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A VERIFICATION OF DESULPHURIZATION PROPERTIES OF PROCESSED BLACK-COAL SLURRIES WITH VARIOUS TYPES OF SOLID FUELS

PORÓWNANIE WŁAŚCIWOŚCI ODSIARCZAJĄCYCH PREPAROWANYCH SZLAMÓW WĘGLA KAMIENNEGO I RÓŻNYCH TYPÓW PALIW STAŁYCH

Abstract

It is possible to make fuel that resembles energetic brown coal in its qualities through a suitable preparation of black-coal slurries by means of a lime component. This coal is used in the majority of large output sources. In contrast to common fuels, the newly developed fuel has higher desulphurization capacities due to the presence of the lime component. The paper describes the procedure and results of laboratory analyses which were supposed to prove the efficiency of desulphurization applying classical solid fuels compared with the newly developed fuel with black-coal slurries.

Keywords: black-colas slurries, solid fuels, lime, desulphurization

Streszczenie

Istnieje możliwość wytwarzania paliw o właściwościach zbliżonych do węgla brunatnego na drodze obróbki szlamów węgla kamiennego przez dodatek wapna palonego. W przeciwieństwie do tradycyjnych paliw, dodatek wapna palonego poprawia właściwości odsiarczające nowo opracowanego paliwa. W artykule przedstawiono badania oraz analizę wyników laboratoryjnych, które miały na celu potwierdzenie korzyści wynikających z poprawy właściwości odsiarczających paliw otrzymanych na bazie szlamów węgla kamiennego w porównaniu z paliwami tradycyjnymi.

Słowa kluczowe: szlamy węgla kamiennego, paliwa stałe, wapno palone, odsiarczanie

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1. Situation in black-coal mining

The situation in the Czech black-coal mining has been characteristic for the run-down which has been in progress since the early 1990s. For many years before 1990 over 20 million tons of black coal had been mined in the CR.

The shrinking reserves, economic reforms and restructuring of the industry and the whole economy after 1990 projected themselves into the reduction in the domestic demand and a gradual decrease in the mining of black coal. In 2006, 13.4 million tons of black coal were produced, out of which 7.4 million tons were cokeable coal (UVPK) and 5.6 million tons energetic coal (ČUE). The export of black coal is historically linked to the period of Austria-Hungary, when Ostrava coal and coke were supplied into all parts of the monarchy. After WWI metallurgical operations and power plants in the countries that were formed in the area of the former Austria-Hungary remained important business partners of Ostrava mines and coking plants. This relationship continued also after WWII, when the market for the export of Ostrava black coal and coke expanded further.

The import of black coal into the CR also has a historical background. Mostly these were cases of special types of energetic coal for technological purposes (chemical industry, cement works, sugar factories, etc). There was a more pronounced expansion of the energetic black coal imports in the 1990s in connection with the ongoing run-down of the domestic mining. Poland has been the decisive import territory.

The import of cokeable coal into the CR had been negligible before 1990. In the 1990s cheaper UVPK started to be imported to the CR from Poland and these imports have lasted to date.

The domestic power-engineering is going to search for a new strategy to find the optimal composition of the energy sources for the future, which will not be easy. The significance of the imported sources will inevitably increase, but the changes should not be too sudden and destabilizing.

Despite the fact that there are quite high geological reserves of black coal within the Czech Republic, the balance of recoverable reserves is very low (only 134 million tons as of 1 January 2007). A full utilization of available balance reserves is inhibited by too high costs of underground mining of black coal. Domestic black energetic coal will be supplied to the Czech market in slightly falling annual volumes – from today’s approximate 3.5 million tons to about 3 million tons by 2015 – and economically interesting parts will be exploited until 2018.

2. Overview of prepared samples and carried out analyses

On the basis of its different chemical composition the coal mass shows different properties after its heat treatment. These properties determine the potential utilization of each fuel (combustion, coking, chemical treatment, etc) and its technological or business classification. There are indexes evaluating those properties, for example calorific value, heating value, swelling index, Rog number, coking capacity (dilation and contraction capacities), ash fusing point, etc.

On the basis of the results of previous works [2], we carried out the second phase of the verification of the application of black-coal slurries as a fuel that provides the benefit of desulphurizing capacity. In the second stage the degree of desulphurization was determined in combination with selected types of black and brown coal. The overview of the prepared samples is in Table 1.

Laboratory analyses in the following scope were carried out with the prepared samples: basic technological analysis (ZTR – the determination of analytical water, ash, calorific value, total sulphur), the determination of the total (W_t^r), remaining (W_h) and gross (W_{ex}) water content, the determination of volatile combustible (V^{daf}) and carbonates, the determination of carbon dioxide from carbonates, the determination of ash fusing point in the oxidizing atmosphere, ash chemical analysis (the determination of SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, K_2O, P_2O_3, SO_3, TiO_2), the elementary analysis of fuel organic mass (the determination of carbon, hydrogen, nitrogen and oxygen), the determination of chlorine and fluorine, the determination of selected trace elements, the determination of emission factors, the determination of loss on ignition and total sulphur in ash. Based on the analyses results, an evaluation of the obtained values of the individual parameters was carried out in terms of potential utilization of the samples for fuel purposes.

