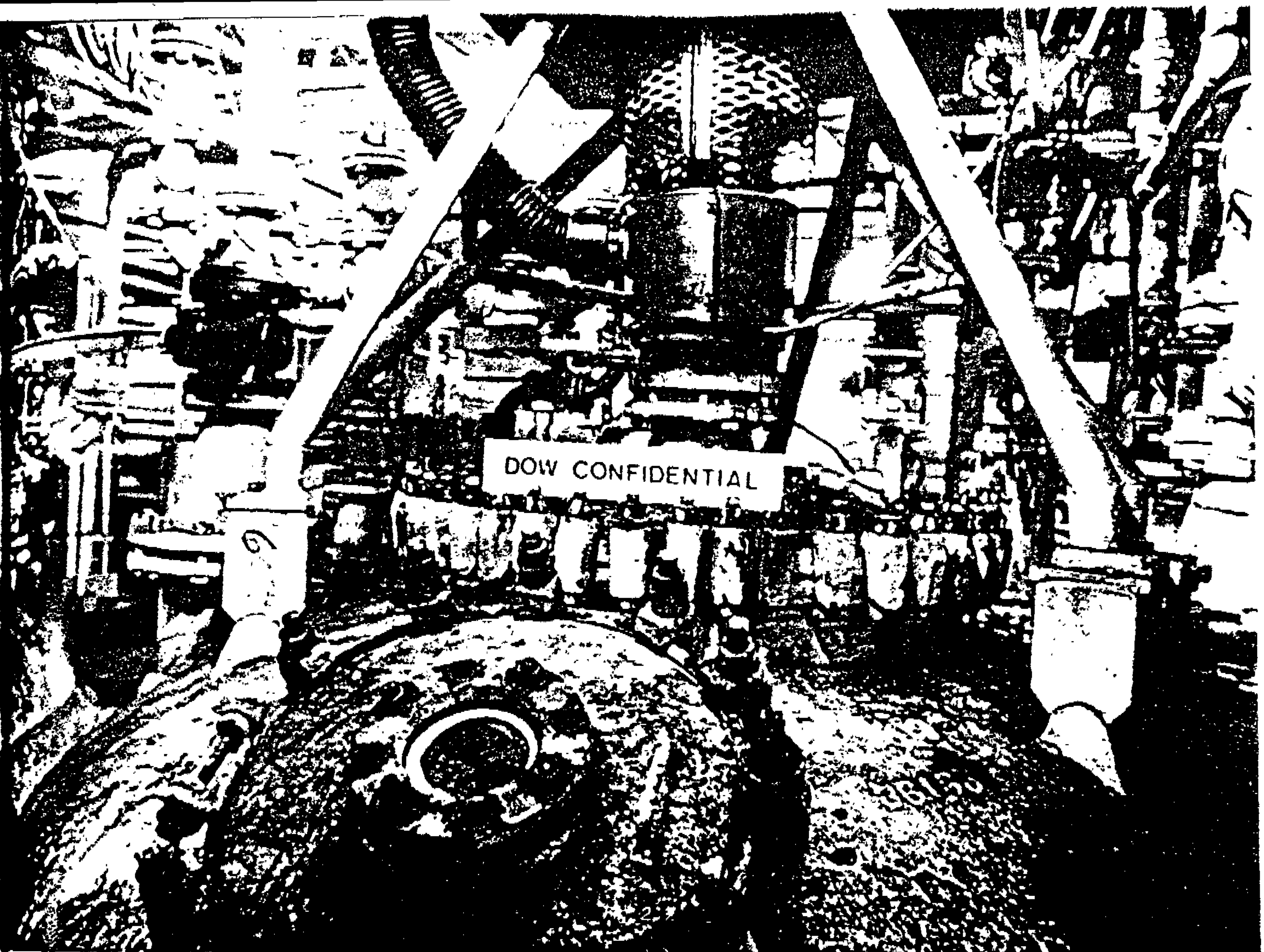

How to control carcinogens in chemical production

Which makes more sense, zero exposure to a few known toxic chemicals or minimizing exposure to all ch micals? The evidence points to the latter.

The symposium title, "Workplace Control of Carcinogens," is enlightening. It indicates that the membership of the ACGIH agrees that carcinogens can be used by industry and that it is possible to control exposures to acceptable levels.

by Ralph R. Langner, Director, Industrial Hygiene Laboratory, Health and Environmental Research, Dow Chemical USA, Midland, Mich.

This acceptance by ACGIH of carcinogens in industrial operations may be ahead of many academic and industrial leaders. There are several research and development directors who have banned the use of the 14 carcinogens, even in research. Of course, these same directors would not ban asbestos, and vinyl chloride wasn't supposed to appear as a carcinogen.

