

CONCEPT FOR THE DEVELOPMENT OF A NEW TYPE CARBON CATALYST DESIGNED FOR PROTECTION AGAINST VAPOURS OF HIGHLY TOXIC SUBSTANCES

КОНЦЕПЦИЯ ЗА РАЗВИТИЕТО НА НОВ ТИП ВЪГЛЕН КАТАЛИЗАТОР ПРЕДНАЗНАЧЕН ЗА ЗАЩИТА ОТ ПАРИТЕ НА ВИСОКОТОКСИЧНИ ВЕЩЕСТВА

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ABSTRACT: A concept is presented for the development of a carbon catalyst for protection from vapours of highly toxic substances, different from the ASC Whetlarite type of impregnated Cu/Cr/Ag carbons, based on the analysis of the disadvantages of the breathing filters of contemporary gas masks. It is concluded that promising carbon catalysts will possess higher stability with respect to aging and better protective properties in regard to a considerable number of industrial toxic compounds.

KEY WORDS: PROTECTION AGAINST CWA, ASC WHETLARITE TYPE CARBON, IMPREGNATED ACTIVATED CARBON, DEACTIVATION OF ASC WHETLARITE TYPE CARBON, CARCINOGENIC Cr⁶⁺

The experience gained during World War I has shown that although activated carbon has the capacity to remove the vapors of the majority of chemical warfare agents by means of physisorption, its application in gas mask filters requires modification due to two reasons:

- activated carbon was found to be ineffective when used against highly volatile non-persistent chemical warfare agents such as hydrogen cyanide, cyanogen chloride, phosgene, arsine and phosphine;
- the disposal of used activated carbon is problematic, as handling such contaminated material becomes difficult and raises concerns over safety.

Furthermore, there is a possibility of cross-contamination due to desorption upon its improper disposal after use [1].

At the end of World War I, as a solution to these problems, was initiated addition of chemical sorbent (typically soda-lime) to the activated carbon in gas mask filters. A typical example of this technology is the American M1 Model gas mask ("1919 Model") [2]. The combination of activated carbon and chemical sorbent increases the protection capacity of gas mask canisters against highly volatile acid gases (Table 1), which is due not only to physisorption that takes place, but also to removal from air and destruction of persistent agents by means of chemisorption. That principle is still in use in modern military gas masks.

In this way, gases which the activated carbon does not hold firmly by physisorption and which are gradually given off by its surface, are caught by soda-lime (a mixture that consists of hydrated lime, cement, kieselguhr, sodium hydroxide and water in various proportions [2]) via chemical reaction (i.e. chemisorption, as mentioned above).

Table 1. Types of chemical warfare agents (CWA) and corresponding materials for their neutralization used in M1 Model ("1919 Model") gas mask canisters.

| Type of CWA | Neutralizing materials |
|---------------------|---------------------------------------|
| Bromobenzyl cyanide | Activated carbon |
| Chloropicrin | Activated carbon |
| Mustard gas | Activated carbon |
| Chlorine | Activated carbon + soda-lime mixtures |
| Phosgene | Activated carbon + soda-lime mixtures |
| Diphosgene | Activated carbon + soda-lime mixtures |
| Hydrogen cyanide | Activated carbon + soda-lime mixtures |
| Lewisite | Activated carbon + soda-lime mixtures |

As a result from the considerable research on modification of activated carbon materials used in gas masks (mainly with inorganic phases) conducted during the period between the two World Wars and especially after the World War II, the sorption capacity of the manufactured carbon materials against the non-persistent chemical warfare agents (given in Table 1) was substantially increased.

Table 2 illustrates different compositions for impregnation of activated carbon in gas masks for protection against non-persistent chemical warfare agents, which have been used by the armies of different countries during World War II.

Table 2. Types of activated carbon impregnants used in gas mask canisters according to [3].

| Type of impregnant | Form of application | Functions |
|--------------------|---------------------------------------|--|
| Copper | Cu, CuO, Cu ₂ O, CuS | Reactant: Cu ₂ O + 2HCN → H ₂ O + 2CuCN CuO + COCl ₂ → CO ₂ + CuCl ₂ |
| Zinc | ZnO, Na ₂ ZnO ₂ | Catalyst: 2AsH ₃ + 3O ₂ → As ₂ O ₃ + 3H ₂ O Reactant: ZnO + 2HCN → Zn(CN) ₂ + H ₂ O ZnO + COCl ₂ → ZnCl ₂ + CO ₂ |
| Silver | Ag, Ag ₂ O | Catalyst: 2AsH ₃ + 3O ₂ → As ₂ O ₃ + 3H ₂ O |
| Pyridine | C ₅ H ₅ N | Reactant: C ₅ H ₅ N + ClCN + H ₂ O → CHOCH=CHCH=CHNHCN + HCl |

The most successful technology for the preparation of activated carbon for gas masks, which is still in use today, is the so called (in the USA) "whetlerization" process, named after two of its originators – J.C. Whetzel and E.W. Fuller. The essence of this process is the consecutive immersing of activated carbon in appropriate mixtures of impregnants, followed by heat treatment. The carbon materials manufactured by this method are called ASC Whetlarite. In the initial period the US whetlerization process consists of immersing activated carbon in ammoniacal copper carbonate solution, draining off the excess liquid and drying the carbon granules at a temperature sufficient to expel substantially all the ammonia from the granules. Analogous process was developed in Germany, which is done by adding aqueous solution of sodium zincate over the activated carbon material.

