Pulmonary effects of acute exposure to degradation products of sulphur hexafluoride during electrical cable repair work

Allen Kraut, Ruth Lilis

Abstract

Six electrical workers accidentally exposed to degradation products of sulphur hexafluoride (SF_6) during electrical repair work were followed up for one year. One degradation product, sulphur tetrafluoride (SF_4), was identified from worksite measurements. Unprotected exposure in an underground enclosed space occurred for six hours over a 12 hour period. Initial symptoms included shortness of breath, chest tightness, productive cough, nose and eye irritation, headache, fatigue, nausea, and vomiting. Symptoms subsided when exposure was interrupted during attempts to identify the cause of the problem. Although exposure ended after several hours, four workers remained symptomatic for between one week and one month. Pulmonary radiographic abnormalities included several discrete areas of transitory platelike atelectasis in one worker, and a slight diffuse infiltrate in the left lower lobe of another. One worker showed transient obstructive changes in tests of pulmonary function. Examination at follow up after one year showed no persistent abnormalities. Preliminary data from this paper were presented at the VIIth international pneumoconiosis conference. Pittsburgh, PA, August 1988.

Sulphur hexafluoride (SF_6), a heavy, colourless, and odourless gas of high chemical stability, was first synthesised in 1902.¹ It is an effective scavenger of electrons and can efficiently retard electrical conduc-

tion. For this reason SF_6 is used as an electrical insulating material in circuit breakers, cables, capacitors, and transformers,² and has allowed for the creation of compact electrical substations.³ Occupational exposure to this compound has increased recently in the United States, from 177 potentially exposed workers in 1971 to over 9000 by the early 1980s.^{4,5} Over half of the exposed workers are electrical and electronic equipment repair personnel.⁵

Sulphur hexafluoride is inert; mice can safely breathe a mixture of 80% SF_6 and 20% O_2 for 12-16 hours.⁶ It degrades to a variety of sulphur oxyfluorides during electrical arcing in the presence of oxygen,^{7,8,9} and under anaerobic and anhydrous conditions sulphur tetrafluoride (SF_4) may be detected.⁷ Sulphur tetrafluoride is highly reactive and forms thionyl fluoride (SOF_2) and hydrogen fluoride (HF) in the presence of water.¹⁰ It possesses an odour similar to sulphur dioxide,¹¹ and is extremely irritating and corrosive to the respiratory tract, skin, and eyes.¹² Toxic pulmonary effects have been reported in animal experiments.^{13,14,15} The toxicity of SF_4 has been compared with that of phosgene.⁶ The degradation product SOF_2 has an odour similar to hydrogen sulphide. It is not irritating to mucous membranes but can cause pulmonary oedema in animals.⁷ Other degradation products of SF_6 include SO_2F_2 , S_2F_{10} , and SO_2 . The precise compounds that are produced depend upon the characteristics of the reaction and the moisture and oxygen content of the surrounding air. Table 1 lists American Conference of Govern-

Table 1 Threshold limit values (TLVs)* for SF_6 and some of its degradation products

Compound	TLV
SF_6	1000 ppm TWA†
SF_4	0.1 ppm ceiling
S_2F_{10}	0.01 ppm ceiling
SOF_2	Compound not listed
SO_2F_2	5.0 ppm TWA 10.0 STEL††
HF	3.0 ppm ceiling

*From American Conference of Government Industrial Hygienists.¹⁶

†TWA = Eight hour time weighted average.

††STEL = Short term exposure limit.

Departments of Internal Medicine and Community Health Sciences, University of Manitoba, NA—618 700 McDermot Ave, Winnipeg, Canada R3E 0W3
A Kraut
Division of Environmental and Occupational Medicine, Department of Community Medicine, Mount Sinai Medical Center, 1 Gustave L Levy Place, Box 1057, New York, NY 10029, USA
R Lilis

ment Industrial Hygienists threshold limit values for SF₆ and some of its degradation products.¹⁶

To our knowledge, only one report of human exposure to SF₆ degradation products has previously been published.¹⁷ Two workers were rendered unconscious following exposure to these compounds in an enclosed space. One of the workers developed pulmonary oedema; SO₂F₂ was identified at this worksite.

Circumstances of exposure and acute symptoms

Concurrent with the loss of a large amount of polybutene insulating oil from an electrical transmission cable, a burnout occurred in circuit breakers at a substation several miles further downline. Four days later a team of six gas operators (workers 1–6) began repair work near the substation. The worksite was an underground space 3 m × 1.2 m × 2.4 m with two openings, each 0.9 m in diameter. Four members of the crew (1–4) worked underground, while the safety officer (5) remained on the surface. The foreman (6) worked above or below ground as needed. All workers were previously healthy, except for worker 5 who had emphysema and asbestosis.

