Mouthpiece respirator cartridge performance evaluation following passive exposure in kraft pulp mills

William H. Bullock, and Zane N. Frund Jr.

ABSTRACT: Respiratory protection program administrators are required by the Occupational Safety and Health Administration (OSHA) to calculate the replacement times for chemical cartridges used with air-purifying respirators. To address this requirement, a method has been developed that enables program administrators to determine cartridge replacement frequencies for escape-respirator cartridges. Cartridges are passively exposed to pulp mill and bleach plant atmospheres for 30, 60 and 180 days. The cartridges are then tested for overall performance following National Institute for Occupational Safety and Health (NIOSH) criteria. Using the service time reduction curves plotted from the performance data, a cartridge replacement frequency can then be determined. This paper outlines the method used in five kraft pulp mills with bleach plants, which resulted in a calculated cartridge replacement frequency of 180 days.

KEYWORDS: Air conditioning, atmosphere, environments, exposure, gas, monitoring, bleach plants, OSHA, performance evaluation, protection, pulp mills, replacement, respiration, service life, test methods.

Mouthpiece respirators are commonly carried by employees in kraft pulp mills and bleach plants in the event that it becomes necessary to escape from chlorine (Cl_2), chlorine dioxide (ClO_2), or hydrogen sulfide (H_2S). Due to a lack of data on the effects of passive adsorption of these gases on cartridge performance, it was not possible to determine cartridge replacement frequency. Therefore, a study was performed at five kraft pulp mills with bleach plants to determine the mouthpiece respirator cartridge performance after passive exposure to gases in the workplace atmosphere.

Selecting a respirator that will provide adequate protection when needed is the responsibility of the program administrator. The Occupational Safety and Health Administration (OSHA) respiratory protection standard 29 CFR 1910.134 requires that the respiratory protection administrator calculate the useful life of air-purifying respirator cartridges. Typically, this is calculated by comparing the task duration with the exposure concentration. For escape respirators, however, many unknown or unpredictable factors exist (e.g., effects and time of passive adsorption, temperature, and humidity). Exposure time is another unknown factor. For instance, employees often carry respirators in gas permeable plastic bags or pouches. Because these bags or pouches quickly develop tears and punctures, the cartridges can be passively exposed to trace levels of gases and humidity in the atmosphere. Others are never placed in any type of sealed container, and consequently receive passive exposure.

Neither the program administrator nor the respirator manufacturer can predict the quantified effects

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such "passive exposures" may have on cartridge performance. Therefore, a method is needed to evaluate the performance of these escape respirators. This paper describes a method which was developed and field tested at five International Paper (IP) kraft pulp mills with bleach plants.

Background

The sulfate or kraft process is a chemical pulping process that dominates the United States pulp production *(1)*. In the kraft process, sulfate liquors are used to remove the fiber-bonding lignin to varying degrees *(2)*. In the production of white papers this process is continued with a bleaching stage that generally requires a combination of chlorine and chlorine dioxide.

Kraft pulp mill atmospheres have the potential to contain reduced sulfur gases. The reduced sulfur gases typically found are hydrogen sulfide (H_2S), methyl mercaptan (CH_3SH), dimethyl sulfide [$(CH_3)_2S$], and dimethyl disulfide [$(CH_3)_2S_2$] *(3)*. Hydrogen sulfide is produced if sulfate liquors come in contact with any acidic compounds. In addition to these sulfur gases, atmospheres in and around the bleach plant area can include chlorine, chlorine dioxide, and chloroform ($CHCl_3$).

A study by Leach and Chung *(4)* showed the concentrations of all four sulfur gases to be less than 1 part per million (ppm), with occasional peaks of dimethyl sulfide to 6 ppm near batch digesters. A Canadian study by Goyer *(5)* showed the concentrations to be less than 0.05 ppm hydrogen sulfide, 0.2 ppm dimethyl disulfide, 8 ppm dimethyl sulfide, and up to 2 ppm methyl mercaptan.

