

FLUE GAS DESULPHURIZATION AND DENITRIFICATION USING ACTIVATED COKE

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In the process of coal treatment is produced the coal sludge. One of the usage options of this sludge is their thermal treatment and conversion to the activated coke. The options for the conversion of coal sludge on activated coke and the testing of its properties was investigated in the laboratory research, whose results are presented in this article. Waste from coal flotation was used for the laboratory production of activated coke. The obtained samples were tested for SO₂ adsorption and NO removal from flue gas. The results achieved were compared with those of industrial activated coke. The wastes from coal flotation represent very good raw material for activated coke production. The activated coke samples prepared from these raw materials under laboratory conditions show similar properties as the industrially produced activated coke by Rheinbraun and Carbo Tech.

Key words: activated coke; desulphurization; denitrification

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1. Introduction

The technology of flue gas purification using activated coke is currently used in many power plants and waste disposal plants [1, 2]. Both the non-regenerative technology with the subsequent combustion of loaded activated coke and the regenerative technology involving pollutant desorption from loaded activated coke and its repeated use for purification [3] are used for flue gas purification. The impurities-loaded activated coke produced in waste disposal plants is eliminated by combustion.

Compared to other purification technologies (e.g. wet technologies using limestone), the activated coke technology features certain benefits, such as higher efficiency of SO₂ removal, the possibility of simultaneous NO_x removal, heavy metals removal, purification temperatures above the flue gas dew point, the possibility for technical use of the desulphurization product (H₂SO₄), low consumption of process water, no waste water production. The considerably higher operating costs compared to wet desulphurization technologies represent one of the activated coke technology disadvantages [4].

The purification technology using activated coke represents one of the few possibilities to reduce PCDD and PCDF levels in flue gas below the emissions limits in municipal waste incinerators [5, 6]. Simultaneously, activated coke serves as an adsorbent for the residual removal of dangerous acidic gaseous pollutants, e.g. HCl, HF, SO₂, NO_x, heavy metals and organic impurities [7, 8]. Given the long term experience with activated coke technology application in waste disposal plants, the future use of this technology can be anticipated.

2. Activated coke and its producers

Carbon-based adsorbents containing less developed porous structure are referred to as activated coke. The BET surface area of activated coke is under value of 400 m²/g. In Europe, activated coke is produced by the German companies Rheinbraun and Carbo Tech. Rheinbraun [9] produces granular activated coke (particle size 1.25 – 5 mm), fine activated coke (particle size 0.1 – 1.5 mm) and powdered activated coke (< 0.4 mm). Low ash brown coal is used as raw material for the production, carried out in plate oven at 950 °C. Annual production in last years ranged up to 200 000 t. The produced activated coke is used first of all as one-way adsorbent in flue gas treatment in power plants and waste incineration plants.

Carbo Tech [10] produces pelletized activated coke (diameter 5 mm and particle length 5 – 10 mm) in multi-step fluidized bed oven using bituminous coal. The produced activated coke is used as regenerable adsorbent for flue gas desulphurization and denitrification in coal fired power plants.

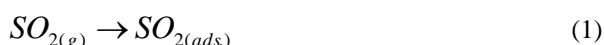
The activated coke consumption in the Czech Republic is currently covered by the import from Germany. It is mainly used for flue gas treatment in waste disposal plants. In consequence to the new legislation in the area of atmosphere protection, the increase of activated coke consumption is anticipated.

Therefore, in collaboration with the University of Freiberg, the ICT Prague developed a new process for activated coke production, using waste from bituminous coal flotation as raw material. The properties of the activated coke samples produced were subsequently compared to those by Carbo Tech and Rheinbraun.

3. Flue gas desulphurization and denitrification using activated coke

There are two different mechanisms of flue gas desulphurization:

1. Sulphur dioxide from flue gas is adsorbed into the porous structure of activated coke and subsequently oxidized by O_2 to SO_3 . SO_3 and the adsorbed water steam react to produce sulphuric acid [11]. The regeneration of H_2SO_4 -loaded activated coke continues by its heating to temperatures above $500\text{ }^\circ\text{C}$. The H_2SO_4 is reduced to SO_2 by the carbon from activated coke, whereby SO_2 rich gas is produced. This gas is used for H_2SO_4 production (technical quality grade) [12,13]. The reactions are described by the following equations:

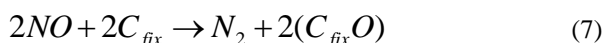


2. Similarity to the first mechanism according equations (1) to (4). During the H_2SO_4 neutralization in the porous structure of activated coke by alkali substances, sulfates are formed. Thermal regeneration of loaded activated coke below $500\text{ }^\circ\text{C}$ is not possible due to the high stability of the sulfates formed. The used activated coke is disposed of by combustion.