Before entering the worksite, routine measurements for natural gas and oxygen concentrations showed acceptable concentrations. Respiratory protective equipment was not available. At around 9.00 am workers began using smith cutters powered with compressed air to open the pipe. About one hour later, the five underground workers noticed a “burning battery” like odour and experienced eye irritation with tears, dry and burning throat, and tightness of the chest. The crew went above ground and symptoms decreased after some fifteen minutes. Similar symptoms recurred and abated as the workers left and returned to the worksite in attempts to determine the source of the problem.

The company chemist called to investigate the worksite did not detect any abnormalities on routine air monitoring but took samples from the partly opened pipe for analysis by mass spectrometry. Repair work was stopped after workers again experienced chest tightness, shortness of breath, headache, fatigue, nose bleed, nausea, and vomiting upon returning to work. At 10.00 pm the crew was sent home as the chemist’s final report was not yet available. At around 1.00 am, all workers were notified by telephone to go immediately to the nearest hospital emergency room as SF₆ had been identified in the air samples from the worksite.

Although the exact sequence of events leading to the exposure could not be determined, a likely sequence was as follows. The loss of insulating oil or the subsequent burnout led to disruption of the valve separating the circuit breakers from the cable. Because of the intense heat of the burnout, SF₆

decomposed. Further breakdown under anaerobic and anhydrous conditions produced SF₄ which was forced into the pipe containing the cable and escaped as the pipe was opened at the worksite. Released SF₄ would then hydrolyse. Although other breakdown products may have been present, SF₄ was the only one reported. As the measurement was qualitative, the level of exposure cannot be given.

Medical evaluation

Five of the workers presented to one emergency room, and the sixth to another. Chest radiographs taken about 26 hours after the start of exposure were reported to be normal in five workers who were discharged a few hours later. Worker 1 who presented with headache, a cough productive of blood streaked sputum, and wheezing and who had three discrete areas of atelectasis, identified by chest radiography, was kept in hospital. Pulmonary function tests (PFT) performed one week later were normal. During his stay in hospital, he developed fever and headache and a productive cough persisted for more than a week.

All six workers chose to come to the Mount Sinai Occupational Medicine Clinical Centre for assessment between two and three weeks after the accident. Table 2 lists individual symptoms and their duration obtained through review of the emergency room records and interviews with the workers at their assessment. Most symptoms resolved within a week of exposure, and almost all had disappeared by one month. Intermittent epistaxis was the most persistent symptom. Evaluation one year after the event did not show any persistent symptoms except for one worker who, although able to maintain his usual lifestyle, complained of persistent fatigue. Physical examination did not detect any pertinent abnormalities at either evaluation.

Review of the initial emergency room chest radiographs showed that worker 6 had a slight diffuse infiltrate in his left lower lung field. All follow up radiographs taken between 10 and 21 days after the accident and again one year later had returned to normal or were unchanged from pre-exposure films.

Pulmonary function tests were not performed during the initial emergency room evaluation but were ordered by the company doctor between three and 10 days after the event for five of the six workers, and for the sixth a few days later. Initial and follow up spirometry performed on five workers did not show any abnormalities that could be related to the exposure. Worker 3 had three sets of PFT in the weeks following exposure. The first was normal. Those taken two weeks after the event showed an obstructive pattern with forced vital capacity (FVC) 109% and forced expiratory volume in one second (FEV₁) 67% of predicted values. Although this worker denied a history of asthma, he complained of

Table 2 Symptoms in workers exposed to degradation products of SF₆

Symptoms	Worker					
	1	2	3	4	5	6
Burning/watering eyes		*	*	*	*	*
Nasal irritation/epistaxis	■		■	■		
Throat irritation	*			*		■
Chest tightness/wheezing/shortness of breath	*	*	■	■□		*
Cough	■	*	*			
Nausea/vomiting	*	*				
Fatigue		■	■	△		
Headache	*		■			

*Symptoms after exposure.
■ Symptoms lasting between one week and one month.
△ Symptom persisting for one year.
□ Symptom recurred after six months, but was probably not related to the exposure.

tightness of the chest and shortness of breath on exposure to cold air for approximately one week after the accident. Repeat testing when asymptomatic and after one year were normal. Diffusing capacities for carbon monoxide were normal in all workers except number 5 who had pre-existing emphysema and asbestosis.

Discussion

Although odour should not be relied on to identify toxic exposures, odours present in areas containing heated SF₆ must be considered to be coming from decomposition products and trigger the use of proper safety procedures.^{7,18} An odour similar to a "burning car battery" was identified by workers, but unfortunately no one taking part in the initial investigation recognised this warning signal.

Workers were exposed for about six hours over a 12 hour period. All five underground workers had respiratory tract symptoms, the sixth who remained above ground experienced only eye irritation. Radiographic evidence of multilobar atelectasis was present in one worker. A second worker developed chest tightness on exposure to cold air and transitory obstructive changes on PFT. These findings are consistent with the known effects of exposure to irritant gases. Examination one year after the event did not show any persistent adverse consequences.