Exposure monitoring conducted by Tulane University's Section of Environmental Medicine *(6)* within bleach plants at IP has revealed ambient concentrations of chlorine and chlorine dioxide to range from less than the limit of detection [5–10 parts per billion (ppb)] for chlorine and chlorine dioxide to 179 ppb chlorine and 19 ppb chlorine dioxide. Although chloroform levels were not monitored during this study, they are expected to be slightly higher than chlorine, but well below the occupational exposure limits of chloroform.

To develop a diverse data base, five large IP facilities that operate under different geographical and process conditions were selected. Two of the selected facilities were from the southeast, two from the northeast, and one from the southcentral United States. The facility construction dates ranged from the 1930s to the 1980s. Each facility consisted of a pulp mill and bleach plant. Consequently, chlorine and sulfur containing compounds were present at each facility. The following is a brief process description of the five facilities selected for this study:

Facility No. 1 has a single Kamyr continuous digester used for both hardwood and softwood. The pulp is washed, then flows through gravity screens and knotters. The bleach plant consists of two lines using chlorine, chlorine dioxide, oxygen, peroxide, and caustic. A noncondensible gas (NCG) system removes reduced sulfur gases from the digester, evaporators, and chip bin.

Facility No. 2 has batch digesters. The pulp is washed in gravitational vacuum brownstock washers. The bleaching process uses chlorine, chlorine dioxide, oxygen, peroxide, and caustic. An NCG system removes reduced sulfur gases from the digesters, evaporators, and blowheat recovery.

Facility No. 3 has two Kamyr continuous digesters. One line is dedicated to softwood and the other is dedicated to hardwood. Each line incorporates knotting, brownstock washing, pressure screening, and a decker. The current bleaching sequences use chlorine, chlorine dioxide, oxygen, peroxide, and caustic. An NCG system removes reduced sulfur gases from the digesters, evaporators, and chip bin.

Facility No. 4 has a single Kamyr continuous digester which is used for both hardwood and softwood. The pulp is then washed and flows through primary pressure knotters and vibrating screen secondary knotters. The pulp then proceeds to screening. The bleaching process uses chlorine, chlorine dioxide, oxygen, peroxide, and caustic. An NCG system removes reduced sulfur gases from the digester, evaporators, and chip bin.

Facility No. 5 consists of a continuous Kamyr digester that runs softwood pulp. The brownstock is washed, screened and cleaned, and then thickened. The bleaching process uses chlorine, chlorine dioxide, oxygen, peroxide, and caustic. An NCG system removes reduced sulfur gases from the digester, evaporators, and chip bin.

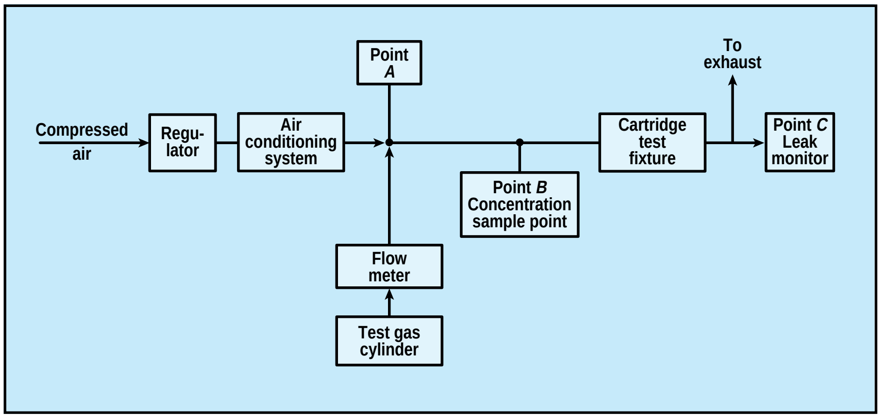
Facility numbers 1, 2, 3 and 5 produce in excess of 1000 tons per day (tpd) of pulp. Facility No. 4 produces approximately 500 tpd.

