

Thermal Method for Testing Small Chemisorbents Samples on the Base of Potassium Superoxide

Pavel V. Balabanov, Daria A. Liubimova, Aleksandr P. Savenkov

Abstract—The increase of technogenic and natural accidents, accompanied by air pollution, for example, by combustion products, leads to the necessity of respiratory protection.

This work is devoted to the development of a calorimetric method and a device which allows investigating quickly the kinetics of carbon dioxide sorption by chemisorbents on the base of potassium superoxide in order to assess the protective properties of respiratory protective closed circuit apparatus.

The features of the traditional approach for determining the sorption properties in a thin layer of chemisorbent are described, as well as methods and devices, which can be used for the sorption kinetics study.

The authors developed an approach (as opposed to the traditional approach) based on the power measurement of internal heat sources in the chemisorbent layer. The emergence of the heat sources is a result of exothermic reaction of carbon dioxide sorption. This approach eliminates the necessity of chemical analysis of samples and can significantly reduce the time and material expenses during chemisorbents testing.

Error of determining the volume fraction of adsorbed carbon dioxide by the developed method does not exceed 12%. Taking into account the efficiency of the method, we consider that it is a good alternative to traditional methods of chemical analysis under the assessment of the protection sorbents quality.

Keywords—Carbon dioxide chemisorption, exothermic reaction, internal heat sources, respiratory protective apparatus.

I. INTRODUCTION

SORBENTS based on potassium are used in respiratory protective apparatus for carbon dioxide adsorption. The protection time of these apparatus depends on the carbon dioxide sorption kinetics, that's why a study on the carbon dioxide chemisorption kinetics is carried out before backfilling the sorbent into the protective apparatus [1], [2]. For this purpose, a sample of the sorbent is taken. A gas mixture containing sorbate (carbon dioxide) is blown through the sample during a fixed time. Then, a chemical analysis of the adsorbed CO₂ concentration is conducted. Similar experiments are performed with several samples at varying duration of blowing. This approach requires a significant amount of time (5-6 hours).

The operational methods and tools that can be applied for the investigation of the carbon dioxide sorption kinetics are known from literature. Tools for its implementation are calorimeters. Calorimeters, based on the measurement of the

heat flux power at a constant temperature or at a constant heating rate (Calvet type calorimeter) are widely used to study the kinetics of chemical reactions [3]-[7]. One problem of using such calorimeters to study the kinetics of CO₂ sorption is the complexity of recreating the conditions of the process directly in the calorimeter.

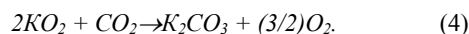
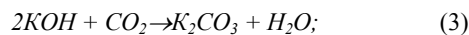
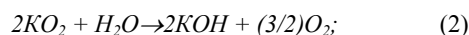
In order to decrease the time of the experiment, authors of the paper developed a method and a device for studying the carbon dioxide sorption by chemisorbents based on the potassium superoxide.

II. METHOD AND MATHEMATICAL MODELING

We consider the chemisorbent layer with thickness h (Fig. 1) through which the gas mixture containing sorbate is blown. At the same time with the gas flow the quantity of heat is supplied. The internal heat sources act in the layer, as a result of exothermic reaction of sorption. The volumetric power of these sources varies with time. The quantity of heat is moved out with the gas flow. The internal heat sources power is naturally related to the rate of the carbon dioxide chemisorption and can be described by (8)

$$q_v(\tau) = \frac{\partial \varphi(\tau)}{\partial \tau} H_x \rho_{CO_2} \quad (1)$$

where φ – volume fraction of adsorbed CO₂ in the volume of sorbent, (m³ of CO₂)/(m³ of sorbent); ρ_{CO_2} – the average density of the carbon dioxide at the temperature of the measurement, kg/m³; H_x – the total thermal effect of chemical reactions of carbon dioxide chemisorption which are described by:



H_x is equal 4200±506 J/g CO₂ for the chemisorbents on the base of potassium superoxide [9].

