

STUDIES ON LIGNITE QUALITY DEPENDING ON STORAGE CONDITIONS

Vasile BOBEI¹, Daniela CIOLEA^{2*}

¹ Technical University of Cluj-Napoca, Cluj-Napoca, Romania, vasile.bobei@ceoltenia.ro

² University of Petroșani, Petroșani, Romania, danielaciolea@upet.ro

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Abstract: *A small increase in the relative humidity in the air in a coal deposit can cause a 1% increase in the moisture content of the deposit resulting in the probability of spontaneous ignition. By depositing the freshly extracted coal over the coal already in the deposit, there is a direct contact between the two surfaces that have different characteristics in terms of physical and chemical properties, so that the latter acts as a primer. The coal with a higher temperature gives up the excess temperature to the coal with a lower temperature, thus initiating the formation of self-heating nuclei followed by self-ignition ones. The phenomenon is easy to observe in the colder periods of the season and especially usually after rain, when the vapors resulting from the exchange of temperature between the two types of coal are released into the atmosphere. The common cause is the movement of water vapor through the deposit correlated with the adsorption on the coal granules. The heat of condensation of vapor at storage temperature is about 580 cal./gram of water. Condensing the amount of water required to increase the content from 3% of the weight of the coal to 4% leads to an increase in the temperature of the coal by more than 170°C. This increase in temperature is sufficient to increase the oxidation rate by 5 times.*

Keywords: *coal oxidation, lignite, calorific power, the storage process*

1. Introduction

Coal oxidation is an unwanted phenomenon that occurs due to the interaction of coal with atmospheric oxygen, a phenomenon that takes place during the life cycle, namely from the moment the coal is extracted until it is consumed. From an economic point of view, the oxidation of coal causes significant losses of a qualitative and quantitative nature both in the producing and consuming units, as a result of not finding the initial parameters existing in the deposit.

In order to reduce this phenomenon, it is necessary to carefully follow the behavior of the coal over time in the technological warehouses, the periodic measurement of the temperature of the stocks, the continuous monitoring of the areas predisposed to auto-ignition, the methodical recording of all the factors involved in the oxidation of the coal.

The results of research on oxidation on different types of coal carried out by specialists in the field over the years, were not quite conclusive due to the multitude and complexity of the factors involved, and the investigations, no matter how well they were carried out, well conducted and interpreted, did not were completely satisfactory.

The motivation for supporting this theory lies in the fact that regardless of our will, oxidation takes place to a greater or lesser extent in the processes of excavation-transport-storage-storage of the coal and until its consumption.

Due to the lack of general accepted and established procedures for determining the degree of coal degradation, most conclusive results on the structure and reactivity of coal presented in the literature were obtained on laboratory samples, observations that were later extended to an industrial scale.

* Corresponding author: Daniela Ciolea, Assoc.Prof. PhD. Eng., University of Petroșani, Petroșani, Romania, contact details (University st. no. 20, Petroșani, Romania danielaciolea@upet.ro, 0254542580, int. 236)

Coals naturally contain oxygen in different proportions depending on the degree of carbonization. The content of carbon and oxygen is inversely proportional. This fact leads to the conclusion that the weight of the carbon content represents a first assessment of the change in the progressive compositional changes.

It can be considered that what changes in the degradation process is the oxygen content. Therefore, the oxygen content can be used as the main parameter for coal classification.

In a fresh, non-oxidized state, coal contains oxygen, and oxygen can be used to measure the degree of degradation. This property is rarely used for this purpose due to the difficulties of determining the degree of degradation, whatever it may be.

The oxygen content can be found by determining the oxygen by 'difference', by adding up the content of the other chemical components determined by elemental analysis and subtracting it from the total content. The 'natural' oxygen content of coal is altered by degradation. Degradation and oxidation of coal change its physical and chemical properties. The quality of the coal depends on its behavior in the processes of technological use, and alteration leads to significant qualitative and quantitative losses over time.

Observations regarding the behavior in the oxidation process of different types of coal on different samples taken in the study, can be made by following the simultaneous loss of CO₂, CO, and H₂O content.

