The Generation of Absorption Qualities of Lignite Absorbents under Conditions of Alkali Activation

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Abstract. The article presents the research of absorbent qualities of carbon materials generated by an alkali activation of lignite from the Kharonorsk deposit. The mass ratio of potassium hydroxide/lignite R_{KOH}=1 g/g under thermal impact and further thermolysis for 60 min at 800 °C allowed to create samples with almost 100% iodine absorbent activity (1000 mg/g). In order to improve economic and environmental performance of absorbent production with lignite activation by potassium hydroxide, the research explored qualitative characteristics of absorbents generated with R_{PH}<1 g/g: 0.25; 0.5 and 0.75 g/g. It has been established that if the ratio of KOH/lignite is lowered to 1.0-0.25 g/g, the absorbent activity for iodine reduces without any significant impact on the output of the product. The iodine adsorption activity for generated carbon materials at R_{PH}<1 g/g meets the requirements for this indicator of industrially produced activated carbons that are in demand in the market. To generate absorbents from Kharonorsk lignite with iodine adsorption activity not less than 40%, the recommended ratio of KOH/lignite R_{KOH}=0.25 g/g and the duration of isothermal exposure is t=30 min; NTL 80 % - RK_{OH}=0.5 g/g and t=30 min; NLT 90 % - RK_{OH}=1.0 g/g and t=30-60 min.

1. Introduction

One of the main methods of absorbent production from fossil carbon is chemical activation. The advantages of the chemical activation in comparison to steam-gas activation are: a shorter process, low temperature and smaller gas consumption and also better homogeneity of pores of generated absorbents. For the modification of carbon-bearing raw materials, various chemical agents are used (potassium hydroxide, NaOH, H_{3}PO_{4}, ZnCl_{2}, AlCl_{3}, K_{2}S, K_{2}CO_{3}, MgCl_{2}, NH_{4}Cl, etc.), but today only two methods of chemical activation are used in industry, sulphuric-potassium and chloride-zink ones [1-4].

There is a number of research projects [5-18] that prove the efficiency of fossil carbon activation by alkali metal hydroxide (LiOH, NaOH, KOH) with a view to generate carbon materials with high-quality pore structure. Despite the pore structure, alkali ensure a high proportion of micro-pores, tight distribution of pores by size and considerably reduces the ash content in the porous material due to the reaction with mineral components of the raw material [4-6]. But the alkali activation method also has its disadvantages, such as: large amounts of catalyst are needed and there are issues associated with its recovery and an additional washing phase.

The qualities of absorbents generated by alkali activation mainly depend on the following factors:
- temperature, regime and thermolysis duration;
- alkali activity as an activating agent;
- natural characteristics of the raw carbon-bearing substance and the mass ratio of alkali/precursor.

The thermolysis of carbon with alkali metal hydroxide is conducted at 600-900 °C for 30-90 min under constant heating or thermal shock.

Potassium hydroxide (KOH) is the main activating agent among the alkali metal hydroxide activation. The lignite grid in contact with potassium hydroxide begins to transform even at room temperature [7], and KOH when heated produces more pores in carbon than sodium hydroxide and lithium hydroxide [13-15].

The function of porous structure generation efficiency and the ratio of alkali/precursor is specific for different carbon-bearing materials. For example, for fossil carbons, the ratio of alkali/precursor grows in direct correlation to the carbon metamorphism [5]. Lignite activation up to certain adsorption activity degree happens when the alkali consumption is considerably lower, than in the case of the activation of mineral coals and antracites. As the cost of lignite is quite low, it becomes a promising raw material for absorbent generation by alkali activation.

Efficient ratio of KOH/lignite (RKOH) is within the range of 1-1.5 g/g [7-12]. Experiments with the lignite from Kharanorsk deposit (Zabaikalsky krai) with RKOH=1 g/g allowed to generate materials with iodine absorbing activity of more than 90%, which meet the requirements for mass produced high-quality activated coals that are suitable for absorption from the liquid phase and for ore cleaning [17-19].

However, despite the fact that RKOH=1 g/g is not a big mass ratio in comparison to the one needed for the activation of mineral coals and antracites, under the proposed method for absorbent generation [17], 1 ton of absorbent with 40% output requires: more than 2.5 t of lignite (depending on its humidity); 2.5 t of potassium hydroxide; 0.9-1.5 thousand litres of concentrated hydrochloric acid (to reduce the duration of the neutralization of the absorbent cleaning waters alkaline medium); several hundred m³ of cleaning water (depending on the technology). We also have to consider that the market price of KOH is several times higher than the price of lignite and is close to the price of mass produced absorbents with poor adsorbing qualities. What is more, the process of absorbent production generates a large amount of alkali-contaminated water that corresponds to the consumption of water and acid.

