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# Adsorption performance of activated carbon towards toxic industrial chemicals



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## English summary

One of the main goals in the project “1238: CBRN-vern” was to extend the present-day knowledge on the current CBRN filter and respirator systems and their possible improvement, in order to give the Norwegian Armed Forces a necessary expertise on their operative performance. This report summarizes the literature survey carried out in connection with the project, focusing on the filter canisters based on activated carbon used in the gas masks. Together with a gas mask the filters give the necessary respiratory protection against CBRN agents and a variety of toxic gases, including Toxic Industrial Chemicals (TICs). Knowledge on the adsorption mechanisms and the materials used in the filters is a key to understand and predict their operative performance against TICs. Activated carbon is of particular interest, since its unique properties make it the most commonly used adsorbent in the filters for civilian and military applications. Here, the preparation techniques, structure, different types of adsorption, effect of humidity and possible impregnation methods of activated carbon are reviewed, and the emphasis is put on the aspects of filter performance most relevant for the military applications. Adsorption mechanisms of selected TICs on activated carbon are presented, and a brief introduction to mathematical models useful for prediction of the filters lifetime is given. Finally, the report presents the conclusions from the literature findings, as well as recommendations for the future research activities at FFI and the possible evaluation of filter performance.

## Sammendrag

Gjennom prosjekt “1238: CBRN-vern” skal kunnskapen om eksisterende CBRN-filter og åndedrettsvernssystemer utvides og utdypes for å gi Forsvaret bedre innsikt i deres operative evner og mulige forbedringer. I forbindelse med dette arbeidet er det gjennomført en litteraturstudie over materialer som anvendes til filtrering av pusteluft i personlig beskyttelsesutstyr, nemlig vernemasker. Sammen med vernemaske gir filtre med aktivkull nødvendig åndedrettsbeskyttelse både mot kjemiske stridsmidler og giftige industrikjemikalier (Toxic Industrial Chemicals – TICs). Fokuset i denne rapporten har vært TICs og deres adsorpsjon på aktivkull. Denne rapporten oppsummerer adsorpsjonsegenskapene til aktivert karbon, det filtermaterialet som er mest brukt for adsorpsjon av giftige komponenter. Kunnskap om aktivkullets evner og adsorpsjonsmekanismer er avgjørende for å forstå og predikere ytelsen til aktivkull-basert filtreringsteknologi. Preparering, struktur, ulike typer av aktivkull, effekt av fuktighet og forskjellige adsorpsjonsmodeller er beskrevet med hensyn til aktivkull-typer som er eller kan benyttes av Forsvaret. Videre er det sett på mulige impregneringsteknikker, og hvordan valget av impregneringskomponenter påvirker kullets adsorpsjonsegenskaper mot utvalgte TICs. Adsorpsjonsisotermer og hvordan de kan brukes er diskutert, og en kort veiledning til matematiske modeller for predikasjon av gjennombruddstid og levetid er inkludert. Til slutt presenteres konklusjoner over litteraturfunn sammen med anbefalinger for framtidige forskningsaktiviteter ved FFI og mulige evalueringsmetoder av filters ytelser mot TICs.

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# 1 Introduction

The development of chemical industry around the world has contributed to a higher risk of exposure to Toxic Industrial Chemicals (TICs) both for civilians and the military. Several chemical compounds are listed as TICs, both inorganic and organic in nature, with different classes of toxicity. Some of these substances are or were considered as Chemical Warfare Agents (CWA), e.g. hydrogen cyanide (AC, blood agent), phosgene (CG, pulmonary agent) or chlorine. Taking into account the amounts of chemicals that may be released and their toxicity, it is clear that under certain circumstances TICs can pose a risk comparable or equal to chemical weapons. For instance, during one of the worst industrial accidents in the world in Bhopal, India in 1984 more than 3000 people were killed and approximately 50000-150000 people were injured when 40 tons of methyl isocyanate leaked from a chemical plant to the surrounding area [1]. Another example is chlorine, which is used by many industrial process facilities. In the USA, there have been several rail car accidents where chlorine has been released, all causing major rescuing and environmental challenges (Festus in 2002, Macdona TX in 2004 and Graniteville in 2005) [2]. Finally, the exposure to high amount of TICs could be also a consequence of a terrorist attack. Probability of being exposed to TICs can be considered even higher during military operations as a result of accidental damage or malfunction of the industrial installations or transporting vehicles in the area, or as an intentional release in lieu of CWA.

So far activated carbon is the most common medium used for removal of toxic chemicals from breathable air, and it is usually applied as an adsorbent for breathable air filtration. However, this particular material also has its limitations and a suitable type of carbon has to be carefully chosen to ensure safe operations in environments where TICs can be present. To achieve this, knowledge on whether CRBN filters and respirator systems used will protect against certain compounds, and for how long, must be gained. Even though there are thousands of toxic chemicals used in the industry, filter challenge tests for practical reasons are performed using few chosen chemical substances with properties representing different classes of poisonous chemicals. In Europe the Respiratory Protective Equipment (EPR) undergoes standardized testing and certification procedures according to European Committee for Standardization (CEN). Examples of commercially available filters suitable for different contaminants and their color code in accordance with European regulations are given in Table 1.1 [3].

Table 1.1 Types of commercially available filters and their color codes in accordance with European regulations on respiratory protection.

| Color  | Type       | Application   | Class | Gas Concentration  | Standard |
|--------|------------|---|-------|--|----------|
| brown  | A          | Organic gases and vapors - boiling point > 65°C   | 1     | 1000 ml/m <sup>3</sup>   | EN 141   |
|        |            |   | 2     | 5000 ml/m <sup>3</sup>   |          |
|        |            |   | 3     | 10000 ml/m <sup>3</sup>  |          |
| gray   | B          | Inorganic gases and vapors (not CO), i.e chlorine Cl <sub>2</sub> , hydrogen sulfide H <sub>2</sub> S, hydrogen cyanide HCN | 1     | 1000 ml/m <sup>3</sup>   | EN 141   |
|        |            |   | 2     | 5000 ml/m <sup>3</sup>   |          |
|        |            |   | 3     | 10000 ml/m <sup>3</sup>  |          |
| yellow | E          | Sulfur dioxide and acidic gas and vapors  | 1     | 1000 ml/m <sup>3</sup>   | EN 141   |
|        |            |   | 2     | 5000 ml/m <sup>3</sup>   |          |
|        |            |   | 3     | 10000 ml/m <sup>3</sup>  |          |
| green  | K          | Ammonia and organic ammonia Derivatives   | 1     | 1000 ml/m <sup>3</sup>   | EN 141   |
|        |            |   | 2     | 5000 ml/m <sup>3</sup>   |          |
|        |            |   | 3     | 10000 ml/m <sup>3</sup>  |          |
| brown  | AX         | Organic gases and vapors - boiling point <65°C - of low boiling substances groups 1 and 2                                   |       | gr.1: 100 ml/m <sup>3</sup><br>(max 40 minutes)  | EN 371   |
|        |            |   |       | gr.1: 100 ml/m <sup>3</sup><br>(max 20 minutes)  |          |
|        |            |   |       | gr.2: 1000 ml/m <sup>3</sup><br>(max 60 minutes)<br>gr.2: 5000 ml/m <sup>3</sup><br>(max 20 minutes) |          |
| blue   | NO         | Nitrogen oxides e.g NO, NO <sub>2</sub> , NO <sub>x</sub>   |       | (max 20 minutes)   | EN 141   |
| red    | Hg         | Mercury vapors  |       | (max 50 hours)   | EN 141   |
|        | CO         | Carbon monoxide   |       |  | DIN 3181 |
| gold   | Reactor P3 | Radioactive iodine  |       |  | DIN 3181 |
| white  | P          | Particles   | 1     | Low efficiency (80%)   |          |
|        |            |   | 2     | Medium efficiency (94%)  |          |
|        |            |   | 3     | High efficiency (99.95%)   |          |

EN – European standard, DIN – German national standard

As can be seen from Table 1.1, filters are classified according to the gas they are able to remove. Within each group marked by an alphabet letter (A, B, E, K) different classes can be distinguished:

- Class 1 – low capacity, up to 1000 ppm
- Class 2 – medium capacity up to 5000 ppm
- Class 3 – high capacity, up to 10000 ppm

Analogically, the efficiency of the filters used by the military for respiratory protection is specified in NATO directives issued by NATO Standardization Office (NSO).

In this report focus is set on the TICs chosen on the basis of chemicals listed in the European standard EN14387 for gas filters (“Respiratory Protective Devices – Gas filters and combined filter(s) – Requirements, testing, marking”) and the screening tool presented by Blakey et al. in 2013 [4]. In their publication Blakey et al. categorize different TICs based on a risk matrix shown in Table 1.2, where the risk score is defined as follows:

*risk score = (probability of exposure) \* (maximum hazard posed by the chemical).*

The risk matrix is shown in Table 1.2.

Table 1.2 Risk matrix for categorization of chemicals.

| Severity of hazard | Probability of exposure |          |            |          |          |
|--------------------|-------------------------|----------|------------|----------|----------|
|                    | Frequent                | Likely   | Occasional | Seldom   | Unlikely |
| Extreme            | Extreme                 | Extreme  | Extreme    | High     | Moderate |
| Major              | Extreme                 | High     | High       | Moderate | Low      |
| Significant        | Extreme                 | High     | Moderate   | Low      | Very low |
| Moderate           | High                    | Moderate | Low        | Low      | Very low |
| Minor              | Moderate                | Low      | Very Low   | Very Low | Very low |

According to Blakey et al. ammonia has a risk score “high”, whereas AC, phosgene, carbon monoxide, chlorine, and hydrogen sulfide all have risk score “extreme”. Interestingly, according to the same screening tool CWA such as sarin and sulfur mustard have risk scores “moderate” and “low”, respectively. This is because the CWA are considered to be rather unavailable to the public, whereas there is higher probability of a release in case of highly volatile and toxic TICs. However, CWAs are still a primary threat in the military operations and are of interest of the terrorist groups, as their toxicity is usually much higher than TICs. For this reason the chemicals considered in this report include both highly volatile CWAs and some of the TICs which are marked as “high” or “extreme”:

1. Hydrogen cyanide (AC, blood agent, also used in the industry as a synthetic gas)
2. Cyanogen chloride (CK, blood agent, precursor for organic syntheses)
3. Phosgene (CWA used during WWI, used in chemical and pharmaceutical syntheses)

4. Carbon monoxide (a component of industrial gases, also released in significant amounts during fires with limited availability of oxygen)
5. Ammonia (raw material for chemical and pharmaceutical industry, important in e.g. fertilizer production)
6. Chlorine (CWA used during WWI, synthetic gas and important for water cleaning systems)
7. Hydrogen sulfide (synthetic gas in chemical industry, used as precursor and reagent in chemical analysis)
8. Sulfur dioxide (main ingredient for sulfuric acid production)
9. Nitrogen oxides (synthesis of nitric acid, released during fuel combustion and byproduct of industrial processes)

## 2 General properties of activated carbon

Several different types of respirators are currently available on the market. The simplest devices, such as particulate respirators protect against dust particles; half or full gas mask respirators are used for air purification from toxic gases or fumes; powered air-purifying respirators (PAPR) which contain a fan for drawing the air through the filter making breathing easier; finally, a self-contained breathing apparatus (SCBA), which employs an air tank for clean air supply. The choice of an optimal respiratory device requires knowledge on types (gas, particle, vapor or mixture of all the above) and concentration of contaminants present in the environment, as well as number of other factors, such as oxygen level, Occupational Exposure Limits (OEL), time of exposure etc. Nevertheless, a gas mask often provides sufficient protection for many uses, especially if combined with a proper protection suit covering the body, as certain substances will absorb also through the skin and mucus membranes.

In order to carry its functions the gas mask requires a filter canister or a cartridge. A typical canister is a multilayered assembly of different filters: an aerosol filter, which consists of metal grid and folded cellulose sheet or glass fiber and a layer of adsorbent, e.g. activated carbon for removing the chemicals from the air stream (Figure 2.1) [5]. The construction of a cartridge is analogical except the amount of adsorbent which is usually smaller than in a canister. Among other types of adsorbents used, activated carbon remains unquestionable leader due to its excellent adsorbing properties, low cost, availability, durability and lifespan. Activated carbons are therefore commonly used in various filters for individual and collective protection to remove toxic gases and vapors from air for civilian and military applications.

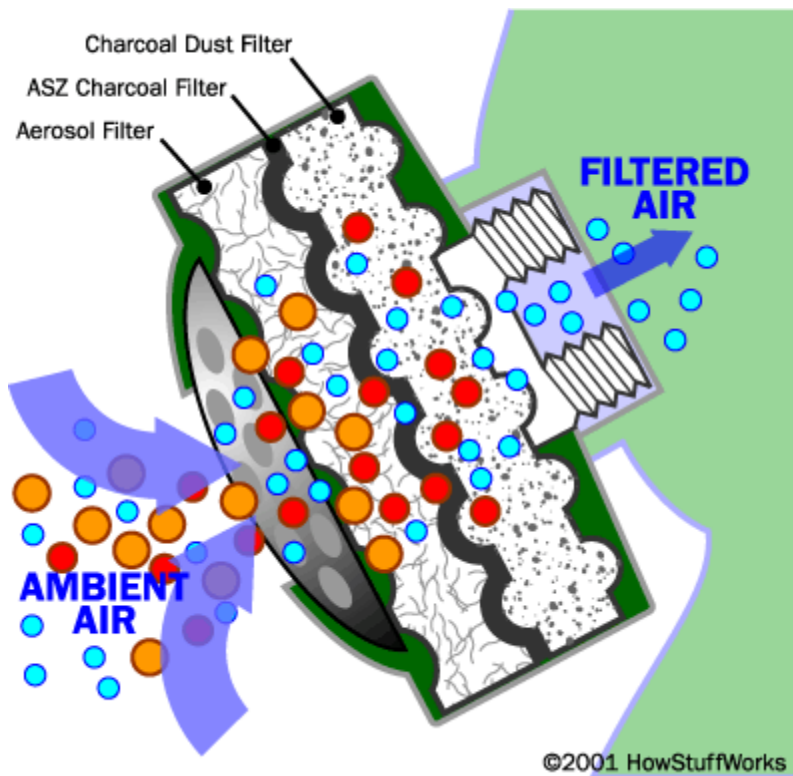


Figure 2.1 Cross-section of disposable filter cartridge for respiratory protection [5].