The differential heat transfer equation for the chemisorbent layer [8]:

$$q_v(\tau) = c_{ch} \frac{\partial T_{ch}(\tau)}{\partial \tau} + w c_g \frac{\partial T_g(\tau)}{\partial x} \quad (5)$$

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where c_{ch} , c_g are volumetric heat capacity of the chemisorbent and a gas at the temperature of the test preliminary determined by the known methods; T_{ch} , T_g are the average temperatures of the chemisorbent and the gas; w is the velocity of the gas mixture, which is determined from the measured flow rate.

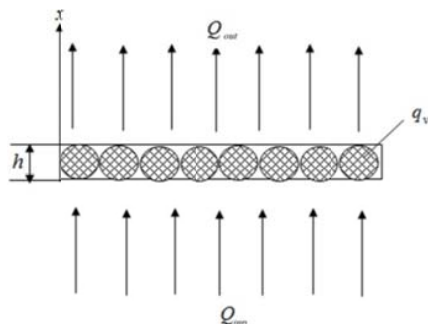


Fig. 1 The thermal scheme of the measurement cell

Equation (5) is written with the consideration of the following assumptions. The loss of heat on the end sides of the layer in the measuring cell is negligible small. The heat capacity of the material is constant if the temperature during the experiment varies slightly (in practice the range is 20–40 °C).

The velocity of the gas mixture is constant, as the volume of oxygen liberated for all time the test is significantly smaller than the total amount of purged gas mixture. The temperature of the chemisorbent at any point is the same and equal $T_{ch}(\tau)$. The heat transfer by the convective gas mixture flow is much greater than the heat transfer by thermal conductivity.

By replacing partial derivatives by finite increments, (5) were transformed to a form (6) for more convenient practical calculations of internal heat sources power at a time moment τ_i :

$$q_v(\tau_i) = c_{ch} \frac{T_{ch}(\tau_{i+1}) - T_{ch}(\tau_{i-1})}{\tau_{i+1} - \tau_{i-1}} + w c_g \frac{T_g^{out}(\tau_i) - T_g^{inp}(\tau_i)}{h} \quad (6)$$

where $T_g^{out}(\tau_i)$, $T_g^{inp}(\tau_i)$ - the temperature of the gas mixture at the output and the input to the layer.

Consequently, the power of the internal heat sources can be calculated from (6) by measuring the temperature of the chemisorbent and gas mixture at the input and the output of the layer. The equation for calculating the rate of carbon dioxide chemisorption at any time moment is obtained from (1)

$$\frac{\partial \varphi(\tau)}{\partial \tau} = q_v(\tau_i) / (H_{\Sigma} \rho_{CO_2}) \quad (7)$$

The value of the current carbon dioxide adsorption φ_i during the time τ_i can be determined from the expression

$$\varphi_i = \int_0^{\tau_i} \frac{\partial \varphi(\tau)}{\partial \tau} d\tau. \quad (8)$$

III. CONSTRUCTION OF THE MEASURING DEVICE

The design of the measuring device for the sorption kinetics investigation is shown in Fig. 2. One-grain sorbent layer is placed on the grid of stainless steel, which is fixed on the end surface of the metal tube 1. The thickness of the layer should be 3–5 mm (depends on the size of the sorbent grains), the layer diameter $d = 40$ –60 mm is limited to the glass ring 11 fixed on the grid 2.

The temperature of the layer $T_{ch}(\tau)$ is measured by three thermocouples 3a–3c, the obtained data are averaged. The thermocouple 3a is placed in the center of the investigated chemisorbent layer thermocouple 3b and 3c - at a distance less than $d/4$ from the central thermocouple with the expectation that in the temperature measuring points the influence of the heat loss on the end surfaces can be neglected.

On the top, the layer of the investigated substance is locked by grid 7 fixed on the end surface of the tube 6.

The gas temperature at the output from the layer T_g^{out} is measured by thermocouples 8a–8c and averaged. The gas mixture is blown through the chemisorbent layer with a predetermined carbon dioxide concentration, relative humidity, temperature and flow rate. The gas mixture is supplied through the pipe 9 and through the deflector 4 and uniformly distributed over the surface of the layer. The temperature of the gas mixture at the input T_g^{inp} is measured by a thermocouple 5.

