Impregnated Active Carbon-Shelf Life Studies and Its Evaluation Against Cyanogen Chloride with and without Canister

Beer Singh[▲], Amit Saxena, Avanish Kumar Srivastava,
Devendra Kumar Dubey and Arvind Kumar Gupta

Defence Research and Development Establishment, Jhansi road, Gwalior-474002 (MP), India

[▲]e-mail: beerbs5@rediffmail.com

(Received August 13, 2007; Accepted September 27, 2007)

Abstract

Samples of active carbon of 1150 m²/g surface area were impregnated with ammoniacal salts of copper, chromium and silver, with and without triethylenediamine. The samples of impregnated carbon were aged at 50°C, with and without 90% RH (relative humidity), for a little more than one year and chemically evaluated periodically. Initially copper (II) and chromium (VI) reduced very fast in the samples in humid atmosphere to the extent of 30% and 60% respectively in four months. These values were found to be unaffected by the presence of triethylenediamine (TEDA) indicating that the chemical did not retard the reduction process of chromium (VI) and copper (II). However, in the absence of humidity the reduction of the impregnants was significantly less (10-12%, w/w) in four months. It was quite evident; therefore, that the moisture was mainly responsible for the reduction of chromium (VI) and copper (II) species in impregnated carbons. The prolonged ageing of the samples with and without triethylenediamine after four months with and without humid atmosphere showed that the extent of reduction of chromium (VI) was very low, i.e. 5-10% and of copper (II) was 2-25%. Silver is not reduced due to carbon, as it remained unchanged in concentration on storage. The impregnated carbon samples (100 g) without triethylenediamine, which were aged at room temperature for 5 years in absence of humidity and unaged when evaluated against cyanogen chloride (CNCl) at a concentration of 4 mg/L and airflow rate of 30 lpm showed a high degree of protection (80-110 minutes).

Keywords : Activated carbon, impregnated carbons, impregnation and cyanogen chloride

1. Introduction

Chemical warfare (CW) agents are highly toxic chemicals, which are used in wars to harm or incapacitate human. Protection against them can be achieved by using suitable material, which can perform the function of physisorption followed by chemisorption in filtration systems. Impregnated active carbon has been proven as the best adsorbent material for filtration systems [1]. This initially adsorbs the CW agent (physisorption) and then degrades it by reacting with it to give non toxic products. One such material, active carbon, impregnated with ammoniacal salts of copper (II), chromium (VI) and silver (I) salts has been proven to be an efficient material for the removal of low boiling and low molecular weight gases such as cyanogen chloride, hydrogen cyanide, phosgene, etc [1-4]. Under ambient conditions, this adsorbent material hydrolyses cyanogen chloride and phosgene effectively to convert them into non-toxic products.

On aging in hot and humid atmosphere, these material lose their protection capacity against chemical warfare agents due to reduction of copper (II), chromium (VI) to their lower oxidation states [5-9]. The literature [5-8] reveals the characterization of impregnated carbons aged under hot and humid conditions/atmosphere for the reduction of copper

(II), chromium (VI), and their concentration and chemical compositions. This investigation was undertaken to examine the reduction of copper (II), chromium (VI), silver (I) content in bulk impregnated carbon with triethylenediamine. The objective of the study was also to investigate the ability of TEDA to provide stability to chromium (VI) in impregnated carbon on storage.

2. Experimental

Active carbon of coconut shell origin, 12×30 BSS mesh size and 1150 m²/g surface area from M/s Active Carbon India Ltd. Hyderabad, was impregnated with ammoniacal solution of copper (II), chromium (VI), silver (I) salts [10] alone and along with TEDA. The impregnated carbons were characterized for surface area, copper (II), chromium (VI), total chromium and silver contents [11]. The results are summarized in Table 1. Sample I was prepared by impregnating carbon first with copper, chromium, silver and then with TEDA, however, sample II was prepared by impregnating carbon first with TEDA and then with metal impregnants.

Impregnated carbon containing-copper (II), chromium (VI)

Table 1. Characterization of Impregnated Carbons

Sample	TEDA (%)	Silver (%) found calcd.	Copper (%) found calcd.	Chromium (VI) (%)	Total Chromium (%) found calcd.	Surface area (m ² /g)
I	3	0.24 0.24	6.3 6.5	2.08	2.7 2.8	950
II	3	0.15 0.16	6.3 6.5	2.26	2.6 2.8	960
III	Nil	0.17 0.16	6.4 6.5	1.97	2.7 2.8	1030
IV	3	0.16 0.16	6.6 6.5	0.947	2.6 2.8	960

Sample I & II were dried at 110°C for 6 hrs.