It was found that even after 20 years of oxidation, coal still produces carbon oxides. The release of CO₂ in these experiments was estimated to be 88% of the absorbed oxygen. Under normal conditions, CO production is between 1 and 4% of absorbed oxygen [1].

2. Coal oxidation in the storage process

In the case of studying the oxidation phenomenon in peat, no release of CO was observed. Therefore, any net increase in oxygen content is far from being accurately reproduced.

Some methods allow the comparison of freshly mined coals with older and oxidized ones. In order to expand the research, it is necessary to correct the data obtained in the two cases with the characteristics of the existing coal in the layer.

No matter how restrictive the tests used, or which are proposed, in connection with the oxidation of coal, only some of them can accurately indicate the oxidation processes. [2]

Through the phenomenon of oxidation, a series of changes occur in the natural properties of coal, namely:

- reduction of calorific power;
- reduction of combustion properties;
- substantial modification of the surface of the granules;
- modification of carbonization and pyrolysis properties.

The results closest to reality were obtained in the case of analyzing samples in the laboratory at medium and low temperatures, in this context, the limitation refers to the study of oxidation on different models up to a temperature of 150°C. [3]

Sometimes the data from some of the authors' studies contradict the results obtained from other works, while others completely reject these hypotheses. This temperature level may seem arbitrary, but it is primarily based on experience in the field.

These phenomena were and are being debated by specialists in the field from several countries in the world, a problem that is being approached very seriously. In our country, the concerns are in the early stages and the results are inconclusive. The main cause of this is the lack of concern as well as the wrong optics of the factors of responsibility, the motivation being the relatively high expenses caused by experimentation in the laboratory phases or in the pilot installations, although the consequences of improper storage management are much more expensive.

For the energetic lignite extracted in the mining basin of Oltenia, the problem of methodically following its behavior over time has not yet been acutely raised, given the fact that the coal's stationary period in its own deposits was in most cases relatively short, of up to 3 months so that in few cases areas of self-heating or self-igniting coal appeared.

Currently, the situation has changed radically as a result of a reduced and fluctuating demand for coal from thermal power plants, a fact that led to the increase of the coal storage period in own depots over 3 months and implicitly to the appearance of problems related to oxidation-self-heating - self-ignition.

From this point of view, there is a need to manage coal stocks from the quarries in Oltenia [4] by taking technological measures aimed at:

- reduction of coal granulation to 0÷80 mm, by installing crushers on the conveyor belt circuits from the flow to the entrance to the warehouses;

- depositing freshly separated coal in stacks and not on top of the old one;
- compaction of stacks with technological equipment (compactor cylinders, blade bulldozers);
- measuring the temperature of coal stocks and following the oxidation, self-heating and self-ignition processes over time;
- the separation of self-heating and self-igniting coal from storage, its extinguishing and delivery to thermal power plants in the shortest possible time.

A new orientation is required in terms of coal production forecasting at month and year level, by scheduling the operation of open-pit excavators with a greater weight in relation to their operation for coal extraction. The purpose of this action is to ensure a greater flexibility of the correlated production in relation to the oscillating coal demand from the beneficiaries, through a directed storage that falls within the prescribed time limits that does not affect the quality parameters of the coal.

It is necessary that in the calculation of the cost price of coal, the additional expenses caused by the arrangement and preservation of the coal stacks from the own warehouses for a longer stationary period should be foreseen, so that the mining operations can carry out their activity profitable.

3. The auto-oxidation tendency of lignite

The main characteristics of coals that have a strong tendency to auto-oxidize and by default to auto-ignite are:

- characteristic high oxidation rate;
- high friability;
- the presence of finely divided pyrites in the coal mass.

The characteristic high oxidation rate is often a characteristic of lower coals that have a relatively high content of moisture, oxygen, volatile matter and pyrite.

It was found that the moisture from the freshly deposited coal in the stacks and the one existing in the ambient environment has multiple effects in triggering the self-ignition process. First of all, the moisture in the deposit, or the moisture of the entire mass of coal in the stack is associated with the large internal surface, especially after the coal has dried, through the release of pores and the free access of oxygen through the deposit.