So, finding best conditions for alkali activation of lignite with lower activating agent consumption is a relevant scientific and technical task for improving economic and environmental performance.

2. Experiment

Experiments with lower mass ratio of KOH/lignite for iodine absorbing qualities were conducted using the lignite B2 from Kharanorsk deposit (Zabaikalsky krai).

The initial qualities of 0.2 mm lignite (%): laboratory moisture of the sample (Wr³ – 10.6; analytical moisture ratio (Wa¹ – 11.1; ash on the dry basis (Ad¹ – 7.5; dry ash-free volatile content (Vd³₀) – 45.7; iodine adsorption activity of coal precursor (X₀ – 16.6).

Potassium hydroxide was introduced into the coal by impregnation. The ratio KOH/lignite in the tested samples is 0.25, 0.5, 0.75 and 1 g/g, and for the purposes of comparison, the sample that has not been soaked in alkali was also tested. The amount of alkali for soaking the coal was calculated based on the KOH/lignite ratio expressed in KOH in grams per 1 g of dry coal. The solution of potassium hydroxide was added to the coal and mixed manually till it becomes homogenous. Then the carbon alkali mixture was conditioned in an air-proof closed container for 2 hours. After the established soaking period, the potassium hydroxide impregnated lignite in a closed laboratory container is immediately exposed to thermolysis at 800 °C. The isothermal exposure lasts for 30 or 60 min. After that, the produced solid product is taken out from the muffle furnace, cooled down at room temperature, cleaned from alkali first with 0.1 N hydrochloric acid solution, and then with distilled water to generate a neutral reaction of cleaning waters. After the samples became air-dried basis, their qualities were tested.
3. Results and discussion
The results of the laboratory testing of qualitative and adsorption qualities of the samples are shown in Table 1.

| R_{KOH}, g/g | t, min | X, % | n | Y, % |
|-------------|--------|------|---|------|
| 0           | 30     | 15.3 | 10.3 | 9.9 | 16.0 | 0.96 | 52.3 |
|             | 60     | 14.1 | 11.1 | 10.1 | 23.3 | 1.4  | 50.9 |
| 0.25        | 30     | 16.2 | 7.6  | 9.3  | 49.9 | 3.0  | 41.7 |
|             | 60     | 14.9 | 10.9 | 10.3 | 52.7 | 3.2  | 44.0 |
| 0.50        | 30     | 19.9 | 10.0 | 11.9 | 84.9 | 5.1  | 45.6 |
|             | 60     | 19.8 | 10.5 | 11.6 | 83.2 | 5.0  | 45.9 |
| 0.75        | 30     | 19.6 | 10.8 | 12.2 | 83.9 | 5.1  | 43.4 |
|             | 60     | 20.0 | 12.8 | 11.9 | 92.0 | 5.5  | 46.2 |
| 1.00        | 30     | 20.4 | 11.7 | 12.1 | 94.9 | 5.7  | 42.9 |
|             | 60     | 20.9 | 11.4 | 14.1 | 99.9 | 6.0  | 44.2 |

In the Table: t - isothermical exposure of the sample, min; X - iodine adsorption activity; n - relative iodine adsorption activity n=X/X₀; Y - output.

The table shows that the activation of lignite with potassium hydroxide and RK_{OH}=0.25-1 g/g allows to increase the initial iodine absorption activity of lignite by 3-6 times. The output of the main product in all alkali impregnated lignite is similar with about 40%, in non-impregnated samples with 50%, which is caused by lower quantity losses due to the cleaning stage.

![Figure 1](image_url)

**Figure 1.** The iodine adsorption activity of the samples generated with the mass ratio of KOH/lignite from 0 to 1 g/g.
When RKOH=0.25 g/g, the iodine adsorption activity is close to not meeting the requirements for high-quality activated coal (X≥50 % [20]). However, there is considerable demand for absorbents with lower absorption activity, for example БАУ-Ац (X≥50 %), КДС, ОУ-ВК, БАУ, БАУ-К (X≥45 %), ДАК, ДАК-5 (X≥30 %).

When RKOH changes from 0.25 to 1 g/g, X is slowly growing. The most considerable increase of iodine absorption activity is registered within the range of 0.25-0.5 g/g (when t=30 min and t=60 min, X grows by 70 % and 58 %, respectively). Further, as the alkali consumption grows within the range 0.5-1 g/g, X does not grow that much.