Sample III & IV were dried at 135°C for 6 hrs.

Table 2. Cyanogen Chloride Protection Time of Copper, Chromium and Silver Impregnated Carbon with and without Canister

Sl. No.	Sample	N ₂ Flow rate (lpm)	CNCl conc. (mg/l)	CNCl protection time (min)	Corresponding CNCl protection time at 4 mg/l CNCl conc.(mg/l)
1	Carbon (4.7 gm, 2 cm bed height)	1.2	5.03	59.38	74.5
2	Carbon (4.7 gm, 2 cm bed height)	1.2	6.43	51.58	83.00
3	Carbon (12.3 gm, 5.0 cm bed height)	6.3	29.24	14.7	107.2
4	Carbon (12.3 gm, 5.0 cm bed height)	6.3	13.87	31.4	108.9
5	Carbon (12.3 gm, 5.0 cm bed height)	0.6	100.8	24.5	616.9
6	Carbon (12.3 gm, 5.0 cm bed height)	30.0	29.59	5.1	37.7
7	(12.3 gm, 5.0 cm bed height)	30.0	7.41	19.58	36.1
8	Canister ^a	30.0	69.94	2.0	35.0
9	Canister ^a	30.0	6.37	85.8	136.0
10	Canister ^b	30.0	10.69	38.28	102.3
11	Canister ^b	30.0	9.47	42.7	110.5

(a) Canister from M/s Pradeep Packages, Bombay, aged for 5 years, at ambient conditions, with plugs intact at both ends.

(b) Canister from M/S Purohit Filters, Bombay.

and silver (I) salts with and without TEDA were stored at 50°C and separately, at 50°C and 90% RH. The samples were then taken out at regular intervals and analyzed for impregnants using wet analytical methods [11] and the results summarized in Fig. 2, 3 and 4 except for silver, which remained unchanged during aging process. Copper (II), chromium (VI) and silver (I) salts impregnated carbons as such and loaded in canisters were also evaluated against cyanogen chloride using the test schematic of which was shown in Fig. 1, and the results in Table 2.

Evaluation of carbon/canister against cyanogen chloride

As per Fig. 1 cyanogen chloride was taken from cylinder (4) through valve (5) and flow meter (6), mixed with nitrogen in a mixing chamber (7). Nitrogen (N₂) was taken in required flow rate (Table II) from cylinder (1) through valve (2) and flow meter (3). CNCl-N₂ mixture was passed through two traps (17&18). Methanolic sodium hydroxide (20 mL methanol + 25 mL 10⁻² N sodium hydroxide) at 100

1. Nitrogen Cylinder	10 Scrubber
2, 5, 9, 11 & 15 Control Valves	13 Carbon column/canister
3, 6, 12 & 16 Rotameters	14 & 19 Detector systems
7 Mixing Chamber	17 & 18 Cyanogen chloride traps
8 Two way valve	

Fig. 1. Experimental set-up for CNCl adsorption.

Fig. 2. Chromium (VI) concentration in aged impregnated carbon.

mL/min flow rate measured through flow meter (16) and controlled through a valve (15). This solution was used to measure the concentration of CNCl in CNCl- N₂ mixture following the standard method [12].

CNCl-N₂ mixture was passed also through a test specimen (carbon column/canister No. 13) and a flow meter (12) by controlling the flow rate using a control valve (11). The CNCl breakthrough was monitored at the outlet of test specimen and CNCl concentration measuring traps with a detector paper [14-19] prepared using standard method. Time difference between the instant of the breakthrough time and beginning time gave the protection time of carbon/canister against CNCl.

3. Results and discussion

Function of impregnated carbon versus aging is shown in Figure 2, 3 and 4 in terms of chromium (VI), total chromium and copper (II) respectively.

Table 1 shows the impregnants in carbon and also drying temperature. Carbon after impregnation with ammoniacal solutions of copper (II), chromium (VI) and silver (I) salts is dried at 130° to 140°C for 6 to 8 hrs which results in 70 to 75% chromium(VI) loading in impregnated carbon. However, the carbon with the above impregnants and with triethylenediamine when heated at 130°C to 140°C, chromium (VI) content was found to bare reduced significantly and only 35% chromium (VI) Of total chromium (VI) loading could be achieved (Table I, sample IV). It was

Fig. 3. Copper concentration in aged impregnated carbon.