This type of reasoning is also practiced by many industrialists. They ask, "Is the proposed material on the NIOSH list of 1500 suspected carcinogens?" If it is, they search for and are willing to use a substitute product for which little or no toxicological information is available.

PROVEN WAYS Carcinogens can be controlled in chemical operations using the same proven techniques used with other toxic materials. The emphasis on eliminating exposures to carcinogens may result in employee overexposure to other toxic chemicals, some of which may prove to be carcinogens in the future. Few, if any, processes use only one chemical. As professional industrial hygienists, we should be looking at the "total system." It is unrealistic to discuss zero exposure to a select few chemicals. Rather, we should be working toward minimizing exposures to *all* materials.

What are the proven techniques? Substitution, containment, local exhaust ventilation and continuous area monitors equipped with alarms—have all been used successfully by industry to control overexposures to toxic chemicals, including carcinogens.

Experienced industrial hygienists know that substituting a material of unknown toxicity for a known toxic material is a misuse of the substitution concept for controlling industrial hazards. This practice is foolish and fails to recognize our modern technological ability to control releases and to minimize employee exposures.

SUBSTITUTIONS What are some realistic substitutions? Some of those that come to mind are toluene for benzene as a hydrocarbon solvent; 1,1,1-trichloroethane for 1,1,2-trichloroethylene in vapor degreasing; a select organophosphate insecticide for ethylene dibromide in grain fumigation.

REACTOR STUFFING BOX COVER

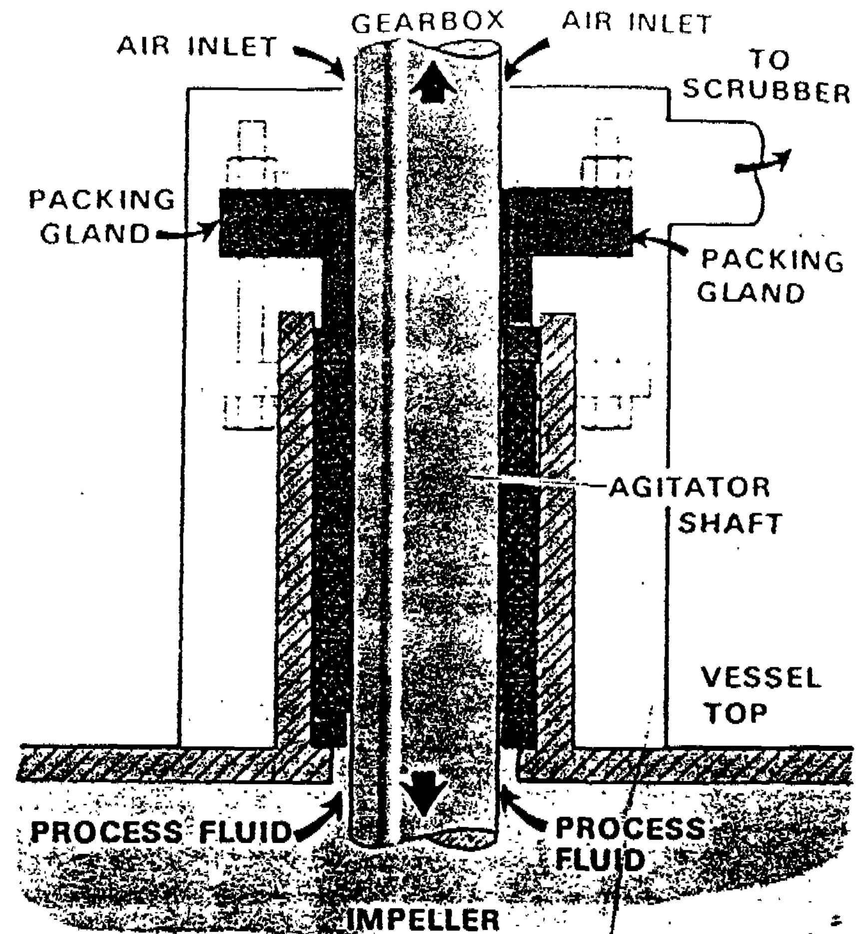

Fig. 1

Carcinogens can be controlled just like other toxic chemicals.

Likewise, the substitution of flammable hydrocarbons or the use of highly corrosive caustic solutions rather than trichloroethylene for metal degreasing should be thoroughly studied. Technically, both have been used successfully, but the risk of human injury, under field conditions, and the lack of data demonstrating that trichloroethylene has caused health problems, when used properly as a degreasing solvent, poses a benefit/risk question.

It is impossible for any of us to determine if it is worse to die from burns than from cancer. Is blindness from caustic at age 30 worse than a remote possibility of cancer at age 65? Overreaction to carcinogens can lead to unwise decisions.

