Occupational Health & Safety Practitioner

Reading

CASE STUDY: HYDROFLUORIC ACID

January 2006



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Overview

Objectives

After reading this information you should be able to:

- understand the physical/chemical/toxicological properties of 70% w/w hydrofluoric acid;
- recall the principles of hazard identification, risk assessment and control and apply them to this case study; and
- identify the significant faults that led to the accident and the importance of applying the hierarchy of controls to prevent further accidents.

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SECTION 1: INTRODUCTION

1.1 Hydrofluoric acid is dangerous

Hydrofluoric acid is a corrosive and toxic liquid that is potentially

fatal even following dermal exposure to small amounts (Burke et al., 1973). The fatality described below highlights the potential for relatively small quantities of concentrated hydrofluoric acid to produce acute systemic toxicity and it is clear that laboratory personnel underestimated the risks associated with the acid. The purpose of this information is to raise

Small amounts of concentrated hydrofluoric acid on the skin can be fatal.

KEY POINT

awareness of the inherent dangers associated with dermal contact with concentrated hydrofluoric acid and of the importance of observing strict precautions when handling it.

This reading is based on a short communication first published in *Ann. Occup. Hyg.*, Vol. 40, No. 6, pp. 705-710, 1996.

SECTION 2: ACCIDENT DESCRIPTION

2.1 Hydrofluoric acid is used to examine fossils for oil potential

A palynological technique used by geologists involves the dissolving of sedimentary rock with mineral acids (hydrochloric and hydrofluoric acid) to liberate acid-insoluble microscopic fossils. The fossils are then examined by microscopy to determine the age of the rock and oil potential.

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2.2 Unsafe system of work

A 37 year old male laboratory technician was performing acid digestion of oil well core and ditch samples with 70% w/w concentrated hydrofluoric acid in a fume cupboard. He was believed to be seated when he knocked over a small quantity (100-230 ml) of hydrofluoric acid onto his lap, splashing both thighs. The only personal protective equipment (PPE) worn was two pairs of wrist length rubber gloves and a pair of polyvinyl chloride (PVC) sleeve protectors. As a result of the fact that the technician was working alone, it is unclear whether the spill was from the digestion cup or the 2 litre. bulk acid container.

2.3 Calcium gluconate was not available

The technician sustained burns to 9% of his body surface area, despite washing his legs with water from a makeshift plumbing arrangement that supplied water at 6 litres per minute. No calcium gluconate gel was applied to the affected area (this gel is an effective topical treatment for hydrofluoric acid burns) and contaminated clothing was not removed during the flushing with water. Following

KEY POINT

Calcium gluconate is the topical (on the skin) treatment most effective in binding fluoride ion on the skin.

flushing, the technician, who appeared to be in severe pain and shock, immersed himself in a chlorinated swimming pool at the rear of the workplace, where he remained for approximately 35-40 min before ambulance help arrived.

2.4 He died from multi-organ failure 15 days later

The injured man was hypothermic and hypocalcaemic (lack of calcium) on admission to an intensive care unit at a nearby hospital, and soon became unconscious. His condition continued to deteriorate despite subcutaneous injections of calcium gluconate and administration of intravenous calcium and magnesium. His right leg was amputated 7 days after the incident. He subsequently died from multi-organ failure 15 days after the hydrofluoric acid spill.

SECTION 3: LIKELY CONTRIBUTING FACTORS

3.1 Amount of fluoride ion absorbed

The most significant factor influencing acute systemic toxicity of hydrofluoric acid is the total amount of fluoride ion absorbed. In dermal exposures this is a function of the duration of exposure, the total surface area affected and the concentration of the hydrofluoric acid (Krenzelok, 1992).

3.2 Body surface area exposed

It is clear that one of the main factors that contributed to the systemic effects in this case was the dermal exposure of 9% body

surface area to concentrated hydrofluoric acid. Wounds as small as 2.5% of the body surface area from concentrated hydrofluoric acid can produce hypocalcaemia of potentially lethal extent within 2 or 3 hours (Greco *et al.*, 1988).

KEY POINT

An area the size of the hand (approx. 2.5% of the body surface area) is generally seen as the minimum for potential lethal action following contact with concentrated hydrofluoric acid.

3.3 Inadequate personal protective clothing and equipment

Adequate personal protective equipment during the handling of concentrated hydrofluoric acid could have prevented this death. Full-length PVC coveralls with sleeves to the wrist or a full-length PVC apron with sleeves protectors, a face shield, rubber boots, safety goggles and mid-arm length PVC gloves should have been worn by the deceased when hydrofluoric acid was being used in the fume cupboard.

