EFFECT OF ADDITIVES IN PHASE COMPOSITION OF CARBON CATALYSTS OTHER THAN ASC WHETLERITE TYPE CARBONS ON THEIR REMOVAL EFFICIENCY AGAINST HYDROGEN CYANIDE VAPORS IN THE AIR

ЕФЕКТ НА ДОБАВКИТЕ ВЪВ ФАЗОВИЯ СЪСТАВ НА ВЪГЛЕН КАТАЛИЗАТОРИ РАЗЛИЧНИ ОТ ASC WHETLERITE ТИП ВЪГЛЕНИТЕ ВЪРХУ ТЯХНАТА ЕФЕКТИВНОСТ В ОЧИСТВАНЕТО НА ПАРИТЕ НА ЦИАНОВОДОРОДА ОТ ВЪЗДУХА

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ABSTRACT: *Canisters for present-day gas masks are usually filled with impregnated ASC Whetlerite activated carbons. To solve the inherent problems of the carbon catalysts new types of Cu/Zn-based impregnated carbons with complete substitution of Cr with Mo and by addition in the impregnating solution of alkaline K_2CO_3 and TEDA in some cases were prepared. The removal efficiency of these samples against HCN vapours in air tested under standard conditions demonstrated that the content of K_2CO_3 to ~ 4% in Cu/Zn samples extends the protection effect to practically equal to the same parameter for the ASC Whetlerite. The inclusion of TEDA in the phase composition of the catalysts does not impair the protection properties towards HCN of the carbon catalysts.*
KEY WORDS: GAS MASK'S CANISTERS, IMPREGNATED ACTIVATED CARBON, ASC WHETLERITE TYPE CARBON, Cu/Zn-BASED IMPREGNATED CARBONS, ADDITIVES IN PHASE COMPOSITION,

1. Introduction

HCN is widely used, strongly toxic precursor for many laboratory and industrial syntheses, whose world production exceeds 0.5 million tons per year, besides, HCN is formed in the ignition of a series of materials of domestic use. Historically, HCN is used as chemical warfare agent during the World War I. Despite the restricted opportunity to use HCN by the modern armies as a CWA, it represents a highly effective potential terroristic poisonous substance.

An optimal protection of the respiratory organs of the armed forces staff and the population in case of terroristic actions and the occurrence of centers of chemical contamination, they provide for the filtering breathing masks, founding their effect in terms of most of the known toxic substances on physical adsorption of activated carbon materials in the breathers or the filtering adsorbing elements.

Since the physical adsorption of highly volatile non-persistent chemical warfare agents such as hydrogen cyanide, cyanogen chloride, phosgene, arsine and phosphin of the non-impregnated activated carbons is weak and hence, reversible at room temperature, the breathers of the modern breathing masks and filter-absorbent of the collective means for protection, are equipped with impregnated activated carbons. As of the moment, to remove the vapours of HCN, ClCN, $COCl_2$, AsH_3 and PH_3 from the air by the breathers of gas masks and filter absorbents, the activated carbons have found the widest application, impregnated with Cu and Cr salts, known as ASCWhetlerite carbons.

Despite of their proven high efficiency in terms of the protection from the vapors of the highly volatile non-persistent chemical warfare agents, the impregnated carbons containing Cr^{6+} are considered as non-perspective by the specialists, such as the ones of the US Environmental Protection Agency [1] due to:

- risk of cancer-producing effect of some of the forms of Cr^{6+}[9] for the production personnel and the army staff, using the relevant gas masks and collective means of protection [2];
- a problem with annihilation of this type of impregnated carbon, after the expiration of the term of use defined by the manufacturer;
- the irreversible deactivation that this type of impregnated carbons are easily susceptible to as a result of the increased temperature [3] and/or enhanced humidity [4-6].

A solution of the problems referred is the creation of a generally new types of impregnation compositions on a basis other than the one of Cu/Crcompositions. Such impregnated carbons are the ones on a Cu/Znbase, alike the American impregnated carbon of new generation, ASZM-T, developed by Calgon Corp. [7].