Methods and materials

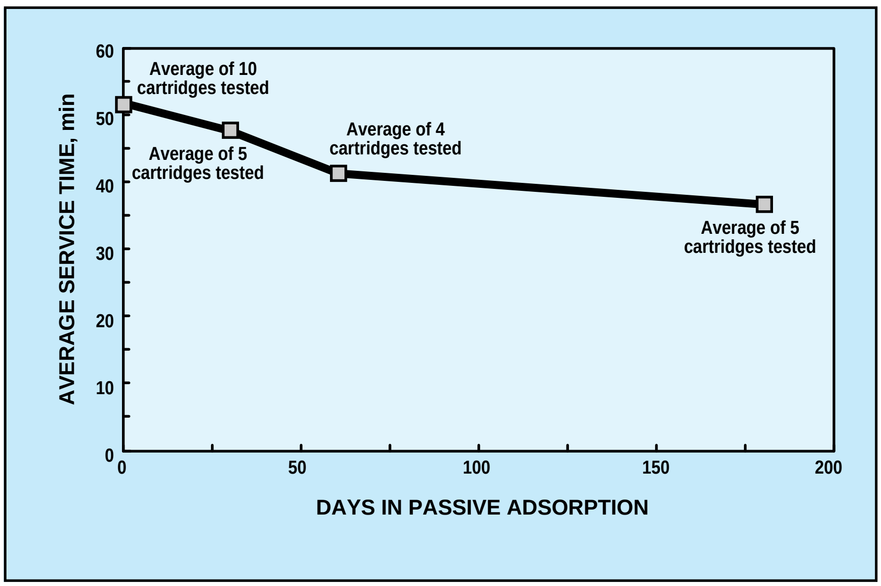
Fifty Mine Safety Appliances Co. (MSA) mouthpiece respirator cartridges, all from the same production lot (lot ID code 0593), were used in the study. Ten cartridges were retained by MSA's Chemistry Group for benchmark testing. Forty cartridges were supplied to IP for placement in mill and plant environments.

MSA's Chemistry Group tested the ten cartridges, which they retained for breathing resistance and sulfur dioxide (SO_2) service time in accordance with an approved National Institute of Occupational Safety and Health (NIOSH) testing method *(7)*. SO_2 was selected as the test agent since it has been found to be the most difficult acid gas (specified by NIOSH) to adsorb. If a cartridge effectively adsorbs or filters out SO_2, it will filter out chlorine, chlorine dioxide, and hydrogen sulfide. These test results were used as the "benchmark service times" to measure the effects of passive expo-

1. Schematic of cartridge test apparatus



2. IP pulp mill average cartridge service times. SO_2 service time tested at 500 ppm SO_2 challenge concentration, 64 L/min air flow, 50% RH, 25°C.



sure to kraft pulp mill and bleach plant environments on cartridge performance.

IP Industrial Hygiene supplied eight cartridges to each of the five geographically diverse facilities. At each pulp mill or bleach plant, two of the eight cartridges were maintained as field blanks, which were never exposed to the facility environment. The remaining six were divided into two groups of three. Each group was placed into ridged plastic containers that had eight 1.25-in. diameter holes bored into the sides. These containers were designed to permit trace level gases and humidity within the area to contact the cartridges, yet prevent liquid water from contacting the cartridges during area cleaning. One container (housing three cartridges) was placed on the pulp mill operating floor, and the other container was placed on the bleach plant operating floor. The containers were placed 5–6 ft above the ground level to further prevent liquid water from contacting the cartridges. Samples were identified by four digit numbers corresponding to the facility, location within the facility, and sample number.

All cartridges were exposed continuously during the study period. Operating conditions were logged throughout the study by area personnel. No upset or nonroutine conditions were reported at any facility during the entire study period. The first cartridge from each container was removed from exposure after 30 days. The second cartridge was removed from exposure after 60 days. The final cartridge was removed following 180 days of exposure.