OPEN WINDOWS? Ventilation is another technique used to control employee exposures. Historically, general ventilation—a concept burrowed from the sanitary engineer—has been used widely. Open the windows and dilute the contaminant to an acceptable level!

Today the industrial hygienist must work side-by-side with the waste control engineer and, in many small plants, they are one in the same. It is no longer acceptable to exhaust toxic vapors into the ambient air. Although general ventilation is still used, the high energy cost of moving and heating large volumes of air has caused industrial hygienists and ventilation engineers to look for better solutions.

Localized ventilation is too seldom used and, when used, too frequently abused for controlling exposures to chemicals. When properly designed and operated, local ventilation offers one of the lowest cost control methods available. Not only is the volume of air reduced, but it allows the point of capture to be strategically placed to minimize employee exposures. Because the volume of air is small, filters and scrubbers can be used efficiently to remove the contaminant and, in some cases, to recover and recycle enough material to pay for the operating costs.

PRECAUTIONS With toxic materials such as carcinogens, local ventilation can be installed as a precautionary measure, *i.e.*, it is operating if a leak develops in a pump, valve, or seal. If the exhaust air is monitored, minor leaks can be detected and the necessary repairs made before employee exposure/overexposure is imminent.

Another technique used to prevent employee overexposure is area monitoring. Continuous, sequential area monitoring has been used in our plants for many years. In recent years, area monitoring has been questioned and the use of personal monitoring has gained in popularity.

Emphasis on documenting employee exposures, proving noncompliance, and forgetting the ultimate goal of all industrial health practitioners *i.e.*, the prevention of employee overexposure, have caused many industrialists to shy away from this valuable tool. Continuous, sequential area air analysis is the most effective method of controlling employee overexposure to all chemicals.

ALERT These instruments, when equipped with alarms and readout devices, allow the employee to know the airborne level in an area before entry. Appropriate respiratory protection can be worn to prevent exposure while completing a work assignment

SAMPLING BOX, SIDE VIEW

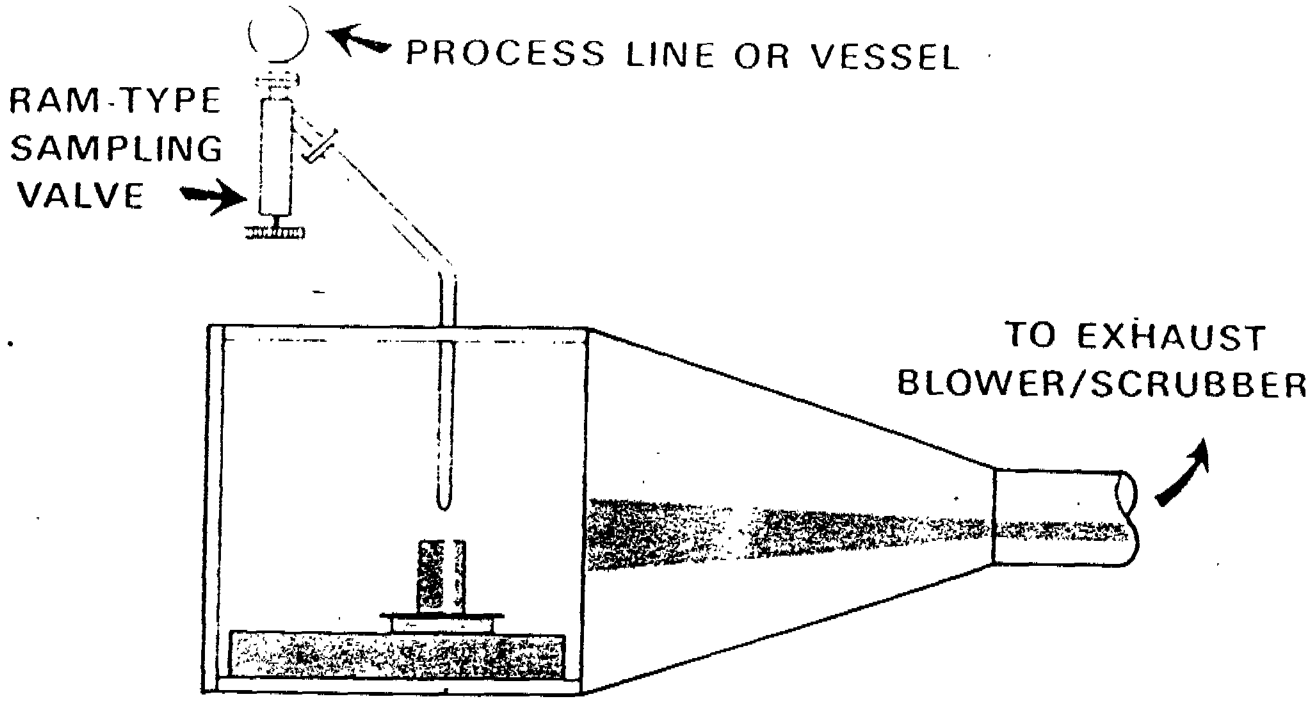

Fig. 4

or while making necessary adjustments or repairs.