Due to the complex nature of the removal of vapours of HCN by the impregnated carbons and the existence of a relation between the reaction capability of vapours and other highly volatile non-persistent chemical warfare, it was decided that the studies of the impregnated carbons on Cu/Znbase start namely with the vapours of HCN.

The absence of Cr^{6+} in the impregnation compositions, on the other hand, leads to the forming as a by-product of $(CN)_2$ as a result of the decomposing of the chemically unstable $Cu(CN)_2$, a product of the removal of HCN. To solve this problem, we have received and studied a new type of impregnated carbon onCu/Znbase, with addition of insignificant amounts of Agand Cr (< 0.6%). This type of impregnated carbon, signified withVSZC, is characterized with protection effect against the vapours of HCN, practically equal to the same parameter for the ASC Whetlaritetype of impregnated activated carbons however with impaired parameter in terms of the forming of $(CN)_2$compared to them.

The last can be corrected via the increase of the content of Cr^{6+}, which is however inadmissible due to its cancerogenity, via overall replacement ofCr, with Mo or via the introduction in the impregnation composition of VSZCof an alkaline additive – for instance K_2CO_3. In the presence of K_2CO_3 in the active phase, the removal of HCN runs on a two-grade mechanism whereat the instable cupricyanide reacts with KCN in alkaline medium, forming $K_2[Cu(CN)_4]$.

It is a practical interest to study the impact on the protection effect against the vapours of HCN and on the forming as a by-product of $(CN)_2$in the impregnated carbons on Cu/Znbase of the complete replacement of Cr, with Mo or the introduction in the impregnation composition of VSZC of an alkaline additive – K_2CO_3.

Therefore the objective of this work is to study the effect of Mo and of the alkaline ingredient (K_2CO_3) in the composition of the active phase of the impregnated carbons on Cu/Znbase, in terms of efficiency of defusing HCN vapours from the air, compared to the same in the ASC Whetlerite type of carbons.

2. Experimental part
2.1. Samples

The activated carbon used in the studies is a commercial product obtained from apricot shells with particle size 1.0 – 1.5 mm, signified as ACVM.

The textural parameters of the starting and the impregnated activated carbons as well as the impregnation compositions of the latter are presented in Table 1.

The samples were obtained via standard impregnation procedure of the activated carbon. The following salts (individually or in suitable combinations) were used to prepare the impregnation solutions: basic copper carbonate, zinc oxide, chrome oxide, molybdenum oxide and silver nitrate. The indicated compounds were dissolved in a solution of ammonia carbonate, water and ammonium hydroxide (25 %). In some of the cases, the impregnation solution was added up with TEDA.

Each of the samples was obtained via slow spraying of the relevant impregnation solution on the activated carbon in a rotating flask on a modified rotary evaporator.

The samples prepared in this way were signified as follows:

VSZ – activated carbon, impregnated with mixed ammoniacal copper zinc + silver nitrate solution.

VSZ-A2 - activated carbon, impregnated with mixed ammoniacal copper zinc + silver nitrate solution, containing 2 mass % K_2CO_3.

VSZC - activated carbon, impregnated with mixed ammoniacal copper zinc + chromic acid solution.

VSZC-T - activated carbon, impregnated with mixed ammoniacal copper zinc + chromic acid solution, containing TEDA.

VSZC-A2 - activated carbon, impregnated with mixed ammoniacal copper zinc + chromic acid solution, containing 2 mass % K_2CO_3.

VSZC-A4 - activated carbon, impregnated with mixed ammoniacal copper zinc + chromic acid solution, containing 4 mass % K_2CO_3.

VSZC-A6 - activated carbon, impregnated with mixed ammoniacal copper zinc + chromic acid solution, containing 6 mass % K_2CO_3.

VSZC-A8 - activated carbon, impregnated with mixed ammoniacal copper zinc + chromic acid solution, containing 8 mass % K_2CO_3.

VSZM - activated carbon, impregnated with mixed copper ammoniacal zinc molibdate + silver nitrate solution.