After removal from the test areas, the cartridges were sealed in plastic bags and shipped to MSA's Chemistry Group for evaluation. All were tested for breathing resistance at 85 L/min and SO_2 service time according to following NIOSH test criteria: 500 ppm SO_2 challenge concentration, 64 L/min air flow, 50% RH, and 25°C. Testing was terminated when a 5 ppm breakthrough occurred.

A schematic of the test setup is presented in **Fig. 1**. Laboratory compressed air, which was regulated, filtered and preconditioned, was mixed at Point *A* with SO_2 from a regulated compressed gas cylinder.

A sample of the challenge gas was taken at Point *B*. After it had been verified that the challenge gas was at the proper NIOSH conditions, a mouthpiece cartridge was mounted in the cartridge test fixture and tested. The effluent air was continuously monitored at the Point *C* to determine the concentration of SO_2 breaking through the cartridges.

Wet chemistry techniques were used to determine the challenge and breakthrough concentrations. The challenge concentration was determined by passing a sample of the challenge gas (at Point *B*) through a glass bubbler which contained an iodine solution to absorb all of the SO_2. This solution was then titrated with a sodium thiosulfate/starch indicator solution to determine the concentration of SO_2 present in the airstream.

The leakage of SO_2 through the cartridge was determined by continuously flowing a sample of effluent air (at Point *C*) into a bubbler that contained an iodine/starch indicator solution. A 5-ppm leakage occurred when the solution changed from blue to clear in 60 s.

Results and discussion

The SO_2 service times for the tested cartridges exposed in kraft pulp mills and bleach plants are presented in **Figs. 2 and 3**, respectively. The breathing resistance results are given in **Table I**. All of the cartridges, even after 180 days of continuous exposure to pulp mill or bleach plant atmospheres, met NIOSH's breathing resistance and SO_2 service time requirements.

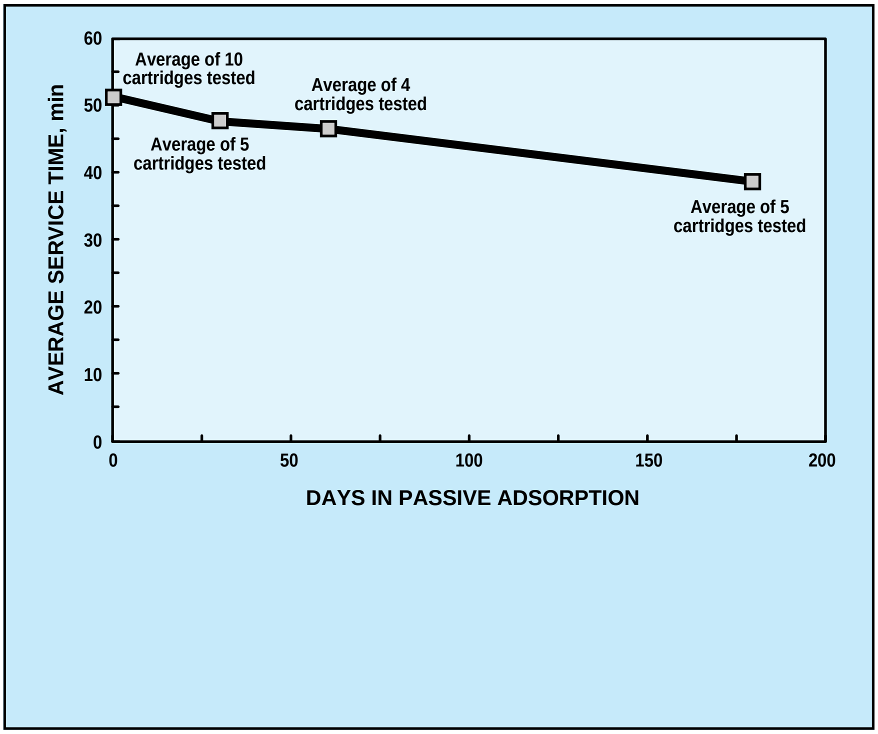
Although there was no significant change in the breathing resistance of cartridges, there was an overall reduction in their service time with exposure. This reduction in SO_2 service time was due to the unpackaged cartridges passively adsorbing trace levels of gases present in the mill and plant atmospheres. The field blanks which had no exposure, had service times comparable to new cartridges. In fact, previous testing by MSA has indicated that mouthpiece cartridges that have been sealed in their polyethylene bags for 3 years perform as well as new cartridges.