Table 1

Overview of prepared samples

Sample No.	Sample designation
1	black coal + 20% CaO – 85% + 15%
2	black coal + 20% CaO – 90% + 10%
3	black coal + 20% CaO – 93% + 7%
4	black coal + 20% CaO – 95% + 5%
5	brown coal + 20% CaO – 85% + 15%
6	brown coal + 20% CaO – 90% + 10%
7	brown coal + 20% CaO – 93% + 7%
8	brown coal + 20% CaO – 95% + 5%
9	black coal + slurry – 85% + 15%
10	black coal + slurry – 90% + 10%
11	black coal + slurry – 93% + 7%
12	black coal + slurry – 95% + 5%
13	brown coal + slurry – 85% + 15%
14	brown coal + slurry – 90% + 10%
15	brown coal + slurry – 93% + 7%
16	brown coal + slurry – 95% + 5%
17	brown coal
18	black coal

Table 2 shows the results of the basic technological analysis carried out with such prepared samples.

In the case of the pure slurry sample combined with brown coal the water content is almost identical in all the samples, with the decreasing trend along with higher amounts of CaO. This corresponds to the fact that the slurry sample has a slightly higher water content than the brown coal sample and adding slurry to brown coal makes the water content go up. The same situation occurred in the case of ash content, which confirms a higher ash content in the black-coal slurry sample. As for the heating value, again, it went down in relation with the amounts of the added slurry, whose heating value was slightly lower than that of brown coal. However, coal with added 15% of slurry has a comparable heating value with common energetic coal. A lower sulphur content caused its gradual decrease in relation to the added black-coal slurry.

Table 2

Basic technological analysis of the prepared fuel samples

Sample description	W_t^r [%]	A^r [%]	A^d [%]	Q_i^r [MJ/kg]	S^d [%]
black coal + 20% CaO – 85% + 15%	7.8	14.32	15.53	25.13	0.27
black coal + 20% CaO – 90% + 10%	7.63	11.83	12.81	25.97	0.31
black coal + 20% CaO – 93% + 7%	7.53	10.37	11.21	26.5	0.29
black coal + 20% CaO – 95% + 5%	7.46	9.31	10.06	26.78	0.32
brown coal + 20% CaO – 85% + 15%	23.36	20	26.1	16.22	1.15
brown coal + 20% CaO – 90% + 10%	24.11	18.09	23.84	16.49	1.31
brown coal + 20% CaO – 93% + 7%	24.56	17.01	22.55	16.59	1.38
brown coal + 20% CaO – 95% + 5%	24.85	15.79	21.01	16.87	1.37
black coal + slurry – 85% + 15%	9.61	12.86	14.23	24.83	0.31
black coal + slurry – 90% + 10%	8.83	11.15	12.23	25.63	0.37
black coal + slurry – 93% + 7%	8.37	10.15	11.08	26.08	0.35
black coal + slurry – 95% + 5%	8.07	9.51	10.34	26.33	0.35
brown coal + slurry – 85% + 15%	25.17	19.01	25.41	15.68	1.36
brown coal + slurry – 90% + 10%	25.31	18.23	24.41	15.9	1.42
brown coal + slurry – 93% + 7%	25.4	17.64	23.65	15.97	1.47
brown coal + slurry – 95% + 5%	25.46	17.29	23.19	16.03	1.48
brown coal	25.6	16.1	21.64	16.23	1.37
black coal	7.29	7.71	8.32	27.44	0.34

Combining pure slurry and black coal made the water content rise gradually as the water content in the slurry sample was higher than in the black coal sample. The higher ash content in pure slurry caused an increase in the ash content in the mixed sample as the ash content of black coal was lowered by roughly 75%. Nevertheless, the ash content value in the sample with added 15% of slurry is at the level of quality types of black coal. Similarly, the heating value went as low as 24.83 MJ/kg. This is also an acceptable value in black coal used for power generating purposes. The sulphur value did not change significantly.

In samples prepared combining brown coal there was a drop in the water content, again, with the gradual addition of 20% CaO sample. The ash content went up. However, this value would not dramatically influence the course of combustion. The heating value had a downward trend and the sulphur content decreased considerably by about 20%.

In samples prepared combining black coal the water content increased more slowly than in the case of pure black-coal slurry, which confirms a lower value of the water content in 20% CaO sample. On the contrary, the ash content rose significantly. The heating value decreased gradually and the final value is, again, acceptable for power generating purposes. The sulphur content value did not change much due to similar values in the input samples of black coal and CaO 20%.

3. Determination of desulphurization degree

Tables 3 and 4 show the determination of the laboratory desulphurization degree.

The samples were dried in a drier at a temperature of 105–110°C into a constant mass. The dried samples were later annealed in a muffle furnace at 900°C with a gradual temperature increase and time lag (30 min.) at 700°C. The total annealing time of the doped partial samples lasted 10 hours. After annealing and ash cooling a visual inspection of possibly unburnt particles was carried out. Simultaneously, the loss on ignition was identified with each sample. Such ash obtained from the individual samples underwent analyses to identify the total sulphur content S_t^d using the Eschka method in accordance with the ČSN 44 1379 Standard. In order to compare the content of sulphur in ash it was necessary to establish a "steady state". In this way the recalculation referred to the identical ash content. It was possible to determine the sulphur content that transferred into the ash material during combustion and that was emitted in such prepared samples.