Fig. 4. Chromium (total) concentration in aged impregnated carbon.

probably due to the decomposition of a complex formed by chromium (VI) and triethylenediamine. This was confirmed when a compound crystallized (green shining needles) from a mixture of two moles of chromiumtrioxide and one

mole of triethylenediamine from aqueous solution, was checked for its melting point, and which decomposed at 120°C. In view of this, the carbon was impregnated with copper (II), chromium (VI) and silver (I) salts and triethylenediamine and dried at 110°C below the decomposition temperature of chromium (VI) compound of triethylenediamine. The required loading of chromium (VI) (70 to 75%) out of the total chromium (VI) could be achieved in impregnated carbon on which is of utmost importance as it is mainly responsible in the detoxification of cyanogen chloride [13], phosgene, etc.

In samples I & II (Table 1), the only difference is the order of addition of triethylenediamine, Sample I was impregnated with metal salts first and then with triethylenediamine while for sample II the order was reversed. However, the sample II showed further improvement in chromium (VI) loading and this indicated that this is a more suitable way of impregnating carbon.

The carbons thus impregnated (Table 1) were aged under two different conditions. One was their storage at 50°C and another, at 50°C and 90% RH. Fig. 2 gives the aging process of chromium (VI) and indicates that at 50°C and 90% RH, chromium (VI) reduction due to carbon in samples I & II was rapid and significant during the initial period of four months (64 to 70%). Afterwards it almost leveled off in next eight months additionally to 2-3%. The reduction of chromium (VI) in sample II was very high initially, i.e. 55% in 30 days. The same sample when aged at 50°C in absence of humidity, chromium (VI) reduced very slowly, in sample I, the reduction of chromium (VI) was very less, i.e. 5% in one year. However, in sample II the chromium (VI) reduction was 12.5% during the initial 4 months giving overall reduction of 15.4% in a year. In sample III where triethylenediamine was not present, the chromium(VI) reduction was 63% during the first four months and in next eight months the reduction was merely 5% under chamber conditions of 50°C and 90% RH. The results indicated that the absence of TEDA in impregnated carbon neither caused fast aging of the material nor its presence retarded the chromium (VI) reduction. Sample IV, which initially contained a very low loading of chromium (VI) after heating at 140°C for 6 hrs showed its reduction to chromium (III) by 47% in 40 days which increased to 59% within four months and later negligible reduction of chromium (VI) in last next eight months. Probably moisture catalyses/activates the chromium (VI) and copper (II) reduction to their lower oxidation species.

The data indicated that triethylenediamine did not provide any stability to chromium (VI) species in impregnated carbon in hot and humid atmosphere. This was also confirmed by the fact that impregnated carbon/canister/filters (NBC) can be stored at 30°C away from moisture for a period of 5 years as the reduction of chromium (VI) to chromium (III) is hardly 5% to 15%. However, under hot

and humid condition, i.e. 30°C and 90% RH the sample storage life could reduce, if functional requirement are to be satisfied.

Fig. 3 indicates that the reduction of copper (II) to its lower oxidation state by carbon under chamber conditions of 50°C and 90% RH was a continuous process which initially was rapid. In samples I, II, III & IV the initial reduction of copper (II) during four months was 20.3 to 28.7% and except sample I, it increased to 42 to 51.3% in other samples in one year. In sample I, it increases to 22.8% from 20.3% during the eight next months. The data of chromium (VI) and copper (II) reduction (Fig. 2 & 3) showed that the sample I where carbon was impregnated with TEDA after Cu, Cr & Ag. the reduction of chromium (VI) and copper (II) reduction by carbon on aging in sample I and II indicates that the carbon should be impregnated as per the method of sample I preparation.

Fig. 3 also indicated that under chamber conditions of 50°C and without moisture/humidity reduction of copper (II) was slow at 10.4 to 10.9% during the initial four months and 11.9 to 16.6% in the next 8 months after slow and continuous reduction.