Flue gas from conventional power plants mainly contains NO_x in the form of NO (85 – 95 %) and NO_2 (5 – 15 %). At temperatures above $120\text{ }^\circ\text{C}$, NO_2 can be reduced to elementary N_2 using the activated coke carbon according to the following equation:

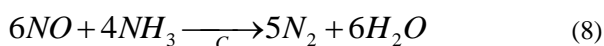


The reactivity of NO is lower than that of NO_2 . Higher temperatures above $150\text{ }^\circ\text{C}$ are necessary for its direct reduction to elementary N_2 [14]. Such conditions enable the reaction according to the following equation:



The oxygen from NO remains on the surface of the activated carbon and its increasing concentration moves the reaction equilibrium to the left, decreasing the reaction's efficiency.

Therefore, in technical scale, the NO reduction using gaseous ammonia as a reduction agent is given preference [15]. The activated coke catalyzes the NO reduction according to the following equation:



4. Preparation of laboratory samples of activated coke

To the preparation of laboratory samples of activated coke was used coal sludge from the coal treatment plant of Coal Mine Darkov (CZ). To determine the basic properties of the sludge, the sludge sample was dried and prepared for the basic analysis. The results of the analysis of coal sludge are listed in table 1.

Tab. 1 Basic properties of coal sludge used for the preparation of activated coke

Parameter	Value
Ash content, A ^(d)	20.41%
Content of volatile matter, V ^(daf)	22.37%
Water content, W ^(a)	38.59%
Carbon content, C ^(d)	69.42%
Content of hydrogen, H ^(d)	3.97%
Oxygen content, O ^(d)	1.05%
Sulphur content, S ^(d)	0.56%
Content of nitrogen, N ^(d)	4.59%
Lower calorific value, Q _i	27.3 MJ/kg
Higher calorific value, Q _s	28.2 MJ/kg

d – dry; *a* – analytical sample; *daf* – dry ash, free

Coal sludge was first mixed with the binder in a ratio of 95:5 and subsequently agglomerated. As the binder pulped waste paper was used. The resulting mixture was extruded through a matrix of holes diameter 4 mm. Manufactured pressed pieces should be 8 - 10 mm in length and a diameter of approx. 3 - 4 mm. Optimal moisture for mixtures was determined in the range of 25 - 30%. The pressed pieces were subsequently dried in air oven at $105\text{ }^\circ\text{C}$. Hydrated lime stone was added to some of produced samples due to the expected increase of adsorption and catalytic properties of produced activated coke samples. Some samples were prepared with the addition of 2 % or 4 % calcium hydrate.

Dried pressings were subsequently carbonized in stationary muffle furnace and then activated in the rotary kiln.

Carbonization conditions:

- the temperature gradient: 5 K/min,
- final temperature carbonization: 800, 900 or 1000 $^\circ\text{C}$,
- the time remaining on the final temperature carbonization: 60 min,
- the inert gas flow (nitrogen): 100 dm^3/h .

Weight decreases individual samples ranged from 26.6 to 29.1 %. Carbonized samples were subsequently activated using water vapor in a rotating electrically heated kiln under the following conditions:

- temperature gradient: 20 K/min,
- final temperature of activation: 800, 900 or 1 000 $^\circ\text{C}$,
- the time remaining on the final temperature: 60 min,

- the consumption of the activation reagent (distilled water): 50 ml,
- nitrogen flow: 100 dm³/h,
- the speed of rotation of the furnace: 3 rpm,
- the water vapour concentration in the gas: aprox. 40 % vol.

The weight decreases of the samples during activation is ranged from 6.3 to 6.7 % (samples activated at 800 °C), over the 14.7 - 17.2 % (samples activated at 900 °C) up to 32.8 - 41.3 % (samples activated at 1 000 °C). Description of the prepared samples is given in table 2, their basic properties are indicated in table 3.

Tab. 2 Used activated coke samples description

Sample	Conditions of sample preparation
A1 800	Activated coke made from bituminous coal waste without additive addition, carbonized and activated at 800 °C
A1 900	Activated coke made from bituminous coal waste without additive addition, carbonized and activated at 900 °C
A1 1000	Activated coke made from bituminous coal waste without additive addition, carbonized and activated at 1000 °C
A2 800	Activated coke made from bituminous coal waste loaded with 2 % limestone hydrate, carbonized and activated at 800 °C
A2 900	Activated coke made from bituminous coal waste loaded with 2 % limestone hydrate, carbonized and activated at 900 °C
A2 1000	Activated coke made from bituminous coal waste loaded with 2 % limestone hydrate, carbonized and activated at 1000 °C
A3 800	Activated coke made from bituminous coal waste loaded with 4 % limestone hydrate, carbonized and activated at 800 °C
A3 900	Activated coke made from bituminous coal waste loaded with 4 % limestone hydrate, carbonized and activated at 900 °C
A3 1000	Activated coke made from bituminous coal waste loaded with 4 % limestone hydrate, carbonized and activated at 1000 °C
Rheinbraun	Sample of industrial activated coke (by the Rheinbraun company), lot 1583 (granular activated coke, grain size 1.25 – 5 mm)
Carbo-Tech	Sample of industrial activated coke (by the Carbo Tech company) (extruded activated coke, diameter 5 mm, length 5 to 10 mm)

5. Preparation of laboratory samples of activated coke

The tests of industrially produced activated coke samples (Rheinbraun and Carbo Tech) and samples made from bituminous coal wastes (laboratory prepared samples) to be used for flue gas desulphurization and denitrification were carried out in a laboratory unit outlined in Fig. 1.