VSZM-T - activated carbon, impregnated with mixed ammoniacal copper zinc molibdate + silver nitrate solution, containing TEDA.

VC5W - ASC Whetlerite type of carbon, obtained as per standard procedure („whetlerization process").

After each application of the precursors, the samples were allowed to stand in a controlled closed volume at room temperature for 2 hours.

The samples prepared in this way were heated at not higher than 423 K in a draft oven (under pressure), as in the case of the VSZC-T and VSZM-T samples, the heating temperature was maintained to preserve the main part of the pyridine.

2.2. Test methods

The characterization of the specific surfaces and porous texture of the initial activated carbon (ACVM) and the impregnated samples was carried out via low temperature adsorption of nitrogen (77.4 K) using Quantachrome Instruments NOVA 1200e (USA) apparatus.

Based on the adsorption – desorption nitrogen isotherms, via the specialized software set in the equipment, the following texture parameters were calculated: specific surface area (A_{BET}) according to the Brunauer–Emmett–Teller (BET) equation, for the interval $P/P_O = 0.05 - 0.35$ (adsorptive N_2, 77.4 K); total pore volume (V_t) as per the Gurvich-rule for $P/P_O = 0.95$ (adsorptive N_2, 77.4 K); micropore volume (V_{MI}) using the density functionale theory (DFT) (adsorptive N_2, 77.4 K); volume of the mesopores (V_{MES}) as a difference between the total volume and the micropore volume (adsorptive N_2, 77.4 K); average radius of the pores (R_P) as a ratio of the double V_t and A_{BET} (adsorptive N_2, 77.4 K); the half-width (x_O) of the micropores (as per the flat parallel model) for the maximum of the distribution curve as per the simplified equation [8,9].

The textural parameters of the samples calculated by the methods referred are presented in Table 1.

The copper, zinc, chrome, molybdenum and silver were determined by atomic absorption using a Pye Unicam SP 90B spectrometer.

The photoelectrons and Auger specters of the samples were registered using an ESCALAB MkII (VG Scientific) XR photoelectron spectrometer with AlK_α (1486.6 eV) source. The C 1s peak at 284.6 eV, was used as an internal standard for calibration of the connecting energies. The samples surface composition according to XPS, was determined based on the photoelectron intensities estimated by the corresponding Scofield cross sections.

2.3. Adsorption –dynamic studies

The experimental dynamic equipment and the procedures for study of the sorption, resp. protective properties of the impregnated carbons against HCN, are analogous to the ones described in [4].

The predried (378 K, 2 hours) impregnated carbons were reproducibly packed in glass dynamic tubes and air (HCN)- vapor flow was passed through the samples, following the parameters set:

- sample bed depth   3.0 cm
- sample bed diameter   2.0 cm
- volume flow rate   1.57 l/min
- relative humidity   50%
- temperature   293 + 3K
- HCN challenge concentration 3 ± 0.3 mg/l
- HCN breakthrough concentration 10 ml/m^3
- $(CN)_2$ breakthrough concentration 5 ml/m^3

The removal efficiency of the impregnated carbons was evaluated indirectly, during the (t_B) removal action, against HCN and $(CN)_2$ (in the cases when free dicyan is formed), as the resolution of HCN and $(CN)_2$ is based on the difference in the interaction of the two substances with $AgNO_3$ solution.

The registration of the relevant breakthrough concentrations was carried out by:

- reaction between HCN and aqueous solution containing benzidine, copper acetate and acetic acid;

- reaction between $(CN)_2$ and aqueous solution of KCN, containing 8-hydroxyquinoline.

3. Discussion of the experimental results
3.1. Adsorption-textural characterization

Via comparing the adsorption textural parameters of the impregnated samples with the ones of the initial activated carbon (Table 1), it was estimated that the impregnation process concerns more the microporous than their mesoporous textures, respectively their specific surfaces.

The reduction of the micropore volumes is most likely due to blocking parts of the micropore space of the samples or to blocking the access to the micropores.