Reducing the risk of spontaneous combustion can only be done based on the application of an appropriate management of coal stocks based on experience in the field.

By depositing the freshly extracted coal over the coal already in the deposit, there is a direct contact between the two surfaces that have different characteristics in terms of physical and chemical properties, so that the latter acts as a primer.

The coal with a higher temperature gives up the excess temperature to the coal with a lower temperature, thus initiating the formation of self-heating nuclei followed by self-ignition ones. The phenomenon is easy to observe in the colder periods of the season and especially usually after rain, when the vapors resulting from the exchange of temperature between the two types of coal are released into the atmosphere.

The common cause is the movement of water vapor through the deposit correlated with the adsorption on the coal granules. The heat of condensation of vapor at storage temperature is about 580 cal/gram of water. Condensing the amount of water required to increase the content from 3% of the weight of the coal to 4% leads to an increase in the temperature of the coal by more than 17°C. This increase in temperature is sufficient to increase the oxidation rate by 5 times [1].

Only a small increase in the relative humidity in the air in a coal deposit can cause a 1% increase in the moisture content of the deposit resulting in the probability of spontaneous ignition.

For example, when a wet coal is stored on top of another dry coal, the heat content of the wet coal also raises the temperature of the dry coal in one part of the storage thus initiating the cycle that ends in spontaneous ignition. Fire nuclei can appear after 13 days from the storage of fresh coal over one previously deposited for about 3 months, at the separation surface between the old and the new coal. The dry coal was exposed to atmospheric humidity of 100% relative humidity, in this particular case not only the heat of condensation of water vapor is the cause, but also the heat of drying of the wet coal, so that the temperature rises in the old coal and is transmitted through conduction and convection at points in the warehouse, triggering spontaneous ignition.

Based on the above theory, the spread of fires in warehouses can be explained, caused by the evaporation of water by becoming steam as a heat transfer agent.

Lignite during storage exfoliates until complete degradation as a result of the woody structure, due to a drying of the coal block in successive layers from the surface to the center, which causes a contraction of the superficial layers without it having occurred and in the rest of the block. The different tensions that are born in the lignite mass, as a result of the inhomogeneous contractions, lead to the crumbling of the previously dry layers.

In prolonged contact with air, the coals change their physical and chemical properties, that is, they undergo a more or less profound alteration. Alteration begins by absorbing oxygen at the surface and along the cracks in the coal. There is an oxidation on the surface of the organic matter, as well as of some mineral substances.

The practice of storing coals in the open air shows that most types of coals are degraded more if they are not sheltered than those that are covered, which leads to the conclusion that humidity favors the alteration of coals. As a result of the alteration, the coal loses its luster, its hardness decreases and it crumbles easily.

Alteration also affects other coal properties [1], as follows:

- lowers the calorific value;
- the agglutination and coking capacity decreases;
- decreases the carbon and hydrogen content;
- increases the amount of oxygen;
- increases the ash content, etc.

At the same time, iron hydroxides, sulfates and carbonates of iron and calcium are deposited on the cracks. It was found that, usually, humic coals deteriorate more easily than bituminous ones. The explanation lies in the fact that humic substances are less resistant to oxidation than bitumens. Vitrite and clarite alter easily, durite is more resistant, and fusite is more difficult to alter.

Auto-oxidation occurs as a result of low-temperature oxidation of coals. Autooxidation is always followed by autoheating, which has a relatively long duration [3]. When the critical temperature ($400\div 600^{\circ}\text{C}$) is reached, the actual combustion starts. It is a very complex physical-chemical process, which depends on many local geological, technical-mining factors, etc.

The intensity of oxidation, which will trigger self-ignition, is directly related to numerous factors, among which I mention:

- the amount of oxygen in the coal;
- the amount of oxygen that enters the coal mass, through absorption;
- the state of the coal surface;
- the amount of volatiles in the coal;
- release of heat to the environment.