Tab. 3 Basic characteristics of activated coke samples

Sample	BET surface area (m ² /g)	Adsorption pore volume (cm ³ /g)	Ignition temperature (°C)
A1 800	147	0.077	422
A1 900	250	0.129	420
A1 1000	441	0.245	430
A2 800	179	0.101	410
A2 900	254	0.144	415
A2 1000	390	0.258	425
A3 800	149	0.094	405
A3 900	260	0.156	410
A3 1000	260	0.216	420
Rheinbraun	263	0.191	378
Carbo Tech	13	0.010	401

This unit consists of a quartz reactor (diameter 42 mm) with electric heating. The volume of activated coke used for all tests was 70 cm³. The activated carbon samples of the original grain size were used for the test. The test gaseous mixture passes down through the reactor and then through the cooler and gas analyzers.

The desulphurization and denitrification tests were carried out separately to eliminate possible interaction. The test gas mixture used for the desulphurization tests consists of 0.26 % vol. SO₂, 5 % vol. H₂O, 5 % vol. O₂, residue N₂. The activated coke sample tests were carried out at 120 °C for 6 hours. The results obtained were used to calculate the average desulphurization grade and the dynamic saturation of activated coke at the end of each experiment.

The same concentrations of oxygen and water steam were used for the denitrification tests. Instead of SO₂ the NO in the concentration of 0.035 % vol. was used. The activated coke temperature was increased to 150 °C for the denitrification tests, each denitrification experiment lasted for 3 hours.

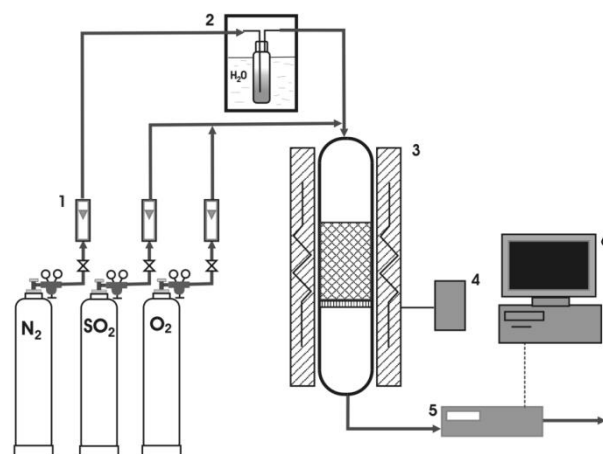


Fig. 1. Laboratory unit for testing of adsorbents;
Description: 1- flow gas regulation; 2- gas saturation of water; 3- reactor and electric heater ; 4- electric heater regulation; 5- SO₂ analyzer; 6- data recorder.

The average denitrification grade was calculated from the results obtained. The dynamic saturation of activated coke at the end of the experiment was not determined due to the catalytic reaction of activated coke with NO (see equation 7). The tested activated coke samples are given in tab. 2.

6. Results

BET surface area and adsorption pore volume were estimated for all activated carbon samples. The tests were carried out using Pore analyzer Coulter SA 3100+ (nitrogen adsorption and desorption isotherm measured at -196 °C, pore distribution calculated using the Barrett, Joyner and Halenda method). Furthermore, ignition temperatures of the activated coke samples were estimated (using air as carrier gas). The results are given in tab. 3.

The results of the desulphurization and denitrification tests are given in tab 4. and drawn at Fig. 2 – Fig. 4 (results of gas desulfurization) and Fig. 5 – Fig. 7 (results of gas denitrification).

Tab. 4 Results of desulphurization and denitrification tests

Sample	Average de-sulphurization grade (%)	Dyn. saturation of activated coke (mg SO ₂ /g activated coke)	Average de-nitrification grade (%)
A1 800	52	39	22
A1 900	72	56	15
A1 1000	26	37	6
A2 800	62	47	25
A2 900	70	54	21
A2 1000	27	41	5
A3 800	52	42	18
A3 900	63	52	17
A3 1000	21	12	7
Rheinbraun	33	27	16
Carbo Tech	27	26	16