In the period after World War II, the composition of active additives for ASC Whetlarite type of carbon materials is supplemented with Cr⁶⁺ and so the active oxide phase of the gas

mask carbon material consists of Cu-, Cr- and Ag-compounds (with or without organic additives).

The ASC Whetlerite type of carbon materials became first choice solution in terms of providing individual and collective protection for the main armies from the second half of 20th century up to now.

The manufacturers of this type of impregnated carbon materials use typically the same components in the production process, although their ratio may vary among different producers. Overall, the Cu-Cr-Ag phase combined with appropriate adsorption and texture parameters of the activated carbon support ensures simultaneous neutralization of practically all types of chemical warfare agents by means of physisorption, catalytic sorption and chemisorption.

The ASC Whetlerite carbon materials are also called activated carbon catalysts based on their catalytic sorption function which they perform in the neutralization of CWA.

At present, the research on the mechanism of removal of non-persistent CWA by ASC Whetlerite is focused primarily on the neutralization of cyanogen chloride (CICN, an instant break through gas-mask canister's CWA) and hydrogen cyanide (HCN), because of its wide application as a semimanufacture product and feedstock for various industrial productions.

The importance of the active additives for ASC Whetlerite for the removal of phosgene (COCl₂) is not significant, assuming the fact that canister's carbon material catalyses considerably the decomposition of COCl₂, especially in the presence of moisture.

Arsine (AsH₃) and phosphine (PH₃) are presently not used as CWA and regarding organofluorine compounds, the importance of active additives is not fully clarified.

The destructive removing of CICN by ASC Whetlerite is a complex process, which, depending on Cu:Cr ratio, the presence of moisture and temperature, is carried out by catalytic sorption, chemisorption (to a less extent) and physisorption (at lower temperatures, ≤ 253 K).

The dominating catalytic sorption in the above mentioned case is not expressed as a strictly defined process, but is an aggregate of parallel processes which result in the irreversible poisoning of the active additives in ASC Whetlerite by the reaction products or intermediate compounds.

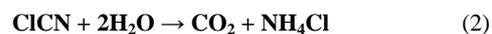
Among catalytic reactions, the two-stage hydrolysis process plays the role of a limiting factor.

During the first stage, the hydrolysis of CICN is catalyzed by Cu²⁺ to a mixture of cyanic acid (in equilibrium with isocyanic acid) and HCl:

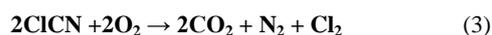


It has been proven that if the active additives for ASC Whetlerite contain only Cu²⁺, the chemical reaction ends at the first stage.

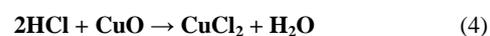
The second stage is ensured by the presence of Cr⁶⁺. The reaction is catalyzed by HCrO₄⁻ to the separation of CO₂ and NH₃:



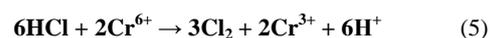
The parallel catalytic oxidation of CICN is also possible:



Part of the HCl separated during the first stage of the reaction (hydrolysis) reacts with NH₃, while the greater amount of HCl combines with CuO, poisoning it irreversibly:



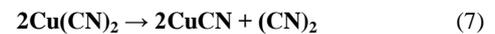
After the depletion of CuO the hydrochloric acid reacts with the chromates (i.e. reduces Cr⁶⁺ to Cr³⁺):



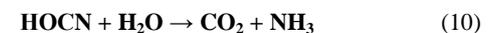
Despite of the considerable research that has been conducted, the actual mechanism of HCN neutralization by ASC Whetlerite carbon is not fully known. At present, it is accepted that Cu²⁺ are the most important ingredient of the active additives for ASC Whetlerite for this purpose. This is due to the significant importance of the reaction between CuO from the additive phase and HCN:



Copper cyanide (Cu(CN)₂) produced in this reaction is an unstable compound and decomposes quickly by the following reaction:



The latter reaction yields cyanogen (dicyan, (CN)₂) which is a highly toxic gaseous substance that can be neutralized by the following reactions:



According to [4] around 15 – 20 % of HCN are neutralized by ASC Whetlerite (depending on Cu/Cr ratio) at the expense of the catalytic oxidation. The reaction is catalyzed by Cu²⁺:



The obtained cyanic acid decomposes typically to CO₂ and NH₃ under the action of Cr⁶⁺ (Reaction 10).

