

Evaluation of protective action of poisoned gas substances of new generated activated carbon for gas mask application

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Abstract: The object of the paper is the dynamic adsorption of new type generated gas mask carbons for respiratory protection, based on apricot shells and the impact of the protective properties of some poisonous gases or warfare poisonous substances. A study performed examined the impact on the breakthrough times of different quantities of K_2CO_3 (2 mass.% - 8 mass. %) and TEDA in the capacity of additives to the impregnation composition of the standard ASC Whetlerite type and newly obtained carbons.

Keywords: ACTIVATED CARBONS, PHYSICAL ADSORPTION, PROTECTIVE EFFECT DURATION

1. Introduction

Impregnated activated carbons represent a basic component of gas mask equipment, gas respirators, powered air purifying respirators and filter absorbers. In order to provide an effective protection against the warfare poisonous gaseous, some industrial toxic substances, and also because of the slight effect of aging processes during their storage and utilization as promising elements in the composition of the active phase of new type of gas carbons (carbon catalyst) are considered Cu, Zn, Mo, Ag, and are referred also potassium carbonate (K_2CO_3) and the organic compound like TEDA are considered [1-4]

Due to the high number of chemical warfare, potentially terroristic poisons and industrial toxic substances and various mechanisms of their detoxification from carbon catalysts, in order to test their protective properties, it is necessary to choose representative of the three mechanisms of toxic substances detoxification.

In the rescue services and armies of many countries for this aim Cl_3CNO_2 is chosen (for toxic substances which are neutralized by physical adsorption), HCN (for poisonous substances via chemisorptions) and carbon dichloride oxide- $COCl_2$ (for the toxic substances that are detoxification by catalytic sorption [5-7]).

The inclusion of alkaline carbonate - K_2CO_3 as supplements in the impregnation composition, leading to the development of meso- and micro-porosity can essentially affect the protection properties of the gas mask carbons [3,8] against the representative highly toxic compounds such as $COCl_2$ and HCN. Although $COCl_2$ has partially lost its significance as a combat poisonous substance, it is considered as an individual or mixed type potential terrorist-poison substance with a high probability of use, due to its high toxicity. In addition to its industrial production, small amounts from the toxic gas can be generated as a result of decomposition and combustion processes of organo-chlorine compounds.

The chlorinated solvents used for oil removal in aim to clean metals from different oil impurities, for example car breaks cleaners can be also converted to phosgene by the UV rays and arc welding processes.

The goal of the presented work is the examination of the impact on the protective properties (in particular the breakthrough times of different quantities of K_2CO_3 (2mass% - 8 mass %) and TEDA as additives of new synthesized type gas carbons to the vapor of $COCl_2$.

2. Experimental

A. Samples

The activated carbon used in the studies is a commercial product (signified as ACVM), obtained based on apricot shells through vapor gas activation (973 K), specific with its granulometric size 1.0 – 1.5 mm.

For the activated carbons (gas carbon catalyst) preparation was used different impregnation solutions: copper carbonate, zinc oxide, molybdenum oxide and silver nitrate. They were dissolved in aqueous solution of ammonium carbonate and ammonium

hydroxide (25%). Potassium carbonate was added and TEDA was added to the impregnation solutions.

Samples of gas mask carbons VSZC, VSZC-A2, VSZC-A4, VSZC-A6, VSZC -A8, VSZM and VSZMA2 were obtained using the standard impregnation procedure for obtaining carbon catalysts [8,9]

The selected gaseous (Cl_3CNO_2 , $COCl_2$, HCN) are representative for all toxic substances, which can be neutralized and detoxified by the following mechanisms:

□ Physical adsorption, by the volumetric filling of the micropores, particularly for the Cl_3CNO_2 . Although it is not considered a warfare substance, it is representative of the so-called well-absorbed toxic substances in testing of warfare toxic substances of gas mask carbons, including respiratory protective equipment [10].