The measuring cell is placed in an air thermostat. Signals from the thermocouples are entered into a computer 12 by means of the data acquisition board 13.

The correction for the temperature (measured by the sensor D) of the thermocouples cold junctions (placed in the box of cold junctions compensation 14) is introduced in the program for processing the results of the experiment.

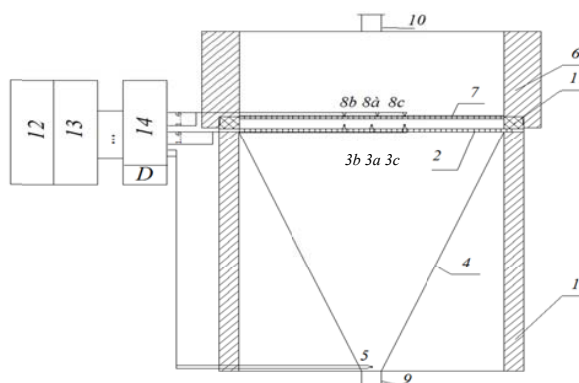


Fig. 2 The scheme of the measurement cell

IV. EXPERIMENTS AND DISCUSSION

In this work we consider an example of investigating the chemisorbent on the base of KO_2 with the grain 2-3 mm. The gas mixture is blown through the 1-grain thickness chemisorbent layer with the carbon dioxide concentration of 2%, relative humidity 68%, temperature of 20°C and a rate of gas mixture 1.5 l / min. The weight of the investigated sample in the experiment was 5.9 g.

The dependence of the chemisorbent layer temperature and the power of the heat sources q_v on time are shown in Fig. 3. The dependencies $\partial\varphi/\partial\tau = f(\tau)$ and $\varphi = f(\tau)$ are shown in Fig. 4.

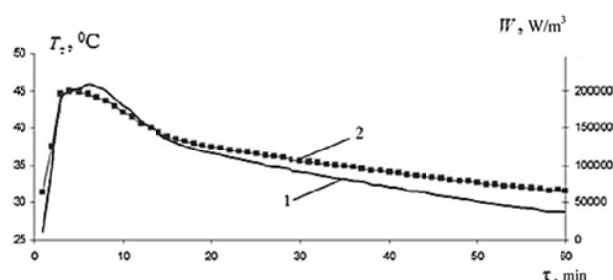


Fig. 3 The dependence of the chemisorbent layer temperature (curve 1) and the power of the heat sources q_v (curve 2) on time

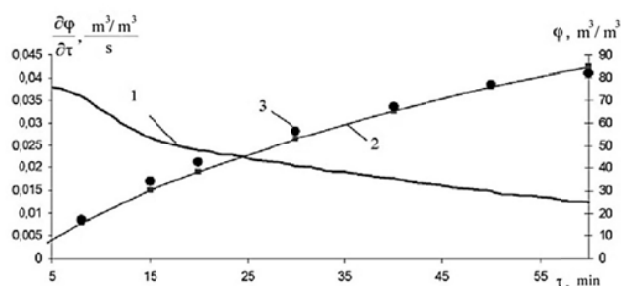


Fig. 4 The time dependences, obtained by the developed and the traditional method respectively. 1 – the dependence $\frac{\partial\varphi}{\partial\tau} = f(\tau)$; 2 our method; 3 – traditional method $\varphi = f(\tau)$

With the help of the developed method and the measuring device, the investigations of the carbon dioxide sorption kinetics by sorbents were conducted. The conditions of the experiments were following: the density of sorbent based on the potassium superoxide is in range 1100-1650 kg/m^3 , the temperature of the gas mixture is in range $20-90^\circ\text{C}$, the moisture content is 0.007-0.023 $\text{kg}/(\text{kg of dry air})$. The concentration of carbon dioxide in the gas mixture was 1- 4%. The size of product grains is 2-3.5 mm. The velocity of the gas mixture is 0.1 m/s. In addition, the experimental conditions correspond to the temperature, humidity (relative humidity 25-70%) and carbon dioxide concentrations for most effective in operating conditions individual and collective protection apparatus.