In the case of pure slurry samples no high sulphur removal was recorded either combining black or brown coal. The slurry contains only a high share of CaO, but this does not enter the desulphurization reaction and the desulphurization ranged on average from 7% in black coal to 15% in black coal. In the case of the inerts content there was no significant increase and it amounted to around 49% in brown coal and 19% in black coal.

Table 3

Sulphur content in ash

Description	W_t^r	A^r	A^d	S^d	S^{pop}
black coal + 20% CaO – 85% + 15%	7.8	14.32	15.53	0.27	3.18
black coal + 20% CaO – 90% + 10%	7.63	11.83	12.81	0.31	3.74
black coal + 20% CaO – 93% + 7%	7.53	10.37	11.21	0.29	3.44
black coal + 20% CaO – 95% + 5%	7.46	9.31	10.06	0.32	2.46
brown coal + 20% CaO – 85% + 15%	23.36	20	26.1	1.15	3.41
brown coal + 20% CaO – 90% + 10%	24.11	18.09	23.84	1.31	2.6
brown coal + 20% CaO – 93% + 7%	24.56	17.01	22.55	1.38	1.97
brown coal + 20% CaO – 95% + 5%	24.85	15.79	21.01	1.37	1.47
black coal + slurry – 85% + 15%	9.61	12.86	14.23	0.31	0.44
black coal + slurry – 90% + 10%	8.83	11.15	12.23	0.37	0.35
black coal + slurry – 93% + 7%	8.37	10.15	11.08	0.35	0.4
black coal + slurry – 95% + 5%	8.07	9.51	10.34	0.35	0.23
brown coal + slurry – 85% + 15%	25.17	19.01	25.41	1.36	0.38
brown coal + slurry – 90% + 10%	25.31	18.23	24.41	1.42	0.43
brown coal + slurry – 93% + 7%	25.4	17.64	23.65	1.47	0.36
brown coal + slurry – 95% + 5%	25.46	17.29	23.19	1.48	0.34

Table 4

Determination of laboratory degree of desulphurization

Description	Recalculated S in ash	Sulphur emissions	Sulphur removal in [%]	Inerts
black coal + 20% CaO – 85% + 15%	0.49	–0.22	182.91	23.33
black coal + 20% CaO – 90% + 10%	0.48	–0.17	154.55	20.44
black coal + 20% CaO – 93% + 7%	0.39	–0.10	132.97	18.74
black coal + 20% CaO – 95% + 5%	0.25	0.07	77.34	17.52
brown coal + 20% CaO – 85% + 15%	0.89	0.26	77.39	49.46
brown coal + 20% CaO – 90% + 10%	0.62	0.69	47.32	47.95
brown coal + 20% CaO – 93% + 7%	0.44	0.94	32.19	47.11
brown coal + 20% CaO – 95% + 5%	0.31	1.06	22.54	45.86
black coal + slurry – 85% + 15%	0.06	0.25	20.20	23.84
black coal + slurry – 90% + 10%	0.04	0.33	11.57	21.06
black coal + slurry – 93% + 7%	0.04	0.31	12.66	19.45
black coal + slurry – 95% + 5%	0.02	0.33	6.79	18.41
brown coal + slurry – 85% + 15%	0.10	1.26	7.10	50.58
brown coal + slurry – 90% + 10%	0.10	1.32	7.39	49.72
brown coal + slurry – 93% + 7%	0.09	1.38	5.79	49.05
brown coal + slurry – 95% + 5%	0.08	1.40	5.33	48.65

A reversed situation occurred combining the 20% CaO sample. In brown coal a pronounced increase in the desulphurization degree from 22 to 77% was observed. In black coal a high degree of desulphurization was recorded already with added 5 wt % of the slurry sample combined with 20% CaO. This degree significantly grew and the next sample practically showed a hundred-percent desulphurization.

4. Conclusion

The paper deals with an analysis of a number of samples that were prepared combining pure black-coal slurry, black-coal slurry with added 20 wt.% of CaO and representative samples of black and brown coal types. These samples were analyzed on a complex basis necessary for the potential utilization in power-engineering. A degree of desulphurization was set in the samples, which simulates the desulphurization process in industrial facilities. The slurry sample did not show a high degree of desulphurization and thus it cannot be recommended as a fuel when a high sulphur removal is expected. In the case of the sample that contained 20 wt.% of CaO there was a high degree of desulphurization both in brown and black coal. However, it was only a laboratory determination under the so-called ideal conditions. The quantity of CaO significantly affects the fusing point of ash. The amount of CaO in the slurry sample shows a “luxury” desulphurization degree and, for further use, an identification of a suitable CaO quantity will be considered with regard to the desulphurization degree and effect of CaO on fusing points of ash for a specific heat source.

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