The potential for toxic exposures to decomposition products of SF₆ are well documented in its safety data sheet.⁸ None of the exposed workers, however, some with over 20 years experience in the electrical industry, had heard of SF₆ or SF₄ before the accident or were aware that their work could lead to exposure to respiratory irritants. Had the workers or company officials been aware of the potential for this exposure, it would likely have been of much shorter duration. Proper education may have prevented the adverse health effects experienced by these workers.

Because of the increased use of SF₆ in the electrical transmission industry¹⁹ it is likely that further

exposures to decomposition products of SF₆ will occur in the future. Occupational health personnel should be aware that exposure to SF₄ and other SF₆ degradation products are important health hazards for workers repairing damaged electrical systems containing SF₆.

Requests for reprints to: Dr A Kraut, Departments of Internal Medicine and Community Health Sciences, University of Manitoba, NA-618 700 McDermot Ave, Winnipeg, Canada R3E 0W3.

1 Moissen H, Lebeau P. Etude des Fluorures et Oxyfluorures de Soufre. *Annales de Chimie et de Physique* 1902;26:145-78.
2 Eibeck RE, Myers W. Fluorine compounds, inorganic. In M Grayson, ed. *Kirk-Othmer encyclopedia of chemical technology*, 3rd ed vol 10. New York: John Wiley and Sons, 1980:799-811.
3 Basileco J. Substation Design. In: Fink DG, Beaty HW, eds. *Standard handbook for electrical engineers*, 12th ed. New York: McGraw, 1987;17:1-51.
4 National Institute of Occupational Safety and Health. *National occupational exposure survey*. Cincinnati: NIOSH, 1978. (HEW (NIOSH) pub no. 78-114.)
5 National Institute of Occupational Safety and Health. *National occupational hazard survey*. Cincinnati: NIOSH, 1990. (DHEW (NIOSH) publ pending.)
6 Smith WC, Tullock CW, Muetterties EL, et al. Fluorination reactions of SF₄. *American Chemical Society Journal* 1959; 81:3165-6.
7 Boudene C, Cluet JL, Kreb G, Wind G. Identification and study of some properties of compounds resulting from the decomposition of SF₆ under the effect of electrical arcing in circuit breakers. *Revue Generale de l'electricite*. 1974;185:45-78.
8 Air Products and Chemicals Inc. *Air products specialty gas material safety safety sheet sulfur hexafluoride*. Allentown Pa: APCI, 1986.
9 Sauers I. By-product formation in spark breakdown of SF₆/O₂ mixtures. *Plasma chemistry and plasma processing* 1988;8: 247-62.
10 Sauers I, Adcock JL, Christophorou LG, Ellis HW. Gas phase hydrolysis of sulfur tetrafluoride: A comparison of the gaseous and liquid phase rate constants. *Journal of Chemical Physics* 1985;83:2618-9.
11 Center for Chemical Hazard Assessment, Syracuse Research Corporation. *Information profiles on potential occupational hazards: sulfur tetrafluoride*, Report No SRC TR 81-549. Syracuse, NY: (CHASRC, (Report No SRC TR 81-549).
12 Air Products and Chemicals Inc. *Air products specialty gas material safety safety sheet sulfur tetrafluoride*. Allentown, Pa: APCI, 1986.

- 13 American Conference of Government Industrial Hygienists. *Documentation of the threshold limit values for substances in workroom air*. 5th ed. Cincinnati: ACGIH, 1986.
- 14 Air Products and Chemicals. *Inc Sulfur Tetrafluoride*, Bulletin. Allentown, Pa: APCI. (Bulletin No C174BuB-O.)
- 15 Clayton JW. the toxicity of fluorocarbons with special reference to chemical constitution: *J Occup Med* 1962;4:262-73.
- 16 American Conference of Governmental Industrial hygienists. *Threshold limit values and biological exposure indices for 1989-1990*. Cincinnati, Ohio, 1989.
- 17 Pilling KJ, Jones HW. Inhalation of degraded sulphur hexafluoride resulting in pulmonary oedema. *J Soc Occup Med* 1988;38:82-4.
- 18 Amalric J, Fallau M, Mazingarbe E, Tellier R, Vigreux J. practical consequences of research on the decomposition by arc of SF₆. *Revue Generale de l'electricite* 1974;185:78-85.
- 19 Troger H, Boeck W, Hogg B, et al. The state of international development and experience with SF₆ insulated high voltage switchgear. *International conference on large high voltage electrical systems*. Paris: CIGRE, 1982: Session 23.01:1-6.

Accepted 15 May 1990

Destruction of manuscripts

From 1 July 1985 articles submitted for publication will not be returned. Authors whose papers are rejected will be advised of the decision and the manuscripts will be kept under security for three months to deal with any inquiries and then destroyed.