Due to the properties of MSA's adsorbent media, the effects of humidity will be minimal. According to NIOSH protocol, these cartridges meet performance requirements at low and high humidity conditions (25, 50, and 85% RH). Laboratory testing at NIOSH conditions has revealed that as the moisture content within the adsorbent increases, the mouthpiece cartridge's service time increases.

These mouthpiece cartridges adsorb challenge gases by a chemisorption process. Therefore, variations in the air temperature will have a minimal influence on the kinetics of the reaction between the challenge gases and the adsorbent, and will have little influence on the cartridges' capacity for a challenge gas.

When determining the cartridge replacement time for mouthpiece respirators, IP required a built-in safety margin. IP wanted to ensure that if an employee needed to escape from an area, a cartridge that had been in the facility for an "unknown" period would have sufficient capacity remaining to protect the employee during escape. IP decided that an overall reduction in service time (adsorptive capacity) of 25% (75% capacity remaining) would be the target for cartridge replacement. An additional safety factor of only using cartridges that initially perform 50% greater than the NIOSH minimum SO_2 service time (e.g., 45 min SO_2 service time instead of NIOSH's 30-min requirement) is also required.

3. IP bleach plant average cartridge service times. Test conditions as in Fig. 2.



Using the average SO_2 service time of 52 min for the unexposed MSA cartridges in this study (see Figs. 2, 3, and 4), and assuming a 25% reduction in service time, it was determined that after the SO_2 service time was reduced to approximately 39 min the cartridge should be replaced.

The service time reduction plots in Figs. 2 and 3 indicate that after 180 days of continuous exposure, the SO_2 service time is reduced to 39 min for bleach plant exposure and 38 min for pulp mill exposure. Employees carrying these escape respirators in IP facilities are exposed to both bleach plant and pulp mill atmospheres on any given day.

For cartridges having an initial SO_2 service time of 45 min (our 50% safety margin), and using the reduction rate from this study, the SO_2 service time should be reduced by 25% after 180 days to 33 min. (**Note:** This is still above the NIOSH minimum criteria for a new cartridge's performance.)

Conclusions

In summary, MSA mouthpiece cartridges exposed to 180 days of continuous exposure to pulp mill and bleach plant atmospheres will still provide an individual with respiratory protection against chlorine, chlorine dioxide, and hydrogen sulfide for escape purposes.

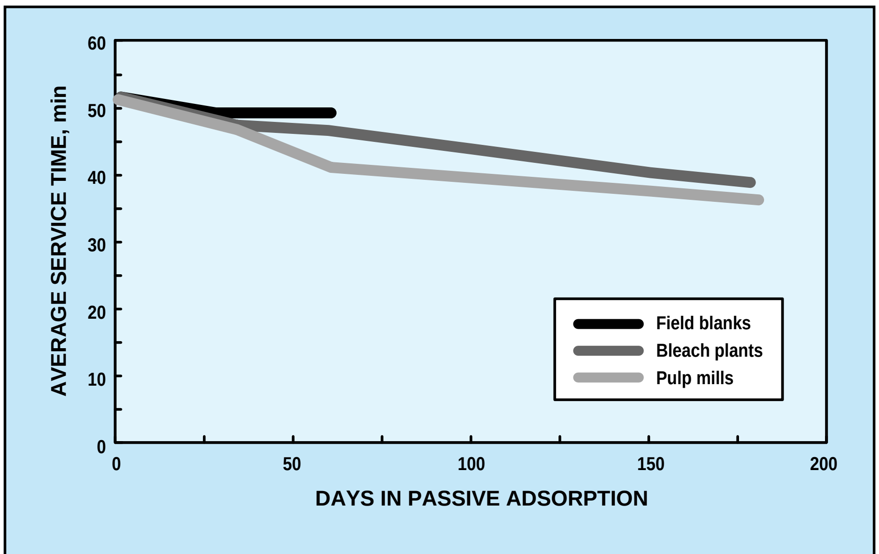
It is recommended, however, that mouthpiece respirator cartridges