Different substances become immobilized (adsorbed) on the surface of carbon depending on both the type of adsorbate (a substance being adsorbed) and adsorbent (a solid surface). To understand how various compounds adsorb on different surfaces, knowledge on different types of adsorption, the effects of carbon structure and surface treatment, environmental conditions and adsorbate properties must be achieved. Furthermore, it is important to get an overview over adsorption models, as these can be used for prediction of filter performance, i.e. adsorption capacities and breakthrough times. In particular, prediction of the breakthrough time (the time it takes to reach a chosen outlet concentration of the gas of removal) is valuable, as it gives the life-time of the filters.

Activated (also called active) carbon is a form of porous carbon processed to yield a high surface area, which for commercially available carbons is usually between 500 – 1500 m<sup>2</sup>/g [6]. Possible applications of activated carbon are almost countless, especially in the field of air and water filtration technologies, where a remarkably high surface area of activated carbon is utilized for adsorption of contaminants or undesired biological and chemical components. Additionally, once the activated carbon becomes exhausted it is possible to regain its adsorptive powers by regenerative processes, e.g. heating or washing with chemicals, which makes the entire filtering process economically beneficial. For these reasons activated carbons are utilized worldwide as adsorbents in various filtration systems for industrial, personal and military applications.

## 2.1 Preparation

Filtration of gas requires low resistance to gas flow through the carbon bed to avoid pressure drop. Therefore carbons for this application are in the form of hard granules, hard pellets, fibers, cloths or monoliths (Figure 2.2).

Production process of activated carbon may vary depending on the manufacturer, but typically it consists of two main steps: carbonization of the material with high carbon content via pyrolysis and activation of the product by oxidizing agents. A scheme of activated carbon production is given in Figure 2.3 [7].

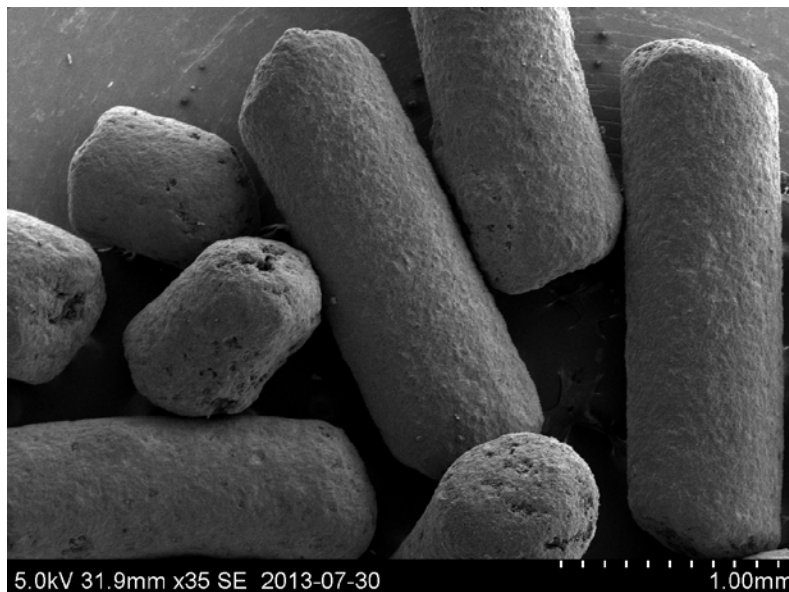


Figure 2.2 Scanning Electron Microscope (SEM) image of activated carbon granules used in gas mask filters.

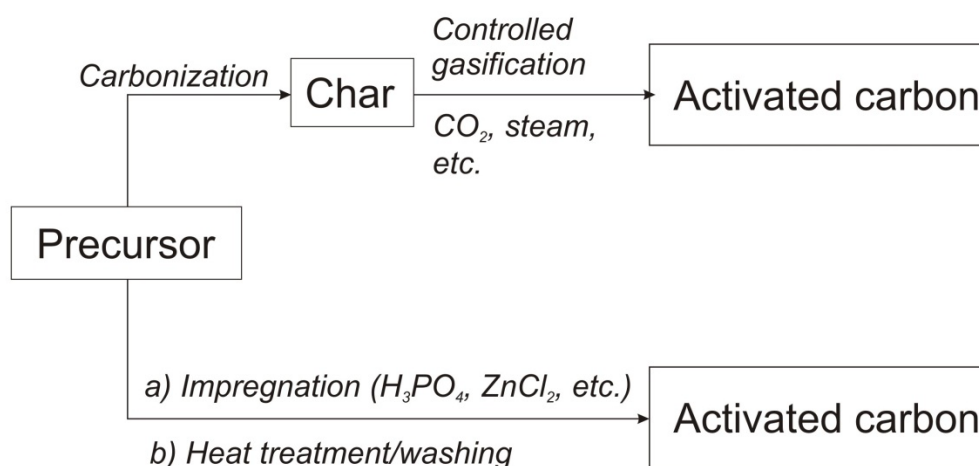


Figure 2.3 Flow sheet for activated carbon manufacturing [7].

Almost any material rich in carbon can be transformed into activated carbon. The choice of the source material and conditions for activated carbon production depends on the future applications, e.g. coconut shells are the source of chars for adsorption of gases and vapors, whereas bones were used for chars employed in sugar refining [8]. This is due to the microstructural features of the source material, which contribute to the shape and size of pores forming during activation. Some of the carbonaceous materials used for activated carbon production are listed below [9]:

- Bituminous coal\*
- Bones
- Coconut shells
- Lignite
- Peat
- Pecan Shells
- Petroleum-based residues
- Pulp mill Black-ash
- Sugar
- Wastewater treatment sludges
- Blood
- Wood

\* *bituminous coal-based carbon (BPL) is one of the most commonly used types of activated carbon*

During pyrolysis the source material is annealed at elevated temperatures with limited access of oxygen. Temperature (usually below 600°C) should be high enough to separate and volatilize substances other than carbon. Prior to this step the source material is often impregnated with dehydrating salts, such as metallic chlorides solutions (CaCl<sub>2</sub>, ZnCl<sub>2</sub>, MgCl<sub>2</sub>) [9].

The resulting product consists mostly of carbon atoms and it has a developed surface area due to multiple pores formed during evaporation of more volatile content of source material. It is believed that those pores are partially blocked by the tar formed during the carbonization. However this surface area requires further increase by means of activation process. During activation the carbonization product is simultaneously heated and exposed to oxidizing agents such as steam, air, CO<sub>2</sub> or chemicals (Table 2.1). Tar and some carbon atoms are removed: carbon atoms are partially burnt off resulting in widening of the open pores and perforation of the closed ones. This creates a porous network and increases the surface area available for adsorption.

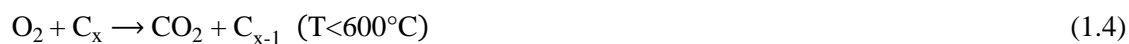
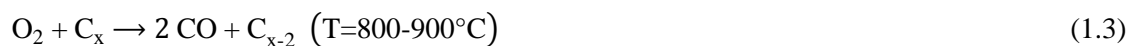
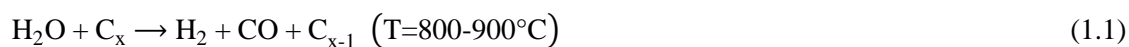
*Table 2.1 Chemicals studied as potential activation agents [9].*

|   |                          |
|---|--------------------------|
| <b>Ammonium salts</b>                   | <b>Hydrochloric acid</b> |
| <b>Borates</b>                          | <b>Manganese dioxide</b> |
| <b>Boric acid</b>                       | <b>Nickel salts</b>      |
| <b>Calcium oxide</b>                    | <b>Nitric acid</b>       |
| <b>Cyanides</b>                         | <b>Sulfur</b>            |
| <b>Iron(II) and iron(III) compounds</b> |                          |

Carbon can be activated chemically or physically [10]. Chemical activation in industrial scale employs water solutions of ZnCl<sub>2</sub> or H<sub>3</sub>PO<sub>4</sub>, which are mixed with carbon precursors and heated.



The carbonaceous material is etched; as the water molecules are removed, the cross-links are formed between the carbon atoms. Physical activation requires higher temperatures and is accompanied by the following reactions taking place between chars and oxidizing gases [8;9]:



The most important parameters affecting the adsorptive capacity of the product are as follows [8;9]:

- Chemical composition and concentration of the oxidizing gas
- Temperature during activation process
- The extent to which activation is conducted
- Concentration and chemical composition of mineral ingredients in the char and the inorganic additives during oxidation.

Activation parameters and the presence of mineral salts are crucial for establishing adsorptive properties of the final product, such as adsorptive capacity or selectivity towards certain adsorbates. Non-carbon components contribute to ash formation, but they also bind to carbon atoms forming functional groups on its surface with various adsorptive powers. The exact mechanism of action of the mineral ingredients is not entirely explained, yet they seem to alter the activation mechanisms by e.g. changing water evaporation mechanisms or temperature of activation. Microstructural features of the product, such as pore size or structural arrangement of carbon atoms will also depend on the kind of chemical used during activation. A detailed description of the theories on the role of mineral ingredients can be found in reference [8].

## 2.2 Crystal structure

The atomic structure of graphite, one of the crystal forms of carbon, is a convenient starting point when considering the fine structure of activated carbon. Crystal lattice of graphite is sometimes used for modeling of activated carbon properties, especially its surface (Figure 2.4). Graphite structure is lamellar, e.g. consists of infinite layers of fused hexagons, where carbon atoms are placed periodically in space forming a crystal lattice. The carbon atoms within the layers are joined via covalent bonds, whereas weak van der Waals interactions hold the layers together.

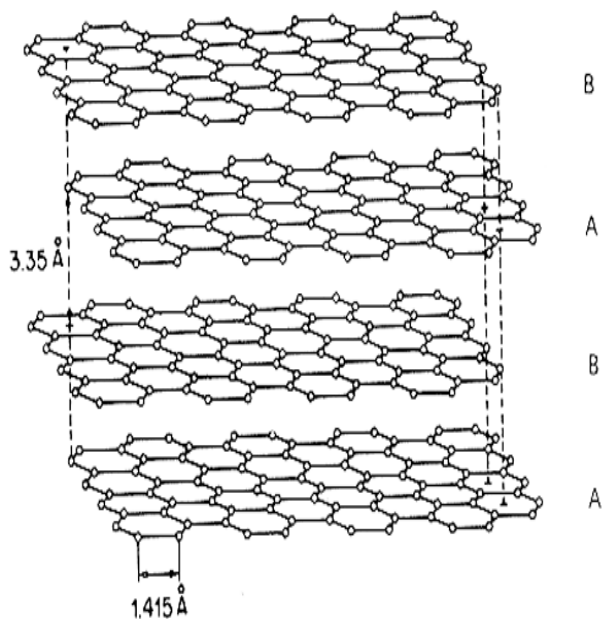
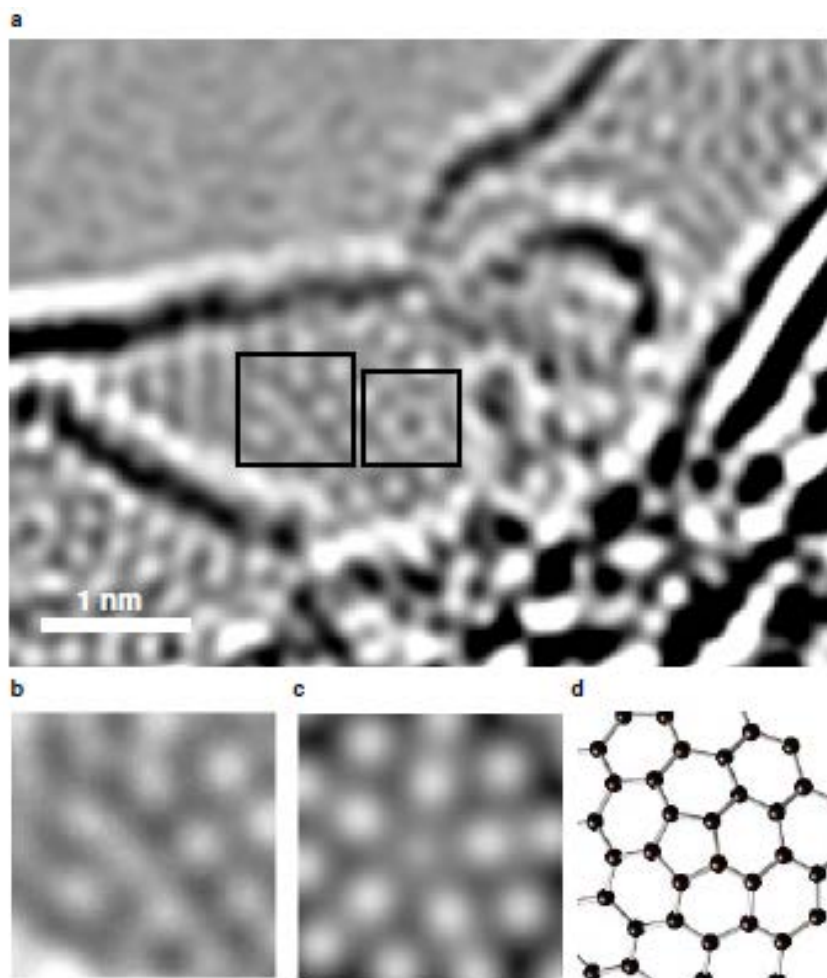


Figure 2.4 Graphite crystalline structure (circles represent carbon atoms). Hexagonal units formed between carbon atoms are arranged in planes joined by Van der Waals forces [11].

