: decrease of the calorific value, decrease of agglutination and coking capacities, decrease of the carbon and hydrogen content; increase of the amount of oxygen and ash content, etc. [9].

The occurrence of the phenomenon of oxidation and auto-ignition may have several causes. The large contact surface of the coal leads to a faster oxidation process, which explains why the coal in powder form or broken into small fragments auto-ignites more easily. Moreover, volatile components react with oxygen more easily, increasing the auto-ignition tendency of the respective coals [10]. The state of the coal surface influences the auto-ignition phenomenon, since oxygen absorption does not take place if the surface is occupied with water molecules in an absorbed state. This explains why, with coals that form humic acids in a humid environment, water can favor the auto-ignition phenomenon. The coals with a higher content of oxygen and a lower content of hydrogen have a greater tendency towards auto-ignition [9].

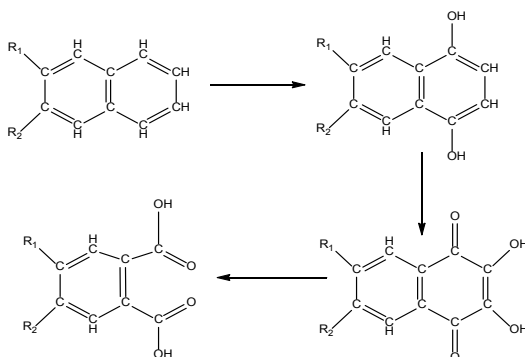
Previous works have shown that, following the oxidation reaction, the coal gains in weight by up to 12% of the initial weight [11]. This shows that the weight of oxygen remaining in the coal-oxygen complex is higher than the weight of the carbon and hydrogen eliminated in the gaseous products. It was reported that mineral bassanite (CaSO<sub>4</sub>×1/2H<sub>2</sub>O), which comes from the calcite in coal, can be used as an oxidation indicator [12].

Humidity is one of the basic parameters in the oxidation process with major influence not only on the oxidation of pyrite, but also on the organic part of the coal. Water can play an important role in the oxidation of coal in which it induces the formation of (hydro)peroxides, initiating oxidative reactions in organic macerals. At a temperature of 150°C, oxidation is slower in humid air than in dry air [13].

The drying of coal can affect its reactivity to O<sub>2</sub> and can initiate other chemical changes. The most conclusive evidence on this subject was brought by Dack and collaborators [14], when examined the effects of the variations of the dry temperature (-15°C to 150°C) on the content of free radicals. It was shown that bulk drying at 100°C produces irreversible (albeit slight) chemical changes of the (acid-base) capacitor type, a phenomenon that occurs when the coal is heated. The results show that, even around the temperature of 100°C, thermal chemical reactions take place. Carbonyl species can be lost through thermal reactions even if they were formed through oxidation. It is considered that oxygen is added to the centers of free radicals, and the addition of O<sub>2</sub> is reversible [15]. The increase in temperature favors the formation of carboxyl groups.

The smallest particles of coal have a weak alkanes content higher than the larger particles that are collected from the base of the stack [16]. Macropore oxidation occurs when the determined rate of the oxidation stage of coal particles is made by the diffusion of oxygen through the core of the entire lump. In the coal oxidation in micropores, the oxidation of coal particles is 'open' and the oxidation is not limited to diffusion. The oxidation of the macropores depends on the granulation. The depth of oxygen penetration in the coal varies between 2 and 4.5 μm and in the hottest areas they could reach even 20-50 μm, if the smallest particles in the hottest areas are completely exposed to oxygenation [16]. These small particles can lose the carbonyl groups after all the active sites have reacted.

