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Two Stage System for the Destruction of Methyl Bromide from Fumigation Ventilation Streams

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Introduction

Large-scale emissions control of methyl bromide from fumigation vent streams presents a formidable scale-up problem. Industry and government representatives have stated that large-scale emissions control is not likely to be technically or economically viable^[1,2] for large tarp fumigations typically done in warehouses. To date, small-scale emissions controls of methyl bromide are commercially done for individual containers of less than 150 cubic meters.

The problem of removing and destroying methyl bromide from large volumes of air > 7, 200 cubic meters, encountered in Quarantine and Pre-Shipment (Q/PS) operations, has been resolved. *Value Recovery, Inc.* has solved this problem by employing a sequential two-stage scrubber system that employs carbon adsorption in the first step followed by de-sorption and simultaneous chemical destruction in the second step (Fig. 1). Previously we have reported^{3,4} on the ability of a chemical scrubber to instantaneously destroy methyl bromide from fumigation vent streams with a thiosulfate solution. The adsorption step removes methyl bromide from the relatively large volume of fumigation air at ambient temperature. The de-sorption step employs much lower air volumes at elevated temperatures to provide a feed stream compatible with the scrubber. Enough carbon is present in the adsorption cycle to ensure that all of the methyl bromide is retained on the bed without breakthrough into the vent stream. The de-sorption step is designed to remove the methyl bromide from the carbon bed with cycle times required for high throughput distribution characteristic of unloading ships at ports.

During the aeration step that follows a typical fumigation, the concentration of methyl bromide in the exhaust streams shows an exponential decay as the methyl bromide is "swept" from the fumigation enclosure with replacement air as diluted air - gas mixture. In most Califor-

nia Q/PS operations, aeration times are four hours with more than 95 percent of the methyl bromide removed in the first 30 minutes. In order to predict the correct sizing of the carbon bed, one must allow for 3.5 hrs of relative pure air displacing this initial methyl bromide concentration "spike." In order to quantify the performance of the carbon and ensure retention of the methyl bromide, experimental work confirming the carbon bed size was performed.

Experimental

Value Recovery built an apparatus (Figure 2) to quantify carbon performance at identical superficial gas velocities needed for industrial scale-up. It consists of a stainless steel insulated column (2.5 cm diameter) filled with carbon particles to a depth of 127.4 cm. Temperature control was maintained with circulating, pressurized hot water in an external heat exchanger jacket that envelopes the full length of the carbon bed. The inlet, outlet and jacket temperature was measured with multiple 3 - wire RTD's. Inlet and outlet temperature probes were welded into the pipe and protruded directly into the air streams. Adsorption and de-sorption air flow-rate was measured using factory calibrated mass flow-meters (Cole-Parmer). The outlet methyl bromide concentration in air was measured via Infra Red absorption with a Spectros Instruments (Hopedale, MA) methyl bromide analyzer. Calibration gas standards of 1.50, 0.76 and 0.18 volume percent methyl bromide in air (Scott - Marin Riverside, CA) were used to check the calibration of the IR analyzer. The calibration standards along with the mass flow-meters were used to simulate the exponential concentration decay flow loading of methyl bromide onto the carbon column. All of these instruments were connected to a National Instruments Labview® data acquisition system connected to a personal computer. Data points for all instruments were taken every 30 seconds and recorded and time-stamped in an excel

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spreadsheet.

Math Model

Professor Genarro Maffia⁵ of Widener University provided a numerical solution for adsorption of an organic compound from liquid streams. The model was modified for gases since it is based on first principals, and the gas density change (< 4 percent) is assumed negligible across the carbon bed. The same model was used to predict both adsorption and de-sorption cycle performance. Inlet gas concentration to the carbon bed was based on a typical exponentially decaying feed stream exiting the fumigation chamber⁴.

Input data parameters for the model are:

Temperature, C

Initial Fumigant Concentration, $c(0,0)$ g/
m³

Fumigation Volume, V, m³

Gas Flow - rate, G, m³/s

Carbon Bed Diameter, D, m

Carbon Bed Length, L, m

Gas Constant, R, 0.0821 Lit - Atm. , Deg
- Gmol

Carbon Particle Length and Diameter, m

Carbon Bulk Density, kg/m³

Methyl Bromide and Air Critical Con-
stants, Tc - Deg K, Pc - Atm

Fumigated Commodity Uptake - Fraction
of "dead volume," dimensionless

Pressure, Atm

Diffusivity Parameter constants

Fruendlich Isotherm Constants for Methyl
Bromide Adsorption on Carbon

Time Increment, dt, sec.