The explanation of the occurrence of the phenomenon of oxidation and autoignition corresponds to the following causes [5]:

- the larger the contact surface of the coal, the faster the oxidation occurs. it follows, therefore, that coals in powder form or broken into small fragments self-ignite more easily;
- volatile components react with oxygen more easily, increasing the auto-ignition tendency of the respective coals;
- the state of the coal surface influences the self-ignition phenomenon by the fact that oxygen absorption does not take place if the surface is occupied with water molecules in an absorbed state; this explains why for the coals that form humic acids in a humid environment, water can favor the self-ignition phenomenon;
- coals with a higher content in oxygen and poorer in hydrogen have a greater tendency towards self-ignition; Another cause that favors auto-ignition is the phenomenon of pyrite oxidation. research has shown that a coal with 3% pyrite can raise its temperature by about 68°C (when it is in a dry state) and by about 114°C , in a wet state;
- due to the activity of some bacteria, which are found in the lower coals, mixtures of CH_4 and CO_2 are formed, which largely contribute to the initiation of self-ignition;
- additional heating of the coals, due to solar radiation, electrical discharges, or random sources of heat, leads to a rise in the temperature of the coal in the warehouses and favors self-ignition.

From the current practice, it is found that after the execution of some repairs to the work fronts (on the coal seams in operation) and to the own warehouses in the premises, due to negligence, a series of foreign bodies remain (wood, rags soaked in oil and diesel fuel, unextinguished fires where the workers warmed up), led to the appearance of direct fires in the coal seams and in warehouses that were difficult to extinguish.

The way coal is stored in silos influences the heat accumulation process. Thus, in large stacks the heat losses in the environment are small and the risks of self-ignition increase compared to small stacks where the risk of self-ignition is reduced [5].

4. The parameters of the oxidation reaction

In general, the qualitative deterioration of coal is due to the action of atmospheric air, humidity and the temperature of the environment. For these reasons, before studying the chemical changes in the organic structure of the oxidized coals, the parameters that could affect the course of the oxidation reactions must be taken into account.

4.1. The mechanism of the oxidation reaction and the physical structure of coal

The reaction mechanism between gaseous oxygen and coal at low temperatures is quite complex. Currently, little is known about the stages of this process.

Experimental works have shown that following the oxidation reaction, the coal gains in weight after oxidation up to 12% of the initial weight [5]. This shows that the weight of oxygen remaining in the coal-oxygen complex is greater than the weight of carbon and hydrogen removed in the gaseous products.

In the experiments where fine coal samples were oxidized at constant temperatures below the ignition point (below 200°C) in most cases - half of them, the consumed oxygen remains in the coal, the other half appears in the gaseous products, CO₂, CO and the water. So it can be understood that steps 2 and 4 taken together have about the same rate as step 3. While in this case step 4 is slower than step 3, their result is that the amount of small solid 'charcoal-oxygen' increases with increasing coal oxidation.

References from the literature on this subject point out that the complex is very stable. However, apparently, at least at low temperature, the oxidized coal samples can be stored for a long time in sealed containers, with no appreciable changes being detected in the analyses. This solid complex does not have a defined stoichiometric composition.

The rapid initial decrease in oxygen consumption when a fresh surface is exposed to air, suggests that the carbon-oxygen complex can be highly resistant to oxidation, and this is how the effect of the attack on the active surface of the coal is manifested, so the decrease in oxygen permittivity under the fresh surface. The carbon-oxygen complex is probably similar to that formed when coal or charcoal is exposed to oxygen and undoubtedly has something in common with the peroxides found in the oxidation of hydrocarbons and other organic materials [1].

By completely oxidizing fine coal at low temperature, a product almost completely soluble in caustic solutions results. In fact the amount of soluble material formed by low temperature oxidation is a good measure of the extent of coal oxidation [3].

These soluble materials are called ullmines, ullmic acid, humines, and humic acids, and some authors assume from their own methods of preparation that they are closely related to the original carbon-oxygen complex.

After precipitation from acid solutions, these solid suspensions consume oxygen from the air at low temperature and have an undefined composition.