Coal oxidation is not a singular reaction but a group of sometimes competing reactions. Moreover, given the heterogeneity of the coal, differences between the data are usually reported [17]. Coal oxidation can occur through exposure to air after the coal is mined. It was found that the occurrence of an increased amount of phenolic-OH and carboxylic groups in the oxidized coal is likely a major factor reducing the hydrophobicity of the coal. The scheme of the coal oxidation process is presented in Figure 1 [18]. Reasons for the observed variation of coal hydrophobicity with rank undoubtedly reflect differences in the chemical composition of the coal, particularly the oxygen containing functional groups of the coal [19].



**Figure 1.** Scheme of the coal oxidation process

Coal autoignition is a serious problem in coal mining. Due to the very large loss of high-quality coal caused by spontaneous combustion, extensive research was conducted on the mechanism of spontaneous combustion of coal [20–24]. Many works have studied the activities of aliphatic chains and oxygen-containing functional groups, such as  $-\text{OH}$ ,  $-\text{CHO}$ ,  $-\text{COOH}$ ,  $\text{C}=\text{O}$ ,  $\text{C}-\text{O}$ ,  $-\text{CH}_3$  and  $-\text{CH}_2$  in coal [25–27]. As a harmful element of coal, sulfur can not only produce  $\text{H}_2\text{S}$  and  $\text{SO}_2$ , which would cause environmental pollution during the burning process, but also limit the rational use of coking coal resources. The sulfur-containing components of coal are mainly divided into two categories [28]: inorganic sulfur, which exists mainly in the form of mineral sulfur, such as pyrite; and organic sulfur, which generally exists in the molecular structure of coal through chemical bonds. According to the theory of molecular orbitals, sulfur atoms and other atoms could form  $\pi$  bonds by using the 3p orbitals. The valence electron shell is far from the atomic nucleus and is less bound to the atomic nucleus, so  $\text{C}-\text{S}$  bonds and  $\text{S}-\text{H}$  bonds are prone to breaking. Because of this, the sulfur atom oxidizes more easily than the carbon atoms [28].

The results of the research on the oxidation of different types of coal carried out by specialists in the field over the years have not been quite conclusive due to the multitude and the complexity of the factors and the investigations involved. Knowledge of the phenomena that favor the oxidation of coal requires a careful analysis of the variation of the physical and chemical properties of lignite, depending on the duration of storage and preservation. The aim of the current study is to assess the characteristics specific to each type of coal within the mining perimeters of Oltenia basin, Romania, from the point of view of oxidation, self-heating and auto-ignition capacity, with a view of preventing qualitative losses in time.

## RESULTS AND DISCUSSION

### *Self-heating and auto-ignition of lignite*

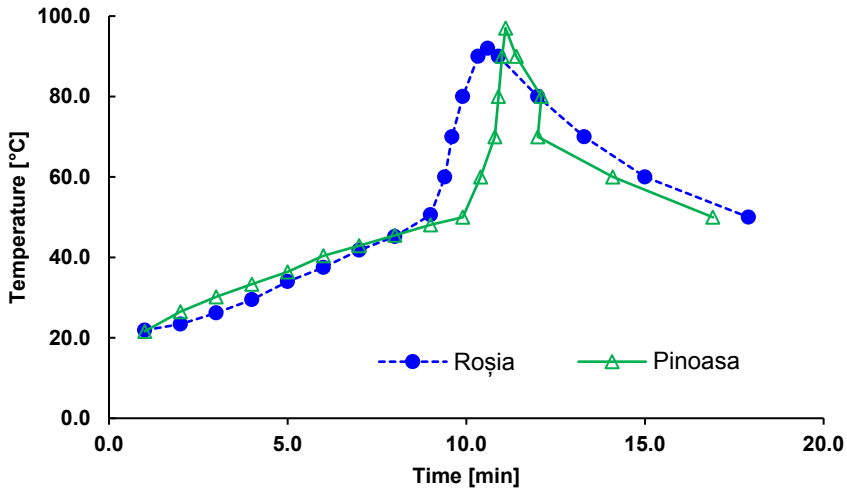
To ensure the prevention of quality losses over time, in the coal industry it is recommended to determine several quality parameters specific to each type of coal. Usually, these parameters refer to autooxidation, self-heating and auto-ignition capacity of coals.