The increase of the microporous heterogeneity of the samples (characterized via the alterations of the values of x_O), best expressed in the impregnated samples VC5W, VSZ-A2, VSZC-T, isrelated to the distribution of the micropores of the initial carbon by size [10], with the stage of heating and attending migration of the active phases and the metal ions nature.

Despite of the fact that as a result of the impregnation and following heating, the parameters of the porous texture and all sample specific surfaces change, Table 1 displays that the biggest changes occur in the samples including in their phases K_2CO_3 and TEDA.

In this sense, the change is bigger of the parameters referred in the samples including TEDA (VSZC-T and VSZM-T) compared to the single type VSZC and VSZM, than the samples containing various quantities ofK_2CO_3.

It must be noted that, with the increase of the content of K_2CO_3 (> 2%), the specific surfaces decrease and the average radiuses of the sample pores increase in synchrony (Table 1), which is an evidence for the simultaneous change of the external and internal surfaces of the impregnated carbons.

Table 1 Elemental phase composition and main texture parameters of the initial activated carbon and of impregnated samples

Samples	Content (mass %)				A_{BET} (m^2/g)	V_t (cm^3/g)	V_{mi} (cm^3/g)	V_{mes} (cm^3/g)	x_O (nm)	r_{Pmes} (Å)
	Cu	Zn	Cr	Mo						
ACVM	-	-	-	-	1060	0.930	0.396	0.534	0.68	17.5
VC5W[a]	7.1	-	2.07	-	892	0.861	0.352	0.509	0.93	19.3
VSZ[a]	6.3	5.6	-	-	882	0.830	0.327	0.503	0.87	18.8
VSZ-A2[a],[b]	6.2	5.6	-	-	851	0.829	0.324	0.505	0.99	19.5
VSZC[a]	5.8	5.4	0.63	-	872	0.820	0.312	0.508	0.82	18.8
VSZC-T[c]	5.7	5.3	0.60	-	823	0.816	0.292	0.524	0.90	19.8
VSZC-A2[a],[b]	5.6	5.3	0.62	-	846	0.813	0.300	0.513	0.85	19.2
VSZC-A4[a],[b]	5.5	5.2	0.61	-	829	0.814	0.284	0.530	0.85	19.6
VSZC-A6[a],[b]	5.7	5.4	0.61	-	817	0.812	0.263	0.549	0.75	19.9
VSZC-A8[a],[b]	5.7	5.3	0.59	-	776	0.808	0.272	0.536	0.86	20.8
VSZM[a]	5.5	5.2	-	1.9	827	0.807	0.309	0.498	0.87	19.5
VSZM-T[a],[c]	5.6	5.3	-	1.8	783	0.788	0.252	0.536	0.77	20.1

[a] - Sample contains about 0.05 mass % Ag

[b] - Sample contains K_2CO_3, in a quantity (mass %) indicated after "A"

[c] - Sample contains about 3 mass % TEDA

3.2. Chemical analysis and sample surface analysis

The content of Cu, Zn, Cr and Mo in the studied samples was determined via atomic absorption. The results are presented in Table 1.

The determination of the oxidative state of the studied elements in the impregnants, element composition of the sample surface as well as the location of the impregnants on the surface or in the sample volume, was carried out via XPS.

Due to the higher sensitivity of the Auger signal towards Cu (1+), as well as the relative invariance with respect to the oxidation state of Zn in the values of the Zn 2p photoelectron peak, Auger spectroscopy was also used to characterize the copper and zinc phase. The photoelectron specters obtained for the Cu 2p photoelectron area, in all copper containing samples, demonstrate binding energies for Cu (2+) oxidation state of the Cu $2p_{3/2}$ peaks, whose shoulders to the higher binding energies on their turn demonstrate the presence of incompletely decomposed $CuCO_3$ and $Cu(OH)_2$ phases. Via studies using Cu $L_3M_{4,5}M_{4,5}$ Auger specters, presence of Cu (1+) was not found in the samples of Table 1.