□ Catalytic adsorption, combined with the chemisorptions of the semi-products of the impregnate components. Representative poisonous substance is $COCl_2$, referring to the acid gases, which hasn't lost its use as a chemical weapon, used especially in various poisonous formulations.

□ Chemisorption of toxic substances combined with catalytic sorption. Representative toxic substance selected is HCN, which apart from combat purposes has wide industrial application.

The samples obtained through standard impregnation procedure for carbon catalysts obtaining are presented in Table 1.

Table 1 carbon catalysts obtained [10].

Sample type signification	
ACVM	-
VC5W ASC Whetlerite type	Cu/Cr/Ag
VC5W-A2 ASC Whetlerite type	Cu/Cr/Ag + 2 % K_2CO_3
VC5W-T ASC Whetlerite type	Cu/Cr/Ag + TEDA
VSZ ASZ type	Cu/Zn/Ag
VSZ-A2 ASZ type	Cu/Zn/Ag + 2 % K_2CO_3
VSZC ASZC type	Cu/Zn/Cr/Ag
VSZC-A2 ASZC type	Cu/Zn/Cr/Ag + 2% K_2CO_3
VSZC-A4 ASZC type	Cu/Zn/Cr/Ag + 4% K_2CO_3
VSZC-A6 ASZC type	Cu/Zn/Cr/Ag + 6% K_2CO_3
VSZC-A8 ASZC type	Cu/Zn/Cr/Ag + 8% K_2CO_3
VSZC-T ASZC type	Cu/Zn/Cr/Ag + TEDA
VSZM ASZM type	Cu/Zn/Mo/Ag
VSZM-A2 ASZM type	Cu/Zn/Mo/Ag + 2% K_2CO_3
VSZM - T ASZM type	Cu/Zn/Mo/Ag + TEDA

The specific surface of the samples were determined using low temperature nitrogen adsorption of N_2 (77K) by the BET method. Data from the adsorption-textural parameters and distribution curves (micro- and mesopore size) are presented in [10,11]. The total volume of the pores (V_t) was determined based on the Gurvich rule [12] at the relative pressure p/p_0 of 0.95. The volume of the mesopores (V_{MES}) was estimated based on the Dubinin Radushkevich equation [13] (table 2).

III. Results and Discussion

A. Adsorption – textural characteristics

Based on the results for adsorption textural parameters (table 1) it can be seen that the impregnation procedure leads to increase of microporous heterogeneity, respectively specific surface of the impregnated samples compared to the initial activated carbon ACVM.

Table 2. Specific surfaces and basic texture parameters of Cu/Zn/Cr/Mo/Ag gas mask carbons

Specimen	A_{BET} m ² /g	A_{MEL} m ² /g	V_p cm ³ /g	W_0 cm ³ /g	V_{MA} cm ³ /g	V_{MS} cm ³ /g	V_{MEL} cm ³ /g	α_p (nm)	r_p Å
¹ ACVM	1060	165	0.930	0.396	0.377	0.019	0.534	0.68	17.5
² VCSW	892	280	0.861	0.352	0.202	0.150	0.509	0.93	19.3
³ VCSW-A2	881	363	0.851	0.313	0.185	0.128	0.538	0.78	19.3
⁴ VCSW-T	864	320	0.805	0.310	0.198	0.112	0.495	0.82	18.6
⁵ VSZ	882	354	0.830	0.327	0.264	0.063	0.503	0.87	18.8
⁶ VSZ-A2	852	365	0.829	0.324	0.226	0.098	0.505	0.99	19.5
⁷ VSZC	872	340	0.820	0.312	0.240	0.072	0.508	0.82	18.8
⁸ VSZC-A2	846	322	0.813	0.300	0.201	0.099	0.513	0.85	19.2
⁹ VSZC-A4	829	374	0.814	0.284	0.189	0.095	0.530	0.85	19.6
¹⁰ VSZC-A6	817	383	0.812	0.263	0.178	0.085	0.549	0.75	19.9
¹¹ VSZC-A8	776	417	0.808	0.250	0.142	0.108	0.558	0.86	20.8

The study of the protection properties (in particular the breakthrough times) was carried out with highly poisonous substances $COCl_2$ [14] synthesized by us.