In our study, the autooxidation tendency was assessed using coal granules with a grain size of 0.2 mm reacted with a perhydrol solution ( $H_2O_2$  20% - obtained by dilution of  $H_2O_2$  30% from Merck Millipore catalog number 107209) as oxidant, through the methodology described by Ionescu and collaborators [29]. The increase of the temperature of coal mixture following the perhydrol addition was registered. In identical working conditions (initial temperature, weight, granulation), the coals may have different behavior because of the different characteristics (petrographic, elemental composition, etc.).

The experiments were carried out on coal samples taken from two representative quarries in the mining basins of Oltenia, in order to find some notable similarities or differences between them, knowing in advance the specific geological characteristics of each mining area. The lignite samples for the experiment were taken from ten points (from holes dug 30 cm deep) on each coal stacks (finished production) belonging to the two quarries, which were then put together, to form two representative samples, according with the former Romanian standard SR ISO 1988:1996 and ISO 18283:2022 - Coal and coke - Manual sampling.

In the studied area the climate is temperate. The mild climate with moderate temperatures and abundant precipitation is also due to the circuit of southern, southwestern and western air masses. From the analysis of the monthly air temperature averages, it is found that the coldest month of the year is January (the average temperature being  $-2.5^{\circ}C$ ). The warmest month is July (average values between  $20.6-21.4^{\circ}C$ ). During the year, the highest average monthly precipitation amounts are recorded at the end of spring (in May, between  $86-103$  l/m<sup>2</sup>) and at the beginning of summer (in June, between  $92-98$  l/m<sup>2</sup>) [31].

The Roșia and Pinoasa quarries belong to the Rovinari Mining Basin and the obtained results showed that the differences between them in terms of the heating-cooling time and the heating-cooling speed are insignificant, as presented in Figure 2.



**Figure 2.** The variation of the heating-cooling temperature of the coal from the Roșia and Pinoasa in Rovinari basin

The results of the experiments regarding the auto-heating of the lignite from Rovinari (Roșia and Pinoasa quarries) are presented in Table 1.

**Table 1.** Auto heating parameters of the lignite from Roșia and Pinoasa quarries

Coal source	$T_{in}$ [°C]	$T_{max}$ [°C]	Time [min]	Gradient [°C/min]
Roșia	21.4	92.0	10.6	7.37
Pinoasa	21.4	97.0	11.1	6.85

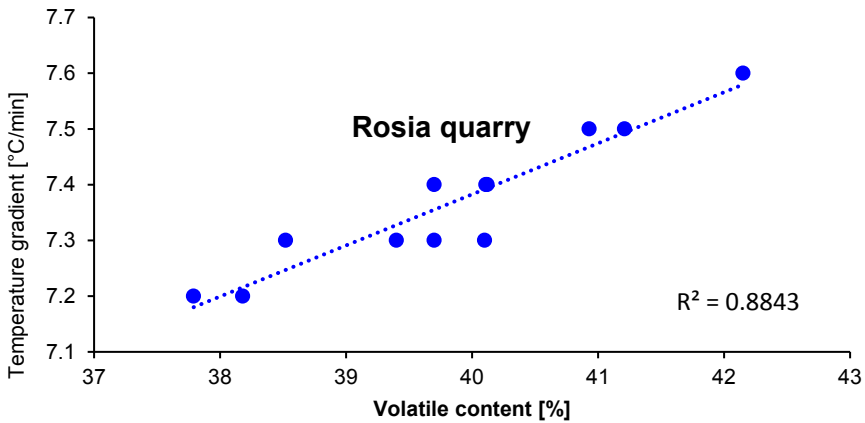
According to the previously presented model, tests were carried out to determine the auto-oxidation capacity for coals from the Roșia quarry, for different values of the volatile matter content. The obtained experimental results are shown in table 2.