When oxidized coal is heated to temperatures below the decomposition temperature of coal, or oxygen is continuously added to the reaction, the coal-oxygen complex decomposes to form carbon dioxide, carbon monoxide, and water, the components appearing in varying proportions. Sometimes other complex decomposition products are found. It has also been reported that, upon discharge at 200°C, there is a decomposition and evolution of carbon dioxide, carbon monoxide and water and the characteristic oxidation rate of coal is restored to values close to those of fresh coal.

Consequently, a stable carbon-oxygen complex is formed at 200°C. The properties of the complex can differ greatly depending on the formation conditions and the type of coal. Studies on the initial appearance of carbon dioxide when fine coal is rapidly heated in oxygen showed that for preoxidized Illinois coal, carbon dioxide first appeared at about 125°C, while for fresh coal it first appeared at about 93°C [5]. Both for fresh coal and oxidized coal heated in oxygen, these results are not a good criterion for the stability of the coal-oxygen complex, except for the indication that the complex is not extremely unstable at these temperatures.

Under these circumstances, coals preheated to 300°C in vacuum doubled the characteristic oxidation rate for some coals and for others it was largely unaffected.

The interaction of oxygen with coal takes place at the gas-solid interface. As a result of the colloidal nature of coal the external surface of the sphere or cube of coal of known dimensions not understanding the equality of the surface of the solid-gas interface that reacts with oxygen at low temperatures.

In other words, the coal contains pores, so that oxidation at low temperature takes place on a surface that is the sum of the external surfaces and interiors. It is little known how the value of the total surface varies with the granulation, the type of coal, etc.

Currently, experiments are carried out using the method of obtaining isothermal adsorption at low temperature with argon. Preliminary tests indicated that the total adsorption surface of this gas is 10...1000 times greater than the external surface [1]. The factor depends on the coal type and granulation.

Despite the fact that adsorption experiments indicated that a very large surface area is available for gases, oxygen does not penetrate deep into the coal.

As a result of these considerations, it seems correct to assume that ordinary oxidation is reduced as a result of the pores, but that this surface is much larger because of the pores. This total pore surface area would be expected to be greater in coals with a high level of moisture, which responds to the high oxidation rate characteristic of these coals.

The oxygen diffusion rate in these pores can affect the oxidation rate, even at low temperatures. The results show that the measured characteristic rates increase with the cubic root of the equivalent surfaces of the coal particles [5]. If there are no internal surfaces covered by cracks, pores and fissures, a direct proportional relationship is expected. At high temperatures, the oxidation rate of the internal surfaces should be reduced compared to the external surface due to the formation of oxygen diffusion in the pores. In other words, at high temperatures the oxidation rate should be expected to become proportional to the external area.

First of all, coal minerals will be taken into account in order to emphasize their presence in its structure and which can have considerable influences in the oxidation process.

4.2. The minerals

Examining coal samples taken from an exploration front with the Fourier transform infrared (FTir) spectroscopy, a quantitative mineralogical low temperature ash analysis (LTA) was applied. It was found that the mineral bassanite ($\text{CaSO}_4 \times 1/2 \text{H}_2\text{O}$) can be used as an oxidation indicator. Bassanite originates from coal calcite (CaCO_3) [1].

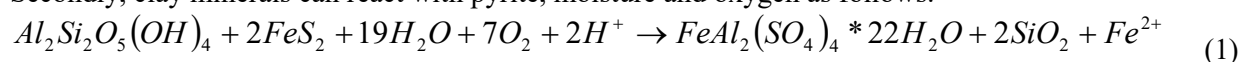
Further oxidation studies by Painter P.C., in 1984 on bituminous coal from Pennsylvania, artificially oxidized at 60°C and 140°C in dry air, it was observed that the minerals are represented by a series of spectral bands of the mineral components that can overlap those of the organic phase. The spectral bands around 1040 cm^{-1} show breaks in various spectra. The same result was obtained from the spectra taken before and after oxidation.