Certainly, this approach is far better than placing an adsorption tube in the breathing zone of the employee, using a carefully calibrated air sampling pump and a validated analytical procedure to document what the exposure *was*. When these area analyzers are equipped with a computer to handle vast amounts of data, daily printed exposure records are possible. If posted in the work area, the calculated exposure record can be a valuable training tool for operating personnel. Gas chromatographs, infrared units, ultraviolet and nonspecific combustion analyzers have all been adapted to this use.

Substituting an unknown chemical for a known carcinogen is dang rous.

MONITORING The OSHA vinyl chloride standard accepts continuous area monitoring as a method of determining employee exposure. NIOSH could make a valuable contribution by collecting and analyzing the data from the many vinyl chloride plants using the various monitoring techniques and reporting to industry those systems that are acceptable as well as those that have been shown to be inadequate.

Containment, or the use of closed systems, is another method to control exposure to toxic chemicals. The BCME (bis-chloromethyl ether) problem was associated with exposures that occurred during "open kettle" operations in the 1950's and 1960's. Employees working in the closed system plants did not develop the characteristic oat-cell carcinoma nor have new cases of cancer been reported in employees working only with closed systems in older plants. New plants have closed systems equipped with vent scrubbers that minimize both employee and public exposures.

SAMPLING Changes in process sampling have reduced potential employee exposure. Opening of process lines for sampling has been eliminated in many cases and reduced in others. In-line analyzers are being used in most new plants and they have been added to many of the older processes. Gas chromatographs are used in most plants for quality control. They require microliter quantities. The past practice of draining quantities of material into an open container to obtain a representative sample has been eliminated.

Local ventilation is an effective way of ridding an area of fumes.

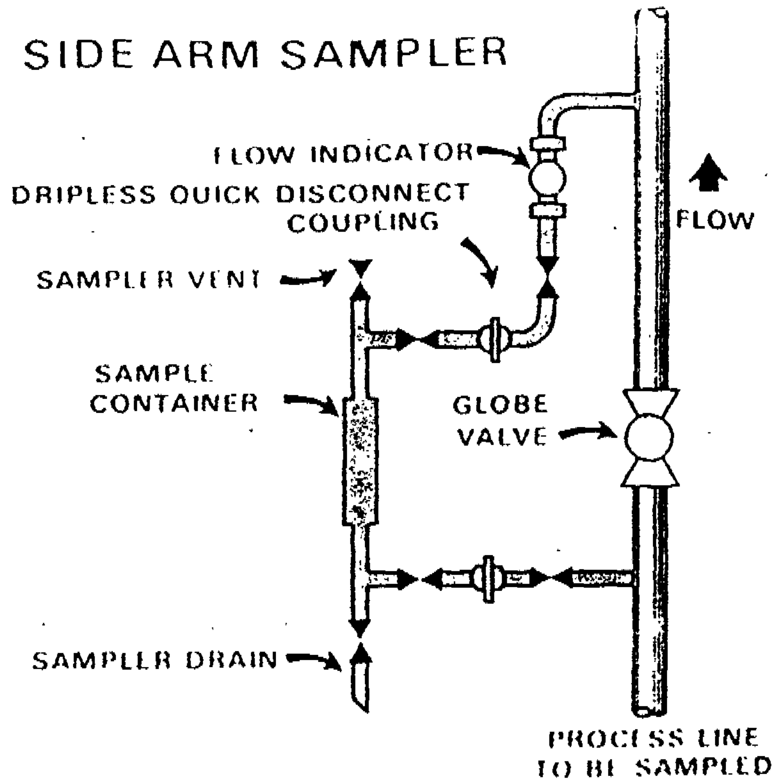

Fig. 5

Let's look at some of these techniques, as installed in operating plants. (Fig. 1) This is a drawing of a shroud that can be placed around a reactor agitator shaft or other moving part that is subject to leaking. Fig. 2 shows a shroud on a old-style reactor handling CMME (chloromethyl methyl ether). The exhaust system uses a low flowrate. Yet, there is a high capture velocity at the point of potential leak. New plants would use mechanical seals rather than packing glands.

PUMPS LEAK. A similar shroud can be used on pumps. Pumps leak. The question is, when? Continuous area samplers can be used to detect early leaks. After spending thousands of dollars on research, we have developed an air monitoring technique that measures (sequentially) both CMME and its carcinogenic impurity, BCME, at the 1 ppb level.