When 0.5≤RKOH≤1 g/g, the absorbent samples of high quality were generated that the requirements for КАД-молотый (X≥80 %) and УАФ (X≥70 %). The porous structure is best developed when RKOH=1 g/g and the thermolysis duration is t=60 min (Figure 1). Iodine adsorption activity reaches 99.9% and meets the requirements for high-quality activated carbon СКТ-0 with no less than 95%.

Similar results for X were achieved during experiments with various mass ratios of KOH/lignite:
- at RKOH=1 g/g, t=30 min (X=94.9 %) and RKOH=0.75 g/g, t= 60 min (X=92.0 %);
- at RKOH=0.75 g/g, t=30 min (X=83.9 %) and RKOH=0.5 g/g, t= 60 min (X=83.2 %) and RKOH=0.5 g/g, t= 30 min (X=84.9 %).

The longer duration of thermolysis with RKOH=0.75 g/g up to 60 min allows to produce samples with the same iodine absorption activity as the samples with RKOH=1 g/g and t=30 min, and, therefore, to reduce the alkali consumption per the absorbents production by 25 %. What is more, the longer isothermal exposure of the samples with RKOH=0.75 and 1.0 g/g up to 60 min allows to increase iodine absorption activity in comparison to t=30 min by 9.7 and 5.2 % respectively.

The difference in the thermolysis duration has not produced any effect on the samples produced with RKOH=0.5 g/g. X with RKOH=0.5 g/g, t=30 min and RKOH=0.5 g/g, t= 60 min are equivalent, and on par with the sample (RKOH=0.75 g/g, t=30 min). So, among the samples that we have described above, the best and most energy and alkali consumption efficient option for the purposes of absorbent production with X≥80 % is the one with RKOH=0.5 g/g and t=30.

4. Conclusions
When lignite from the Kharanorsk deposit is impregnated with potassium hydroxide in the ratio of 0.25; 0.5; 0.75 and 1.0 g/g and undergoes further thermolysis at 800 °C, the carbon materials with iodine absorbent activity 3-6 times higher than for the carbon-precursor are produced, which meet the requirements for the mass-produced activated carbons.

The ratio of KOH/lignite 1 g/g for the alkali activation with further isothermal exposure in an airtight container for 60 minutes at 800 °C allows to produce absorbents with the iodine absorption activity of about 100% (1000 mg/g) from lignite from the Kharanorsk deposit. This iodine absorption activity is 2-3 times higher than the absorption of some of widely used activated carbons (ДАК, БАУ, КДС, ОУ-ВК, etc.) and is comparable to the iodine absorption activity of high-quality АУ by СКТ-0 (X ≥ 950 mg/g).

As a result of smaller KOH/lignite ratio, from 1.0 to 0.25 g/g, iodine absorption activity of the produced absorbents is lower, but it does not affect the product output. To enhance the absorption qualities of the produced samples even more with the mass ratio of KOH/lignite of less than 1 g/g, we should prolong the duration of isothermal exposure from 30 to 60 min.

To produce absorbents with iodine absorption activity of not less than 80% due to alkali lignite activation within the range of KOH/lignite 0.25-1 g/g, the best economic and environmental option is 0.5 g/g along with the isothermal exposure for 30 min.

The issue of smaller alkali amount for chemical activation depends on the requirements for the quality of produced absorbents. Today there is demand in the market for absorbents of different quality. If it is necessary to produce high-quality absorbents from lignite with X≥90 %, the smaller amount of alkali (RKOH<1 g/g) and the thermolysis duration (t<60 min) are not feasible. At the same time, if it is required that iodine absorption activity of the manufactured product was X≥40 %, the ratio KOH/lignite can be selected that are less than 1 g/g. The alkali activated lignite from the
Kharanorsk deposit with the mass ratio of KOH/lignite (R_{KOH}) and after the isothermic exposure (t), allows to achieve the iodine absorption activity (X):  
- X≥40 % with R_{KOH}=0,25 g/g, t=30 min;  
- X≥80 % with R_{KOH}=0,5 g/g, t=30 min;  
- X≥90 % with R_{KOH}=1,0 g/g, t=30-60 min.  

The quality of the produced absorbents must be assessed for every individual raw material on the basis of technical and economic calculations of production feasibility considering the needs of the market for absorbents of a certain type and possibilities to reduce the environmental burden.