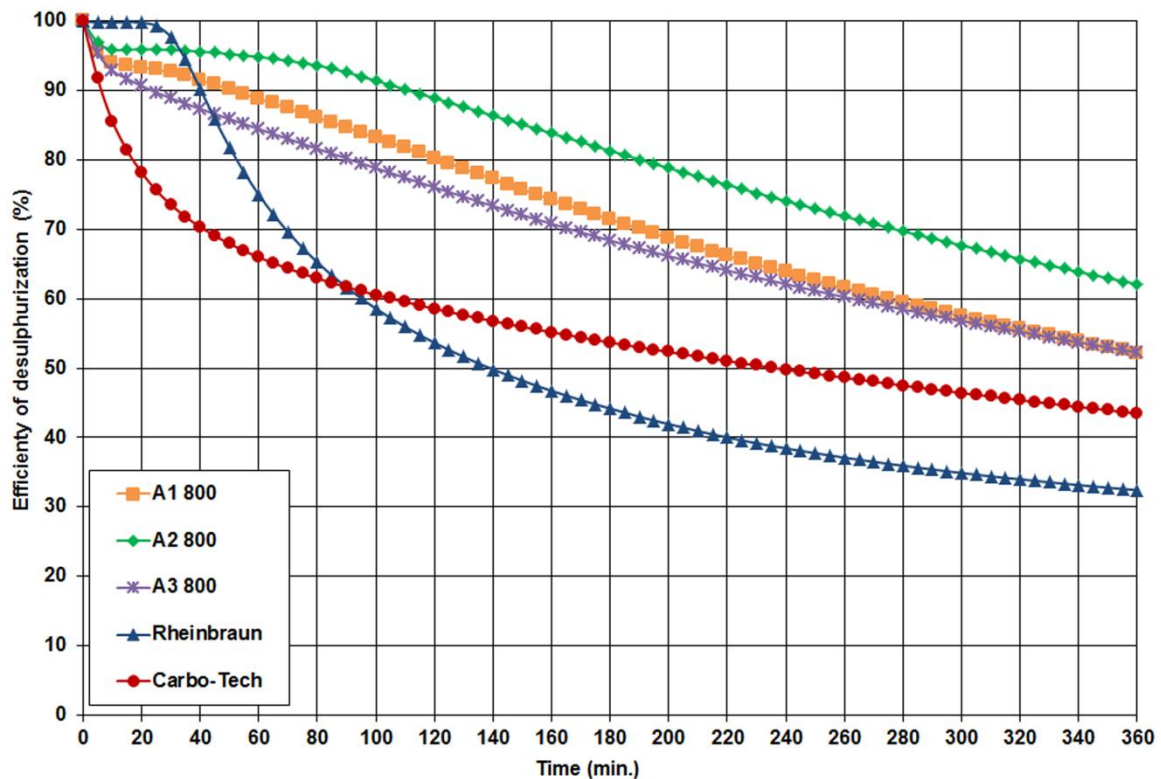


Fig. 2 Flue gas desulphurization using various activated coke samples

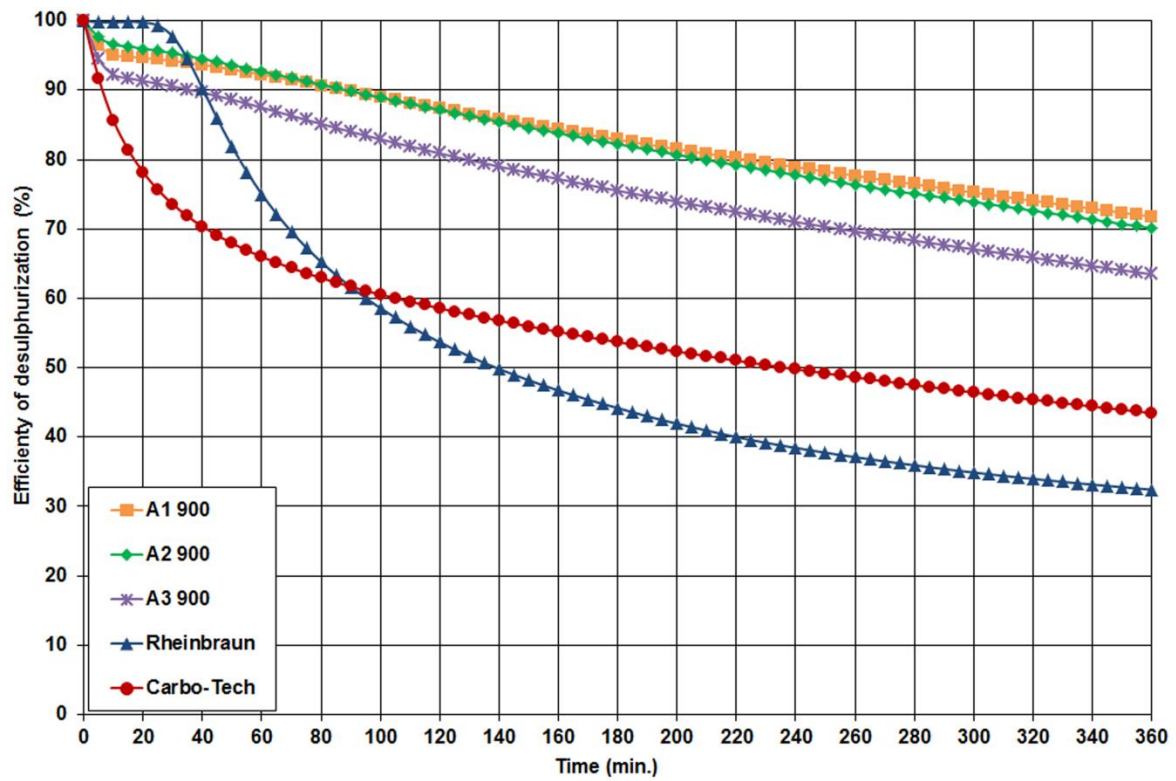


Fig. 3 Flue gas desulphurization using various activated coke samples

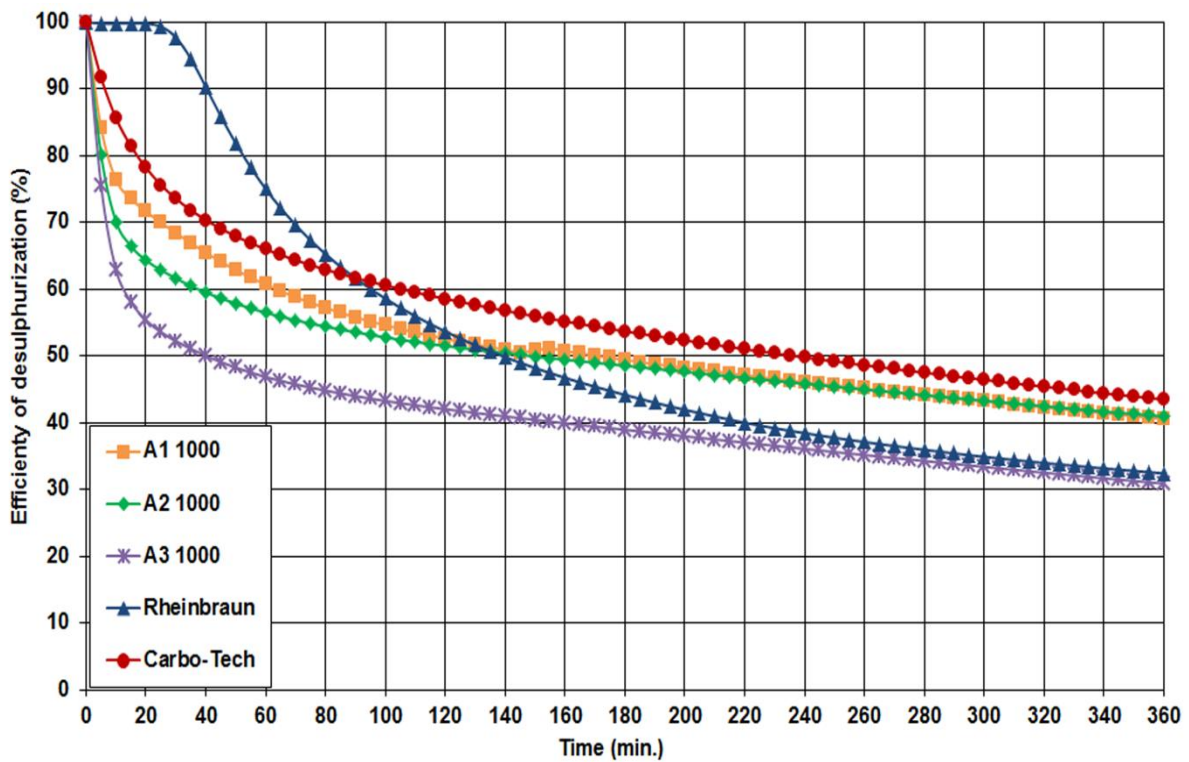


Fig. 4 Flue gas desulphurization using various activated coke samples

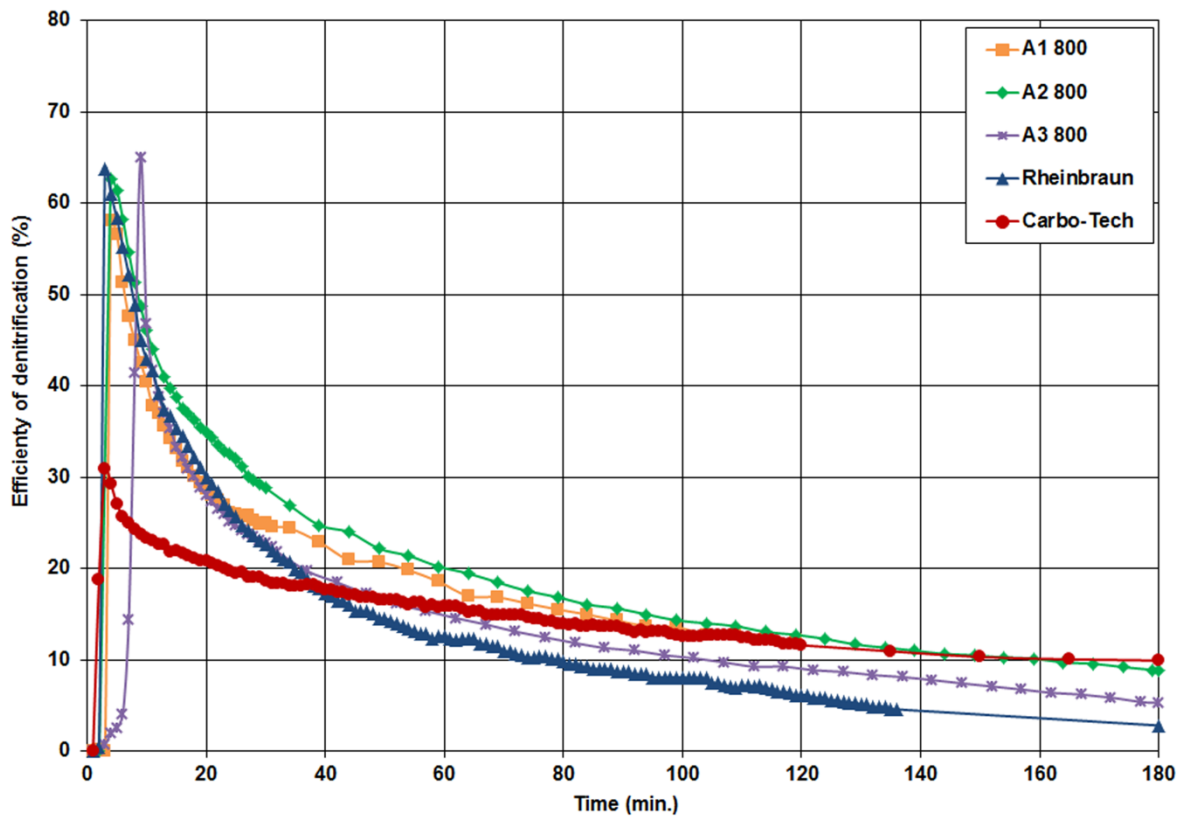


Fig. 5 Flue gas denitrification using various activated coke samples

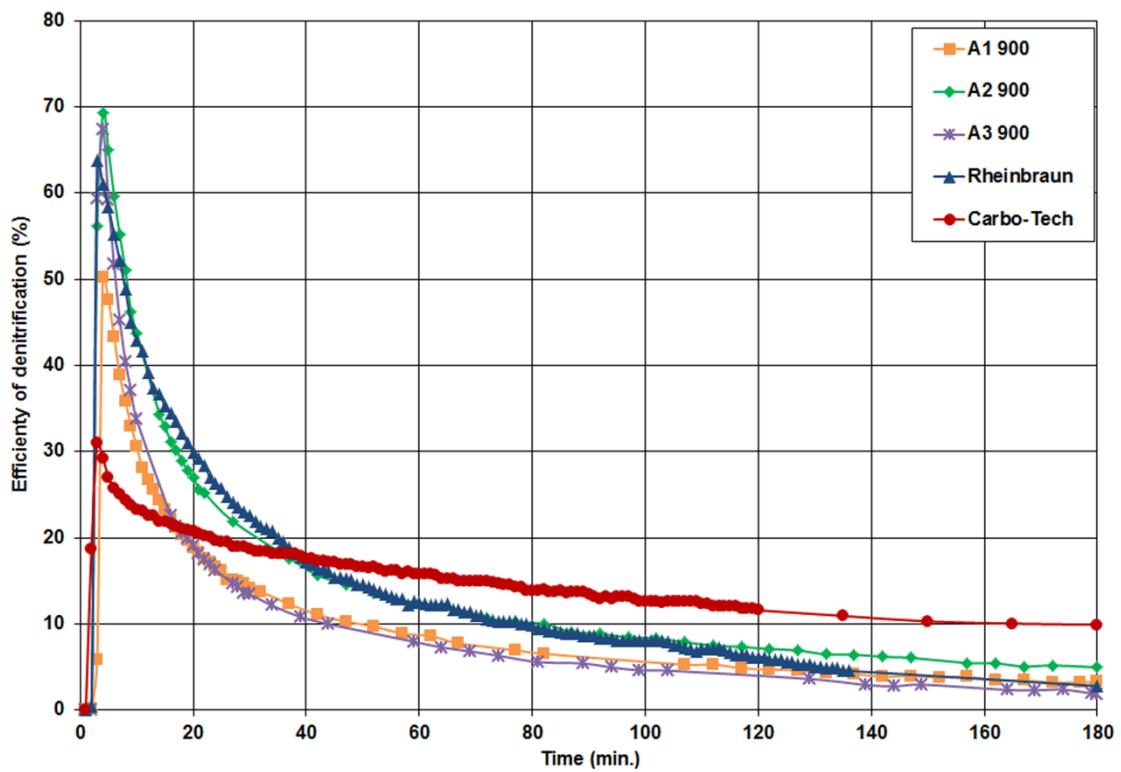


Fig. 6 Flue gas denitrification using various activated coke samples

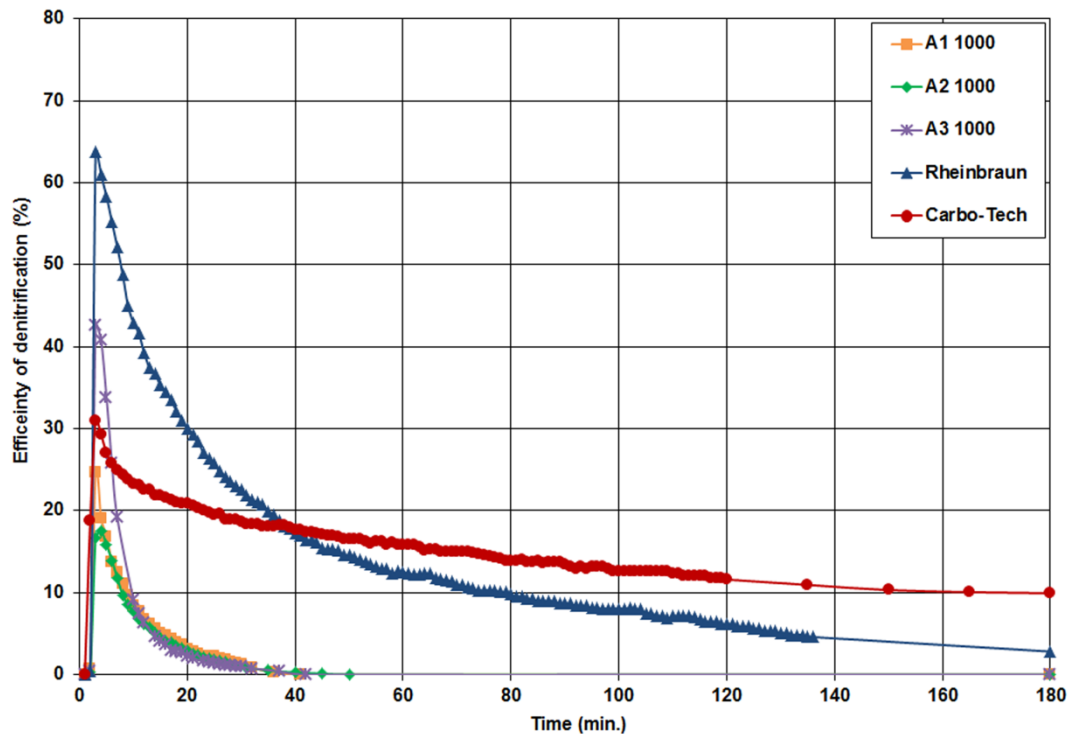


Fig. 7 Flue gas denitrification using various activated coke samples

7. Discussion

