

GENERAL COMPANY TECHNICAL REPORT

Addendum Report #3: Additional Studies on VCM Adsorption

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A number of VCM exposures involving new adsorbants, commercial adsorbants at low VCM exposures, and a variety of exposure conditions have been carried out. During the course of this continuing study we have replaced the Century OVA with a Bendix Hydrocarbon Analyzer. In summary we have found:

- (1) The Bendix analyzer far outperforms the Century analyzer in terms of stability, background and accuracy,
- (2) carbon remains to be the best adsorbant for VCM,
- (3) the life-time of the Welsh cartridge in terms of 1 ppm breakthrough ranges between 30 minutes and 90 minutes,
- (4) the Welsh canister outperforms anything evaluated to date.

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Introduction

Our last report (B.F.G. Technical Report, March 8, 1974) on the subject of VCM adsorption covered evaluations of new adsorbants and larger carbon canisters and cartridges. Since that report we have continued our studies in this area and have also prepared VCM standards in support of other investigations (gas chromatographic, chemical desorption, x-ray studies). This current report is a summary of this work. A summary of all experiments is provided in Table I. No detail is given for the Analytical Gas Standards (A.G.S.) prepared for other studies; a permanent record of this work will be retained.

During the course of this work we replaced the Century OVA with a Bendix Total Hydrocarbon Analyzer. One of the advantages with the Bendix instrument is the ability to determine VCM breakthrough times below T_5 . An attempt was made to do this with the Century OVA at T_5 (see #33, 34) but there is considerable error in the values. The main reason is due to the inherent 5-10 ppm background in the Century analyzer. This background can be zero suppressed with the Bendix instrument. We have also found that the baseline is much steadier with the Bendix instrument. Baseline drift is probably the greatest source of error with the Century OVA analyzer, especially in the 0-5 ppm region. The agreement between the two methods considering the above limitations with the Century is not that bad. Testing the Welsh cartridge (7500-1) at 15 liters/min. and 10 ppm of VCM we obtained the following breakthrough times (T_5)* for the two analyzers: $T_5 = 162$ (Century) and $T_5 = 120$ (Bendix) (see Experiments #33 and #63). Previously we had determined a 12% deviation in determining T_5 with the Century analyzer.

In Table I, we have analyzed the Welsh 7500-1 cartridge at 30 l/min. and 10 ppm two times (#64 and #71) with the Bendix analyzer. The average T_0 is 50 ± 4 minutes which represents an 8% deviation. In our next report we will broaden the data base on this deviation analysis but reproducibility seems better with the Bendix instrument.

Effect of Rate on Breakthrough Time

Comparing experiments #63 and #64 a significant decrease in T_0 (initial breakthrough) takes place when the rate is increased from 15 l/min. to 30 l/min. A number of people have requested that more experiments be carried out at the 15 l/min. rate rather than the 30 l/min. rate. While the information obtained at 15 l/min. is of interest, it should be remembered that in our approach we correlate to the OSHA standard when we test at 30 l/min. not at 15 l/min. Since final acceptance of any device is based on the OSHA standard, most of our testing should be in the 30 l/min. range (or whatever rate best correlates to the standard).

T_1 Values

Our initial data involving the Welsh cartridge at 10-20 ppm (30 l/min.) indicates that T_1 is reached between 1 and $1\frac{1}{2}$ hours. Although we have not yet

* T_5 is defined as the time to .5 ppm VCM/

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determined T_1 at 50 ppm, previous work with the Century analyzer at 50 ppm indicates a $T_1 = 41$. We believe this value is high, again due to the inherent problems with the Century analyzer at these low levels. Nevertheless in terms of the problem, the values (T_1) indicate the approximate life-time of the Welsh cartridge. If the concern is worker exposure to 1 ppm of VCM, the Welsh cartridges exhibit a life of $\frac{1}{2}$ to $1\frac{1}{2}$ hours depending on the concentration of VCM in the atmosphere.

Welsh Canisters

In our last report we showed the significant increase in protection offered by the Welsh canister (7800-1M). At 30 l/min. and 100 ppm, T_5 was reached after 11 hours. Recent studies with this canister (Experiment #70) indicate that initial breakthrough, T_0 , at 10 ppm and 30 l/min is almost 17 hours and T_1 is not reached until ~20 hours. To date we have seen nothing that approaches the performance of the Welsh canister.