At the same time, process research has continued to reduce the formation

COMPARISON OF EXPOSURE LEVELS TO ETHYLENIMINE PLANT PERSONNEL 1966-1974

JOB CLASSIFICATION	8-HOUR TWA EXPOSURE LEVELS (PPM, V/V) ETHYLENIMINE	ETHYLENE DICHLORIDE
ASSISTANT SUPERINTENDENT (1966)	0.06	4.9
SUPERINTENDENT (1974)	<0.1	1.4
SENIOR PRODUCTION ENGINEER (1966)	0.04	2.8
PRODUCTION ENGINEER (1966)	0.06	4.9
R&D ENGINEER (1966)	0.08	8.8
PRODUCTION ENGINEERS (1974)	<0.02	5.9
PRODUCTION CHEMIST (1966)	0.04	2.8
TECHNICIAN (1966)	0.08	7.9
FOREMAN (1966)	0.08	8.8
FOREMAN (1974)	<0.02	6.6
CONTROL "A" OPERATOR (1966)	0.04	2.8
CONTROL "A" OPERATOR (1974)	<0.01	1.0
CONTROL "C" OPERATOR (1966)	0.17	13.5
CONTROL "C" OPERATOR (1974)	<0.04	10.2
CONTROL "C" (SRO) OPERATOR (1966)	0.04	8.4
CLERK (1966)	0.02	1.5
JANITOR (1966)	0.02	1.5

Fig. 6

AREA SAMPLES
TOTAL CHLORIDE CALCULATED AS CMME

DATE	NO. OF SAMPLES	AVG. (PPM)	RANGE (PPM)
1949	7	5.2	2.2-8.7
1952	3	1.1	0.15-2.65
1957	230	0.7	0-12
1961	8	2.5	1-8

Fig. 7

of by-product BCME. This research was done even though the existing OSHA standards for CMME and BCME neither require measurements nor offer an incentive for industry to do this type of work. A vinyl chloride pump shroud is shown in Fig. 3. Sealless pumps are available for some materials, but they do not perform in all operations.

The use of remotely operating valves also reduces employee overexposure. Even though the valve is operating remotely, the area monitor will detect leakage and the operator will be able to put on proper respiratory protection before he leaves the pressurized control room.

Monitors can be set up to alert workers to a rise in contaminant level.

Let's move on to sampling devices. The use of an enclosed sampling box with cross ventilation will minimize exposure. (Fig. 4) The sample valve also minimizes the quantity needed to obtain a representative sample. By-pass sampling prevents the need for open systems. (Fig. 5) A "double ended cylinder" can be used to collect gas samples with little or no release. These sampling techniques can be used effectively in noncarcinogen plants also.

THE RECORD Now, let's turn our attention to employee exposure records from plants using this technology. (Fig. 6) Measured employee exposures in our ethylenimine plant in 1966 and 1974 demonstrate good control. This plant, put in operation in 1963, uses a gas chromatograph for sequential area air monitoring. There has been little change in the airborne levels. Has the posting of "CANCER SUSPECT AGENT" signs in 1973 and the resulting mental anguish benefitted these employees?

The measured airborne levels of contaminant in the CMME plant provide an interesting study in the evolution of the chemicals industry and in the technology used by industrial hygienists. (Fig. 7) The early samples taken in the 1950's were collected using a hand-operated sampling pump and silica gel as the adsorbent.

The silica gel was burned and the resulting chloride was scrubbed and measured using the Volhard colorimetric method. The presence of BCME was unknown and it and all other airborne chlorides were calculated as CMME. Repeat samples in 1952 demonstrated continued good control. In 1957, a new technique, infrared, became available. This instrument allowed us to be more specific and measured primarily CMME. By attaching a multipoint sequential sampler, many analyses were possible. Again, good control was demonstrated. Repeat sampling in 1961, 1966 and 1970 showed little change. (Fig. 8)

OVERREACTION In 1969, the report on the carcinogenetic effect of BCME was published. Results of analyses from the various producers indicated that CMME contained 7-10% BCME. Industry responded by developing analytical techniques for monitoring BCME and these methods have been published. We were now able to measure both CMME and BCME and, in general, everyone overreacted to measuring the known carcinogen, BCME.