In activated carbon the infinite planes are disrupted – the carbon atoms are arranged in hexagonal lamellas, but the arrangement of the lamellas is lacking a long-range order. This is reflected by the X-ray diffraction patterns with broad peaks of low intensity. The unsaturated bonds at the edges of the lamellar structures contribute to the adsorption phenomenon. The real structure of activated carbon is also affected by impurities (atoms other than carbon), vacancies (empty spaces in the structure which should be occupied by carbon atoms) and voids between the lamellas (pores).

The exact structure of activated carbon, especially types of carbon prepared at lower temperatures is difficult to derive experimentally, even with most advanced microscopy. Transmission Electron Microscopy (TEM) is often used for imaging atom arrangements in crystalline materials. However, the resolution of most of the instruments is insufficient to analyze the carbon-bonds in activated carbon (the C-C bond distance is 0.1415 nm within the layers) and the amorphous nature of the material is yet another challenge to be faced. Figure 2.5 presents unique TEM images of activated carbon collected by Harris et al. [12] who analyzed samples of commercial Norint® carbon, as-received and treated at 2000°C. The images were then used to illustrate the symmetry of carbon rings.



*Figure 2.5 (a) TEM image of activated carbon treated at 2000°C; (b) and (c) enlargement of the analyzed area; (d) simulated image of the atomic structure showing pentagonal arrangement of carbon atoms [12].*

TEM results seem to confirm the hypothesis that activated carbon can be represented by fullerene-like, bent planes with pentagonal, hexagonal and heptagonal rings rather than parallel planes with hexagonal arrangement (Figure 2.6). Nevertheless, the fresh carbon sample was too disordered to confirm its structure without any ambiguities. It was found that the applied thermal treatment promotes the development of hexagonal network without affecting the pentagonal carbon rings. For more detailed information on the subject of carbon structure the reader can refer to references [7;12;13].

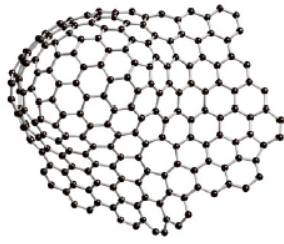


Figure 2.6 A section of curved carbon showing pentagonal, heptagonal and hexagonal rings [12].

### 2.3 Porosity and surface properties

Activated carbon owes much of its sorptive powers to its porosity (Figure 2.7). The porosity in activated carbons is due to spaces and voids between defected and crumpled graphitic lamellas with low packing density. Pores with various shapes and sizes are formed during carbonization and activation processes, and their distribution depends on the source materials and the procedures included in carbon preparation.

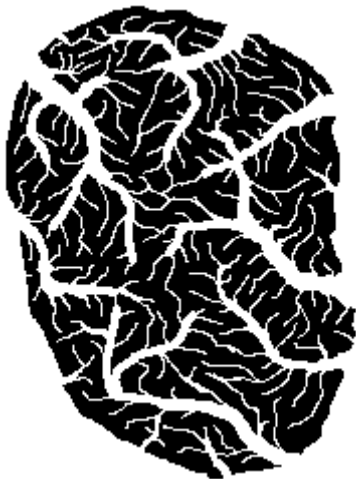


Figure 2.7 Schematic representation of the activated carbon cross-section showing the porosity structure [14].

According to IUPAC (International Union of Pure and Applied Chemistry) recommendations the pores can be divided into the following categories depending on their size:

- Macropores:  
 $r > 50$  nm; responsible for adsorption of large organics (viruses, bacteria)
- Mesopores (transitional pores)  
 $50 \text{ nm} > r > 2$  nm; monomolecular and polymolecular adsorption
- Micropores  
 $r < 2$  nm; size order corresponds to the size of molecules

Despite their minute size micropores contribute to the 95% of the specific area of the activated carbon. As can be seen from Figure 2.8, macropores open directly to the surface of carbon grain, and they are connected with meso- and micropores in the bulk of the grain. Macropores serve mostly as transportation channels for the molecules which enter the micropore network.

In general the pore size corresponds to the size of the species adsorbed by activated carbon (Figure 2.8) [15]. Nevertheless, the adsorptive powers of activated carbon cannot be explained entirely by its enormous porosity which provides the extended surface area. Activated carbon contains numerous imperfections – the leftovers of inorganic matter including metal ions, as well as the unsaturated carbon bonds from the partially burnt off layers of graphite. Those imperfections affect the electronic density on the surface, thus influencing the adsorptive properties towards polar or polarizable substances.

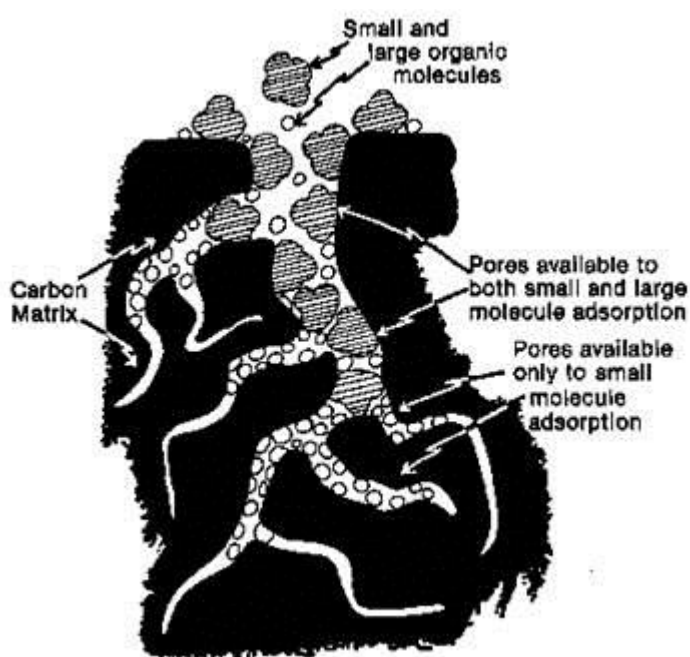


Figure 2.8 Schematic representation of the activated carbon pore structure [15].

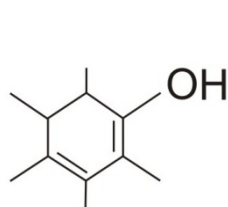
Another important factor is the presence of heteroatoms chemically bonded to the surface. Surface groups have different electron and ion-exchange properties, which is manifested by the preferential adsorption of polar compounds. In addition, those groups can also affect other groups in their vicinity so that the final properties of the surface, such as acidity or polarity can be enhanced or weakened. In pure carbons oxygen chemisorbed at the edges of carbon planes contributes to formation of polar sites, whereas in carbons of lesser purity other heteroatoms play this role [16].

Due to adsorptive properties of activated carbon and the mutual interactions between the surface groups it is difficult to establish their exact nature in direct experiments. Nevertheless, it is agreed that the oxygen surface complexes have general formula of  $C_xO_y$  and can be acidic or basic [17]. Acidic complexes are formed during carbon exposure to oxygen at 200 – 500°C or to aqueous

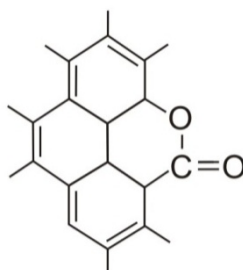
oxidizing solutions, whereas basic complexes formation requires stripping off the surface oxides by annealing in vacuum or reducing atmospheres [18;19]. Examples of functional groups contributing to acidic and basic surface oxides are given in Figure 2.9 [18].

A titration method was proposed by Boehm to analyze the acidic surface groups qualitatively and quantitatively [20]. Titration method utilizes the neutralization of the particular surface group by one of the four bases of different strength. Carboxyl groups are neutralized by  $\text{NaHCO}_3$ , lactones by  $\text{Na}_2\text{CO}_3$ , phenols by  $\text{NaOH}$  and carbonyls by  $\text{NaOC}_2\text{H}_5$ . For the basic groups a titration with strong acid can be applied, but their nature is less known and hence difficult to determine [21]. Other techniques include TPD (temperature-programmed decomposition), where a sample of activated carbon is heated under controlled atmosphere and the evolving gaseous products are analyzed quantitatively and qualitatively [22] by using e.g. Infrared Spectroscopy (IR) and X-ray Photoelectron Spectroscopy (XPS) [23].

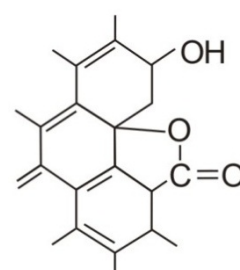
### Acidic groups



Phenolic

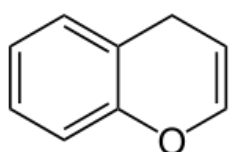


n-lactone

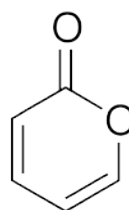


f-lactone

### Basic groups



Chromene-like  
(2H-1-benzopyran)



Pyrone-like  
(2-pyrone)

Figure 2.9 Examples of functional groups on activated carbon surface with acidic and basic properties.

Depending on the dominating surface oxides, L-type carbons (majority of acidic oxides) and H-type carbons (majority of basic oxides) can be distinguished. In aqueous environments L-type carbons are hydrophilic; they display negative surface potential and adsorb strong bases; H-type carbons are hydrophobic, with positive surface potential and the ability to adsorb strong acids [18;19;24] (Table 2.2). The hydrophobic or hydrophilic behavior of activated carbon influences

their adsorptive characteristics when water vapor is present. More information on water interaction with activated carbon can be found in section 3.4.

Table 2.2 Differences between L-type and H-type activated carbons.

| L-type activated carbon   | H-type activated carbon  |
|---|--|
| <b>Lower activating temperature (450-600°C) with the appropriate impregnating chemical agent such as H<sub>3</sub>PO<sub>4</sub> or ZnCl<sub>2</sub> used</b> | Higher activating temperature (800-1000°C) with the appropriate activating vapor/gas in the reaction chamber (H <sub>2</sub> O, CO <sub>2</sub> ) used |
| <b>Surface oxygen groups present originating from precursor material</b>  | Surface oxygen groups originating from partial oxidation mechanism by the activation atmosphere  |
| <b>Wider micropores present due to the formation of smaller polyhexagon sheets but with larger aliphatic and hydrogen content</b>                             | Smaller micropores present due to different polyhexagon sizes being linked by oxygen bridging in the intersheet spacings                               |
| <b>Pore size distribution obtained by N<sub>2</sub> adsorption indicates that L-type carbons have large micropores but narrow mesopores</b>                   | Pore size distribution obtained by N <sub>2</sub> adsorption indicates that H-type carbons have narrow micropores but wider mesopores                  |
| <b>Lower particle size reduction and higher yields in chemically activated carbons</b>  | Higher particle size reduction and lower yields in physically activated carbons  |

### 3 Impregnation of activated carbons and the interactions with chosen chemicals

#### 3.1 Physisorption versus chemisorption

In general different species may become trapped on the activated carbon surface during the filtration process due to so-called physical or chemical adsorption. In porous materials like activated carbon the physical adsorption will take place in the pores, and both monomolecular (surface covered with one layer of molecules) and multimolecular layers (surface covered with several layers of molecules) can be formed. This kind of adsorption is non-specific.

In case of physical adsorption (physisorption), the main interaction between the adsorbate and adsorbent is weak van der Waals forces and no real chemical bonds are created, whereas in chemisorption the interaction between the adsorbate and adsorbent is much stronger. In chemisorption, chemical bonds are created at the activated sites on the carbon surface or at impregnates. Whether a molecule is physisorbed or chemisorbed on a surface depends e.g. on the characteristics of the adsorbate and the adsorbent, the surface reactivity, the surface area of the adsorbent, and the temperature and pressure of adsorption. Physical adsorption occurs in all adsorbate-adsorbent systems, whereas chemisorption is system-specific. The adsorption processes are exothermic, but the amount of heat released in case of chemisorption is much higher than in physisorption [25-27]. Organic molecules with low vapor pressure such as nerve or blister agents usually become strongly bonded due to physical adsorption followed by slow hydrolysis on

activated carbon. On the other hand, physical adsorption of chemicals with low vapor pressure (e.g. choking or blood agents) is poor. For this reason activated carbon is impregnated with e.g. metal ions to create active sites on its surface where chemical adsorption of volatile compounds can take place.