The wastes produced by bituminous coal flotation serve as good raw material for activated coke production. The properties (BET surface area, adsorption pore volume) of activated coke samples produced from these wastes are comparable to those of the Rheinbraun activated coke. The Carbo Tech activated coke features lower values.

Tab. 3 shows that the BET surface area and adsorption pore volume values increase with increasing activation temperature. The limestone hydrate addition shows no distinct impact on these parameters.

The ignition temperatures of bituminous coal waste activated coke samples are higher than those of the Rheinbraun and Carbo Tech activated coke samples. Ignition temperature increases with the rising activation temperature. The limestone hydrate addition decreases ignition temperature slightly.

The estimated average desulphurization grade of the bituminous coal activated coke samples is much higher than for the Rheinbraun and Carbo Tech activated coke. In some samples, it reaches double values. The best results were obtained in samples activated at 900 °C. The impact of the additive is not distinct, it causes the decrease of the desulphurization grade in most samples.

The dynamic saturation of activated carbon samples by SO₂ shows similar values for all samples. These values appear to be affected by grain size and density of

the adsorbents used (the weight of the tested samples is different due to the different density).

The best denitrification test results were obtained using samples activated at 800 °C. The samples by Rheinbraun and Carbo Tech show comparable results. Only the samples made at 1000 °C show worse results than the industrial samples. The decrease of the activated coke reactivity to NO is probably caused by the changes in carbon structure due to high temperature of the carbonization and activation.

The results in Tab. 4 show that the NO reduction using activated carbon has no technical significance compared to the gas desulphurization and therefore is not industrially used. On the other hand, by the industrial use of flue gas desulphurization using activated carbon is achieved high saturation grade of activated coke for SO₂ (e.g. flue gas desulphurization in the power plant in Arzberg, Germany).