In reality, if the CMME was controlled, the BCME (less than 10% of the CMME) would be controlled also. Data from our plants demonstrated that both were being controlled. After 27 years of controlled

TIME-WEIGHTED AVERAGE EXPOSURE TO CMME (PPM)

JOB	1966	1970	1971	1972
OPERATOR #1	0.5			
OPERATOR #2			2.4	0.29
OPERATOR #3			1.8	0.3
OPERATOR #4			0.6	0.1
OPERATOR #5				0.43
OPERATOR #6		0.34	0.08	0.24
OPERATOR #7			0.04	0.10
OPERATOR #8			0.04	0.24

Fig. 8

8-HOUR TWA EXPOSURE TO BIS-CHLOROMETHYL ETHER (PPB, V/V) BY QUARTER, 1972-1975

YEAR	FIRST QUARTER	SECOND QUARTER	THIRD QUARTER	FOURTH QUARTER	AVERAGE
OPERATOR #1					
1972	2.7	0.15	0.35	0.33	0.89
1973	1.2	0.65	0.64	0.44	0.74
1974	0.99	0.33	1.8	0.34	0.87
1975	0.80	0.11	0.24	0.18	0.33
OPERATOR #2					
1972	3.1	0.07	0.12	0.12	0.87
1973	0.36	0.33	0.77	0.23	0.42
1974	0.40	0.10	0.83	0.07	0.35
1975	0.15	0.07	0.18	0.06	0.12
OPERATOR #3					
1972	0.51	0.11	0.09	0.11	0.21
1973	0.40	0.26	0.16	0.18	0.22
1974	0.42	0.19	0.91	0.16	0.41
1975	0.37	0.04	0.08	0.09	0.14

Fig. 9

8-HOUR TWA EXPOSURE TO BIS-CHLOROMETHYL ETHER (PPB, V/V) BY QUARTER, 1972-1975

YEAR	FIRST QUARTER	SECOND QUARTER	THIRD QUARTER	FOURTH QUARTER	AVERAGE
OPERATOR #4					
1972	3.0	0.23	0.17	0.15	0.64
1973	0.23	0.15	0.32	0.11	0.20
1974	0.08	0.05	0.05	0.06	0.06
1975	0.06	0.04	0.05	0.03	0.04
OPERATOR #5					
1972	2.2	0.25	0.17	0.18	0.71
1973	0.31	0.24	0.50	0.17	0.31
1974	0.14	0.07	0.07	0.10	0.10
1975	0.09	0.06	0.07	0.04	0.06
OPERATOR #6					
1972	0.64	0.08	0.08	0.06	0.19
1973	0.10	0.06	0.14	0.04	0.08
1974	0.03	0.02	0.02	0.02	0.02
1975	0.02	0.02	0.02	0.01	0.02
HEAD OPERATOR					
1972	3.0	0.30	0.29	0.18	0.92
1973	0.26	0.17	0.37	0.13	0.23
1974	0.11	0.06	0.06	0.07	0.07
1975	0.07	0.04	0.06	0.03	0.05

Fig. 10

TIME	LOC 1	LOC 2	LOC 3	LOC 4	LOC 5	LOC 6	BLANK
8:06 AM							3.3
8:25 AM	2.8	3.2	3.4	3.3		2.8	3.1
10:24 AM	3.1	4.6	8.2	6.0	6.2	7.3	4.8
1:00 PM	5.5	7.9	6.4	5.8	5.3	6.3	6.9
3:19 PM	8.6	7.2	7.4	4.6	5.0	6.6	6.8
5:37 PM	7.9	7.8	20.1	12.3	10.7	7.9	4.1
7:55 PM	6.5	5.3	6.4	3.6	5.6	4.9	3.9
10:14 PM	4.2	2.8	5.4	4.5	4.2	2.4	3.3
12:32 AM	3.9	3.4	3.6	3.1	3.2	3.2	3.1
2:50 AM	3.1	3.0	3.0	2.9	3.4	3.2	3.0
5:09 AM	3.0	2.8	3.4	3.0	3.0	3.1	2.9
7:27 AM	3.0	3.2					
AVERAGES							
SHIFT 1	5.0	5.7	6.4	5.1	5.8	5.5	4.5
SHIFT 2	6.2	5.3	10.6	6.3	6.4	5.5	5.0
SHIFT 3	3.3	3.1	3.4	3.0	3.2	3.2	3.1
DAY	4.7	4.6	6.7	4.9	5.2	4.8	4.1