### 3.2 Impregnation

Despite the extended pore network and high surface area the adsorption capacity of activated carbon towards several chemical compounds is insufficient for many applications, such as filter canisters for personal respiratory protection in military and civil services. The performance of the filtering agent is greatly enhanced when chemisorption and/or catalytic decomposition occurs on its surface. For this reason activated carbon, such as BPL, is impregnated to improve the adsorptive properties towards one or more particular contaminants present in the air stream. In principle, the impregnation blocks part of the porosity, but in return it makes the filter more capable in terms of chemical adsorption, necessary for trapping several highly volatile contaminants with low molecular weight, such as cyanides. Chemisorption is more selective than physical adsorption, where the size of molecules is crucial for effective trapping process. In case of chemisorption certain chemical bonds have to be formed between the surface of activated carbon and the adsorbed substance, therefore the choice of the impregnating salts will depend on the application. Table 3.1 lists some of the possible combinations of adsorbates (adsorbed substances) and impregnating agents [28].

Table 3.1 Commercially used impregnations against industrial hazards [28].

| Impregnating agent     | Chemisorbed species   |
|------------------------|---|
| Sulfuric acid          | NH <sub>3</sub> , amines, mercury   |
| Phosphoric acid        | NH <sub>3</sub> , amines  |
| Potassium carbonate    | Acid gases (HCl, HF, SO <sub>2</sub> , H <sub>2</sub> S, NO <sub>2</sub> ), CS <sub>2</sub>                 |
| Iron oxide             | H <sub>2</sub> S, mercaptanes, COS  |
| Potassium iodide       | H <sub>2</sub> S, PH <sub>3</sub> , Hg, AsH <sub>3</sub> , radioactive I <sub>2</sub> and CH <sub>3</sub> I |
| Triethylene diamine    | radioactive I <sub>2</sub> and CH <sub>3</sub> I  |
| Sulfur                 | Hg  |
| Potassium permanganate | H <sub>2</sub> S from non-oxidizing gases   |
| Manganese (IV) oxide   | Aldehydes   |
| Silver                 | PH <sub>3</sub> , AsH <sub>3</sub> , bacteria   |
| Copper                 | H <sub>2</sub> S, HCN in cigarette filters  |
| Zinc oxide             | HCN   |

A wide variety of impregnated carbons is available commercially from several companies and the abbreviated names are given to those carbons depending on the chemicals used for impregnation. Those abbreviated names are to a large extent universal, even though some variations occur. Most common types of activated carbon include [29]:



AC<sup>1</sup> – activated carbon

ASC – AC impregnated with copper (Cu) and chromium (Cr) salts

ASZ – AC impregnated by Cu (II), zinc (Zn) (II) and silver (Ag) (I) salts

ASZM - AC impregnated by Cu (II), Zn (II), Ag (I) and molybdenum (Mo) (VI) salts

ASZM-T (ASZM-TEDA) - ASZM impregnated by Cu, Zn, Ag, Mo salts and triethylenediamine (TEDA)

It is worth mentioning that the abbreviations may also vary depending on the producer, therefore it is recommended to verify whether the specifications are in accordance with application requirements. For instance, Table 3.2 shows an example of abbreviations and impregnating substances used by the activated carbon manufacturer Splagro ®, India ([www.splagro.com](http://www.splagro.com)).

Table 3.2 Different types of impregnated carbons and their abbreviations (Splagro ®).

|                 |  |
|-----------------|--|
| <b>ASV</b>      | <b>Activated Carbon with Copper, Silver, Vanadium</b>                                  |
| <b>ASVT</b>     | Activated Carbon impregnated with Copper, Silver, Molybdenum                           |
| <b>ASVT</b>     | Activated Carbon impregnated with Copper, Silver, Vanadium & Tartaric Acid             |
| <b>ASMT</b>     | Activated Carbon impregnated with Copper, Silver, Molybdenum & Tartaric Acid           |
| <b>ASMVT</b>    | Activated Carbon impregnated with Copper, Silver, Molybdenum, Vanadium & Tartaric Acid |
| <b>ASZ</b>      | Activated Carbon impregnated with Copper, Silver & Zinc                                |
| <b>ASZ-TEDA</b> | Activated Carbon impregnated with Copper, Silver, Zinc & TEDA                          |

---

<sup>1</sup> Since AC is already used as an abbreviation for hydrogen cyanide it will not be used for description of activated carbon in this report

From military point of view, the types of activated carbon most important for personnel protection are **whetlerite** and **ASZM-TEDA**. Whetlerite, a type of activated carbon impregnated with copper, silver and with or without chromium (ASC whetlerite) has been known since World War I. For whetlerites typical content of activated metal ions varies between 6 and 8% for Cu, 2 to 3 % for Cr and less than 0.5% Ag [30]. In reference [28] the following chemical composition for ASC-type whetlerite established by XPS (X-ray Photoelectron Spectroscopy) is given: 78.9% C, 13% O, 4.1% Cr, 1.3% Cu, 2.7% N. Since XPS is a surface sensitive technique with the probing depth usually less than 10 nm, such results can also indicate surface segregation of certain impregnates on the carbon grains.

ASC whetlerite is an effective adsorbent of cyanogen chloride (CK), hydrogen cyanide (AC) and cyanogen. Whetlerizing solution contains Cu and Cr ammonia complexes, stabilized by excess ammonia present in the solution [31]. It was also suggested that ammonium carbonate from whetlerizing solution participates in formation of acidic and basic sites, the later playing an important role in CK hydrolysis [31]. However, filters using whetlerite produced by this method were found to release ammonia, especially in hot and humid conditions, leading to irritation of respiratory track. Since copper ammonium chromate complexes remain in the impregnated activated carbon despite drying and temperature treatment, it was proposed that they undergo hydrolysis when a humidified air stream is passing the filter, yielding free ammonia. Interestingly, ammonia release is also observed upon adsorption of toxic gases: AC or CK on activated carbon, but the mechanism behind it is not entirely understood [31].

There is a general consensus that Cu and Cr form complexes with  $\text{NH}_3$ , where the predominant oxidation state for Cr is +6 and +2 for Cu. The exact formula of these compounds is debated. Changing the oxidation state of these elements is associated with loss of adsorptive properties for cyanides removal. It is worth mentioning that even in freshly prepared whetlerite some part of copper and chromium is already reduced to  $\text{Cr}^{+3}$  and  $\text{Cu}^{+1}$ . Exposure to atmosphere and humidity causes further reduction in oxidation state of those ions, leading to weathering of the filter and a decrease in its capacity towards cyanides [32].

It should be mentioned that Cr (VI) compounds are toxic (teratogenic) and there are environmental issues related to Cr-impregnated carbon production and disposal. The latest REACH (**R**egistration, **E**valuation, **A**uthorisation and **R**estriction of **C**hemical substances; European Community Regulation on chemicals and their safe use) directive from 2013 restricts the use and production of Cr(VI) compounds. In addition, accidental inhaling of carbon particles containing Cr(VI) can cause respiratory track diseases. For these reasons the filters are currently being withdrawn from production and replaced with other types of carbon, such as ASZM-TEDA.

ASZM-TEDA is another type of impregnated activated carbon-based filter effective towards TICs and CWAs. ASZM-TEDA has been in use by U.S. military as a part of NBC (Nuclear, Biological and Chemical) protection system since 1993 [33]. TEDA (triethylenediamine or DABCO: 1,4-diazabicyclo[2,2,2] octane) is an amine which has been used successfully for removal of radioactive iodide and iodide-compounds. TEDA does not desorb easily from activated carbon

surface and it has been found that simultaneous use of TEDA and chromium for impregnation increases the adsorption capacity against CK [34]. As an impregnate TEDA alone does not provide equally good protection against CK, but it may reduce amounts of other impregnates, such as chromium and copper, needed for adsorption of cyanide compounds. In case of ASZM-TEDA, possible interactions and synergism between impregnates is still debated [34]. General overview on the adsorption mechanisms of some of CWAs on ASZM-TEDA carbon is given in Table 3.3 [33].

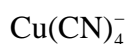
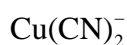
Table 3.3 Mechanisms of CWA vapor filtration by ASZM-TEDA.

| <b>Agent</b>                           | <b>Filtration mechanism</b>  |
|--|--|
| <b>Nerve</b>                           | Strong physical adsorption, generally followed by slow hydrolysis of the adsorbed agent.   |
| <b>Blister</b>                         | Strong physical adsorption, generally followed by slow hydrolysis of the adsorbed agent.   |
| <b>Phosgene (choking agent)</b>        | Weak physical adsorption combined with agent decomposition, affected by the impregnates. Phosgene hydrolysis to form hydrogen chloride and carbon dioxide. The hydrogen chloride reacts with the copper and zinc carbonate impregnates to form copper and zinc chlorides.  |
| <b>Cyanogen chloride (blood agent)</b> | Weak physical adsorption combined with agent decomposition, affected by the impregnates. Cyanogen chloride very likely undergoes hydrolysis catalyzed by the triethylenediamine impregnate, followed by removal of the acid breakdown products (hydrogen chloride and cyanic acid) by the copper and zinc carbonate impregnates. Cyanic acid very likely hydrolyzes to form carbon dioxide and ammonia.                                    |
| <b>Hydrogen cyanide (blood agent)</b>  | Weak physical adsorption combined with agent decomposition affected by the impregnates. Hydrogen cyanide reacts with the copper (+2) and zinc carbonate impregnates to form copper (+2) and zinc cyanides. The copper (+2) cyanide converts to cuprous cyanide and cyanogen. The cyanogen reacts with the ammonium dimolybdate impregnate, very likely forming oxamide, which is strongly and physically adsorbed by the activated carbon. |
| <b>Arsine (blood agent)</b>            | Weak physical adsorption combined with agent decomposition, affected by the impregnates. At low relative humidity, arsine is oxidized by copper (+2) to form arsenic trioxide and arsenic pentoxide. At high relative humidity, arsine is catalytically oxidized by the silver impregnate to form arsenic oxides.  |

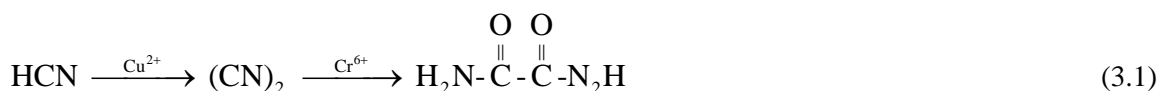
### 3.3 Interaction of chosen chemicals with activated carbon

#### 3.3.1 Hydrogen cyanide, HCN

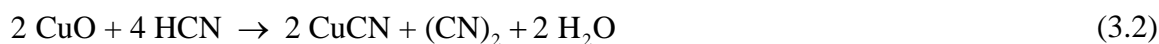
For HCN filtration activated carbon impregnated with copper and chromium ions is mainly used. Both copper and chromium take active part in HCN oxidation, and the capacity for HCN removal is higher when both elements are present in comparison with carbons impregnated with either copper or chromium [35]. This could indicate that the active ingredient is a compound consisting both of Cu and Cr and indeed several different complex compounds have been proposed [28]. Copper ions form active sites for HCN adsorption, since copper can form several cyanide complexes [10]:



In general the process of HCN chemisorption on copper and chromium-impregnated carbon can be described as follows, with the formation of oxamide as final product [28]:



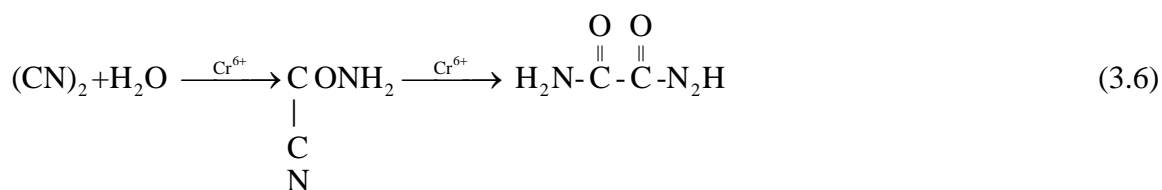
It was established that during HCN passage through the filter toxic  $(\text{CN})_2$  is formed and emerges in the effluent. One of the proposed HCN retention mechanisms involves oxidized copper (in form of  $\text{CuO}$  or  $\text{CuCO}_3$ ) and possibly requires  $\text{Cr}^{6+}$  as a catalyst for hydrolysis reactions. At first HCN dissolves in adsorbed moisture and then reacts with copper ions. The resulting cyanogen  $(\text{CN})_2$  undergoes hydrolysis leading to HCN regeneration, whereas hydrolysis of other product,  $\text{HOCN}$ , yields  $\text{CO}_2$  and  $\text{NH}_3$  [28]:



Another proposed mechanism involves a direct reaction of  $(\text{CN})_2$  with  $\text{Cu}^{2+}$  :



The presence of  $\text{Cu}^{2+}$  plays a key role in formation of toxic  $(\text{CN})_2$ , however Cu is a necessary component of impregnated activated carbon. On the other hand,  $\text{Cr}^{6+}$  improves HCN capacity but mainly it has effect on  $(\text{CN})_2$  retention. It was concluded that it acts as a catalyst in oxamide formation [28]:



If the assumption of purely catalytic role of chromium is correct, the amount of hexavalent chromium in activated carbon should remain unchanged after exposure to HCN. On the other hand, Krishnan et al. [30] observed a significant decrease (over 90% of initial value) in  $\text{Cr}^{6+}$  upon HCN exposure. Chromium degradation as a result of water vapor present in the testing gas mixture was excluded in a separate test, where the samples were subjected to 80% relative humidity for 16 hours. It was found that ACS adsorbs water to a large extent, probably due to water molecules affinity to impregnating salts [36]. Still, exposing activated carbon to water vapor contributes to only 7% loss of  $\text{Cr}^{6+}$ . Thus purely catalytic role of hexavalent chromium in HCN neutralization on impregnated carbon is disputable.