**Table 2.** Moisture, ash content, net calorific power, volatile mater content and results for the autooxidation tests on lignite from Roșia quarry

Sample	Moisture W [%]	Ash content A <sub>anh</sub> [%]	Net calorific power Q <sub>inf</sub> [kcal/kg]	Volatile mater content V [%]	Autooxidation rate [°C/min]
1	41.03	36.39	1838	39.70	7.4
2	37.64	35.41	2006	40.93	7.5
3	40.12	38.11	1812	39.40	7.3
4	42.69	39.43	1692	38.52	7.3
5	39.35	39.35	1817	37.79	7.2
6	42.53	38.76	1719	38.18	7.2
7	40.26	35.97	1897	40.11	7.4
8	42.00	38.81	1726	39.70	7.3
9	38.27	35.97	1977	40.10	7.3
10	40.48	38.44	1787	40.12	7.4
11	38.57	36.51	1932	42.15	7.6
12	38.62	37.72	1889	41.21	7.5
Average	40.13	37.57	1841	39.83	7.4
Min	37.64	35.41	1692	37.79	7.2
Max	42.69	39.43	2006	42.15	7.6
Standard deviation	1.70	1.44	101	1.26	0.12
RSD%	4.23	3.84	5.53	3.17	1.67

In the 12 analyzed lignite samples from Roșia quarry, the moisture content varied between 37.64 – 42.69 %. The ash content was in the range of 35.41 – 39.43 %, while the net calorific value ranged between 1692 – 2006 kcal/kg. In general, a very low variability of the measured parameters was observed, with a relative standard deviation (RDS %) below 5 %, which indicates a homogenous composition of the coal in the studied quarry. In the specific literature, there are extremely poor data on the autooxidation characteristics of lignite from Oltenia. Only Bacalu Ion [30] has carried out tests to determine this characteristic, obtaining values of the heating speed between 2.8 ÷ 7.1 °C/min.

The variation of the autoxidation rate of the lignite from the Roșia quarry, depending on the content of volatile substances, is shown in figure 3. From this figure, the autoxidation rate of coal samples increased with the increase in the volatile matter content; that is, the coal samples with a high volatile content exhibited a higher tendency to autoxidation. Thus, by measuring the volatile content of the coal, its autoxidation behavior may be predicted.



**Figure 3.** Variation of autoxidation rate *versus* volatile matter content in lignite Roșia quarry

According to Figure 3, it can be observed that there is a good correlation between the speed of autoxidation and the content of volatile matter.

### ***Modification of lignite characteristics depending on the storage time***

The analyses carried out regarding the auto-heating and the autoxidation capacity of the coals from the Oltenia Mining Basin revealed that the coal with the highest exposure to qualitative depreciation is the one from the Rovinari Quarries. This study is based on laboratory scale experiments through the analysis of the coal samples from Roșia and Pinoasa quarries.

It was found that, from a qualitative point of view, the coal from Pinoasa Quarry is superior to that from Roșia Quarry. This is highlighted by the results obtained based on chemical and technical analyses (Table 3), as well as by the way in which the parameters evolve under given experimental humidity conditions, in correlation with the period of storage in warehouses.



**Table 3.** The evolution of the quality parameters of lignite according to the storage duration (The Roşia Quarry)

Period [days]	$W_{tot}$ [%]	$A_{anh}$ [%]	$Q_{inf}$ [kcal/kg]	$Q_{sup}$ [kcal/kg]	$C_{tot}$ [%]	$V_{anh}$ [%]
0	39.71	35.21	1940	3580	57.03	36.61
5	39.71	36.48	1896	3507	55.69	36.94
10	39.71	36.75	1887	3492	55.39	37.09
20	39.71	36.90	1882	3483	55.21	37.24
30	39.71	37.11	1875	3471	54.99	37.27