In the case of the samples containing zinc (VSZ, VSZ-A2, VSZC, VSZC-T, VSZC-A2, VSZC-A4, VSZC-A6, VSZC-A8, VSZM, VSZM-T), the oxidation state of Zn was determined by the Zn $L_3M_{4,5}M_{4,5}$ Auger line. The data obtained are likely to demonstrate the presence in our samples, except of a main component of the zinc phase, $ZnCO_3$ and of hydroxicarbonate, with approximate composition $2ZnCO_3 . 3Zn(OH)_2$ (к.e. 988.0 eV), whose composition is not permanent and depends on the conditions of receipt and thermal treatment.

In the case of the samples VSZC, VSZC-T, VSZC-A2, VSZC-A4, VSZC-A6, VSZC-A8, the content of Cr is relatively low (approximately 0.61mass.%, Table 1), which is a reason for the lack of adequate reliability in the results regarding its valent state. Nevertheless, by analogy with VC5W [11], it can be assumed that Cr (6+) appears under the form of $CuOH . NH_4 . CrO_6$ [22]). The latter is close to the adopted composition $CuCrO_4 . NH_3. H_2O$, according to the references cited by Nikolov [4].

It is an obscure picture of the type and nature of the Mo-phase in the case of VSZMand VSZM-T. Various authors assume that in the case of this type of carbon, Mo exists under various forms (above all as a fine dispersed phase, distributed predominantly in the volume of VSZM [12]). However, the one responsible for the removal of the forming $(CN)_2$ is Mo^{6+} [13]. Our

photoelectron specters for the Mo $3d_{2/5}$ photoelectron area provide for ground in the Mo-phase of VSZM (VSZM-T) to distinguish MoO_3 (b.e. 231.7 eV), $(NH_4)_2MoO_4$ (b.e. 232.1 eV) and $(NH_4)_2[Mo_2O_7]$ (b.e. 232.5 eV).

The inclusion of TEDAto Cu- and Zn-phase (regardless of the presence of Cr (VSZC-T) or Mo (VSZM-T) (VSZM-T) affects the copper phase as its content in the volume of the samples referred to increase with about 10% compared to VSZCand VSZM, accordingly, as in parallel, the content of Zn on our surface also increases. On the opposite, the inclusion of $K_2CO_3$to the composition of the impregnants (in the case of samples VSZC-A2, VSZC-A4, VSZC-A6, VSZC-A8) results in the re-distribution compared to VSZC, of the Cu- and Zn-phase between their volume and external surface. Thus, depending on the quantity of K_2CO_3, the content of the Cu-phase decreases in the volume, whereas, otherwise, the content of the Zn-phase on the external surface increases.

3.3. Breakthrough time of the samples

In the case of gas-mask equipment, the service time (t_B) is defined as time during which the concentration of PS in the air vapor flow, after the sorbent bed, reaches a preset value for the relevant experimental conditions.

Table 2 present t_B against HCN and $(CN)_2$ of the studied impregnated carbons and for reference, the ones of the initial activated carbon (ACVM).

As it can be expected, ACVM practically does not remove the vapors of HCN. Table 2 displays that the studied samples (except VSZ, VSZ-A2, VSZC-T) are characterized with t_B against the vapors of HCN > 50 min.

The sample VSZ (appearing to be basic with its Cu/Znactive phase) is characterized simultaneously with the lowest t_B among the rest of the samples both against the vapors of HCN, and against $(CN)_2$. Nevertheless, Table 2 displays that t_B against the vapors of HCN in the case of VSZ is practically the same as of the sample VSZC containing Cr, accordingly less against the vapors of $(CN)_2$ and significantly less regarding this parameter compared to the sample VSZM containing Mo.

Table 2. Breakthrough times for intial and impregnated carbon samples

Образци	t_B (min)	
	HCN	(CN)$_2$
ACVM	2.5-3.0	[a]
VC5W	53.0	[b]
VSZ	49.0	29.0
VSZ-A2	49.0	31.0
VSZC	51.0	32.0
VSZC-T	49.0	33.0
VSZG-A2	51.0	33.0
VSZG-A4	53.0	40.0
VSZG-A6	51.0	38.0
VSZG-A8	51.0	37.0
VSZM	52.0	47.0
VSZM-T	53.0	48.0

[a] - Not determined experimentally. According to literature data it is close to breakthrough time against HCN.