In Fig. 5, the results of a series of experiments are shown. The gas mixture with a moisture content 0.013 $\text{kg}/(\text{kg of dry air})$ was blown through the sorbent layer with density 1300 kg/m^3 . The results of determining the volume fraction of the carbon dioxide in the sorbent, found by the traditional chemical method, are shown in particular points.

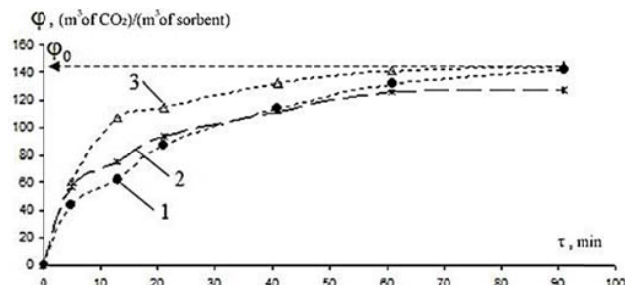


Fig. 5 Graphs of changing the carbon dioxide volume concentration in chemisorbent layer during the time in the input: curves 1, 2, 3; the concentration of CO_2 in the gas mixture 1, 2, 4 % respectively

We used the obtained data for the chemisorbent sorption properties determination.

It is known from literature, that to describe the kinetics of processes of carbon dioxide adsorption by substances based on the potassium superoxide equation of the form (9) is used [10]:

$$\partial\varphi/\partial\tau = \beta C_0(1 - \varphi/\varphi_0) \quad (9)$$

where φ, φ_0 - the current and the limit value of the carbon dioxide volume per chemisorbent volume unit; C_0 - the current concentration of the carbon dioxide in the gas mixture; β - the mass transfer coefficient.

Taking into account, that experiments were conducted in the 1-grain layer, the assumption about constancy of carbon dioxide concentration along the length of the chemisorbent layer was taken.

In this case, the decision of (9) will be following:

$$\varphi = \varphi_0(1 - \exp(-\frac{\beta C_0}{\varphi_0}\tau)) \quad (10)$$

where C_0 - the initial carbon dioxide concentration.

Approximating the experimental data in Fig. 5 by (10), it was found that to describe the interaction kinetics of the carbon dioxide with chemisorbents based on potassium superoxide, (9) can be used with the following parameters:

- $\beta = 5 \pm 0.16$ 1/s at 4% CO_2 concentration;
- $\beta = 6.5 \pm 0.3$ 1/s at 2% CO_2 concentration;
- $\beta = 10 \pm 0.4$ 1/s at 1% CO_2 concentration;
- $\varphi_0 = 140 \pm 5$ m^3 of CO_2 / m^3 of sorbent.

It is clear from the obtained data that the adsorption rate for the 4% concentration is significantly higher than for the 1%

and 2% concentrations. The limit capacity φ_0 of the carbon dioxide for the chemisorbent depends little on concentration.

The developed setup provides the possibility of studying the effect of temperature, the carbon dioxide concentration in the gas mixture, the humidity of the gas mixture on capacity properties of chemisorbents (chemisorbent capacity for carbon dioxide) and the rate of carbon dioxide adsorption.

The setup can be used for testing superoxides of alkali metals in the range of temperature from room to 100 °C (Table I: bulk density 1300 kg/m³, grain size 2–3 mm; Table II: CO₂ concentration 4%). The test requires a small amount of

chemisorbent. It allows using the measuring setup to predict the operation quality of newly synthesized chemisorbents as a part of collective and personal protective apparatus.

Experimental results show that the values of the carbon dioxide volume fraction adsorbed by the sorbent and measured by the thermal method and the traditional chemical method differ from each other by not more than 12 %. Taking into account the efficiency of the thermal method, it can be considered as a good alternative to traditional chemical methods for investigating the properties of potassium superoxide chemisorbents.