Compared to the initial values of the analyses ( $V_{anh}=36.61$ ,  $C_{tot}=57.03$ ,  $W_{tot}=39.71\%$ ,  $A_{anh}=35.21$  și  $Q_{sup}=3580$  Kcal/Kg), under the conditions of a storage period of 30 days, it can be observed that the content of volatile substances ( $V_{anh}$ ) increased by 1.8 %, while the carbon content ( $C_{tot}$ ) decreased by 3.6 %. The ash content ( $A_{anh}$ ) increased by 5.4 %, though the superior calorific value ( $Q_{sup}$ ) decreased by 3.1 % when compared to the initial value. The loss of coal estimated after 30 days of storage is 5,1% from initial mass, that which is mainly found in the reduction of carbon content.

Taking into account that 4.3 % of the oxidized carbon forms carbon monoxide, it follows that, by storing lignite for 30 days, there is an emission of 5.2 kg CO/ton of coal/month. Reported to the amounts of tens of thousands of tons of stored coal, it follows that the emissions of this toxic gas are significant for the storage area.

## CONCLUSIONS

According to the experimental results, the coal storage time depends on two main factors: the production deposited in the stacks and the amount of coal delivered daily. The phenomenon is characterized by a continuous movement of the coal stock in the warehouses. The more deliveries increase, the shorter the downtime, and the quality parameters of the excavated coal keep their initial values. In the case of keeping the coal in the warehouse for an average duration of 30 days, the quality of the coal decreases by more than 3 %.

The time the coal stays in the warehouses is different from one day to another and from one month to another, varying from a minimum duration of a few days to approx. 50 days of storage. The initiation of the oxidation process

and, implicitly, the qualitative deterioration of the coal, takes place around the value of 1900 Kcal/Kg (corresponding to the quality determined during testing), and decreases proportionally with the increase in storage time, reaching a quality loss of approx. 2.6 % after an average storage period of 10 - 15 days. The essential element in the analysis of coal depreciation is the duration of the storage process. The auto-oxidation phenomenon also has an impact on the quality of the environment, mainly the air, through carbon monoxide emissions, which can reach values of 5.2 kg CO/ton of coal/month.

## **EXPERIMENTAL SECTION**

### ***Evaluations of auto-oxidation tendency.***

The hydrogen peroxide oxidation method was used to determine the auto-oxidation tendency of lignite. Already in 1952 Orleanskaya described the use of oxygenated water for evaluating the self-ignition capacity of coals, but by a different procedure [32]. The method was developed by the University of Petroșani in the 70's, and has been widely used to identify coals that are at risk of spontaneous combustion [29]. At that time, it was considered so important that it was also included in the chemistry laboratory curriculum. This method consists of placing 3 g of coal sample in 20 ml of 20% H<sub>2</sub>O<sub>2</sub> in a glass container and monitoring the temperature over time. The maximum temperature obtained and the time in which it is reached are measured.

### ***Monitoring of coal quality evolution during storage***

Coal samples were taken from a coal stack initially, and after 5, 10, 20 and 30 days. The samples were processed to determine certain technical characteristics in accordance with the standards in force as follows: SR ISO 1988:1996 [33] (The standard refers to coal sampling methods, as well as obtaining and preparing samples for analysis and moisture), SR 5264:1995 [34] (The standard establishes the methods for determining the humidity of solid mineral fuels by drying at 105°C), SR ISO 1171 [35] (The standard establishes a method for the determination of ash for all solid mineral fuels, using the gravimetric method, by calcination at 825°C), ISO 1928-2020 [36] (This document specifies a method for the determination of the gross calorific value of a solid mineral fuel at constant volume and at the reference temperature of 25 °C in a combustion vessel calorimeter calibrated by combustion of certified benzoic acid.) and STAS 5268 [37].( The determination consists of heating the sample, in the absence of air, at 850°C for 7 minutes and calculating the mass loss)

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