TIME-WEIGHTED AVERAGE EXPOSURE TO CMME

JOB CLASS	SHIFT 1	SHIFT 2	SHIFT 3
ANION OP	4.43	5.33	2.68
FINE OP.	2.75	2.75	1.57
LDR-PKGR	1.71	2.35	1.02

ND = NOT DETECTED (0.5 PPB MINIMUM DETECTABLE)
MS = MISSED SAMPLE
M/C = MAINT. OR CALIB. PERIOD BEGINS

Fig. 11

TIME	LOC 1	LOC 2	LOC 3	LOC 4	LOC 5	LOC 6	BLANK
8:06 AM							ND
8:25 AM	ND	0.7	ND	ND		ND	0.8
10:24 AM	ND	ND	ND	0.7	ND	ND	0.5
1:00 PM	ND	ND	ND	ND	ND	ND	ND
3:19 PM	ND	ND	ND	ND	ND	ND	ND
5:37 PM	ND	ND	0.9	ND	ND	ND	ND
7:55 PM	ND	ND	ND	ND	ND	ND	ND
10:14 PM	ND	ND	ND	ND	ND	ND	ND
12:32 AM	ND	ND	0.7	ND	ND	ND	ND
2:50 AM	ND	ND	ND	ND	ND	ND	ND
5:09 AM	ND	ND	ND	ND	ND	ND	ND
7:27 AM	ND	ND					
AVERAGES							
SHIFT 1	ND	ND	ND	ND	ND	ND	ND
SHIFT 2	ND	ND	ND	ND	ND	ND	ND
SHIFT 3	ND	ND	ND	ND	ND	ND	ND
DAY	ND	ND	ND	ND	ND	ND	ND

TIME-WEIGHTED AVERAGE EXPOSURE TO BIS

JOB CLASS	SHIFT 1	SHIFT 2	SHIFT 3
ANION OP	0.04	0.04	0.13
FINE OP.	0.08	0.01	0.03
LDR-PKGR	0.00	0.03	0.06

ND = NOT DETECTED (0.5 PPB MINIMUM DETECTABLE)
MS = MISSED SAMPLE
M/C = MAINT. OR CALIB. PERIOD BEGINS

Fig. 12

OPERATOR JOB TITLE	DATE	VINYL CHLORIDE	VINYLIDENE CHLORIDE
POLYMER OPERATOR #1	1-08-75	2.4	1.5
	2-13-75	—	10.1
	5-12-75	0.2	0.2
	6-13-75	4.5	1.0
POLYMER OPERATOR #2	3-12-75	1.7	4.5
	3-27-75	0.6	1.0
	4-10-75	10.5	1.1
	5-21-75	5.7	5.9
	6-16-75	1.1	0.4
POLYMER OPERATOR #3	1-06-75	17.4	5.0
	2-13-75	2.3	0.7
	3-12-75	0.9	2.0
	4-02-75	0.4	0.7
	5-12-75	0.3	0.4
	6-17-75	0.5	0.2
POLYMER OPERATOR #4	2-27-75	0.3	0.8
	3-12-75	4.7	1.3
	4-10-75	2.9	0.3
	5-21-75	3.6	0.7
	6-16-75	1.3	0.3
POLYMER OPERATOR #5	3-13-75	2.9	1.1
	4-24-75	0.8	0.8
	5-19-75	0.2	0.1
POLYMER OPERATOR #6	3-13-75	0.7	2.7
	4-24-75	5.9	1.5
	6-03-75	0.3	0.1

operation, using closed systems, no cases of oat-cell carcinoma have been observed in these employees.

We recently built a new CMME plant and, as the exposure data show, the process research which lowered the BCME formation has also lowered the BCME level in the environment. (Figs. 9-13) Has the cost of this research benefitted these employees or society? Since plants using closed systems were already safe, it is difficult to demonstrate a health benefit from this costly research.

VINYL The last carcinogen plant to be discussed is vinyl chloride. I know of no vinyl chloride plant, either producer or user, that doesn't use respirators. The emphasis on documenting employee exposure rather than controlling exposure has been very costly. Certainly, OSHA and/or NIOSH owe both the employees and employers a report on the results of the present standard. (Figs. 14-15) What are the benefits of a 1 ppm standard versus a 10 ppm standard? Both employees and employers are very much aware of the cost to them in comfort and dollars, respectively.

Technology is available to control toxic chemicals, including carcinogens. Industry is being forced to use this technology to remain competitive. The bottom of the industrial cancer iceberg has failed to appear and the rate of lung cancer due to smoking tobacco is rapidly increasing. (Fig. 16) Dermatitis continues to be

COPOLYMER PLANT
OPERATORS' 8-HOUR TWA
EXPOSURE IN PPM (V/V)

OPERATOR JOB TITLE	DATE	VINYL CHLORIDE	VINYLIDENE CHLORIDE
OPER #1	1-07-75	3.8	1.7
	1-20-75	0.3	0.3
	4-02-75	0.2	0.2
	6-16-75	0.9	0.1
OPER #2	1-13-75	0.9	0.6
	3-10-75	0.4	0.3
	4-10-75	0.1	0.2
	5-08-75	0.3	0.1
	6-06-75	0.4	0.1
OPER #3	2-27-75	10.2	15.4
	3-10-75	0.6	3.0
	4-29-75	0.6	0.8
OPER #4	3-10-75	0.6	3.0
	4-29-75	0.6	0.8
OPER #5	5-20-75	0.2	0.3
	6-18-75	0.3	0.1

Fig. 15

the leading industrial disease. Are we using our limited industrial hygiene resources effectively?