TABLE I
TESTING THE CHEMISORBENT ON THE BASE OF KO₂ AT THE TEMPERATURE 99 °C

TESTING THE CHEMISORBENT ON THE BASE OF KO ₂ AT THE TEMPERATURE 99 °C									
The time of blowing τ , min	CO ₂ concentration 1%			CO ₂ concentration 2%			CO ₂ concentration 4%		
	The moisture content in the gas mixture, kg/(kg of dry air)								
	0.007	0.013	0.026	0.007	0.013	0.026	0.007	0.013	0.026
	φ , (m ³ of CO ₂)/(m ³ of sorbent)								
5	41	43	33	53	57	44	71	60	68
13	59	61	56	75	75	60	97	107	86
21	81	87	71	94	94	88	110	115	105
41	110	114	88	115	112	98	129	132	117
61	135	132	97	116	126	104	141	141	146
91	138	143	97	125	127	105	144	144	145
φ_0 , (m ³ of CO ₂)/(m ³ of sorbent)	178	140	178	178	127	178	178	144	178
β , l/s	5.0	10	5.0	5.0	6.6	5.0	5.0	5.0	5.0

TABLE II
TESTING THE CHEMISORBENT ON THE BASE OF KO₂ AT THE TEMPERATURE 25 °C

TESTING THE CHEMISORBENT ON THE BASE OF KO ₂ AT THE TEMPERATURE 25 °C							
The time of blowing τ , min	Bulk density 1100 kg/m ³			Bulk density 1300 kg/m ³		Bulk density 1650 kg/m ³	
	The moisture content in the gas mixture, kg/(kg of dry air)						
	0.007	0.013	0.026	0.007	0.013	0.007	0.026
	φ , (m ³ of CO ₂)/(m ³ of sorbent)						
5	44	63	89	43	71	34	43
13	62	91	113	65	96	47	57
21	82	114	133	89	119	52	78
41	111	156	162	127	161	73	14
61	127	174	177	136	183	89	188
91	134	193	-	146	207	106	-
φ_0 , (m ³ of CO ₂)/(m ³ of sorbent)	137	192	178	145	206	106	180
β , 1/s	2.3	3.2	5.0	2.5	3.4	3.3	5.8

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REFERENCES

- [1] P. C. Wood, T. Wydeven "Improved Oxygen Sources for Breathing Apparatus: report NASA", *NASA Ames research. Moffett field. Calif.*, 61 p., 1985.
- [2] P. C. Wood, T. Wydeven, "The use of superoxide mixtures as air-revitalization chemicals in hyperbaric, self contained, closed circuit breathing apparatus", *NASA Ames research. Moffett field. Calif.*, 61 p., 1985.
- [3] Lee D. Hansen "Calorimetric Measurement of the Kinetics of Slow Reactions". *Ind. Eng. Chem. Res.*, no. 39, pp. 3541-3549, 2000.
- [4] V. Hemminger, G. Khene "Calorimetry. Theory and practice". *Moscow, Chemistry*, 176 p., 1990.
- [5] R. E. Tapscott, L. D. Hansen, E. A. Lewis "Calorimetric Studies of Stereoselective Vanadyl (IV) Tartrate Reactions". *J. Inorg. Nucl. Chem.*, №. 37, pp. 2517-2519, 1975.
- [6] O. Sohnel, M. Kroupa, G. Frankova, V. Velich "Calcium Oxalate Crystallization Kinetics from Calorimetric Measurements". *Thermochimica Acta*, vol.306, Issues 1–2, 17, pp. 7-12, November 1997.
- [7] V. P. Lehto, E. A. Laine "Kinetic Study of Polymorphic Transition of Anhydrous Caffeine with Microcalorimeter". *Thermochimica Acta*, vol. 317, Issue 1, 6, pp. 47-58, July 1998.
- [8] P. V. Balabanov, S. V. Ponomarev "The use of the theory of the two-alpha method to investigate the thermophysical characteristics of regenerative products and chemical absorbents". *Measurement Techniques*, vol. 53, no. 11, pp. 1256-1263, February 2011.
- [9] P. V. Balabanov "A thermal method of measuring the chemisorption characteristics of regenerative products". *Measurement Techniques*, vol. 55, no. 5, pp. 589-594, August 2012.
- [10] A. A. Krimshcheyn, S. V. Plotnikov, V. I. Kononov, B. V. Putin "Simulation of isolating devices chemical oxygen" *Journal of Applied Chemistry*, vol. 65, no. 11, pp. 2463-2469, November 1992.