

ABSTRACT OF Ph.D. THESIS

***The influence of some expired pharmaceuticals on the course
of coking process of weakly caking coals***

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Scientific progress and civilization development in every country depend on the state of its economy. In most cases, such state is determined by the amount of pig iron and steel being produced. A predicted increase in steel production is strictly connected with the demand for metallurgical coke. Raw materials for production of metallurgical coke are caking coals, the resources of which ran low due to an intensive exploitation in previous years. The lack of coals with good caking abilities involves the use of coals having worse technological values in this process.

Expired pharmaceuticals comprise a specific group of dangerous wastes, the presence of which in natural environment causes water and soil pollution. The unused pharmaceuticals are biologically active substances that are thermally utilized. This is connected with high costs. Similar to utilization of plastic wastes during coking process, there are some activities to be taken in order to explain the possibilities of utilization of expired pharmaceuticals during the process of coke-making of coal charges. Before taking such steps, it should be checked whether the introduction of expired pharmaceuticals into the coke-making practice will worsen technological properties of coals.

The main aim of this doctoral dissertation was an investigation of the influence of addition of expired paracetamol and naproxen on the course of pyrolysis and coke-making processes of low-rank and high-rank coals.

The subject of research were the three commercial samples of coals originating from mines belonging to Jastrzębska Spółka Węglowa SA: Coal Mine Knurów (a lower rank coal having a high yield of volatile parts), Coal Mine Pniówek (a medium rank coal that is characterized by a good caking ability and the ability to form compact coke residue) and Coal Mines Borynia – Zofiówka – Jastrzębie (a higher rank coal that during coke-making tends to generate a dangerous coking pressure). The two non-steroidal anti-inflammatory drugs were

applied as the additives in the amount of 2% wt. The first drug was paracetamol (N-(4-hydroxyphenyl)-acetamide), the second one - naproxen (acid 2-(6-methoxynaphthalene-2-yl) propane). The sample of a medium-rank coal had a better caking ability and the ability to form a compact residue. That is why the thermal behaviour of this sample was chosen as a reference for determination of the influence of additives on the changes in lower rank and higher rank coals taking place during pyrolysis and coke-making.

The samples of coals and their blends with additives were subjected to pyrolysis in a TG/FT-IR measuring set and coke-making in a laboratory unit that made it possible to X-ray the heated charge. The samples of the material from the zones of plastic layer that were obtained during preparation of the cooled charge were analyzed by the FT-IR (DRIFT) technique and extracted in a mixture of chloroform/methanol (50:50) with the help of ultrasound. The obtained extracts were investigated by the FT-IR (ATR) and UV-Vis techniques. The relief of the surface of plasticized samples was presented by the SEM technique. However, the investigation of the material of extracts was conducted by the STEM-HAADF technique.

It was established on the basis of the conducted research that paracetamol and naproxen added to the charge in the amount of 2% wt change the thermal behaviour of studied low-rank coals in a different way. The addition of paracetamol decreased the yield of solid product of pyrolysis of the blend with lower rank coal by 0,47% and the addition of naproxen - by 7,72% compared to the sample of this coal without additives. Moreover, the first additive facilitated the formation of a more condensed and less porous coke residue and hardly changed the yield of volatile products of pyrolysis. The results of deconvolution of the ATR spectra (in the range of $3700-2400\text{ cm}^{-1}$) of the material of the extracts from the charge of blend with paracetamol pointed out to the decomposition of hydrogen bonds and the bonds of $C_{al}-H$ and $C_{ar}-H$ type between the zones of the plastic layer that was similar to the decomposition of these bonds in the plastic layer of medium-rank coal. Based on the data in literature it can be concluded that paracetamol facilitates the process of artificial maturation of low-rank coal during its coke-making.

It was determined that under the influence of naproxen during the pyrolysis of a higher rank coal there was an increase in the mass loss of this coal. This increase was 1,5 times higher than the amount of the additive. The addition of paracetamol also increased the mass loss of this coal but to the amount that was 3 times less than the amount of applied additive. The used additives broaden the temperature range of the occurrence of viscous-liquid state and decreases the temperature of appearance of this state by 10°C . This points out to a plasticizing effect of both additives. Moreover, the addition of naproxen causes an increase in volume of the layer of



heated charge between the heating wall and the marker. The volume of this layer at the stage of swelling of coal grains increased by 20% compared to the layer of coal charge without additives. However, the addition of paracetamol reduced the increase in volume of the charge layer by ca. 1,4 times.

In the extracted materials from the zones of the plastic layer of coal charges and their blends with additives, for the first time by the use of the STEM-HAADF technique there was determined the presence of nano-objects of different topological structure and elemental composition. The elemental mapping of the material of extracts of all three coals proved that the elemental composition of the material of extracts becomes more and more various in a row from low-rank coal to high-rank coal. The presented data suggest that the arrangements of heteroorganic compounds formed during carbonization of commercial samples of low- rank and high-rank coals with additives can be catalysers of chemical reactions. The differences in composition and structure of these heteroorganic arrangements predetermine the differences in the course of pyrolysis process, plasticization and carbonization of lower rank and higher rank coals.

The results of conducted research showed that expired paracetamol (that contains an active substance with proton-donor properties) can be used as an additive to the charges of coals with a worse caking ability. The first proof for this suggestion is a more dense carbonizate that was obtained from the partly carbonized charge of the blend of this additive with a lower rank coal having a high content of volatile parts. Secondly, during coking of the blend of paracetamol with a higher rank coal, there is a decrease in volume of the charge layer at the stage of coal grain swelling contrary to an increase in volume of the coal charge without additives.

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