8. Conclusions

The wastes from bituminous coal flotation represent very good raw material for activated coke production. The activated coke samples prepared from these raw materials under laboratory conditions show similar properties as the industrially produced activated coke by Rheinbraun and Carbo Tech.

The BET surface area and adsorption pore volume of the prepared samples are dependent on the preparation conditions. The addition of limestone hydrate has no distinct impact on these parameters.

By the gas desulphurization at 120 °C, the activated coke samples made from bituminous coal show higher loading capacities for SO₂ than industrial coke made by Rheinbraun and Carbo Tech resp. The optimum activation temperature for the achieving of maximal desulphurization efficiency is 900 °C.

Direct denitrification (NO reduction) in flue gas using both laboratory and industrial activated coke at 150 °C provides unsatisfactory results for industrial use.

References

- Li, J.; Kobayashi, N.; Hu, Y. The activated coke preparation for SO₂ adsorption by using flue gas from coal power plant. *Chem. Eng. Process.* **2008**, *47*, 118–127.
- Jastrzab, K. Properties of activated cokes used for flue gas treatment in industrial waste incineration plants. *Fuel Processing Technology* **2012**, *101*, 16–22.
- Kojima, N.; Mitomoto, A.; Itaya, Y.; Mori, S.; Yoshida, S. Adsorption removal of pollutants by active cokes produced from sludge in the energy recycle process of wastes. *Waste Management* **2002**, *22*, 399–404.
- Jastrzab, K. Changes of activated coke properties in cyclic adsorption treatment of flue gases. *Fuel Process. Technol.* **2012**, *104*, 371–377.
- Everaert, K.; Baeyens, J. Removal of PCDD/F from flue gases in fixed or moving bed adsorbers. *Waste Management* **2004**, *24*, 37–42.
- Olson, D.; Tsuji, K.; Shiraishi, I. The reduction of gas phase air toxics from combustion and incineration sources using the MET–Mitsui–BF activated coke process. *Fuel Process. Technol.* **2000**, *65*, 393–405.
- Knoblauch, K.; Richter, E.; Juntgen, H. Application of active coke in processes of SO₂ and NO_x removal from flue gases. *Fuel* **1981**, *60*, 832–838.
- Zaini, M.; Amano, Y.; Machida, M. Adsorption of heavy metals onto activated carbons derived from polyacrylonitrile fiber. *Journal of Hazardous Materials* **2010**, *180*, 552–560.
- Sobolewski, A. Slovak brown coals as a feedstock for the active coke production. *Acta Montanistica Slovaca* **1998**, *3*, 414–420.
- Ogriseck, S.; Vanegas, G. P. G. Experimental investigations of ammonia adsorption and nitric oxide reduction on activated coke. *Chem. Eng. J.* **2010**, *160*, 641–650.
- Richter, E.; Knoblauch, K.; Jüntgen, H. Mechanisms and kinetics of SO₂, adsorption and NO_x, reduction on active coke. *Gas Separation and Purification* **1987**, *1*, 35–43.
- Gaur, V.; Asthana, R.; Verma, N. Removal of SO₂ by activated carbon fibers in the presence of O₂ and H₂O. *Carbon* **2006**, *44*, 44–60.
- Mochida, I.; et al. Removal of SO₂ and NO_x over activated carbon fibers. *Carbon* **2000**, *38*, 227–239.
- Richter, E.; Schmidt, H. J.; Schecker, H. G. Adsorption and catalytic reactions of NO and NH₃ on activated carbon. *Chem. Eng. Technol.* **1990**, *13*, 332–340.
- Tsuji, K.; Shiraishi, I. Combined desulfurization, denitrification and reduction of air toxics using activated coke 1. Activity of activated coke. *Fuel* **1997**, *76*, 549–553.

Souhrn

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Odsíření a denitrifikace spalin s použitím aktivního koksu

V procesu úpravy uhlí vznikají uhelné kaly. Jednou z možností využití těchto kalů je jejich tepelné zpracování na aktivní koks. Možnosti pro přeměnu uhelného kalu na aktivní koks a testování vlastností vyrobených adsorbentů byly zkoumány během laboratorních experimentů, jejichž výsledky jsou uvedeny v tomto článku. Pro výrobu laboratorních vzorků aktivního koksu byl použit odpadní kal z flotace uhlí. Získané vzorky adsorbentů byly testovány na adsorpci SO₂ a odstranění NO_x ze spalin. Dosažené výsledky byly porovnávány s výsledky získanými s použitím průmyslově vyráběných aktivních koksu.

Odpad z flotace uhlí představují velmi dobrou surovinu pro výrobu aktivního koksu. Vzorky aktivního koksu připravené z tohoto odpadu v laboratorních podmínkách vykazují podobné vlastnosti jako průmyslově vyráběné aktivní koks firmy Rheinbraun a Carbo Tech.