It can be concluded that the formation of (CN)₂ and HOCN as a result from chemical reaction (6) and the catalytic oxidation of HCN (Reaction 11) are due to Cu²⁺ in the composition of ASC Whetlerite impregnated carbon, while Cr⁶⁺ ions take part in the catalytic decomposition of (CN)₂ (Reaction 8) and HOCN (Reaction 10). Nevertheless, the removal of copper from the impregnation compositions for activated carbon is unacceptable, as CuO ensures or participates in the neutralization of the vapors of other non-persistent chemical warfare agents such as phosgene, arsine and chlorine.

Despite of their proven high efficiency in respect to protection against highly volatile non-persistent chemical warfare agents, the ASC Whetlerite type of impregnated carbon materials containing Cr⁶⁺ are regarded by the specialists (for example, from the US Environmental Protection Agency) as non-perspective because of the following reasons:

- some forms of Cr⁶⁺ are carcinogenic [5] and pose risk to the production staff and army personnel, which use the respective gas masks and collective protection equipment;
- the problems associated with the disposal of this type of impregnated carbon materials after the end of their expiration date (defined by the manufacturer);
- the irreversible deactivation during use and storage of ASC Whetlerite with increased pre-adsorbed moisture content [4, 6, 9], which is connected to reduction of Cr⁶⁺ to Cr³⁺ and strong decrease of the sorption capacity of carbon materials towards CICN.

The above mentioned problems dictate the need for creation of a new generation of impregnated active carbon materials for gas mask protection against the vapors of airborne non-persistent chemical warfare agents and some industrial poisonous substances [10]. The composition of the active additives (the active phase) has to ensure:

- high efficiency, no less than that of ASC Whetlerite carbon materials;

- increased aging stability during storage and exploitation;
- composition of the active phase containing no (or minimal amounts of) Cr^{6+} and not allowing (or limiting to a maximum) the formation of side products (like cyanogen) during use;
- increased protection against the vapors of some of the most common poisonous substances in case of industrial accidents or fires.

The analysis of the mechanism of neutralizing HCN, ClCN and COCl_2 vapors by the active additives for impregnated carbon materials with different composition of active phases shows that they have to contain copper and to be composed in such a manner that to ensure:

- high reactivity towards HCN by simultaneously not allowing the formation of free cyanogen;
- compatibility of the different impregnation components and their participation in common reactions;
- high level of protection against the other types of non-persistent chemical warfare agents such as ClCN.

An opportunity for accomplishment of the above mentioned recommendations is the reduction of Cr^{6+} content ($< 0.6\%$) and the inclusion of Zn instead. Based on our experience, the impregnated carbon materials of this type (called ASZC) ensure protection against HCN vapors equal to that of the ASC Whetlerite carbon materials, but perform poorer than the latter in terms of cyanogen formation.

The addition of an alkaline component (2 % K_2CO_3) to the impregnation composition of ASZC materials solves that problem and increases the protection activity of the carbon catalyst towards some industrial poisonous substances. However, adding more than 2 % of alkaline component changes the chemistry of neutralization of other poisonous substances and has a negative overall effect.

In this sense the most perspective solution according to [7, 11, 12] is the complete replacement of Cr^{6+} in ASZC with Mo or V. At present, such change of the impregnation composition of carbon catalysts is partially accomplished only by the USA army. Such impregnated carbon material of a new generation, designated as ASZM-T, is developed by Calgon Corp. [10] and since 1992 is being used in type C2A1 gas mask canisters.

The perspective for the development of a new type of gas mask carbon material depends also on whether the new technology for application of the precursor solutions and the following thermal treatment of the impregnated carbon materials will distinguish significantly or not from the ASC Whetlerite carbon materials production.

Solution of the problem with ensuring protection against ClCN vapors is achieved by adding 3.5 mass % triethylenediamine (TEDA) to the active additives of ASZM carbon materials. The aging is being reduced by adding TEDA or pyridine.

The additional and mandatory inclusion of TEDA (pyridine) or K_2CO_3 in the impregnation compositions for the new type of carbon materials demands higher requirements towards the texture parameters of the base carbon materials. The latter can be summarized to the following:

- Specific surface area (measured by the BET method) of the base activated carbon materials no less than 1200 m^2/g ;
- Volume of micropores (V_{MI}) no less than 0.7 cm^3/g ;
- Ratio between the volume of micropores and volume of mesopores less than that for ASC Whetlerite carbon materials, at the expense of the volume of supermicropores.

Conclusion

1. The perspective new carbon catalysts will be based on impregnation compositions different from those for the preparation of ASC Whetlerite materials.
2. The new type of carbon catalysts will have no or significantly reduced ($< 0.6\%$) Cr^{6+} content. Instead they will contain Cu, Zn, Mo (V) and also tertiary amines (mostly TEDA) which will improve their anti-aging properties and broaden the area of application against vapors of industrial poisonous substances.
3. The requirements for the texture parameters of the base activated carbon materials are raised, which will increase the final price of the product.

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