I. Breathing resistance of mouthpiece respirator cartridges

New cartridges		*30-Day old cartridges*		*60-Dayold cartridges*		*180-Day old cartridges*	
ID no.	*Breathing rsistance, mm H_2O*	*ID no.*	*Breathing resistance, mm H_2O*	*ID no.*	*Breathing resistance, mm H_2O*	*ID no.*	*Breathing resistance, mm H_2O*
1	27	11-01	25	11-02	24	11-03	24
2	25	12-01	26	12-02	24	12-03	24
3	27	13-01	25	13-02	25	--	--
4	25	21-01	24	21-02	27	21-03	24
5	27	22-01	23	22-02	26	22-03	25
6	26	23-01	26	23-02	U/A[a]	--	--
7	25	31-01	24	31-01	24	31-03	25
8	27	32-01	25	32-02	24	32-03	24
9	24	33-01	25	33-02	27	--	--
10	25	41-01	27	41-01	U/A	41-03	27
		42-01	26	42-02	U/A	42-03	24
		43-01	24	43-02	25	--	--
		51-01	25	51-01	25	51-03	23
		52-01	26	52-02	26	52-03	26
		53-01	26	53-02	25	--	--

Maximum allowable breathing resistance = 40 mm H_2O
[a] Cartridge was unavailable for testing

4. Mouthpiece respirator cartridge average service times following passive exposure in IP kraft pulp mills. Test conditions as in Fig. 2.



exposed to kraft pulp mill and bleach plant atmospheres be replaced following 180 days exposure. This will ensure that they will provide an individual with adequate protection and continue to meet the NIOSH service time requirements. (**Note:** Cartridge replacement time may be significantly different if exposed to atmospheres unlike those described in this study.)

Finally, it will be necessary for the cartridges coming into the plants to have an average SO_2 service time of at least 45 min. If less than 45 min, the cartridge replacement time will have to be shortened proportionally. TJ

Literature cited

1. Casey, J. P., *Pulp and Paper Chemistry and Chemical Technology,* John Wiley and Sons, New York, 3rd edn., 1980, vol. 1, p. 161.
2. Casey, J. P., *Pulp and Paper Chemistry and Chemical Technology,* John Wiley and Sons, New York, 3rd edn., 1980, vol. 1, p. 380.
3. "Atmospheric Emissions from the Pulp and Paper Manufacturing Industry," Report of NCASI–EPA Cooperative Study Project, NCASI Atmospheric Quality Improvement Technical Bulletin No. 69, NCASI, New York, NY, February 1974.
4. Leach, J. M. and Chung, L.T.K., *TAPPI 1982 Environmental Conference Proceedings,* TAPPI PRESS, Atlanta, p. 175.
5. Goyer, N., *Am. Ind. Hyg. Assoc. J.* 51: 390(July 1990).
6. Poovey, H. G. and Rando, R. J., "Determination of Chlorine and Chlorine Dioxide by Non-Suppressed Ion Chromatography and Application to Exposure Assessment in The Paper Industry," Tulane University Medical Center, Section of Medicine, Section of Environmental Medicine, New Orleans, LA, (manuscript submitted to the *J. Liquid Chromatography*).
7. Code of Federal Regulations, Title 30, Part 11, Subpart L, (1991), p. 82, Table 11.

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