[b] – breakthrough concentration of (CN)$_2$ not reached.

In the case of VSZC, after the exhausting of Zn-phase (as a result of the chemisorption of HCN) the function of the direct destruction of (CN)$_2$ is taken by Cr^{6+}. The presence of Cr^{6+} in the composition of the impregnants of VSZC practically does not change t_B by the HCN of the sample compared to the one of VSZ. On the opposite, t_B by (CN)$_2$ increases with about 10% against the same for VSZ, however remains lower than the same parameter for the other sample containing Cr^{6+} (about 2 %) - VC5W (Table 2).

The sample VSZM proves the positive impact of Mo in the composition of Cu/Znactive phase, appearing an alternative variant of the sample with best parameters in the study VC5W. In its case, t_B by HCN is practically the same as of the sample VC5W, and the forming of (CN)$_2$, starts upon spending its time for removal of HCN. The mechanism of effect of the impregnants against HCN, in this type of impregnated carbons is not entirely clear. Our studies demonstrate that there is an analogy in the functioning of Zn- and the Cu-phase in the samples VSZM and VSZC, as, after spending the Zn-phase in VSZM (as a result of the chemisorption of HCN), the (CN)$_2$ being formed reacts with the Mo-phase to tightly bound with the carbon surface, non-toxic product (likely oxamide).

The most likely explanation of the difference (although insignificant) in the values in t_B by HCN and by (CN)$_2$ between VC5W and VSZM are: the less content of the Mo-phase than needed (Table 1) or of some of the Mo-forms, and also increase of the content of the Cu-phase on the external surface, at the expense of the same in the volume in the case of VSZM [M!].

The samples of the type VSZ and VSZC (VSZ-A2, VSZC-A2, VSZC-A4, VSZC-A6 and VSZC-A8) are interesting, containing in the composition of their impregnants K$_2$CO$_3$ (between 2 and 8 mass. %), which, upon removal of HCN impedes or even disables the formation of (CN)$_2$.

Based on the results in Table 2, it can be concluded that the inclusion of K$_2$CO$_3$ in the composition of the impregnants (except the sample VSZC-A4, containing 4 mass. %) does not result in the increase of t_B against the vapors of HCN. The impact of K$_2$CO$_3$ is much more significant regarding t_B against (CN)$_2$. In this case, there is dependence even between t_B and the content of K$_2$CO$_3$, which passes through maximum with the content of K$_2$CO$_3$ about 4 mass. %. Probably in case of content of K$_2$CO$_3$ above the determined, exhausting of the Cu-phase appears viathe binding to K$_2$[Cu(CN)$_4$] and the exclusion of it from the general process of removal of HCN.

The inclusion of TEDA in the composition of the phase of the samples VSZC and VSZM, i.e. the samples VSZC-T and VSZM-T, increases insignificantly t_B by (CN)$_2$ compared to VSZC and VSZM. Analogically, t_B against the vapors of the HCN in the case of the two samples changes within the limits of 2-4 %. Most likely the effect of TEDAin the phase composition of the impregnants can be related to the fact that TEDA to a very slight extent affects the Cu-phase as this is more likely to manifest in the

stronger expressed positioning of the Cu-phase in the mesoporous space of the VSZM-T, compared to the same for the sample VSZC-T. TEDA does not affect the Zn-phase. Generally, it can be concluded that TEDA practically does not affect the chemisorption of HCN.

4. Conclusion

A study has been carried out of the effect of additives to the phase composition of the carbon catalysts on Cu- Zn base in terms of their effectiveness for the elimination of the HCN vapours in the air. It was found that the inclusion in Cu- Zn phase of the samples of Mo, Cr^{6+} (~ 0.60 mass. %), K$_2$CO$_3$ or TEDA results in their commensurable effectiveness in terms of the removal of the HCN vapours in the air (determined as a breakthrough time) with the one of the standard ASC Whetlerite type of carbon.