For HCN removal impregnates other than toxic  $\text{Cr}^{6+}$  are currently investigated, such as in case of ASZM-TEDA carbons. For instance, a wide range of metal (Cu, manganese Mn, Ag, iron Fe, magnesium Mg, aluminum Al) organic salts (acetates, oxalates, tartrates, citrates, stearates) was tested for HCN adsorption on activated carbon cloth [37;38]. Cu and Ag were found to be most effective for HCN removal, whereas Al and Mg show very little or no effect of carbon adsorptive capacities. It was also found that organic salts contribute to improved adsorption of HCN in case of Cu and Ag salts in comparison with inorganic salts of those metals. However no comparison to the benchmark impregnated carbons, such as ASZM-TEDA was done.

Nickolov et al. [35] examined Zn as an alternative impregnate and proposed a reaction, where HCN is initially chemisorbed by Zn ions:



This inhibits  $(\text{CN})_2$  formation since the reaction product, unlike  $\text{Cu(CN)}_2$  is, regarded as relatively stable. Reaction with copper occurs once the Zn phase is consumed. It was also observed that neither of the phases is effective towards HCN adsorption separately. The HCN breakthrough time for carbon sample impregnated with both Cu and Zn was comparable to original ASC Whetlerite sample. Nevertheless, HCN conversion into non-toxic oxidation products was enhanced when some amount of chromium (Cr/Cu ratio of 0.3) was present in the sample.

Finally, Oliver et al. [39] investigated HCN retention on activated carbon produced from porous sulfonated styrene/divinylbenzene resin and impregnated solely with Cu. They analyzed the effluent gas and found that using  $\text{Cu}^0$  or  $\text{Cu}^{1+}$  only does not lead to  $(\text{CN})_2$  formation. The oxidation state of copper was confirmed by XPS analysis, and the following reactions leading to HCN removal on such carbons were suggested:



0 and +1 oxidation states of copper were attributed to the reduction of the impregnating compound during thermal treatment of activated carbon. The performance of such carbon was comparable to chromium-containing ASC whetlerite in terms of HCN breakthrough times. This was attributed to a high Cu loading (28%) in comparison to 7% in tested ASC whetlerite (Chemviron ®). Reaction (3.8), although probable, should be carefully considered since the evolution of H<sub>2</sub> was not confirmed during analysis of the effluent gas.

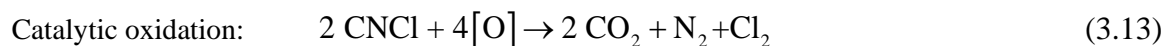
### 3.3.2 Cyanogen Chloride, CNCl

CNCl is only weakly bounded on activated carbon by means of physisorption, therefore chemisorption is necessary for efficient removal of CNCl from the air stream. Similarly to HCN process, CNCl filtration requires both Cu and Cr present as impregnates in the activated carbon. The exact mechanism of chemisorption is still under discussion. Again, it is disputed whether copper and chromium exists in form of pure compounds (oxides, carbonates) or in the form of complexes with NH<sub>3</sub> ligands. For instance, a compound CuCrO<sub>4(3.5)</sub>NH<sub>3(0.5)</sub>H<sub>2</sub>O was found by means of X-ray diffraction analysis of the solid residue after evaporating the impregnating solution [40]. However it cannot be excluded that the crystallization mechanism could be different on activated carbon surface.

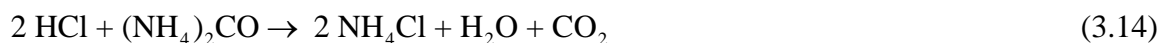
Generally it is accepted that the first step of CNCl destruction on impregnated activated carbon is hydrolysis supported by Cu and Cr ions [41]:



The cyanic acid HOCN, a non-volatile product precipitates on activated carbon surface. In reference [41] a decrease in the BET nitrogen surface area of activated carbon exposed to CNCl was ascribed to retention of HOCN and/or its trimer, cyanuric acid (CNOH)<sub>3</sub>. Other proposed mechanisms are given by reactions [42;43]



HCN formed in (3.12) can then undergo further oxidation (see reaction 3.2) and hydrolysis to oxamide, (CONH)<sub>2</sub>. HCl could eventually react with ammonium carbonate remaining from the whetlerizing solution:



Reaction (3.13) could explain the formation of CO<sub>2</sub> detectable during CNCl passing through whetlerite filters. Indeed, the molar ratio of CO<sub>2</sub> formed to CNCl retained was found experimentally to be 0.5, confirming the suggested mechanism [41]. Apart from that HCl formation in the reaction (3.10) can contribute to deactivation of activated carbon impregnates during the CNCl by destroying active Cu sites and reduction of Cr<sup>+6</sup> [10;43]:



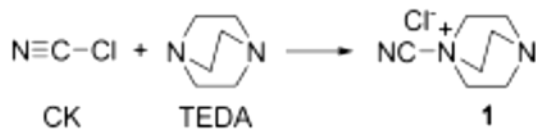
It was shown in [41] that the addition of HCl scavengers to whetlerite, such as alkali activated carbon or fine grist bone charcoal can improve the breakthrough times of CNCl.

The organic impregnates, such as TEDA or pyridine also play active role in CNCl capturing. In case of active carbon impregnated with Cu, Cr, Ag and pyridine the latest can bond ClCN via following reaction [10]:

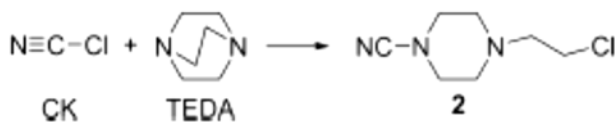


Interaction between CNCl and TEDA-impregnated carbon was studied by Mahle et al. [34], where three different mechanisms of CNCl–TEDA reactions proposed in the literature are mentioned (Figure 3.1). It was found that for BPL samples impregnated with both Cu and TEDA the cyanogen breakthrough time was significantly improved. However, when only TEDA was applied the breakthrough time was almost the same as for untreated BPL carbon. The authors suggest a synergic effect of TEDA and Cu impregnates, leading to formation of water soluble, complex compounds between these two in the presence of water.

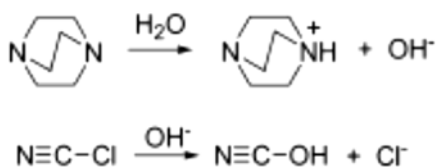




Scheme 1



Scheme 2



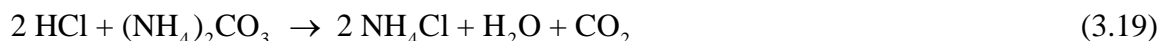
Scheme 3

Figure 3.1 Proposed reaction schemes between CK and TEDA molecules: scheme 1 – CK trapping by TEDA, scheme 2 – analogous von Braun reaction between CK and TEDA, scheme 3 – base production by TEDA in the presence of water and subsequent CK hydrolysis [34].

To summarize, multiple mechanisms have been described for adsorption and decomposition of cyanide compounds on impregnated activated carbon. Inconsistencies regarding specific reactions may be caused by different procedures of sample preparation and experimental conditions, especially during the impregnation step. Whereas the role of Cu ions seem to be quite well recognized, reactions involving Cr and other ions and substances used for impregnation, such as Ag, Zn and Mo seem to be less understood. Gradual poisoning of impregnated activated carbon can be explained partially by exhaustion of the active sites such as Cu and Cr on its surface during irreversible reactions and formation of precipitate layers which limit the surface available for adsorption.

### 3.3.3 Phosgene, $\text{COCl}_2$

The mechanism of phosgene removal by whetlerite was described briefly in reference [41]. In principle, it is analogical to cyanogen chloride removal and can be given by the following reactions:



As in  $\text{CNCl}$  case, the adsorption on active centers (Cu and Cr) is followed by hydrolysis and formation of chemisorbed products, such as HCl and  $\text{NH}_4\text{Cl}$ .

### 3.3.4 Carbon monoxide, CO

CO is a nonpolar, relatively inert and small molecule which adsorbs on activated carbon only in minute amounts. Since the adsorption of CO on activated carbon is poor it remains a subject of academic research rather than a process of practical relevance, and is mostly devoted to separation of CO from mixtures with other industrial gases [44;45]. To the best of our knowledge there are no impregnates which would increase the adsorption capacity of carbon towards CO sufficiently for real-world applications. Usually respirators effective against CO use a catalyst that converts CO into CO<sub>2</sub>, such as *hopcalite* (a mixture of manganese and copper oxides). In this case CO is oxidized into CO<sub>2</sub> in the presence of oxygen from air, and the reaction cannot proceed if there is insufficient amount of oxygen in air. In such case a SCBA (Self-Contained Breathing Apparatus) must be used. Carbon monoxide thus remains one of the poisonous gases that cannot be eliminated directly from the air stream by adsorption on activated carbon.

### 3.3.5 Ammonia, NH<sub>3</sub>

Ammonia is a polar molecule with basic properties; therefore one can expect that the acidic sites of activated carbon, such as carboxyl groups, are crucial in the adsorption process. In reference [22] two adsorption models were postulated. In the first case ammonia molecules bind to proton-donating surface group forming NH<sub>4</sub><sup>+</sup> ions; in the second, the presence of electronegative oxygen-surface groups leads to a decreased electronic density on the graphene layers, allowing for ammonia adsorption due to electrostatic interactions with ammonia lone electron pair [22;46]. Apart from that, microstructural features such as volume and size of the micropores are important [46]. In addition, moisture plays a significant role for increasing the adsorption capacity towards ammonia [28], although some studies found in literature proved otherwise. For instance, in [22] it was found that for high concentrations of acidic oxygen-surface groups, moisture has little effect on ammonia adsorption. The authors concluded that the increased NH<sub>3</sub> adsorption observed in case of pre-humidified carbons is due to ammonia dissolution in adsorbed water.

To increase the adsorption capacity towards ammonia, different techniques such as impregnation with metal ions (zinc, Zn) or pre-oxidation are used. An example here may be a commercially available carbon from Cabot Norit ® company for ammonia and other alkaline gases adsorption: Norit® RZN1 (impregnated with ZnSO<sub>4</sub>).

### 3.3.6 Chlorine, Cl<sub>2</sub>

Chlorine is a strongly oxidizing gas which was first used as a chemical warfare agent during WWI at Ypres battle by the German Army. Today it has multiple applications; apart from being used as a raw material in the chemical industry, chlorine compounds are also employed as water disinfectants, bleaching agents etc. Disinfection of water with chlorine or its compounds leaves aftertaste and is considered to have adverse health effects on the consumers, therefore activated carbon filters are often used for water purification after chlorine treatment. For this reason, a majority of literature studies available on the subject of chlorine interaction and its adsorption on activated carbon is focused on water solutions. In water environment, chlorine molecule reacts with water yielding hypochlorous acid HOCl [47]:



One can expect similar reactions occurring in the presence of water adsorbed on the activated carbon surface, where the hydrolysis of chlorine molecule would be succeeded by adsorption of HCl on active sites such as copper ions [28]:



### 3.3.7 Hydrogen sulfide, H<sub>2</sub>S

In case of non-impregnated activated carbon the effective removal of H<sub>2</sub>S consists of adsorption and oxidation of H<sub>2</sub>S molecules to elemental sulfur and sulfur oxides, and requires the presence of pre-adsorbed water and oxygen (pre-adsorbed or from the air stream). In the absence of water film the adsorption capacity is very small and the removal process is mainly due to physical adsorption in micropores. Oxygen is present on carbon surface in the form of different surface groups, however its amount was found to be insufficient for efficient oxidation of H<sub>2</sub>S. Nevertheless, oxygen-containing groups are mostly acidic and contribute to hydrophilicity of the surface; therefore their presence is beneficial for the water-film formation. On the other hand an increase in oxygen-containing surface groups contributes to low surface pH and in turn weakens dissociation process of weak acid formed from dissolved H<sub>2</sub>S. This suppresses formation of HS<sup>-</sup> ions. Moreover, when the water content on the surface becomes too high, water molecules condense in micropores limiting the available adsorption sites [48].

Several mechanisms for H<sub>2</sub>S adsorption on activated carbon can be found in literature, depending on the surface acidity and oxygen presence in the air stream [48, 49]. On activated carbon surface with acidic properties the proposed process of H<sub>2</sub>S removal assumes that H<sub>2</sub>S from a gaseous phase first undergoes hydrolysis with water present on activated carbon surface. The adsorbed HS<sup>-</sup> ions become oxidized by the adsorbed oxygen to elemental sulfur, which reacts with oxygen (from surface and air stream) forming sulfur oxides. These oxides can undergo further reactions, which yield elemental sulfur as the final product. The whole process is described by the following reactions [49]:



where S\* is dissociated sulfur adsorbed on activated carbon, C<sub>f</sub> is a free adsorption site on carbon, S<sub>x</sub> is elemental sulfur adsorbed on activated carbon.

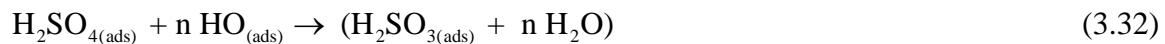
Since simple washing with water restores adsorption capacity of the non-impregnated carbons, their use is economically beneficial. However it is argued that the adsorption capacity of those carbons is too low for practical applications [50]. For H<sub>2</sub>S removal caustic-impregnated and potassium salt-impregnated activated carbons are used [49]. Commercial carbons for H<sub>2</sub>S

removal are impregnated with KOH and NaOH, and high pH of the surface causes an increase in HS<sup>-</sup> concentration and more efficient removal of H<sub>2</sub>S from the air stream. Other impregnation compounds include KI and KMnO<sub>4</sub> for improved H<sub>2</sub>S oxidation [51]. It is worth mentioning that the adsorption is accompanied by heat release which makes those carbon beds prone to self-ignition [51].

