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Specialty 161 (05.17.07)

PRODUCTION OF THE HIGH-QUALITY COKE FROM THE COAL BLENDS WITH INCREASED CONTENT OF GAS COALS USING THE METHOD OF PARTIAL BRIQUETTING OF THE COAL BLEND. Report 1. Coking of partially briquetted coal blends using individual hydrocarbon products of coke production and their mixtures as a binder with an assessment of the properties of coke obtained from briquetted blends

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The research which are described in the article continues the study of the possibility of using hydrocarbon-by-products of coke production as a binders for partial briquetting of a coal blends.

In 5 kg laboratory coke oven designed by the SE UKHIN the basic, two experimental and ten variants of partially briquetted coal blends have been coked. The amount of briquettes in partially briquetted coke blends was 20 %.

The samples of coke, obtained from experimental coal blends, were used to determine the parameters of technical analysis, structural strength, abrasive hardness, as well as indicators of reactivity and post-reaction strength (CRI and CSR) and indicators of actual and apparent strength and porosity. In addition, the expected strength values (M_{25} and M_{10}) and the CRI and CSR indicators of industrial coke were calculated taking into account the conversion factors from laboratory to industrial data.

It has been established that the using of the partial briquetting method with the hydrocarbon additives as a binders due to the small number of briquettes and the small proportion of the binder in the total coal blend, has practically no effect on the structural characteristics of the obtained coke

As it was expected, the increasing of the gas coal content in the coal blend increases the reactivity of coke according to DSTU 7664: 2014 (km), as well as the reactivity according to DSTU 4203: 2006 (CRI), and decreases the post-reaction strength of coke (CSR). The coal tar pitch, as well as a mixture of coal tar, sludge, tar and oils of the biochemical plant (BCP) and acid tar of the recovery shop in a different ratios were used as a binder for briquetting in the amount of 5 % (by weight) of the briquettes.

It is shown that the using of the screenings of coal pitch as well as a mixture of acid tar with BCP resins and oils as binders in briquetting leads to a deterioration in the strength characteristics (mechanical strength) of the obtained coke compared with these parameters of coke obtained from the same coal blends, but without the use of partial briquette technology with a binder.

Using a mixture of coal tar and sludge in a ratio of 80:20 as a binder during briquetting makes it possible to obtain high-strength blast furnace coke, corresponding to the complex of properties of KDM1 coke, from the coal blend containing 30 % coal of gas group. When the content of gas coal in the coal blend is equal to 35 %, the coking of the partially briquetting coal blend using a binding mixture of sludge, coal tar and acid tar in ratio with 30:20:50 provides metallurgical coke according to a quality properties of the KDM2 mark.

Keywords: hydrocarbon products of coke production, briquetting of the blend, partially briquetted coal blend, coking, coke strength, coke reactivity, gross coke yield.

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SEMI-COKING OF SAPROPELITE COAL OF THE SEPARATE MINES OF THE LVIV-VOLYN COAL BASIN

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Ukraine)

In the article the problem of accumulation of sapropelite coal in the coal's heaps of the coal-mining enterprises of the Lviv-Volyn coal basin is considered. An assessment of its reserves in State Company "Lvivvugillya" enterprises carried out. We suggested using semi-coking process to remove tar, combustible gas and coke from this non-standard raw material. Samples of sapropelite coal were selected from three mines of SC "Lvivvugillya", crushed and fractionated. For them, the technical characteristics were determined; they showed high ash content of all samples, which averaged 36.3%, with average humidity - 1.7% and volatile yield - 25.35% (from the analytical sample).

We used two apparatus for semi-coking: a small one with a loading capacity of 100 g and a large one with a camera volume of more than 1.5 dm³. Semi-coking was carried out in the temperature range 540-550 °C. Using a small apparatus and a wet gasometer, it was found that the gas emission of the samples averages 6.56 dm³ per 100 g. The gas composition is determined by gas chromatography and its higher (22.59 MJ/m³) and lower volumetric heat (10.29 MJ/m³) of combustion in the ideal gas model according to ISO 6976: 1995.