Column Differential Slices, n, dimension-
less

Calculated parameters from the model are:

Space Velocity (V/G) time constant, sec-
onds

Gas Phase Concentration, c , (function of
time and column position), kg/m³

Solid Phase Concentration, q , (function of
time and column position), kg/m³

Equilibrium Gas Phase Concentration, ce ,
(function of time and column position), kg/m³

Carbon Particle Area, A, m²

Number of Carbon Particles in a differenti-
al slice, N_p , dimensionless

Gas Viscosity, μ , kg/m/s

Gas Density, ρ , kg/m³

Diffusivity of Methyl Bromide in Air, D,
m²/s

Reynolds No. , $N_{Re} = dv\rho/\mu$, dimensionless

Schmidt No. , $N_{Sc} = \mu/\rho/D$ dimensionless

Mass transfer constant correlation coeffi-
cient, j_D , dimensionless

Mass transfer coefficient, kc , m/s

Superficial Gas Velocity, v , m/s

Mass of Carbon in Bed, MC, kg

dz - differential column length, m

The key equations for solving for the gas
phase concentrations at all times t , everywhere
in the bed, z are:

$$1. c(t, z) = c(t-1, z) + vdz * dt * (c(t, z) - 1) - c(t-1, z) - (k * A * dt/vd) * (c(t-1, z) - ce(t-1, z))$$

$$2. c(t, z) = c(t, z) + D * dt * (c(t-1, z) + c(t-1, z-2) - 2 * c(t, z-1)) / dz^2$$

$$3. q(t, z) = q(t-1, z) + (k * A * dt / (1 - vd)) * (c(t-1, z) - ce(t-1, z))$$

$$4. ce(t, z) = (q(t, z) / a)^{(1/p)}$$

where

c - gas phase concentration in kg/m³

v - superficial gas velocity, m³/s

dt - differential time, s

kc - mass transfer coefficient, m/s

A - Area of carbon particles in a differenti-
al slice, m²

vd - particle void fraction, dimensionless

ce - gas phase concentration in equilibrium
with adsorbed methyl bromide, kg/m³

D - Diffusivity of methyl bromide in air,
m²/s

q - Adsorbed methyl bromide, kg/m³

a, p - Freundlich Isotherm parameters

For every time increment, dt , the mass bal-
ance and equilibrium concentrations were
solved for the entire column. The mass transfer
coefficient was obtained from a correlation pro-
vided by Sherwood, Pigford and Wilke⁶.

The Freundlich Isotherm parameters were
obtained from a regression of methyl bromide
gas - solid equilibrium data provided by Snyder
and Leesch⁷.

The model runs in True - Basic and prints
out all inputs, calculated values and all three
calculated concentrations for every bed position
at the end of the run. It also plots the gas phase
concentration vs. bed depth as a function of
time on the computer screen while the calcula-
tions are progressing.

Experimental Results and Discussion

During the adsorption step, the mass of

methyl bromide loaded on the column was obtained by summing the flow-rate provided by the mass flow-meters times the known feed concentration while methyl bromide was being fed. During the de-sorption step, the mass of methyl bromide removed was obtained by summing the flow-rate times the concentration of methyl bromide provided by the IR Analyzer. The latter was obtained every 30 seconds over 16 hours (- 1 900 data points).

Table 1 shows data for two corresponding adsorption & de-sorption cycles of methyl bromide on carbon. The loading of methyl bromide is very low, 2.5 wt%. The mass balance closure to within 96% (out/in) for both runs gives us confidence that the methyl bromide is well accounted for and comes off the bed at predicted rates. Temperature control was not used during the adsorption step and the temperatures shown for adsorption correspond to ambient temperatures. The de-sorption cycle time was approximately 4 times longer than the adsorption cycle time. The temperature was set at 98.5 to 101C.

Figure 3 compares the model and experimental data for the methyl bromide concentration in air (PPM) exiting the carbon bed for the de-sorption step. Figure 4 shows the cumulative amount of mass desorbed from the bed as a % of the amount loaded or charged during the adsorption step. The math model predicts that methyl bromide should come off approximately 15 percent faster than that shown by the experimental data. The two experimental runs were in relatively close agreement with regard to the mass balance and cumulative mass desorbed. The data suggests that the discrepancy comes from an extrapolation in the use of Freundlich equilibrium isotherm parameters. We believe that equilibrium data for methyl bromide adsorbed on carbon is needed at higher temperatures to eliminate the discrepancy. However, from a design point of view, knowing that the model and the data differ by only 15 percent still makes the model a valuable scale-up tool.

Conclusion

Experimental data combined with a model show that the scale-up of a two-stage process for destroying methyl bromide from very large scale Q/PS and structural fumigations is a technically and economically feasible option. Predicted mass adsorption and de-sorption of methyl bromide from a carbon bed provide methyl bromide concentration profiles that show that the de-sorption from carbon combined with a chemical

scrubber will destroy methyl bromide in concentration ranges demonstrated in previous commercial trials. The time needed for the de-sorption cycle is four times that of adsorption and is easily allowed for in the design of sequential fumigation operations. Applying this system to large scale operations and smaller ones as well will make a major impact on protecting both bystanders and preserving the ozone layer. A commercial installation of this two-stage system is planned for start-up in 2009 for the Port of Stockton, CA, USA.