B. Adsorption – dynamic studies

The pre-dried (378 K, 2 hours) carbon catalysts were loaded in glass dynamic sorption pipes and were exposed to the steam-air flow from toxic substances, passing through the samples, regarding the following set parameters:

Table 3. Test parameters set [8]

Layer thickness of the studied sample	3.0 cm
Internal diameter of the dynamic pipe	2.0 cm
Volumetric velocity of the vapor gas flow	1.57 l/min
Relative humidity of the flow	50%
Temperature	293 + 3 K
Inlet concentration of Cl_3CNO_2	5 ml/l
Concentration of registration of the Cl_3CNO_2 breakthrough	15 ml/m ³
Inlet concentration of HCN	3 ± 0.3 mg/l
Concentration of registration of the HCN breakthrough	10 ml/m ³
Concentration of registration of the $(CN)_2$ breakthrough	5 ml/m ³

In the gas technique, the protective action of breakthrough time (t_B) is defined as the time for which the concentration of poisonous

substances in the steam-air flow after the sorbent layer reaches a preset value for the relevant experimental conditions.

The breakthrough time of the samples for the toxic substances Cl_3CNO_2 and HCN was investigated in our previous study [8].

A. The breakthrough time of the samples exposed to the vapor of $COCl_2$

The breakthrough time of the vapors of the chloropicrin under the conditions set, for the studied samples are given on figure 1.

According to the currently adopted mechanism [15] $COCl_2$ can be neutralized by physical adsorption combined with impregnation. $COCl_2$ is hydrolyzed from the pre-adsorbed water vapor from the air generating HCl and carbon dioxide $-CO_2$. Afterwards hydrogen chloride reacts with Cu and Zn (predominant basic carbonates) complexes to form Cu and Zn chlorides.

The last one has a negative effect on the possibilities of impregnates to further protection for example against HCN.

From table 1 it can be seen that the initial activated carbon-ACVM has an about two times shorter breakthrough time than the same parameter for all examined gas carbon samples. This strongly proves the role of the impregnated gas carbons in the process of disposing of the vapor of $COCl_2$.

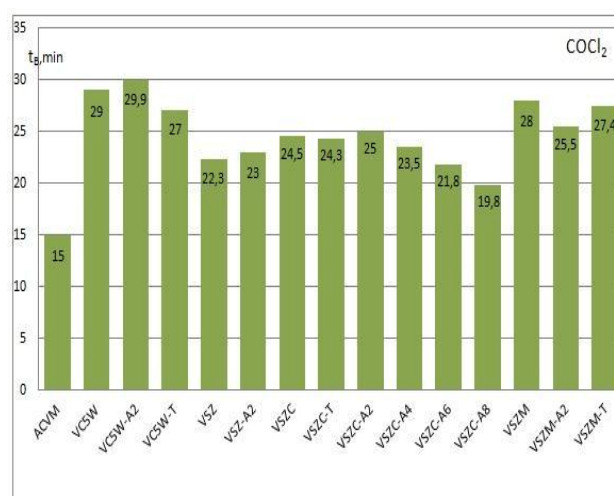


Fig1. Breakthrough time (t_B) of the initial activated carbon and the impregnated samples

Based on the obtained results and the comparison of the all gas type carbons, it can be concluded that the higher values of breakthrough time are shown by the samples of the ASC Whetlerite. Samples from the ASZC type (without samples with high content of K_2CO_3 r.e > 4 mass%) have a breakthrough time a little lower than the samples from ASC Whetlerite and ASZM type, but higher t_B than the samples from ASZ-type.