After a series of experiments carried out on a large installation, we have collected a sufficient amount of primary tar for fractionation and investigation of individual fractions. The tar was a dark brown, moderately viscous liquid, with a high water content. It was found that only part of the water can be separated by the method of separation of unmixed layers. The remainder is separated in light distillation fractions (gasoline and ligroin). The average water content in the tar was 43.7%, of which more than 90% were easily separated on the separating watering can. The relative density of the dehydrated tar samples is in the range of 0.975-0.996.

The fractionation of the dehydrated tar was carried out according to the fuel scheme. On average, the gasoline fraction was (in wt.%) – 3.2, kerosene – 4.28, ligroin – 9.41, diesel – 43.95 and fuel oil – 39.16. For two tar fractions – kerosene and diesel, an IR-spectroscopy was performed to determine the group composition. It has been shown that with increasing boiling point, the decarboxylation of the tar components occurs, and the fractionation product acquires an aliphatic-aromatic character with an admixture of a small amount of oxygen-containing compounds represented by phenols, ethers and alcohols.

Keywords: sapropelite coal, semi-coking, primary tar, combustible gas, fractionation.

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ALKALI PROMOTION OF ANTHRACITE OXIDATION BY OXYGEN

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The aim of this work was to identify the effect of alkali metal hydroxides on the oxidation and functionalization of anthracites in reaction with molecular oxygen.

The interaction of O₂ (200 °C, time ≤ 5 h) with anthracite A (C^{daf} = 94,6 % and 95,6 %) impregnated (1 mmol/g) with alkali metal hydroxides (MOH, M = Li, Na, K, Rb, Cs) has been studied. MOH has been established to promote oxidation: the initial rate increases linearly (by 2,3-2,5 times) with an increase in the cation diameter d_M. A comparison of the different alkalis activity at the same time (5 h) has been performed.

It has been determined that in the series from the initial anthracite (A) to the "A-CsOH" compound, the total amount of O₂ reacted increases by 2,5 ± 0,1 times and the CO₂ yield increases by 3,7±0,2 times; the yield of CO does not change. The amount of oxygen in the functional groups m(OFG) increases linearly (by 1,7-3,0 times) with the polarizability P of the cation. It was established that the content of carboxyl [COOH] and phenolic [OH] groups in oxidation products of "A-MOH" compounds depends on the type of MOH and anthracite and increases by 2,1-9,0 times and 4,3-12,2 times, respectively. With increasing polarizability, [OH] value increases exponentially on the background of linear growth of m (OFG), which indicates additional (in addition to oxidation) routes of OH groups formation initiated by alkalis.

It has been established too, that a more metamorphosed anthracite is oxidized to a lesser extent both on its own and

in the presence of MOH, but the dependences on the size and polarizability of M⁺ cations are qualitatively identical. It is also impossible to exclude the effect of individual structural features of the spatial frameworks of different anthracites, which strongly affect the steric accessibility of arene fragments to MOH and O₂ molecules, as well as the diffusion of reaction products into the external environment. The routes of reactions with MOH are proposed to include a new way of electrons transfer from anthracite to O₂ through complexes "M⁺ - π -system of polyarene", heterolysis of C-C bonds of quinoid anthracite structures with the carboxylates formation and arene hydroxylation with the degree exponentially increasing from LiOH to CsOH.

Keywords: coal, anthracite, alkaline impregnation, oxidation

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THE INFLUENCE OF ROCK DUMPS OF COAL MINING ENTERPRISES AND COAL POWER PLANTS OF UKRAINE ON THE ENVIRONMENT

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Storage facilities for coal sludge and ash disposal facilities require significant areas that fall out of the use zone for a long time and are the centers of accumulation of toxic compounds of heavy and rare metals. Intensive dissolution and migration of heavy and rare metal ions occur in the near-surface zone of the ash dump or coal slime dump under the influence of oxygen, precipitation, filtration fields, and other factors. In this case, depleted and metal-enriched sites with reduced and oxidized forms are formed. On the territory of northern Donbass there are 209 such zones, of which 192 are in industrial-residential areas (their total area is 48.8 km²).