Demineralization with HCl/HF favors air oxidation of coal at low temperature. Observations indicated that, under conditions similar to those of demineralization, coal oxidation occurs in the absence of acid. The role of the acid may be as a catalyst that causes the coal to oxidize at low temperatures. Through coal demineralization, pores are created in its structure, which increase the oxidation surface [1]. To examine the distribution of iron between the iron phases in the samples, Mossbauer spectrometers were used. The spectrum was obtained at 77°K and showed that the iron was generally distributed among the following minerals: pyrites, clay, szomolnokit, jarosite, goethite, lepidocrocite.

The most interesting aspect of the Mossbauer spectrum was that, with increasing oxidation, pyrite was replaced by iron oxyhydroxide. It is considered that this formation of sulfates could be an intermediate step in the oxidation of pyrite. The total content of sulfur contained in the studied coals decreases with the degree of oxidation (they are in the surface area). This is accentuated with the flow of soluble sulfates from naturally degraded coals. As a result of this study, the Mossbauer ratio of $\alpha\text{-FeOOH}$ relative to pyrite was proposed as a measure of oxidation.

First of all, clay tends to be hygroscopic, so it can retain water for a longer time. This water, even in dry periods, can react with the coal.

Secondly, clay minerals can react with pyrite, moisture and oxygen as follows:



4.3. Humidity

Humidity is one of the basic parameters in the oxidation process with major influences 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 150°C, oxidation is slower in moist air than in dry air.

The accelerating effect of moisture on the degradation processes shows that the water comes into action with the oxygen groups on the surface of the coal.

High humidity tends to facilitate the formation of CO₂ and prevents the formation of carbon monoxide. The oxidation is also accelerated by the soluble iron salts in the coal. These can result from pyrite especially in the presence of microbes. So, any effect of moisture on the oxidation of macerals is the opposite of the oxidation of minerals (and successive chemistry), it is difficult to appreciate.

When the coal is simultaneously oxidized and dried, water vapor diffuses out through the pores, partially reducing the oxygen pressure and reducing the reaction rate. If the coal is too dry, the oxidation rate increases. Although it is difficult to extrapolate experimental results found for lower-rank coals such as bituminous coal, the evidence from Australian lignites is valid [5]. The high humidity of the coal during storage seems to 'preserve' the reactivity of the coal in the face of subsequent oxidation. The behavior was explained by invoking 2 processes:

- degradation during storage reduces the reactivity, but it is partially released by the increase induced by the moisture content;
- at low temperature, oxidation is inhibited by humidity and growth.

Other factors that could be considered in the effect of humidity is the opening of the pores of the coal structure and therefore the exposure of new areas to the reaction.

Recent evidence on the role of water in the oxidation of organic macerals from coal seems to support the idea that oxidation reactions are sensitive to water. However, it is a real difficulty to separate the possible different effects of moisture on organic mineral matter.

4.4. Dry and thermal chemistry

The drying action of the coal can affect the reactivity of the coals towards O₂ and can initiate other chemical changes. The most conclusive evidence on this subject was brought by Dack S.W. in 1984 through the studies carried out. He examined the effects of varying the drying temperature (-15⁰C to 150⁰C) on the free radical content.

The results of this study of a sub-bituminous coal indicated that bulk drying at 100⁰C produces irreversible chemical changes (even if weak), of the capacitor (acid-base) type, which occur when the coal is heated. The results show that, right around the temperature of 100⁰C, thermal chemical reactions take place. Carbonyl species can be lost through thermal reactions even if they were formed through oxidation.

It is believed that oxygen is added to the free radical centers, and the addition of O₂ is reversible [1].

The reactions occur as follows:

- thermal decarbonylation/decarboxylation:



- oxidation/decarbonylation at room temperature:



- thermal oxidation (100⁰C):



Increasing the temperature favors the formation of carboxyl groups.

4.5. Granulation and total area

As previously discussed, it has been shown that the smallest coal particles oxidize the fastest. For the smallest particles sampled in the center of the stack (hot space) the intensity decreases. The smaller particles also have a higher weak alkane content than the larger particles collected from the base of the stack.