Monitoring the impact of the modifier TEDA and K_2CO_3 on the breakthrough time of the investigated gas carbons was studied.

$COCl_2$ reacts with the primary amines, to which TEDA does not relate to. The results obtained Fig.1 show that for all type samples, also for the impregnates having TEDA to the composition leads to decrease of the service time (t_B), compared to the samples without TEDA. Therefore, despite its high alkalinity, TEDA does not promote the hydrolysis of $COCl_2$ in the pores of gas masks. The inclusion of K_2CO_3 (2 mass%) in all types of gas carbons except the sample VSZM-A2 (ASZM type carbons) leads to a slight increase of breakthrough time.

The inclusion of alkaline carbonates K_2CO_3 in the impregnation composition leads to:

- pH increasing, which leads to the improvement of the catalytic function of additives with respect to the hydrolysis of $COCl_2$. K^+ ions from the potassium carbonate improves the catalytic function of the carbon surface [17].
- K_2CO_3 reacts with the released HCl (hydrochloric acid) thus protecting the Cu and Zn- compounds (mainly basic

carbonates) of the impregnates. Thus the catalytic function remains for the longer period, respectively the breakthrough time is prolonged. Especially $Zn(CO_3)_2(OH)_6$, protected with K_2CO_3 from HCl, also prolongs the reaction time with HCl, respectively the service time (t_B) of the gas carbons from the type ASZC (2 mass% K_2CO_3).

For the VSZM-A2 sample probably Mo cause an effect interfering with the function of K_2CO_3 .

The impact of the breakthrough time was studied with regard to the increasing content of K_2CO_3 (> 2 mass%). For the sample VSZC-A4 (4 mass% K_2CO_3) it can be seen a slightly decreasing breakthrough time - about 4.1% compared to VSZC. The tendency remains and is strongly expressed in samples VSZC-A6 and VSZC-A8, decreasing with 11% and 19.2% respectively. Therefore, an increase of the K_2CO_3 content with more than 2 to 4 mass%, leads to a decrease in breakthrough time of the sample type ASZC compared to VSZC, reaching about 20% for VSZC-A8.

The results obtained of the gas carbons catalyst, containing K_2CO_3 in the impregnant composition for $COCl_2$ detoxification, can be summarized in two groups, the first one is the samples, comprising $K_2CO_3 < 4$ mass%, and the other one for the samples with $K_2CO_3 > 4$ mass%.

For samples, comprising $K_2CO_3 < 4$ mass%, we can assume that the hydrolysis (including the components of the impregnates, as well as on the surface of the initial activated carbon, promoted with K^+ , do not proceed separately, but in a synergetic mechanism in $COCl_2$ hydrolysis. The weak physical adsorptions probably occurs not only at K_2CO_3 2 mass%, but also at 4 mass% (but probably much less significantly).

For the second modified gas carbons, comprising more than 4 mass% content K_2CO_3 , the catalytic process of hydrolysis weakens, based on the synergistic effect of the impregnates and the surface of the initial carbon weakens (due to the optimal values pH, corresponding to potassium carbonate mass content (2 до 4 mass% K_2CO_3). The physical adsorption of $COCl_2$ from the gas carbon is completely stopped.

IV. CONCLUSION

The protective properties of the obtained gas carbons (carbon catalyst) was studied, including the modified samples on the representative toxic substance ($COCl_2$) with catalytic detoxification combined with chemisorptions of the products of vapor conversion of the toxic substance was studied.

From the examined types of the carbon catalysts in terms of vapor of $COCl_2$, the highest breakthrough time (t_B) was observed in the ASC Whetlerite type samples, and the lowest for the initial samples –ACVM.

The protective properties of the synthesized new type gas carbons (including the modified samples) of the newly obtained carbon catalysts were established, providing a sufficient level of protection against the studied toxic substances.

3. References

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