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3.4 Duration of exposure

The duration of exposure may also have contributed to the uptake of the fluoride ion. Hydrofluoric acid passes through the skin into deep tissue rapidly and the affected area must be flushed with water immediately (Bracken et al., 1985; Greco et al., 1988). The deceased did not have access to an emergency shower to remove the hydrofluoric acid, and instead the skin was washed from a hose that provided water at a very low flow rate. Because of the low flow rate, the volume of water may have spread the hydrofluoric acid onto other parts of the skin, rather than washing the hydrofluoric acid off the skin. After a number of minutes, the deceased immersed himself in the swimming pool.

3.5 Calcium gluconate gel was not available

Although flushing is effective in removing surface hydrofluoric acid, it does not affect the fluoride ion that may have already penetrated deeper (White, 1984). In this instance, no calcium gluconate gel was applied following dermal exposure to hydrofluoric acid; calcium gluconate gel is an effective topical treatment for hydrofluoric acid burns (Trevino *et al.*, 1983).

3.6 Inhalation was another possible route of exposure

In addition to the burns sustained, inhalation may have been another route of exposure due to the relatively high vapour pressure of hydrofluoric acid. Pulmonary oedema (fluid in lungs) was noted at autopsy but it was unclear whether this was due to hydrofluoric acid inhalation or to other causes.

KEY POINT

Due to the high vapour pressure of 70% hydrofluoric acid (15 mmHg at 20°C and 1 atmosphere), inhalation was a possible route of entry for hydrofluoric acid that could have contributed to the fluoride poisoning.

3.7 Substandard design of workstation and inadequate workspace

An ergonomic assessment of the workstation indicated the following:

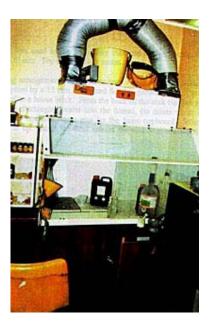
- The working height of the fume cupboard was too low (by between 110 and 160mm) for the deceased to work comfortably in a standing position. Sitting would have increased the body surface area during a spill of hydrofluoric acid. An appropriate bench height working surface should have been provided for the operator.
- 2. Instability of the digestion cups due to lightweight construction, that is, height 75mm, diameter of base 59mm, diameter at top 78mm made of 2mm polyethylene.
- Lack of available working space in general and in particular within the fume cupboard: entrance of the fume cupboard was 470mm wide and 410mm high.
- 4. As a result of the design of the container, decanting from the 2 litre 70% w/w hydrofluoric acid container was awkward, involving the pronation of the forearm (movement downwards and twisting of the wrist). Use of smaller sized bottles or better designed containers (to minimise awkward pouring postures) or introduction of a graduated dispensing unit to negate pouring the acid would have reduced the risk.

KEY POINT

A funnel and narrow perspex opening at the entrance of the fume cupboard prevented safe handling of the hydrofluoric acid because the worker could not adopt an appropriate worker's posture when standing.

Overall, the laboratory did not comply with the requirements of Australian Standard *Safety in Laboratories* (AS 2243, 1992) Parts 1, 2 and 8 in the areas of emergency procedures, safe handling and disposal of the chemical and laboratory design.

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Left: Fume cupboard where the spill of 70% w/w hydrofluoric acid occurred. Note the restricted space of the fume cupboard (a funnel and narrow perspex opening), the digestion cup and 2 litre. bulk hydrofluoric acid container.



Above: The laboratory personnel may have minimised the likelihood of a spill through the introduction of cup supports for the digestion cups.



Above: Provision of a fume cupboard that had more working space, such as in this photograph, would have reduced the risk.

SECTION 4: ENFORCEMENT ACTION AGAINST EMPLOYER

4.1 Notices issued

The following notices were issued by WorkSafe Western Australia inspectors following their investigation of the accident:

- A prohibition notice preventing the use of hydrofluoric acid unless calcium gluconate gel, eyedrops and tablets are at hand.
- A prohibition notice for handling of hydrofluoric acid if persons handling the acid are not equipped with adequate personal protective equipment to protect them from the acid in accordance with the Worksafe Australia Guide for Hydrogen Fluoride 1989.
- A prohibition notice for the handling of chemicals in the workplace unless adequate information for safe use has been provided as contained in the relevant Material Safety Data Sheet.
- An improvement notice was given to the supplier of the hydrofluoric acid to provide a Material Safety Data Sheet whenever the acid is supplied to a workplace.

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4.2 Coroner's inquest findings

The coronial inquiry into the fatal accident delivered the following findings:

WESTERN AUSTRALIA

The Coroners Act, 1920 INQUISITION (Taken without a Jury)

AN INQUISITION taken at the CORONER'S COURT, PERTH, within the State of Western Australia, this 29th day of June, 1995 (and on divers other days by me David Arnold McCANN S. M., Coroner for the said State by law authorised to inquire-

When, where and after what manner (*Name of deceased worker*) came by his death.

Upon inquiry I find:

(a) that the deceased (*Name of deceased worker*) died on 12 November, 1994, at Fremantle Hospital as a result of Multiple Organ Failure following burns with Hydrofluoric Acid.

I find that death arose by way of accident.