Despite of the fact that the inclusion of the additives referred in the Cu-Zn phase composition results in the increase of t_B of the samples against the vapours of (CN)$_2$, by this parameter, they stay behind the ASC Whetlerite type of carbon.

Regardless of the fact that the sample containing Mo in their phase composition is closest to the t_B against the vapours of (CN)$_2$ of the ASC Whetlerite type of carbon, as the same parameter in its case remains smaller, probably due to the smaller amount of the Mo-phase than the needed or of any of the Mo-forms.

The inclusion to the phase composition of the carbon catalysts on Cu- Zn base (containing or not Cr^{6+}) K$_2$CO$_3$, does not result in the increase of t_B against the vapours of HCN (except the sample VSZC-A4, containing 4 mass. %). The impact of K$_2$CO$_3$ however is much more significant in terms of t_B against (CN)$_2$. In this case, there is even dependence between t_B and the content of K$_2$CO$_3$, which passes through a maximum in the event of content of K$_2$CO$_3$ about 4 mass. %.

The inclusion of TEDA in the composition of the phase of samples VSZC and VSZM practically does not affect their effectiveness for the removal of the HCN vapours, but in all cases, it provides further protection also from the ClCN vapours.

5. References

1. Rossin, J., R. Morrison, Spectroscopic analysis and performance of an experimental copper/zinc impregnated, activated carbon, Carbon 29, 1991, 887-892.
2. Николов, Р., Д. Механджиев, Структура и състав на фазата на перспективен медно-цинков въглен катализатор, предназначен за защита от парите на токсични вещества, ВНТИ, Научна сесия „Въоръжение и военна техника на 2000^{та} година", Химия и ядрена физика 8, 1995, 77-82.
3. Bac, N., J. Hammarstrom, A. Sacco, Jr., Thermal decomposition studies on copper-chromium-silver impregnated activated charcoal, Carbon 25, 1987, 545-549.
4. Николов, Р. Дисертация, София, ВТНИИ, 1988.
5. Rossin, J., E. Petersen, R. Lamontagne, L.Isaacson, Effect of environmental weathering on the properties of ASC-Whetlerite, Carbon 29, 1991, 197-205.
6. Zhiqiang, L., Z. Mingrong, C. Kuixue, The investigation for the deactivation mechanism of Cu-Cr impregnated carbon by XPS, Carbon 31, 1993, 1179-1184.
7. Doughty, D. Development of a chromium-free imprergnated carbon for adsorption of toxic agents, Pittsburgh, PA: Calgon Carbon Corporrationm, 1991.
8. Nickolov, R., D. Mehandjiev, Adsorption studies on the changes in microporous texture of an ASC Whetlerite type carbon catalyst modified with Co in an organic medium, Ann. Univ. Sofia "St. Kl. Ohridski" 89, 1997, 229-236.
9. Mehandjiev, D., E. Bekyarova, R. Nickolov, Micropore Size Distribution by a Simplified Equation, Carbon 32, 1994, 372-374.
10. Molina-Sabio, M., V. Perez, F. Rodrigueez-Reinoso, Impregnation of activated carbon with chromium and copper salts: effect of porosity and metal content, Carbon 32, 1994, 1259-1265.
11. Nickolov, R., D. Mehandjiev, Comparative study on removal efficiency of impregnated carbons for hydrogen cyanide vapors in

air depending on their phase composition and porous texture, J. Colloid Interface Sci. 273, 2004, 87-94.

12. Park, S., S. McClain, S. Tian, S. Suib, C. Karwacki, Surface and bulk measurements of metals deposited on activated carbon, Chem. Mater. 9, 1997, 176-183.

13. Rossin, J., R. Morrison, The effect of molybdenum on stabilizing the performance of an experimental copper / zinc impregnated, activated carbon, Carbon 31, 1993, 657-659.