### 3.3.8 Nitrogen oxides, NO<sub>x</sub> and sulfur oxide, SO<sub>2</sub>

NO<sub>x</sub> and SO<sub>2</sub> are acidic gases used for industrial syntheses, such as production of nitric acid, HNO<sub>3</sub> and sulfuric acid, H<sub>2</sub>SO<sub>4</sub>. Apart from that they often receive attention because they appear in the exhaust gases and contribute to environmental pollution (smog, acid rains). Since both SO<sub>2</sub> and NO<sub>x</sub> are present in the flue gases, their simultaneous adsorption on activated carbon is often studied.

SO<sub>2</sub> is formed during combustion of sulfur or sulfur-containing compounds. In presence of humidity and oxygen from air SO<sub>2</sub> undergoes oxidation on the surface of activated carbon, which acts as a catalyst [52]:



NO<sub>x</sub> is a common term for different nitrogen oxides: N<sub>2</sub>O, NO and NO<sub>2</sub>. Those gaseous compounds can be formed at high temperatures from N<sub>2</sub> and O<sub>2</sub> present in air. NO can undergo oxidation to NO<sub>2</sub>, or in case of adsorption in the micropores, NO molecules can react forming dimer N<sub>2</sub>O<sub>2</sub> [53].

In principle, activated carbon is able to adsorb certain amounts of nitrogen oxides on its surface. The adsorption process and its mechanisms are a subject of numerous scientific investigations, and some part of the research is oriented towards developing filters for filtration of car fumes or industrial gases at elevated temperatures. It has been shown that under such conditions catalytic processes occur more efficiently. Apart from carbon surface properties (oxygen-containing groups) temperature, moisture and oxygen content in the gas mixture are the most important factors affecting the adsorption capacity. In addition, the impregnation with potassium salts, such as potassium bicarbonate has been efficient for acidic gases removal [49].

### 3.4 Humidity

Activated carbon in filters that are exposed to air will also be exposed to water vapor due to the presence of humidity. The carbon can either be pre-wetted from storage in humid conditions, or get in contact with water from air flow containing water vapor. Both pre-wetting and humid air flow can influence the filter capacity.

Initially water will be adsorbed to specific adsorption sites by hydrogen bonding. For pure carbons these sites will be chemisorbed oxygen molecules. For contaminated carbon containing hetero atoms, the sites can be other atoms creating polar sites [16]. Freeman et al. [36] studied the mechanisms of water vapor adsorption on BPL grade activated carbon and ASC whetlerite impregnated carbon. For both types, the adsorption isotherms were non-linear. At relative low pressures, the amount adsorbed was relatively small at both carbon types. At relative pressures between 0.4 and 0.6 the adsorption rate increased rapidly. This was explained with regard to two distinct adsorption sites. At first, hydrogen bonds are formed between the water molecules and surface oxides present in the micropores. Secondly, the already adsorbed water act as adsorption sites for new water molecules, also by the formation of hydrogen bonds. The more secondary adsorption sites available, the faster adsorption, and hence the rapid increase at higher pressures. Further, as more molecules adsorb in the pores, the water vapor can condensate into liquid filling the pores. They also found that for low pressures the ASC whetlerite carbon adsorbed more water than the BPL grade carbon. This was most likely due to affinity between the impregnating salts at the ASC whetlerite carbon and the water vapor. At higher pressures the adsorption capacity is determined by available pore volume. The BPL carbon then adsorbs more, since the pores in ASC whetlerite are partly filled with impregnates.

In case of organic vapors it is expected that the adsorption capacity will decrease if the carbon is pre-wetted. This can be explained by water vapor and organic vapor competing about the same adsorption sites, or by condensed water blocking the micropores. Low humidity levels in the airstream are found to only give a small reduction in the adsorption capacity. As the relative humidity in the airflow rises above 50% the adsorption capacity for organic vapor decreases considerably, with the most impact on low organic vapor concentrations [54-56].

For inorganic vapors the consequences of humidity seem to vary more. For systems with phosgene or chlorine adsorbing on the activated carbon Chemviron ASC-TEDA, the breakthrough times were found to remain unchanged both for pre-wetted carbon and for airflows with relative humidity 0-70% [27;57]. On the other hand, for ammonia the adsorption capacity and breakthrough time was unchanged with humid airflow, but increased when the carbon was pre-wetted. A possible explanation to this could be hydrolysis of ammonia molecule by pre-adsorbed water [26]. The breakthrough time for sulfur oxide also rises for pre-wetted activated carbon used in Swiss Army NBC canister [58]. This shows that water can even be a reactant in the chemical process of adsorbing the toxic agent, resulting in improved filter performance.

## 4 Adsorption isotherms

When a gas molecule comes into contact with the surface of a solid it may become immobilized on this surface (adsorption), and after a while return to the gas phase (desorption). The adsorbed molecules form a single layer on the surface (a monolayer) or build up multiple layers if the attraction forces between them are strong. In case of chemical adsorption it is convenient to assume that the adsorbed molecules form a monolayer on the surface, as they bond with the active sites, and that they do not interact with each other. At first the adsorption rate would be high due to a large part of free sites on the surface. As the surface is more and more covered by adsorbed molecules the adsorption rate decreases. On the other hand, desorption rate increases as more molecules can desorb. When the rate of adsorption is equal to the rate of desorption the equilibrium point is reached [59].

The equilibrium amount adsorbed can be written as a function  $f$  of temperature ( $T$ ) and pressure ( $p$ )

$$\frac{x}{m} = f(p, T) \quad (4.1)$$

where  $x/m$  is the amount adsorbed per unit mass of the adsorbent.

If the temperature is kept constant, the equilibrium depends on  $p$  only and can be described as an adsorption isotherm  $f(p)$ . Often the result is expressed in terms of  $p/p_s$ , where  $p_s$  is the saturation vapor pressure. The steeper the isotherms are, the more effective is adsorption on the surface [59].

By studying the isotherms, useful information about the adsorption process, the adsorbent and the adsorbate can be retrieved. This information can help to determine the surface area of the adsorbent, the volume and size distribution of pores, the heat of adsorption, and the capacity of a gas or vapor at a given surface [60].

On the other hand, it is impossible to derive one common equation to fit all adsorbate/adsorbent systems. At low pressures all adsorption isotherms tend to be linear, hence the adsorbed amount  $x$  is proportional to the pressure  $p$ . At high pressures this is no longer the case. Five main categories of adsorption isotherm, shown in Figure 4.1, have been suggested by Brunauer et al. [61]. The categories with the corresponding adsorbate/adsorbent systems are given in Table 4.1.

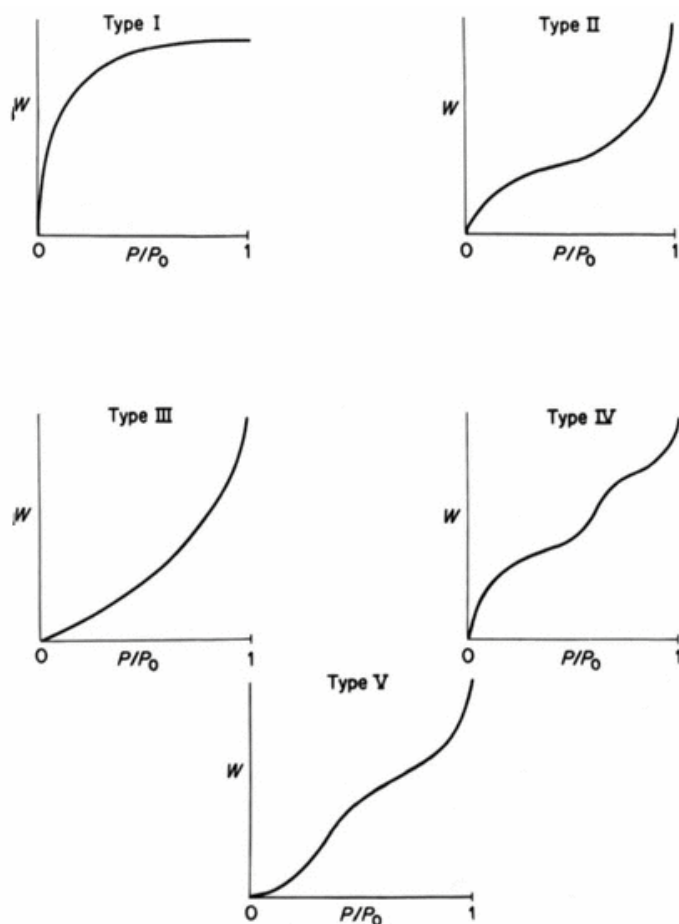


Figure 4.1 The five isotherms classifications used by Brunauer et al. Here  $W$  is weight adsorbed,  $P$  is the adsorbate equilibrium pressure, and  $P_0$  is the adsorbate saturated equilibrium vapor pressure;  $P/P_0$  is the relative pressure [62].

Table 4.1 The five Brunauer types of adsorption isotherms and corresponding adsorbate/adsorbent systems [60].

| Isotherm               | System validity   |
|------------------------|---|
| <b>Type I</b>          | Chemisorption and physical adsorption on highly porous surfaces, such as activated carbon. As the pressure increases, the adsorbed amount reaches a finite value.   |
| <b>Type II</b>         | Adsorption on open surfaces or in micropores and open surfaces with multilayer formation.   |
| <b>Type III and IV</b> | Systems where already adsorbed molecules increase the adsorption of other molecules, i.e. adsorption of water vapor on charcoals or activated carbon. The adsorbate-adsorbate interactions seem to be more important than the adsorbate-adsorbent interactions. |
| <b>Type V</b>          | Solids with pores in mesopore range   |

In addition to the classification of adsorption isotherms, several attempts have been made to find mathematical expressions to derive adsorption isotherms. Among the most common adsorption

isotherms are the Langmuir equation [63], the Freundlich equation [64], the BET (Brunauer, Emmett and Teller) equation [61], and the Dubinin-Radushkevich equations [65]. In the report at hand more details on the Langmuir isotherm and the Dubinin equation will be given. Langmuir equation is important for both chemi- and physisorption, whereas Dubinin-Radushkevich equation is widely used to analyse physical adsorption on porous materials containing micropores, such as activated carbon [60]. More information about different isotherms can be found in e.g. [60, 66].

#### 4.1 The Langmuir isotherm

The Langmuir equation is the first theoretically developed adsorption isotherm, and is of type I. The isotherm describes monolayer adsorption on energetically homogenous surfaces and no interactions between adsorbed molecules. These conditions are very rare, but the isotherm is still important for expressing dynamic adsorption equilibrium, and is important for analyzing both chemi- and physisorption [60]. The isotherm is written as

$$\frac{p}{V} = \frac{1}{V_m b} + \frac{p}{V_m} \quad (4.2)$$

where  $p$  is the pressure of the adsorbate gas,  $V$  the volume adsorbed at pressure  $p$ , and  $V_m$  the volume adsorbed at infinite pressure,  $b$  is the constant

$$b = \frac{\alpha}{\xi \sqrt{2\pi k_B T}} \quad (4.3)$$

where  $\alpha$  is the fraction of molecules bonded to the surface,  $\xi$  epsilon the evaporation rate from a fully covered surface,  $k_B$  the Boltzmann constant and  $T$  the temperature.

#### 4.2 Dubinin-Radushkevich isotherm

Dubinin-Radushkevich isotherm model is based on the potential theory of physical adsorption, introduced in 1914 by Polanyi [67]. In this theory the driving force for physical adsorption is the adsorption potential<sup>2</sup>. The amount  $q$  that is adsorbed under equilibrium conditions can therefore be described as a function of the adsorption potential  $\varepsilon = \text{Gibbs free energy } (\Delta G)$ .

$$q = f(\varepsilon) = f(\Delta G) = f[RT \ln(p_{sat} / p)] \quad (4.4)$$

where  $R$  is the universal gas constant,  $T$  the absolute temperature,  $p_{sat}$  the saturated vapor pressure of the bulk material, and  $p$  the partial equilibrium pressure of the adsorbate.

Polanyi found that for fixed adsorption volumes (volume of condensed like adsorbate), the adsorption potentials,  $\varepsilon$ , were correlated by the affinity constant  $\beta$  [68, 69]:

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<sup>2</sup> Adsorption potential is the work performed by the adsorption forces in bringing a molecule from gas to bond to a surface.



$$\frac{\varepsilon}{\beta} = \frac{\varepsilon_{ref}}{\beta_{ref}} \quad (4.5)$$

By convention, benzene  $C_6H_6$  is chosen as the reference compound for organic compounds and by definition  $\beta(C_6H_6) = 1$ .