Other Adsorbants

A number of other adsorbants involving a number of principles of chemistry were tried. Nothing, so far evaluated, approached the effectiveness of carbon in scavenging VCM. In our last report we found that the coconut charcoal was not as effective as the petro-charcoal. Since that report, Harvard has also tested the coconut charcoal in their apparatus and have arrived at the same conclusion. Thus at this time, coconut charcoal offers no real advantage over the more abundant petroleum based charcoal.

Future Studies

We will continue our studies along the following lines:

- (1) determine reproducibility (T_0 , $T_{.5}$, T_1) at the low (5-20 ppm) exposure concentration,
- (2) follow the Harvard work now in progress in which engineering redesign experiments with the entire masks are underway,
- (3) continue to evaluate new adsorbants, and
- (4) evaluate the standard cartridges and canisters at low levels of VCM (1-5 ppm).

Mike
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Attachment

Table 1

Summary of VCM Adsorption Data Obtained with the VCM Flow Chamber

Experiment No.	Experiment Involving	Flow Rate l/min.	VCM Concentration ppm	T ₅ ^① (minutes)
31, 32 ^③	A.G.S. ^②			
33	Welsh 7500-1	15	10	T ₅ = 162; T ₅ = 278
34	Welsh 7500-1L	15	10	T ₅ = 291
35 - 39	A.G.S.			
40	MSA Cartridge 44135	30	100	13.0
41	Willson R-13	30	100	0.0 ^④
42	Willson R-21	30	100	57.0
43 - 46 ^⑤	calcium carbonate absorbant	30	100	all 0.0
47	repeat of #42 (R-21)	30	100	46.5
48 - 53	A.G.S.			
54	MSA Cartridge 459315	30	50	32.0
55	MSA Cartridge 459315	30	100	25.0
56	Willson R-25	30	100	11.0
57 - 61 ^⑤	TiO ₂ , Lead Acetate absorbants	30	100	All 0.0
62 ^⑥	Welsh 7500-1	15	20	data in error; will be repeated
63	Welsh 7500-1	15	10	T ₀ = 98, T ₅ = 120; T ₁ = 148
64	Welsh 7500-1	30	10	T ₀ = 54, T ₁ = 92
65	Welsh 7500-1	30	20	T ₀ = 35, T ₁ = 57; T ₅ = 77
66 ^⑤	Various carbon filters containing mixtures	30	100	13.0
67 ^⑤	of carbon and other adsorbants; #67 is	30	100	32.0
68 ^⑤	the control containing	30	100	12.0
69 ^⑤	only carbon.	30	100	0.0
70	Welsh canister, 7800-1M	30	10	T ₀ = 1010, T ₁ = 1220, T ₃ = 1335
71	Welsh cartridge 75001 (repeat of #64)	30	10	T ₀ = 46, T ₁ = 81

① T₅ is the time (in minutes) in which the concentration of VCM downstream from the cartridge becomes 5 ppm.

② Analytical Gas Standard.

③ Runs 31 to 61 were made with the Century O.V.A.

④ 0.0 means immediate breakthrough; no VCM adsorption was evident.

⑤ Materials submitted by L. Chandler for evaluation as VCM adsorbants.

⑥ Runs 62 - 71 and all future experiments were made with our new Bendix Total Hydrocarbon Analyzer.

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Exhibit B-1005

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SUMMARY OF SHELL INTERVIEWS WITH
VINYL CHLORIDE/POLYVINYL CHLORIDE MANUFACTURERS
RELATING TO PROTECTIVE EQUIPMENT PURCHASED UNDER
THE TEMPORARY EMERGENCY STANDARD

V.C. or PVC Product	Class of Protective Equipment	Number of Workers Requiring Protective Equipment	Cost of Equipment (1974 Dollars)	Operating and Maintenance Costs (1974 Dollars)	Comments
Air Products	Respiration, half face air supplied	16-20	\$200,000	\$ 25,000	Several tripping accidents have been attributed to respiration and some of the workers are reluctant to wear them. Minute-by- minute supervision required to ensure use.
Calvin City Penacola		16-20	200,000	25,000	
Allied Chemical	Respiration	67	16,000	N.A.	
American Chemical	Respiration, half face air supplied	N.A.	N.A.	N.A.	8 weeks procurement lead time.
Conoco					
Aberdeen	1. Respiration, airline	68	60,000	6,000	
	2. Protective clothing Disposable coveralls Rubber gloves		30 30	300 300	
Lake Charles	Respiration	20	4,150	6,300	MSA type.
Oklahoma City	Respiration, airline	12	14,000	6,600	
Diamond Shamrock	Respiration, airline				
Deer Park		16	13,000	6,600	One incident of fumes and sooty rash from use of air mask.
Delaware City		16	6,000	6,000	
Dow Chemical					
Louisiana	Respiration, pressure demand or continuous flow	6.3	10,000	6,000	
Oyster Creek	Same	3	6,000	6,000	

of the measurements are to be established in the operating instruction.