References  
[1] Mukhin V M, Klushin V N 2011 Production and use of carbon adsorbents (M.: Russian University of Chemical Technology D.K. Mendeleev) 305 p  
[2] Fenelonov V B 2002 Introduction to the physical chemistry of the formation of the supramolecular structure of adsorbents and catalysts (Novosibirsk: Publishing House of the SB RAS) 414 p  
[3] Kinle H, Bader E 1984 Active carbons and their industrial application Per. with him (L.: Chemistry) 216 p  
[4] Keltsev N V 1984 The basics of adsorption technology (M.: Chemistry) 592 p  
[5] Tamarkina Yu V, Tsyba N N, Kucherenko V A, Shendrik T G 2013 Obtaining porous materials by alkaline activation of fossil coals of varying degrees of metamorphism Problems of Chemistry and Chemical Technology 3 pp 132-137  
[6] Kurilkin A A, Mukhin V M, Kireev S G, Kargaltseva L A 2010 Carbon adsorbents modified with potassium hydroxide Sorption and chromatographic processes vol 10 pp 515-521 Beletskaya M G, Bogdanovich N I 2013 The formation of the adsorption properties of nanoporous materials by thermochemical activation Chemistry of plant raw materials 3 pp 77-82  
[7] Kucherenko V A, Shendrik T G, Khabarova T V, Tamarkina Yu V 2009 Influence of the temperature of chemical activation on the formation of the porous structure of adsorbents from brown coal Zh. Sib. Fed. un-that. Chemistry T 2 3 pp 223-231  
[8] Marsh H, Rodriguez-Reinoso F 2006 Activated Carbon Elsevier Ltd. 536 p 2  
[9] Manina T S, Fedorova N I, Semenova S A, Ismagilov Z R 2013 The influence of alkaline treatment conditions on the properties of adsorbents based on naturally oxidized Kuzbass coal Coke and Chemistry 5 pp 25-28  
[10] Kucherenko V A, Shendrik T G, Tamarkina Yu V, Mysyk R D 2010 Carbon vol 48 15 pp 45-56  
[11] Kozlov A P, Zykov I Yu, Dudnikova Yu N, Tsvetkov V E, Fedorova N I, Ismagilov Z R 2018 Brown coal processing into effective sorbents for solving environmental problems and improving the quality of life Bulletin of KuzSTU 3(127) pp 93-100  
[12] Lillo-Ródenas M A 2003 Understanding chemical reactions between carbons and NaOH and KOH. An insight into the chemical activation mechanism Carbon vol 41 pp 267 - 275  
[13] Chesnokov N V, Mikova N M, Ivanov I P, Kuznetsov B N 2014 Obtaining carbon sorbents by chemical modification of fossil coals and plant biomass Zh. Sib. Fed. un-that. Chemistry T 7 1 pp 42-53  
[14] Shendrik T G, Tamarkina Yu V, Khabarova T V et al. 2009 Formation of the porous structure of brown coal during thermolysis with potassium hydroxide Chemistry of solid fuels 5 pp 51-55  
[15] Tamarkina Yu V, Shendrik T G, Kucherenko V A, Khabarova T V 2012 Conversion of Alexandrian brown coal into microporous carbon material under alkaline activation Zh. Sib. Fed. un-that. Chemistry. 5(1) pp 24-36  
[16] Perederiy M A 2000 Sorption materials based on fossil coals Chemistry of solid fuels 1 pp 35-44  
[17] Vorsina E V, Moskalenko T V, Mikheev V A 2015 Obtaining carbon sorbents by chemical modification of brown coal of the Kharanorsk deposit Modern problems of science and education 2-3 URL: http://www.science-education.ru/ru/article/view?id=23990
[18] Vorsina E V, Moskalenko T V, Mikheev V A 2017 Obtaining sorbents from brown coals of the Kharanorsk deposit Geomechanical and geotechnological problems of development of the subsoil of the North: Mining information and analytical bulletin scientific and technical journal 11 special issue 24 pp 146-154

[19] Vorsina E, Moskalenko T, Mikheev V 2018 Obtaining sorbents from brown coals samples of Kharanorskoe coal deposit by way of electromagnetic microwave radiation exposure 7th International Scientific Conference "Problems of Complex Development of Georesources", PCDG 2018 (St. Khabarovsk, Russian Federation) vol 56 DOI: 10.1051/e3sconf/20185603021

[20] Mukhin V M, Tarasov A V, Klushin V N 2000 Active coals of Russia. Under the general editorship of prof. Dr. tech. sciences A V Tarasova (M.: Metallurgy) 352 p