#### 4.2.1 The Dubinin-Raduskevich equation for potential theory

In porous material physical adsorption will happen in the micropores, and a fixed volume  $W_0$  will be filled to a capacity  $W_e$  for any gases at a given relationship of  $\varepsilon/\beta$ . The amount  $W$  adsorbed can then be written as the Dubinin-Raduskevich (DR) equation [70]:

$$W_e = W_0 \exp\left[-(\varepsilon/\beta E_0)^2\right] \quad (4.6)$$

This is a Gaussian function where  $W_0$  is the maximum volume filled, and  $E_0$  is the characteristic adsorption energy for the reference vapor.  $E = \beta E_0$  is then the adsorption energy for another chemical [71]. By inserting Eq. (4.4) into Eq. (4.6), the DR equation can be written as

$$W_e = W_0 \exp\left[-\left(\frac{RT}{\beta E_0}\right)^2 \ln(p_{sat}/p)^2\right] \quad (4.7)$$

#### 4.2.2 Methods of estimating the affinity coefficient $\beta$

The affinity coefficient  $\beta$  is adsorbent specific, and knowing its value is crucial for determining parameters  $E_0$  and  $W_0$  from equation (4.7). The following sections will be therefore devoted to estimations of  $\beta$  most commonly used in the literature. Wood et al. [71;72] summarized different affinity coefficient values for different adsorbates on various activated carbons. Table 4.2 shows a choice of  $\beta$  values for different TICs, together with their values compared to a reference compound. Some affinity coefficients were found directly, whereas others were estimated by fitting the isotherm and capacity data to the DR equation. High  $\beta$  values are most likely due to reactions with surface oxides or impurities.

Table 4.2 Values for affinity coefficients found in literature.

| Compound                             | Activated Carbon | $\beta E_0$ (kJ/mol) | Experimental $\beta$ vs. reference | Molar polarizability | Citation |
|--------------------------------------|------------------|----------------------|------------------------------------|----------------------|----------|
| Sulfur dioxide (SO <sub>2</sub> )    | CAL AC           | 12.64                | 0.69 <sup>a</sup>                  | 10.090               | [73]     |
| Ammonia(NH <sub>3</sub> )            | CAL AC           | 17.28                | 0.95 <sup>a</sup>                  | 5.460                | [73]     |
| Ammonia                              | BPL              | 7.28                 | 0.31 <sup>b</sup>                  | 5.460                | [71]     |
| Phosgene (COCl <sub>2</sub> )        | BPL              | 24.1                 | 0.91 <sup>c</sup>                  | 18.391               | [74]     |
| Hydrogen cyanide (HCN)               | BPL              | 10.8                 | 0.41 <sup>c</sup>                  | 6.37                 | [46]     |
| Ammonia                              | BPL              | 6.8-10.2             | 0.38 <sup>d</sup>                  | 5.460                | [46]     |
| Hydrogen sulphide (H <sub>2</sub> S) | BPL              | 9.24-13.46           | 0.50 <sup>d</sup>                  | 9.75                 | [46]     |
| Isopropanol                          |                  | $\beta^2=0.56$       |                                    | 17.623               | [75]     |

<sup>a</sup> Compared to benzene, C<sub>6</sub>H<sub>6</sub>,  $\beta_{C_6H_6}E_0 = 18.23$ , [73]

<sup>b</sup> Compared to hexane, C<sub>6</sub>H<sub>14</sub>,  $\beta_{C_6H_{14}}E_0 = 23.59$ .

<sup>c</sup> Compared to chloroform, CHCl<sub>3</sub>,  $\beta_{CHCl_3}E_0 = 26.5$ , [74]

<sup>d</sup> Compared to carbon tetrachloride, CCl<sub>4</sub>,  $\beta_{CCl_4}E_0 = 26.5$  [76]

### Affinity coefficients estimated from molecular polarization

Wood et al. [71;72] further studied if  $\beta$  was correlated to other molecular parameters, and hence could be estimated directly from these. It was found that the  $\beta$  values were strongly correlated to molar volume, molecular parachor (an empirical constant derived from molecular volume and surface tension of a liquid) and molar polarization. Since molar polarization,  $P_e$  can be relatively easily calculated from molecular parameters, and is independent of temperature, pressure and density, it was seen as the preferred correlation to use [77]. The affinity coefficient could hence be approximated from the following relation:

$$\beta^2 = \left( \frac{P_e}{P_{e \text{ reference}}} \right)^{1.8} \quad (4.8)$$

### Affinity coefficients obtained from statistical approach

Another approach for estimating the affinity coefficient  $\beta$ , was proposed by Wu et al. [78]. To study adsorption on Norit R1 activated carbon, the authors used Multivariate Data Analysis with Principal Component Analysis (PCA) and statistical design [79-81] to select a set of 8 volatile organic compounds (isopropylamine, heptane, dichloromethane, 2-chloro-methylpropane, 2-butanone, 1-chloropentane, acetonitrile, and benzene), covering five classes of compounds.

Experimental affinity coefficients were then determined from adsorption isotherms. Partial least square projection (PLS) was thereafter used to correlate 45 physico-chemical properties to the measured affinity coefficients. This led to the model

$$\beta = -0.0731 + 0.00182 \cdot M_w + 0.00418 \cdot volume - 0.0132 \cdot E_{inter} \quad (4.9)$$

where  $M_w$  is the molar molecular weight,  $volume$  is Van der Waals volume, and  $E_{inter}$  is the energy of the Van der Waals interaction with the graphite model surface. All three variables can be calculated from molecular structure. More information about calculation of different variables can be found in [82].

## 5 Prediction of the activated carbon breakthrough time

The carbon life time is determined by the breakthrough time - that is how long it takes to reach a certain vapor concentration in the airstream that passed through the filter. This is one of the most valuable parameters characterizing the activated carbon filter from an applicational point of view. In principle the breakthrough time can be found by laboratory experiments. By sending a certain concentration of vapors in airstream through a bed of activated carbon, the inlet and outlet concentration can be measured. The carbon is saturated when the outlet concentration reaches a certain level. Such breakthrough curves in addition to measuring breakthrough times for certain vapors be used to describe adsorbent performance, for predicting behavior for other concentrations, flows etc.

However, in order to avoid testing all activated carbons towards all possible chemicals, it is desirable to use numerical methods to calculate and predict breakthrough times. The breakthrough time depends on adsorption kinetics, bed design, physical and chemical characteristics, pore size distribution, polarity, nature, and concentration of chemical groups on the surface. To predict breakthrough times, all this should be included adding to complexity of the problem [60].

A widely used model to predict breakthrough times on dry activated carbon is the Wheeler-Jonas equation. Originally this equation was developed for organic compounds that are physically adsorbed [83], but lately it is found to be valid also for systems of chemisorbed inorganic compounds [26;27;54;84;85].

The model consist of two terms, one considering the capacity of the system, the other one taking into account the kinetic effect

$$t_b = \boxed{\text{capacity term}} - \boxed{\text{loss due to finite removal kinetics}} = \frac{W_e M}{C_0 Q} - \frac{W_e \rho_b}{k_v C_{in}} \ln \left( \frac{C_{in} - C_{out}}{C_{out}} \right) \quad (4.10)$$

where

- $t_b$  - time (min) to reach the breakthrough fraction  $b = C_{out} / C_{in}$
- $C_{in}$  - bed inlet concentration

- $C_{out}$  - chosen breakthrough concentration  
 $M$  - weight of the carbon bed (g)  
 $W_e$  - equilibrium adsorption capacity for a given vapor, mass of adsorbed vapor (g/g<sub>carbon</sub>)  
 $Q$  - volumetric flow rate (cm<sup>3</sup>/min)  
 $\rho_b$  - bulk density of the carbon bed (g<sub>carbon</sub>/cm<sup>3</sup>)  
 $k_v$  - overall adsorption rate coefficient (min<sup>-1</sup>)

$C_{in}$ , and  $Q$  are environmental conditions,  $M$  and  $\rho_b$  depend on the type of activated carbon, and  $C_{out}$  is a chosen value.  $W_e$  and  $k_v$  are hence the only parameters that need to be estimated.

### 5.1 Validation methods for applicability of the Wheeler-Jonas equation

This section will review four common methods to test whether the Wheeler-Jonas equation can be applied to a chosen adsorbate-adsorbent system.

#### Breakthrough time versus relative output concentration

In the first method the breakthrough time  $t_b$  for a single vapor is plotted versus  $\ln \frac{C_{in} - C_{out}}{C_{out}}$ . For very low output concentrations the graph should be a straight line of the form  $t_b = a - bX$  where  $X = \ln \frac{C_{in} - C_{out}}{C_{out}}$

$$t_b = \frac{W_e M}{C_{in} Q} - \frac{W_e \rho_b}{k_v C_{in}} \ln \frac{C_{in} - C_{out}}{C_{out}} \quad (4.11)$$

#### Breakthrough time versus bed depth

In the second method the bed depth  $L$  is the varying parameter, giving the equation

$$t_b = \frac{W_e A_{bed} \rho_b}{C_{in} Q} L - \frac{W_e \rho_b}{k_v C_{in}} \ln \left( \frac{C_{in} - C_{out}}{C_{out}} \right) \quad (4.12)$$

which also yields a straight line, where  $X = L$ . The mass  $M$  is found from  $M = A_{bed} L \rho_{bed}$ .

#### Breakthrough time versus contact time

A third method includes the contact time,  $t_c$ , between the airflow and the carbon bed. The contact time is defined as the time it would take for a gas to pass through the bed volume if the bed was empty.

$$t_C = \frac{V_{bed} (cm^3)}{Q_{air} (cm^3 / s)} = \frac{A_{bed} (cm^2) L (cm)}{A_{bed} (cm^2) v_L (cm / s)} = \frac{L (cm)}{v_L (cm / s)} \quad (4.13)$$

where  $v_L$  is the superficial velocity. Since the weight of the carbon bed  $M = V_{bed} \rho_b$  it follows that  $M = (t_C \cdot Q_{air}) \cdot \rho_b$ . From this, the breakthrough time can be written as

$$t_b = \frac{W_e \rho_b}{C_{in}} \left[ \frac{t_C}{0.06} - \frac{1}{k_v} \cdot \ln \frac{C_{in} - C_{out}}{C_{in}} \right] \quad (4.13)$$

By varying the contact time  $t_C$  the above equation should also yield a straight line.

### Output concentration versus time

The fourth method comes from combining the Wheeler-Jones equation and the Yoon/Nelson [86] model for exit concentration:

$$\ln \left( \frac{C_{out}}{C_0 - C_{out}} \right) = \frac{k_v C_{in}}{\rho_b W_e} t - k_v \frac{L}{v_L} \quad (4.14)$$

The output concentration  $\ln \left( \frac{C_{out}}{C_0 - C_{out}} \right)$  could hence be plotted as a function versus time  $t$ .

By using any of the four methods listed here, the adsorption capacity  $W_e$  and the rate coefficient  $k_v$  can be found from intercepts with the vertical axis and slopes (if the Wheeler-Jonas equation is fulfilled). All methods should give the same values. However, there might be problems finding how many points should be included to find the best fit, and high uncertainties in the estimates values can follow [72;84;87,88]. Nevertheless, to finally prove the validness of the Wheeler-Jonas equation, the model should be tested for predicative use.

## 5.2 Estimated adsorption capacities and adsorption rate coefficients for organic vapors

For organic vapors, several studies on finding adsorption capacity and rate coefficients have been reported. By investigating the findings and performance of these studies, one can obtain suggestions on how systems with adsorption of inorganic compounds on active coal can be studied.

### Adsorption capacity

The adsorption capacity  $W_e$  for organic compounds on active coal is normally found from an isotherm equation. For organic compounds the Dubinin-Radushkevich equation is most often used and the parameter that must be estimated is  $\beta$ . When estimating  $W_e$  it is noteworthy that even small deviations from real values will produce large errors in breakthrough time calculated

by the Wheeler-Jonas equation. It is therefore advisable to rather underestimate than overestimate  $W_e$ , to avoid predicting too long breakthrough times [82].

### Adsorption rate coefficients

Below follows a short overview on studies performed to find the adsorption rate coefficient  $k_v$ . Wu et al. [82] have shown that the influence of the predicted  $k_v$  values on the estimated breakthrough times is most important for low outlet concentrations ( $C_{out} / C_{in} < 0.1$ ).

Jonas et al. [82;89] studied benzene adsorption on Pittsburgh activated carbon (12-30 mesh BPL grade). They presented a model based on the assumption that the mass transfer from the bulk to the external carbon surface is the rate controlling step. By using the Wheeler-Jonas equation, and plot  $t_b$  versus varying bed weight at fixed  $C_{out} / C_{in}$ ,  $k_v$  was found from the slope and intercept of the regression line. At 1% breakthrough fraction,  $k_v$  could be expressed as follows:

$$k_v = 111.6 \sqrt{\frac{v_L}{d_p^3}} \quad (4.16)$$

where  $v_L$  is the linear velocity (cm/s) and  $d_p$  is the mean diameter (cm) of the activated carbon particles. The adsorption rate is in this model independent of the properties of the organic vapor.