Sampling of contaminated soils near coal slime dumps of a number of enrichment plants and ash and slag dumps of Tripol thermal power plant was performed.

A high content has been established of compounds of heavy and rare metals in the coal slurries of a number of processing plants and dumps of ash and slag waste generated during the combustion of solid fuels at thermal power plants. It leads to seriously polluting of all areas of the natural environment and does not allow to empty or reclaim sludge storages due to their isolation and final disposal without appropriate processing and disposal. Rather stringent standards for the content of harmful substances in industrial waste require special methods for the disposal of coal sludge and ash and slag before final disposal.

The regularity was determined of decreasing the concentrations of Cu, Pb, Cr, Ni, and Zn compounds in soil samples near the coal dumps of processing plants and the ash and slag waste dump of the Tripol TPP.

It was shown that Pb, Ni, Cu, and Cr compounds have high mobility in soils near coal slurry dumps of enrichment plants and dumps of ash and slag waste from thermal power plants, which is why they accumulate in the soil even far from them at neutral and slightly alkaline pH values. It was shown that Zn compounds have low mobility in the soil near coal slurry dumps of processing plants and dump slag ash of TPPs, which is why they accumulate in the soil only near them at neutral and slightly alkaline pH values.

Keywords: coal slurries, ash-slag wastes, coal enrichment, coal-fired power plants, migration of heavy and rare metals, sorption of metal ions by soil particles, waste heaps, slurry ponds, environmental pollution

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THE CLEANING OF RINSING WATERS OF CAVITATION TREATMENT OF OIL FROM CHLORIDE

IONS

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The volumes of the oil production are growing from year to year. The industrial processing of oil lies in its dehydration and demineralization. When treating oil by the method of cavitation, flushing water get enriched by chloride ions. Their presence implies the creation of chloride acid during the following technological stages of the thermal treatment of oil. HCl fumes decrease the volumes of the oil products' production, disrupt the operation mode of oil-processing machines, worsen the calorific value and quality of petrol, and cause the corrosion of oil-processing machines.

The aim of the work is the purification of flushing waters of cavitation treatment from chloride ions.

Objectives of the work: determine the basic parameters of the process of the reactant purification of the cavitation treatment's flushing waters of oil production from chloride ions and optimize its stages.

The work implied the determination of chloride-ions content in periodically collected water samples. The control of the content of silver ions in the solution after the sedimentation was held on the atomic absorption spectrophotometer. The identification of sediment compounds after the sedimentation was carried out by the radiography method. The morphological peculiarities of the compound's surface were studied in accordance with the electron-probe microanalysis method. The assessment of water acidity was carried out by the measuring device – millivoltmeter.

The chemical-reagent method of sedimentation was suggested for the purification of oil flushing waters from chloride ions to the standard level of the technological process. Argentum nitrate was selected as the sedimentation reagent - its optimal amount was defined by the experimental data.

The basic parameters of the reagent-based process of the purification of oil flushing waters from chloride ions have been determined. Its stages have as well been optimized: the amount of the sedimentation reagent AgNO_3 in relation to chloride ions that are present at the sedimentation stage; the boiling time of the AgCl suspension; volume ratios of the decantating flushing water and the AgCl sediment on the stage of their separation; the amount of the NaOH lye necessary to process the solution left after the decantation, with the AgCl sediment; the ratios of the lye solution that is being decanted, and the sediment formed during the separation stage; volumes of water necessary to rinse the sediment; the volumes of the concentrated HNO_3 acid during the stage of the dissolution of the produced sediment.

The suggested method of the purification of flushing waters of the cavitation oil treatment from chloride ions, that involves the chemical sedimentation of chloride ions by the Argentum nitrate, with the subsequent regeneration of the sedimentation reagent, can be used in oil-producing and oil-refining industries.

Keywords: washing waters oil, reagent purification, chloride ions.

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