No. As stated previously, employee exposures to carcinogens can be controlled using the proven industrial hygiene methods. Our efforts should be expended on the total work environment rather than overemphasizing those few compounds that may cause latent disease. **OH&S**

RESULTS OF ANION EXCHANGE PLANT PERSONAL MONITORING

OPERATOR NUMBER	SHIFT	DATE	CONCENTRATION (PPB, V/V) CMME	BCME
61920	AFTER-NOON	3/15	6.50	< 0.01
27635	MIDNIGHT	3/15	15.1	0.07
67145	DAY	3/16	1.42	< 0.01
60450	AFTER-NOON	3/16	0.21	< 0.01
53841	MIDNIGHT	3/16	0.21	< 0.01
66359	DAY	3/17	0.34	< 0.01
61920	AFTER-NOON	3/17	0.47	< 0.01
57244	MIDNIGHT	3/17	1.1	< 0.01
67145	DAY	3/18	0.52	< 0.01

Fig. 13

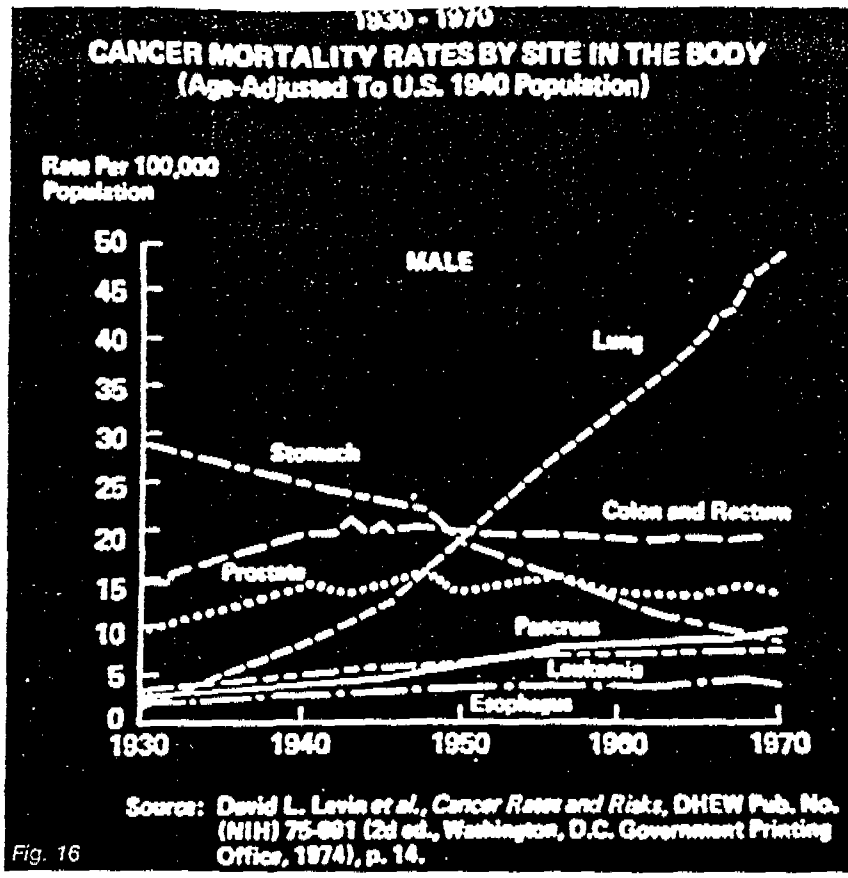

Fig. 16

Health protection must be part of planning, continued from p. 31.

Results of the air sampling program are summarized in Table 1.

From these data it was concluded that respiratory protection was necessary during cleanup and maintenance operations. In addition, some local, spot ventilation (high velocity-low volume) is being considered for certain types of operations. In the interim, respiratory protection will be used to minimize the exposure potential. (Fig. 4).

Exposed skin areas of employees are checked both before and after work shift, using an ultraviolet light (long wavelength). Pre-work skin checks are necessary to be certain the employees are not using lotions, etc. which fluoresce and therefore interfere with the surveillance procedure. This technique is also used to survey tools and equipment leaving the controlled area as well as general area surveys to identify areas contaminated with PNA's for cleanup purpose.

PROGRESS The medical surveillance tests being utilized are those which will lead to early detection of adverse health effects and represent the best currently available tests.

The industrial hygiene program is a simplistic approach to a very complex problem. Certainly, adequate control measures can be developed to minimize the exposure potential. Data interpretation is confounded because of lack of adequate techniques to evaluate the impact of complex mixtures

The hygienist used all his skills and tools to monitor and alert.

on the potentially exposed population. A better technique is needed to quantify exposures.

In the interim, every possible bit of information must be collected in the event that a retrospective study must be done. If it is not, even the retrospectroscope won't help. Everything possible must be done to prevent a repeat of the morbidity-mortality experience seen in the coke workers.

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