Table 1 Methyl Bromide Adsorption and De - sorption Data

Run No. 1	2	
Adsorption		
Grams MB Loaded	7.78	7.73
Loading %	2.50%	2.48%
Temperature, C	16.2	17.8
Time - Hours	4.0	4.0
De - sorption		
Grams MB Removed	7.50	7.49
Temperature, C	98.5	101.0
Time - Hours	16.2	15.1
Mass Balance (Out/In x 100)	96.4%	96.9%

Column Parameters :

Diameter	2.5 cm
Bed Depth	127.4 cm
Carbon Charge	311.8 gms
Carbon Density	0.457 Kg/m ³

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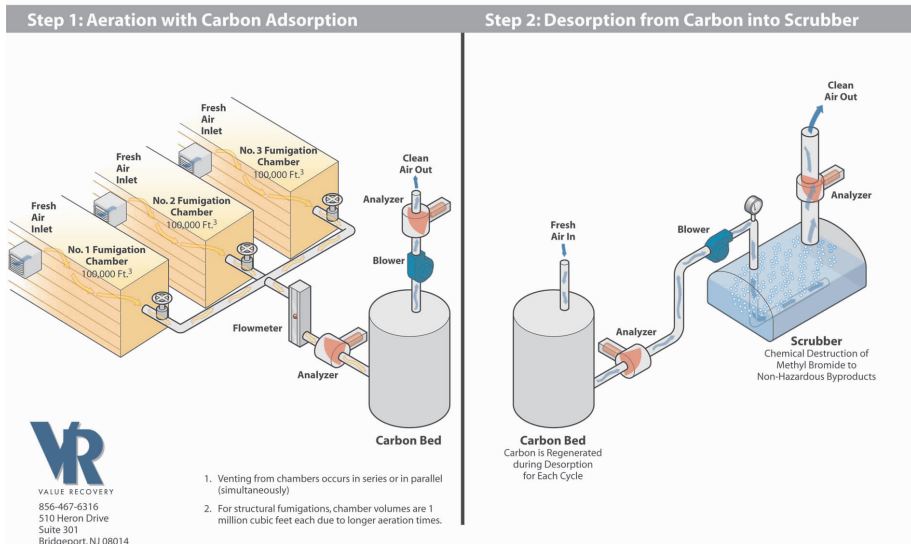


Fig. 1 Value Recovery Methyl Bromide Scrubber System For Very Large Q/PS and Structural Systems

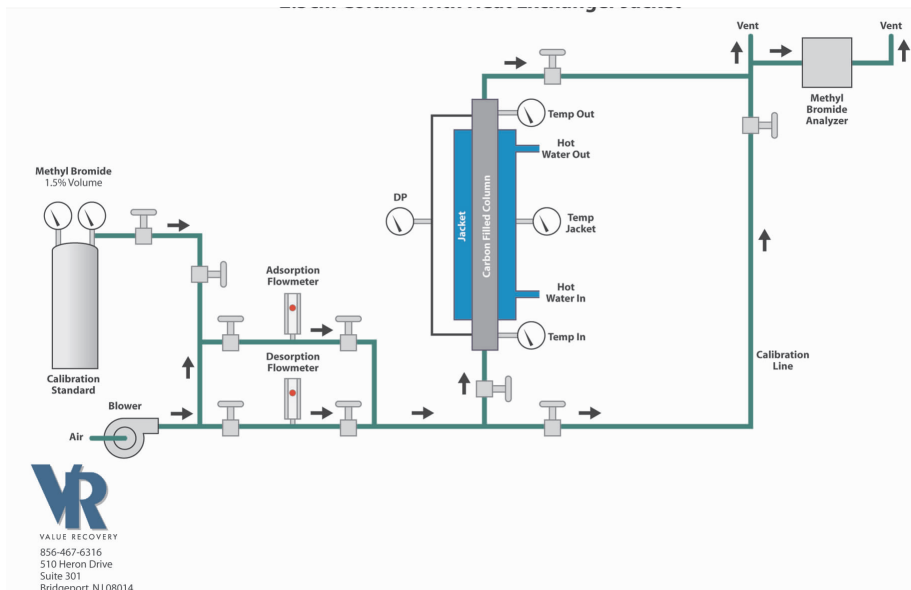


Fig. 2 Experimental Carbon Column 2.5cm Column with Heat Exchanger Jacket

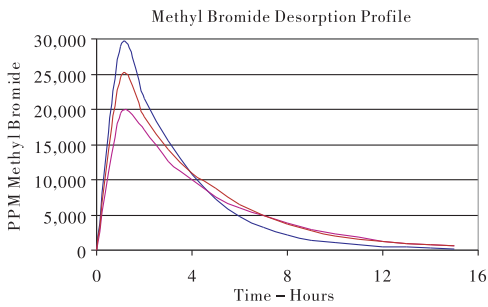


Fig. 3

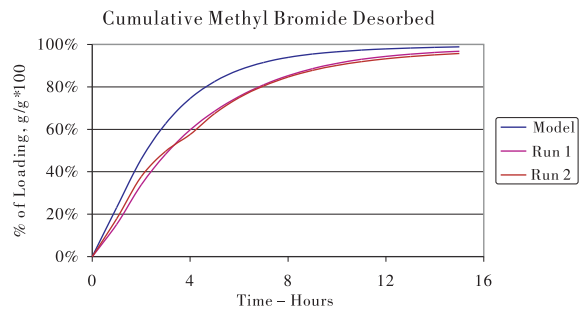


Fig. 4