Macropore oxidation occurs when the determined rate of the oxidation stage of coal particles is made by diffusion of oxygen through the core of the entire lump. In micropore coal oxidation, the oxidation of coal particles is 'open' and the oxidation is not diffusion limited. The oxidation of the macropores depends on the granulation.

For any coal studied, the oxidation is of mixed micro / macropore type. The depth of oxygen penetration in the coal varies between 2 and 4.5 μm and in the hottest areas even reaching 20-50 μm, if the smallest particles in the hottest areas were completely exposed to oxygenation [5]. These small particles can lose carbonyl groups after all the active sites have reacted. An untouched area remains in the smaller areas and in the larger granules.

Studies in the field have shown that there are variations in the reaction rates with granulation. The oxidation of the smallest particles was controlled by surface reaction while the oxidation of larger particles was controlled by surface diffusion. It was observed that the reactivity of sub-bituminous coal was approximately proportional to the fifth power of the specific surface area. The varied nature of coal pores may also help to explain the apparent intensity of some analytical techniques in the oxidation of coals. One test method for surface-only or particulate coal oxidation is to compare results from surface and core analytical techniques.

4.6. The chemical reaction of oxidation

To treat the kinetics of the reactions in the oxidation process, two methods are used:

- adding up a set of 'pure' 'elementary' reactions and combining them;
- obtaining semi-empirical equations.

The second method is usually used, because the complexity of the coal makes it difficult to identify the specific reactive constituents. The problem posed here is valid because the relationships between some kinetic data derived for coal are not well known.

Coal oxidation is not a single reaction but a group of reactions sometimes competing with each other. Moreover, given the heterogeneity of the coal, the defects between the data are not a surprise, as is the finding of the domains, the activation energies of 'oxidation' [1].

The oxidation reactions of coal are controlled by one of the following rates:

- external mass transfer rate from the interior to the solid surface;
- rate of gaseous diffusion in coal;
- the intrinsic rate of the chemical reaction.

Constitutive reactions include:

- reaction with O_2 to form CO_2 and CO directly;
- physical adsorption of O_2 on the coal surface;
- chemical absorption of O_2 in the coal surface;
- the formation of H_2O .

Activation energy estimates were obtained experimentally, concluding that the activation energy for the formation of water was very small. Some authors have studied coal oxidation as a 'single' or 'total' reaction obtaining the corresponding activation energies. It was observed that the effective activation energy decreases over time and the oxidation rate decreases faster for the samples with small grain size. These findings lead to the conclusion that the reaction rate decreases as the reaction progresses in general, the results fit the 'continuous reaction model'.

Based on the data in table 1, regarding the dependence between the heating-cooling time and the heating-cooling speed, the particularities of the coal are highlighted.

Table 1. Results of the experiments regarding the self-heating of lignite from the Roşia Quarry

Temperature initial [°C]	Temperature maxim [°C]	The time of heating [min]	Speed of heating [°C]/[min]	Time of cooling [min]	Speed of cooling [°C]/[min]
28	92	10,5	6,1	7,5	5,6