Total chromium content changes to some species, which are not extractable with sodium hydroxide during aging process. Fig. 4 shows that under chamber conditions of 50°C and 90% RH this change was 34 to 45.5% during 120 days, which initially was very rapid. This increases to 46.3 to 60% in next eight months. However, at chamber conditions of 50°C and without humidity it was hardly significant (0 to 6.8%) during one year, probably due to the presence of triethylenediamine. In samples I & II under condition of 50°C and 90% RH it was 34 to 36% initially during a period of four months. However, later in the next eight months the change seems to be same as the sample in which TEDA was not impregnated. This indicates that TEDA does not retard the reduction of chromium (VI) and copper (II) in impregnated carbon. Silver when analyzed in the aged samples I, II, III, IV at 50°C with and without humidity showed no change indicating that silver does not undergo reduction process.

Table 2 describes the cyanogen chloride protection achieved by carbon as such or in canister. The data indicated that at a higher concentration of cyanogen chloride the protection against cyanogen chloride was less due to the low contact time of adsorbents with impregnated carbon (Table 2, Sr. No.8). The results showed that the canister containing 100 gm of Cu, Cr & Ag impregnated carbon can protect for more than 100 minutes at 30 lpm N₂ flow rate and 4 mg/l CNCl concentration. The required protection time, however, is 30 minutes only. The same applied to the canister, which was stored for five years at ambient conditions (room temperature) with both the canister plugs intact in their places. The carbon bed height, flow rate and CNCl concentration were found to be affecting the CNCl protection time.

4. Conclusion

This study enabled us to develop a suitable impregnation method for carbon suitably with copper, chromium, silver and triethylenediammine. The resulting impregnated carbon contained the required chromium (VI) in required amount (60 to 70% of the total chromium (VI) loading). The study also confirmed that if TEDA was to be impregnated along with other impregnants to achieve additional CNCl protection, it should be impregnated first with metal impregnants and then TEDA in the second step as the aging of the carbon thus impregnated is slower to the carbon impregnated otherwise. The shelf life of copper, chromium and silver impregnated carbon, as such and in NBC canister and filter if stored at 30°C away from the moisture was more than five years. This was in confirmation with the result offered by a canister stored for five years at room temperature (25 to 40°C) and free from humidity, with no deterioration of CNCl protection capacity. However, in the presence of moisture (RH 90%), its shelf life decreases and the functional requirement will have to be adjusted accordingly. The study indicated that humidity was mainly responsible for the reduction of copper (II) and chromium (VI) in impregnated carbon on storage.

Acknowledgements

The authors thank Director, DRDE Gwalior for permitting to carry out and publish this work.

References

- [1] Noyes, W. A. Jr. "Military problems with aerosols and non-persistent gases", Vol. 1, Washington DC, Summary Technical Report of the National Defence Research Committee, Division 10, 1946, 40.
- [2] Aharoni, C.; Barnir, Z. *J. Am. Ind. Hyg. Assoc.* **1978**, *39*, 334.
- [3] Barnir, Z.; Aharoni, C. *Carbon* **1975**, *13*, 363.
- [4] Poziomek, E. J.; Mackay, R. A.; Barret, R. P. *Carbon* **1975**, *13*, 259.
- [5] Hammarstrom, J. L.; Sacco, A. *J. Catal.* **1988**, *112*, 267.
- [6] Bac, N.; Hammarstrom, J. L.; Sacco, A. *Carbon* **1987**, *25*, 545.
- [7] Ehrburger, P.; Heniin, J. M.; Lahye, J. *J. Catal.* **1986**, *100*, 429.
- [8] Ehrburger, P.; Dentzer, R. J.; Lahaye, J.; Dziedzini, P.; Fangat. *Carbon*, **1990**, *28*, 113.
- [9] Ehrburger, P.; Dentzer, R. J.; Lahaye, J.; Dziedzini, P.; Fangat. *Carbon*, **1991**, *29*, 297.
- [10] Singh, B.; Madhusudanan, S.; Padmakumar, C. G.; Sachan, S. R. S.; Pandey, S. K.; Agarwal, S. *Def. Sci. J.* **1998**, *48*, 365.
- [11] Singh, B.; Madhusudanan, S.; Padmakumar, C. G.; Sachan, S. R. S.; Pandey, S. K.; Agarwal, S. *Def. Sci. J.* **1998**, *48*, 365.
- [12] Smisek, M.; Cerny, S. "Active Carbon", Elsevier publication, Amsterdam, **1970**, 188.
- [13] Ross, M. M.; Colton, R. J.; Deitz, V. R. *Carbon*, **1989**, *27*, 492.