Each measurement point must be measured at least one time per shift.

4.4. Safety procedures in the cleaning of polymerization autoclaves.

Units and processes are so fashioned that cleaning processes in the autoclaves are necessary as seldom as possible. Cleaning works by hand are to be extensively excluded.

4.4.1. Mechanized cleaning without entering of the autoclaves.

4.4.1.1. Before the opening of autoclaves, it is to be insured by suitable precautions, e.g. by evacuation, by rinsing with water, by ventilating, by the wearing of protective breathing apparatuses that the personnel are not exposed to an health endangerment by vinyl chloride.

4.4.1.2. Cleaning apparatuses, e.g. mechanically driven spray units, if possible are to be introduced into the container by mechanical apparatuses and to be operated from the outside with covered manhole.

4.4.1.3. If cleaning apparatuses, e.g. spray apparatuses held by hand, are inserted in opened manhole, it is to be insured by suitable precautions, e.g. by evacuation, by rinsing with water, by ventilating, by the wearing of protective breathing apparatuses that the attendant is exposed to no health endangerment by vinyl chloride.

4.4.2. Manual cleaning with entering of the autoclaves.

4.4.2.1. Before the manual cleaning, subject to the regulations of section

4.4.2.2 a mechanized cleaning is to be carried out according to Section 4.4.1.

4.4.2.2. If a mechanized cleaning is not possible stipulated by the process, e.g. in mass polymerization with mischarges, a manual cleaning can be carried out. Since with a cleaning or post-cleaning vinyl chloride can be liberated from gas inclusions in the crusts, the following precautions are to be taken:

4.4.2.2.1. Before the entering and during the working in the inside, the autoclaves are to be ventilated. The air must be introduced in such manner

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that the entire autoclave is sufficiently ventilated. As a rule, the air should be exhausted at the bottom of the container. The effectiveness of the ventilation is to be checked continuously by suitable control measurements of the vinyl chloride concentration. In a post-cleaning, continuous measurement can be relinquished if it is proven that health-endangering vinyl chloride concentrations do not occur.

4.4.2.2.2. With the occurrence of health-endangering amount of vinyl chloride, the personnel must immediately leave the autoclaves.

4.4.2.2.3. If the occurrence of health-endangering amounts of vinyl chloride can not be hindered by ventilating, e.g. in mischarges, protective breathing apparatus independent of the surrounding atmosphere must be worn. The same is true for cleaning with solvents.

4.4.2.3. The duration of the entry is to be limited. The entry time for each person should not exceed 4 hours in two successive shifts.

4.4.2.4. In all manual operations in the autoclaves, tight protective gloves and tight footgear must be worn.

5. First aid

5.1. If a person who deals with vinyl chloride complains concerning health disturbances, a doctor is to be called immediately for consultation. The doctor is to be made aware of the fact that he has been working with vinyl chloride.

5.2. With acute poisoning by vinyl chloride, the victim is to be brought as rapidly as possible into the fresh air or into a well ventilated room. Clothing pieces contaminated with vinyl chloride are to be taken off and removed from the room. To avoid chilling, the victim is to be wrapped in blankets. A doctor is to be called immediately!

5.3. The victim is to be brought into a stable sitting position (without danger of suffocation). The victims must not be left unattended if at all

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possible!

5.4. If the victim is not breathing, an artificial breathing is induced immediately by suitable means, is possible by artificial respiration (mouth to mouth or mouth to nose). If an oxygen breathing apparatus is present, the respiration is to be continued with this. With circulation stoppage, the outside heart massage is to be carried out along with the artificial respiration. However the latter may be carried out only by such helpers who have obtained a special instruction in this method. The remedial measures are to be continued during the transport or until the arrival of a doctor.

5.5. No liquid may be introduced to the unconscious!

6. Industrial medical Precautionary Investigations

The employer may employ only persons in the operations and plant areas according to number 1 which have been evaluated as suitable on the basis of industrial medical precautionary investigations. The investigations are to be carried out according to the rules for industrial medical precautionary investigations of the Employer's Liability Insurance Association of the Chemical Industry.

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