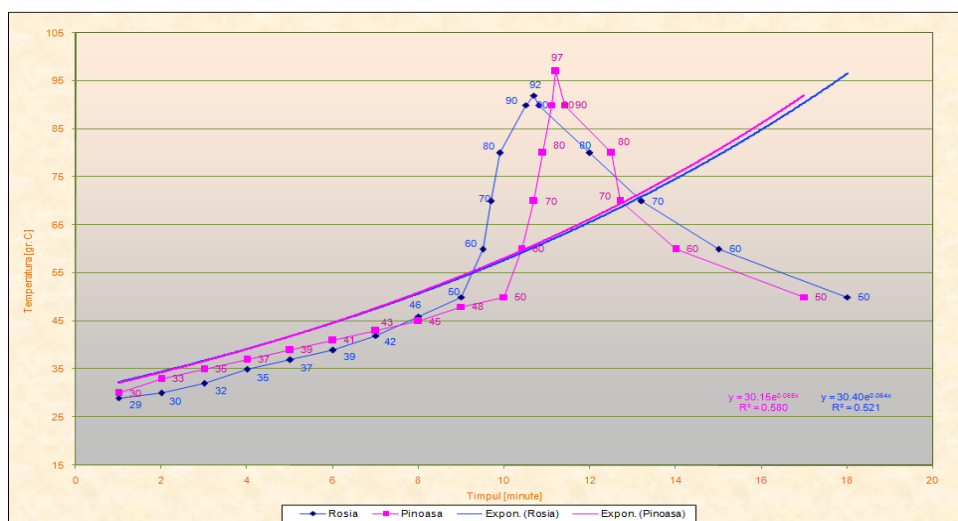


Figure 1. Variation of heating-cooling temperature of lignite

5. Conclusions

The technological process of coal extraction is characterized by the monitoring and management of exploitation works based on quality parameters (total moisture, anhydrous ash, lower calorific value), the values of which are prescribed in the product standards specific to the mining basins and included in the contracts economic contracts concluded with the beneficiaries.

During the excavation-transport-storage processes, it is observed that the values of the parameters mentioned above, register larger or smaller variations compared to the reference values, depending on the internal and external technological factors.

The problems generated by the storage of the extracted production for longer periods of time (over 3 months), have major economic and technological implications resulting in the qualitative depreciation of the coal and the possibility of self-ignition phenomena.

The decrease in the calorific value of the delivered coal has as a consequence the increase in the production price/ton of lignite, by supplementing the storage-conservation expenses and implicitly leads to a decrease in the delivery price to the beneficiaries. Although this aspect is not at all negligible, the most important negative effect is the quality degradation depending on the storage time.

Knowing 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 analysis of the specific quality characteristics of each type of coal from the Roșia quarry, from the point of view of the capacity for oxidation, self-heating and self-ignition, ensures the possibility of preventing qualitative losses in time.

For this purpose, a series of laboratory determinations were carried out to establish the self-heating capacity of lignite at the Roșia quarry, which highlighted the existence of this phenomenon as well as the way the self-oxidation process unfolds.

In view of the laboratory determinations, a method was used which is based on tracking the increase in the temperature of the coal mixture with a strong oxidant (perhydrol - solution with a concentration of 20%). The samples designed for the analysis were made up of the initial laboratory ones where moisture determinations (imbibition, analysis, hygroscopic, total) and ash content during analysis and anhydrous were carried out, following the following stages: homogenization, quantitative reduction, drying, grinding, weighing.

In order for the autoxidation process between the coal granules and the perhydrol solution to be as strong as possible, coal with a grain size of 0.2 mm was used.

The amount of coal that was analyzed was 3 grams/sample, placed in a heat-resistant glass flask, being mixed with 2 ml of distilled water. After this, 9 ml of hydrogen peroxide solution with a concentration of 20% was poured, noting the temperature at the beginning of the reaction by measuring it with the help of a graduated thermometer. The temperature of the mixture of coal with perhydrol was recorded minute by minute, until the temperature of 50°C was reached, and that constitutes the first heating period, characterized by a slow increase in the temperature of the mixture (phase 1 of oxidation). The higher the calorific value of the sample, the shorter the heating time, and vice versa; the lower the quality of the coal, the longer the duration of auto-oxidation.

After the temperature of the mixture has reached 50°C, readings are taken in 10 degree increments until the maximum temperature is reached. This phenomenon manifests itself by increasing the turbulence of the mixture (coal-perhydrol) through the formation of effervescent bubbles that expand towards the upper part of the volumetric flask, in a very short time (reaction phase II). Shortly after reaching the maximum temperature, the reaction begins to decrease in intensity, registering a continuous cooling of the perhydrol-coal mixture. The temperature recording in the cooling phase of the reaction is done from the maximum value to the minimum, from 10 to 10°C, until the temperature of 50°C is reached. Below the temperature level of 50°C, the autoxidation process is no longer representative, so the temperature drop is no longer recorded.

Based on the experiences carried out over a longer period of time, we found that in identical working conditions (initial temperature, weight, granulation), the coals behave differently, precisely because of the different characteristics (petrographic, elemental composition, etc.).

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