In witness whereof I, the said Coroner, David Arnold McCANN S. M., have to this inquisition set my hand, at Perth, in the said State, this 4th day of August 1995.

Coroner

(Section 43(8) of the Coroners Act, 1920, provides that the Coroner shall not express any Opinion on any matter outside the scope of the inquest, except in a rider which, in his opinion, is designed to, and may if given effect to, prevent the recurrence of similar occurrences. A rider is not part of the decision or finding, but it may be recorded, if the Coroner thinks fit.)

4.3 Coroner also wrote to WorkSafe Western Australia

As a rider Coroner McCann wrote to WorkSafe Western Australia on 18 August 1995 stating:

"I ask that you give consideration to the question whether there was a serious breach of the *Occupational Health, Safety and Welfare Act*.

As Coroner, I was precluded from expressing any view on this question. I acknowledge that you may have already done so but, having heard the evidence, I felt it was important to raise this issue with you."

4.4 The prosecution

In November 1995 WorkSafe WA successfully prosecuted the employer in this case. On 1 November 1995 before Mr Roberts SM in the Perth Court of Petty Sessions there were guilty pleas and fines to all the charges. Subsequently, leave to appeal was granted and heard before Judge Ipp on 13 August 1996, and finalised on 22 August 1996. The significant details of the charges were as follows:

- Failure of the employer to provide and maintain a system of work such that so far as was practicable its employee was not exposed to a hazard; contrary to section 19(1)(a); fine \$35,000, reduced on appeal to \$17,500.
- Failure to provide its employee with such adequate personal protective clothing as was practicable to protect him against the hazard of contact with hydrofluoric acid; contrary to section 19(1)(d); fine \$20,000, reduced on appeal to \$5,000.
- Failure to notify the Commissioner for Occupational Health, Safety and Welfare in the prescribed form where an accident at a workplace resulted in an injury to its employee that, on the basis of medical advice, appeared likely to result in the employee being absent from his employment for 10 or more working days; contrary to section 19(3)(b); fine \$1,000.
- Director x being a director of a body corporate when that body corporate was guilty of an offence when that offence was attributable to his neglect; contrary to section 55; fine \$35,000, reduced on appeal to \$5,000.

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SECTION 5: DISCUSSION AND CONCLUSION

5.1 Similar fatality involving 8% burns and no application of calcium gluconate

Mullett *et al.* (1987) described a similar fatality with 70% hydrofluoric acid when a 61 year old male sustained burns to 8% of his body surface area. That individual died from cardiac arrhythmia, secondary to the depletion of ionized calcium by fluoride ion. As in the case reported here, the burns were predominantly on the right leg, the injured person washing his leg with tap water for approximately 15 min. He reached the hospital 35 min after sustaining the injury. Calcium gluconate gel was not applied to the burns site until he reached the hospital and although subcutaneous and intravenous calcium therapy was given at the hospital, he died 15.5 hours after the injury.

5.2 Immediate showering and application of calcium gluconate to 22% burns resulted in survival

By contrast, Greco *et al.* (1988) reported the case of a 50 year old worker who survived burns to 22% body surface area from 70% hydrofluoric acid. He showered immediately, had calcium gluconate gel applied to the wounds and was taken to a nearby hospital where he was promptly treated with subcutaneous and intravenous calcium.

It is evident that apart from the location of burns, the size of the burns and concentration of the acid, washing the affected area immediately and the application of calcium gluconate gel to reduce the uptake of fluoride ion may prevent a fatality.

5.3 Important factors in the development of hypocalcaemia

Greco *et al.* (1988) proposed that the development of hypocalcaemia (lack of calcium) may occur in the following situations:

- burns of ≥ 1% surface area from 50% (or greater concentration) hydrofluoric acid;
- 5% or greater surface area with any concentration of hydrofluoric acid; and
- inhalation of fumes from 60% (or greater concentration) hydrofluoric acid.

5.4 Importance of PPE and emergency procedures

As noted by Stencel and Tobin (1987) and Mansdorf (1987), appropriate protective clothing, prompt first-aid and proper clean-up procedures are critical for workers handling hydrofluoric acid. Failure to wear appropriate PPE and failure to follow appropriate first-aid procedures may result in severe injury and increase the likelihood of death from fluoride poisoning. Nearly 90% of hydrofluoric acid exposures result in the development of some toxic side effects, and approximately 80% of patients require treatment in a health care facility (Krenzelok, 1992).

5.5 Adequate risk assessment and compliance with legislation and standards are essential

It is clear that the laboratory did not comply with relevant Australian Standards for Safety in Laboratories. Compliance with the Australian Standards would have significantly reduced the likelihood of this accident. Proper risk assessment in compliance with the Occupational Safety and Health Regulations and in accordance with the Code of Practice for the Control of Workplace Hazardous Substances would have prevented fatalities such as the one described here.

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REFERENCES AND FURTHER READING

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Further reading

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