Another approach based on 679 different experimental breakthrough curves for 147 compounds (27 hydrocarbons and fluorocarbons on dry whetlerite (ASC) carbon was proposed by Wood and Stampfer in 1993 [59;81;82]. The rate coefficient was calculated from the difference between stoichiometric time (obtained from integration of whole breakthrough curve),  $t_{sto}$ , and measured breakthrough times at outlet concentration of 1 and 10%. The reciprocal value of  $k_v$  could then be found from the rearranged Wheeler-Jones equation:

$$\frac{1}{k_v} = \frac{W(t_{sto} - t_b)}{\rho_B Q t_{sto} \ln(C_0 - C_{out}) / C_{out}} \quad (4.17)$$

The reciprocals were found to be independent of vapor concentration. The reciprocals were then averaged for each compound, and found to be correlated to molar polarization. From this they suggested the equation:

$$k_v = \left\{ \left[ \left( \frac{1}{v_L} \right) + 0.027 \right] \cdot \left[ 0.000825 + \frac{0.063 - 0.0058 \ln \left( \frac{C_{in} - C_{out}}{C_{out}} \right)}{P_e} \right] \right\}^{-1} \quad (4.18)$$

Lodewyckx and Vasant proposed in 2000 a third model to estimate  $k_v$  [80]:

$$k_v = A_f (\text{min}^{-1}) f_1\{v_L\} f_2\{d_p\} f_3\{\beta\} \quad (4.19)$$

where

- $A_f$  - fitting parameter (including transfer from sec to min)
- $v_L$  - linear velocity (cm/sec)
- $d_p$  - mean diameter of activated carbon particles (cm)
- $\beta$  - similarity constant of the DR equation
- $f_1, f_2, f_3$  - fitting functions

By calculating  $W_e$  from the inverse DR-equation [72] and measuring the breakthrough time experimentally,  $k_v$  was calculated from the Wheeler-Jonas equation, Eq.(4.10). In total they studied 55 breakthrough tests with 12 adsorbates on 7 different activated carbons.  $C_{out} / C_{in}$  was in all cases 0.1%. The correlation between  $k_v$  and flow rate,  $v_L$ , were found by measuring the breakthrough times at different flow rates. The mean diameter  $d_p$  from the activated carbon particles were estimated by spherical model and the  $\beta$  values were mostly calculated from molar polarization.  $A_f$  was found by plotting all available data. No correlation between bed depth, carbon type, contact time or inlet concentration were found. The influence by temperature could not be tested by their experimental set up. In total this gave the equation:

$$k_v = \frac{48\beta^{0.33}v_L^{0.75}}{d_p^{0.75}} \quad (4.20)$$

By including more experiments the equation was expanded by Wood et al. [81], yielding the following:

$$k_v = 800 \frac{\beta^{0.33}v_L^{0.75}}{d_p^{1.5}} \sqrt{\frac{W_e}{M_w}} \quad (4.21)$$

where  $W_e$  is the adsorption equilibrium capacity, and  $M_w$  (g/mole) the molecular weight of the vapor.

All the above models are based on experimental results and the estimated rate coefficients are hence very much influenced by experimental errors. Wu et al. presented in 2005 a method with less influence from experimental errors [90]. By using Multivariate Data Analysis<sup>3</sup> on eight representative volatile organic compounds (VOC) and three different dry carbon surfaces they found a model to predict  $k_v$ .

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<sup>3</sup> Wu et al. used Principal Component Analysis on 68 common organic chemicals to find 45 parameters describing them. Fractional factorial design were then used to select eight of the compounds for further testing.

$$k_v = 3920 + 165.2v_L - 2060PS(70\%) - 32.2Diel \quad (4.22)$$

where  $v_L$  is the linear flow velocity ( $\text{cm}^3/\text{s}$ ),  $PS(70\%)$  is particle size parameter (mm) corresponding to 70% on the cumulative size distribution curve, and  $Diel$  is a Dielectric constant. The model is valid for those compounds and carbon surfaces tested, at dry conditions and 20% breakthrough fraction [79].

### 5.2.1 Testing the Wheeler-Jonas equation for inorganic compounds adsorbing on activated carbon

Even though the Wheeler-Jonas equation was originally developed for organic gases adsorbing on activated carbon, it would be very desirable if the Wheeler-Jonas equation could be used for inorganic gases as well. Reported studies have in fact found that the Wheeler-Jonas can be applied for a wide range of inorganic substances, such as chlorine ( $\text{Cl}_2$ ), ammonia ( $\text{NH}_3$ ), phosgene ( $\text{COCl}_2$ ), sulfur dioxide ( $\text{SO}_2$ ), cyanogen chloride ( $\text{CNCl}_2$ ) and hydrogen cyanide ( $\text{HCN}$ ) [26;27;57;84;85]. For inorganic vapors the parameters for carbon-gas interaction are however more complicated than for organic vapors due to specific chemical bonds. Theoretically methods to estimate adsorption capacities and adsorption rates on a general basis are at time not found. The Wheeler-Jonas equation are for now, hence seen as most useful for extrapolation of experimental data. More work must be done to find theoretical estimates also for such systems. Short summaries of some specific studies on adsorption of inorganic vapors on activated carbon are given below.

#### **Ammonia, $\text{NH}_3$**

Verhoeven et al. investigated the validity of the Wheeler-Jonas equation on system with adsorption of ammonia on activated carbon [26]. By plotting the breakthrough time versus  $\ln[(C_{in} - C_{out}) / C_{out}]$  for varying outlet concentration they found a straight line, indicating that the Wheeler-Jonas equation was fulfilled. The adsorption capacity values,  $W_e$ , (and hence the breakthrough times) were found to be 10-100 times smaller than published values for organic vapors. Values calculated by using Eq. (4.20) with  $\beta$  value of 0.28 [72] compared to showed good agreement with measured  $k_v$  values. The magnitude of the  $k_v$  values was also at the same magnitude as for physisorption, and showed that rate controlling step is surface diffusion similar to the case physisorption.



## Cyanogen chloride, CNCl

The adsorption of cyanogen chloride(80% RH) on Chemviron ASC/T GAC was studied by Osmond et.al [85]. They found the time for 1% breakthrough concentration could be estimated by

$$t_{1\%} = 1.36 * 10^6 \frac{1}{C_{in}^{0.98} v_L^{0.9}} (d_p - 0.4v_L^{0.5}) \quad (4.22)$$

A rearranged version of Wheeler-Jonas at 1 % equation can be written

$$t_{1\%} = W_e \rho \frac{1}{C_{in} v_{L B}} \left[ d_p - \frac{v_L}{k_v} \ln(100) \right] \quad (4.23)$$

By inserting  $k_v = v_L^{0.5}$  into Eq.(4.22), it becomes similar to Eq.(4.23), suggesting that the Wheeler-Jonas equation is also suited to predict the adsorption of CNCl on activated carbon.

## Various gases: CNCl, H<sub>2</sub>S, SO<sub>2</sub>, Cl<sub>2</sub>, COCl<sub>2</sub> and NH<sub>3</sub>

Lodewyck et al. [84] have studied the adsorption of CNCl, H<sub>2</sub>S, SO<sub>2</sub>, Cl<sub>2</sub>, COCl<sub>2</sub> and NH<sub>3</sub> on ACS. The Wheeler-Jonas equation is found to be valid for all these carbon-gas systems. The adsorption capacities seemed to have a separate value for all carbon-gas couple and could not be estimated from the Dubinin-Radushkevich equation. For some of the gases at very low concentrations, it was observed that the value of  $W_e$  varied. This could indicate that the adsorption mechanism depends on the inlet concentration of the gas. No common equation for the adsorption rate was found, some of the systems fulfilled Eq.(4.21), whereas this was not the case for other systems. This suggests different rate-determining processes. Further work within this topic should be performed.

### 5.2.2 The influence of humidity on the Wheeler-Jonas equation

The original Wheeler-Jonas equation was developed for systems with dry activated carbon in dry air. In a real life the carbon will often be exposed to humidity. It should therefore be tested whether the equation can be used for such environments. For some systems this is already done. For ammonia on prewetted carbon, the breakthrough time decreased [26], but the breakthrough curve still yielded a straight line, indicating that the Wheeler-Jonas equation was still valid. Other systems that have been investigated are CNCl<sub>2</sub>, H<sub>2</sub>S, SO<sub>2</sub>, Cl<sub>2</sub>, and COCl<sub>2</sub> on prewetted carbon. These also turned out to fulfill the Wheeler-Jonas equation [84].

The parameters that will be affected by the humidity are the adsorption capacity and adsorption rate. As already discussed in section 3.4, humidity will reduce both the adsorption capacity and the adsorption rate in systems with organic compounds on activated carbon. The decreased capacity has the most impact on breakthrough time, but the lower is the output concentration, the

more impact comes from the adsorption coefficient [91]. For systems with inorganic compounds the influence on  $W_e$  and  $k_v$  varies.

If the Wheeler-Jonas equation also is valid in humid conditions, it should be possible to find expression for  $W_e$  and  $k_v$  that includes the moisture. The results of research devoted to this problem based on 7 different organic vapors on three different carbon have been published by Lodewyckx et al. [54;91]. It was found that the reduction of the adsorption capacity will be due to the reduced micropore volume  $W'_0$ , which can be estimated from:

$$W'_0 = W_0 - W_{pre} - \Delta W_{air} + \Delta W_s \quad (4.25)$$

where

- $W_{pre}$  - volume taken by the preadsorbed water (cm<sup>3</sup>/g)
- $\Delta W_{air}$  - volume taken (or liberated) by the humidity of the airstream (cm<sup>3</sup>/g)
- $\Delta W_s$  - volume of adsorbed water replaced by the organic vapor during the adsorption (cm<sup>3</sup>/g)

The value of  $W'_0$  can then be directly inserted in the Dubinin-Raduskiw equation. Details on how to calculate the different parameters in Eq.(4.25) can be found in [54].

The influence on the adsorption rate seemed to be more complex, but was suggested to be estimated from

$$k'_v = k_v \left( 1 - \frac{A_{tot}}{TPV} \right) \quad (4.26)$$

where

- $k'_v$  - overall adsorption rate coefficient under humid conditions
- $k_v$  - overall adsorption rate coefficient in dry circumstances
- $A_{tot}$  - total pore volume occupied by water in the absence of organic vapors
- $TPV$  - total pore volume

Calculated breakthrough times from the Wheeler-Jonas equation with estimates from the equations above showed overall good agreement with breakthrough times obtained [84]. More details on the calculations of the different parameters are found in [91].

## 6 Conclusions and further work

Activated carbon based filters are the most commonly used filters for individual and collective respiratory protection in military and civilian applications. This report has focused on adsorption of Toxic Industrial Chemicals (TICs) on activated carbon. Preparation methods, structures of activated carbon, adsorption properties, and mathematical models to predict the life time of carbon-based filters have been reviewed. Different kinds and mechanisms of adsorption on activated carbon surface show that organic compounds are mostly physisorbed in the pores of the carbon, whereas many volatile inorganic compounds create strong chemical bonds with the impregnates on the carbon surface. In case of filters for military purposes the emphasis is put first and foremost on the filtration of the CWA and other substances which can be used as a chemical weapon. Therefore the preparation process and impregnating chemicals are chosen to perform most effectively against those substances. However impregnation can also have a beneficial effect on the retention of TICs and in some cases the military filters performance can surpass the civilian filters, [28]. It should be noted that up to date testing against TICs is not a part of standard evaluation procedure for the military filters.

Crucial parameters describing the properties of activated carbon include surface area, porosity, adsorption capacity and the breakthrough time. The adsorption isotherms and activated carbon microstructures are important for the development and improvement of filtering technology. Even though the adsorption isotherms provide useful information about several relevant parameters of the adsorbent under equilibrium, they cannot provide complete data on adsorbent performance under operating conditions, such as kinetics. For this purpose the breakthrough curves are recorded. Briefly, a certain amount of adsorbent, such as activated carbon is placed in the reactor and the contaminated airstream is run through it while the concentration of contaminant is monitored simultaneously on both sides of the adsorbent layer. Once the adsorption sites are saturated the filter becomes exhausted and the contaminant concentration on the other side of the layer can be measured. Such breakthrough curves can either be used for describing adsorbent performance, or for predicting behavior for other concentrations, flows etc. However measuring the breakthrough curves can be cumbersome, time-consuming and often requires handling concentrated chemicals of extremely high toxicity. To avoid testing the filters against all possible chemicals, mathematical models can be used for prediction of breakthrough time and hence estimation of life time. The most common model is the Wheeler-Jonas equation, which originally was developed for adsorption of organic compounds on activated coal. Recent studies have shown that the equation also can be used for systems with inorganic compounds adsorbing on activated carbon. Nonetheless, so far it is mostly employed for prediction of filter life time in changing environmental conditions, and not for the inorganic chemicals in general.

Despite remarkable adsorptive properties of activated carbon and introduction of other types of adsorbents, such as MOFs or zeolites in filtering technologies, the filters are efficient provided that the oxygen concentration in the air is high enough to sustain breathing. In addition, the presence of multiple chemical substances at the same time can contribute to a substantial reduction of the breakthrough time and adsorption capacity of the filter. For this reason, a careful

analysis of the risk factors and identification of the chemical compounds which may be present at the event place is required.

Further work at FFI on activated carbon in filters will focus evaluating the filter performance by measuring breakthrough curves with chosen TICs using activated carbons from various canisters. These curves will be used for prediction of life time and to assess whether the Wheeler-Jonas equation can be used as a model to describe the adsorbent-adsorbate pair. More effort should however be put in defining which TICs are regarded high risk chemicals for soldiers in operation. Those chemicals could be then divided into groups according to their chemical structure, physical properties etc. From these groups the filtering properties of different filters towards several chemicals should be outlined, based both on laboratory experiments and theoretical calculations. Such work would be important for assessing the performance of the filters against different TICs under various environmental conditions. In addition, some of the emerging materials such as MOFs should be also included in further research activities, as these may play more important role in the future filtration technologies.

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## Appendix A Physical data chosen toxic industrial chemicals

| Name             | Formula           | Boiling point<br>(SI chemical data) |
|------------------|-------------------|-------------------------------------|
| Sulfur dioxide   | SO <sub>2</sub>   | -10 °C                              |
| Chlorine         | Cl <sub>2</sub>   | -34 °C                              |
| Phosgene         | COCl <sub>2</sub> | + 8.2 °C                            |
| Ammonia          | NH <sub>3</sub>   | -33 °C                              |
| Hydrogen cyanide | HCN               | +25 °C                              |
| Hydrogen sulfide | H <sub>2</sub> S  | -60 °C                              |
| Carbon Monoxide  | CO                | -191.5 °C                           |