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An Improved Method for Emergent Decontamination of Ocular and Dermal Hydrofluoric Acid Splashes*

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ABSTRACT. Accidental hydrofluoric acid (HF) splashes often occur in industrial settings. HF easily penetrates into tissues by initial acid action allowing fluoride ions to penetrate deeply, chelating calcium and magnesium. Resultant hypocalcemia and hypomagnesemia can be fatal. This report describes the utilization of Hexafluorine® — a hypertonic, amphoteric, chelating decontamination solution — in workplaces where water decontamination followed by calcium gluconate inunction failed to prevent HF burns and systemic toxicity. Between 1998 and 1999, 16 cases of ocular and dermal HF splashes with either 70% HF or 6% HF/15% nitric acid (HNO_3) were decontaminated with Hexafluorine® at the worksite. HF burns did not develop and medical treatment other than initial decontamination was not required in 12/16 (75%). In 7/16 (44%) cases, lost work time corresponded to duration of hospital observation (mean < 1 d).

Hydrofluoric acid (HF) is a weak acid (pK = 3.2) widely utilized in industrial settings in areas such as metallurgy, paper production, ceramics, microelectronics, glass cutting and etching. Workers can be exposed in such operations as metal stripping and polishing, decanting or maintenance. Risks of HF splashes include the development of severe burns, as well as systemic intoxication that is sometimes fatal with exposure to high concentrations. Decontamination with water followed by inunction of calcium gluconate gel has been relatively efficacious for skin splashes with low concentrations of HF, but is not capable of preventing either burns or systemic toxicity with exposure to high concentrations. This report describes the results of an improved protocol using Hexafluorine® for decontamination of HF splashes in a Swedish metallurgy facility.

METHODS

Avesta Polarit Group is a company working with stainless steel, including pickling operations. In different workplaces, HF is utilized as a 70% concentrate or a dilute mixture of 6% HF/ 15% HNO_3. Splashes with either concentrated HF or the dilute HF/HNO_3 mixture occurred mainly during repair or maintenance operations.

Prior to 1998, an HF splash protocol of initial water decontamination followed by inunction of calcium gluconate gel used in this facility did not produce satisfactory results (see following Case Report). The facility first made an inventory and minimized the risks, and where a risk of HF splashes persisted, evaluated where it was necessary to pre-position first aid devices containing Hexafluorine® HF and acid decontamination solution.

As a second step, the facility established a major education campaign for personnel with potential HF exposure which included the importance of using adequate personal protective equipment and the immediate and delayed effects of HF exposure, depending on the concentration.

A new decontamination protocol was then put into effect: initial decontamination of all ocular or dermal HF splashes should consist of Hexafluorine® lavage within 1 min of exposure. In the absence of Hexafluorine® in close proximity to the accident site, initial decontamination with water should be done. Following all HF splashes decontaminated with Hexafluorine®, the victim should also have a consultation with a hospital-based medical specialist.

An internal maintenance program was established for safety equipment and particularly for the Hexafluorine® DAPs (stand-alone portable showers) to guarantee proper functioning in an emergency. A tracking system for accidents and their outcomes was also established.

CASE REPORT

In August 1996, while checking a leaking valve, an operator received a splash with concentrated 70% HF in his face and on his throat, one arm and the abdomen. There was an immediate sensation of pain. The victim was immediately undressed and lavaged with water for 15 min. The worker was transported to the hospital, arriving about 30 min after the accident. Bandages where then immediately soaked with a calcium chloride solution (20 g/2 L of water) and placed on the burned areas of the

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skin. Subcutaneous injections of calcium gluconate (0.5 ml/cm^2) at a concentration of 9 mg of Ca^{2+}/ml were given, followed by calcium gluconate via an iv infusion with 30 ml/2 h in 1,000 ml of Ringers lactate. The ionized serum calcium was 0.67 mmol/L (laboratory normals = 0.9–1.32 mmol/L). Topical application of 2.5% calcium gluconate gel was also done.

About 4 h after exposure, ventricular fibrillation developed that responded to defibrillation, but recurred 4 times over the following 2 h, each time requiring defibrillation. The patient was anesthetized and intubated, the vital signs were stabilized, and hemodialysis was done. Serum levels of calcium and magnesium were then normal. The concentration of fluoride in the urine was 5800 mmol/L before starting hemodialysis, and was 3800 mmol/L following hemodialysis (reference range < 105 mmol/L). The following day, the patient was transferred to the Burn Center at the Karolinska Hospital in Stockholm for treatment of deep dermal burns, where skin grafting was done. The patient was released in mid-September 1996. In August 1997, 1 y after the accident, the patient returned to work.

RESULTS

During 1998-1999, there were 16 HF ocular and dermal splashes at the Avesta Polarit plants. Victims were aged 39 ± 11 y and 80% were males. One-third of exposed workers were external workers. Two dermal chemical splashes involved 70% HF, and 1 ocular splash involved an unknown HF concentration (Table 1). Twelve splashes were with the 6% HF/15% HNO_3 mixture, pH = 1 (Table 2). One exposure was to a mixture of 6% HF/15% HNO_3 that also included an unknown concentration of sulfuric acid, pH = 1 and involved both 1 eye and facial skin (Table 2). In 2 dermal splashes involving the hand and arm or the face and oral cavity, exposure was to the 6% HF/15% HNO_3 pickling acid mixture that had been heated to 45 C (Table 2).

All workers with HF or mixed acid exposure were initially decontaminated with Hexafluorine® which began within 1 min of the splash in 12/16 (75%) of cases. In 3 cases involving the dilute 6% HF/15% HNO_3 mixture, decontamination began 1 h after exposure.

All HF-exposed workers reported immediate pain relief during or after Hexafluorine® decontamination. More than 60% of exposed workers were transported to the hospital for medical examination, but no systemic toxicity was noted.

The worker with an ocular splash with an unknown concentration of HF developed some delayed irritation several hours after the accident that proved an allergic reaction to an instilled topical medication. A small corneal lesion was treated with topical cortisone. In the worker with facial and oral cavity exposure to 6% HF/15% HNO_3, some blistering on the outside of the eyelid was noted 1 d following the accident.

Table 1. Results from chemical splashes with hydrofluoric acid (HF).

Cases	Body surface area	Time until decontamination	Lost work time (d)
Splashes with 70% HF			
1	Left forearm	< 1 min	0
1	Oral cavity	< 1 min	1
Splashes with an unknown concentration of HF			
1	One eye	< 1 min	0

Table 2. Splashes with a mixture of 6% HF/15% HNO_3

Cases	Body surface area	Time until decontamination	Lost work time (d)
2	One eye	< 1 min	0-0
1*	Face and one eye	3-5 min	3
1	Both eyes	< 1 min	0
1	One thigh	< 1 min	0
2	Both thighs	1 h-1 1/2 h	2-2
2	Face + oral cavity, forehead	< 1 min	1-1
3	Forearm, arm + hand, right and left arm folds	< 1 min	0-0-1
1	Wrist	2 h	0

* Mixture also included an unknown concentration of sulfuric acid ($H2SO_4$).

No permanent sequelae or severe burns were observed in any of these 16 HF-exposed workers. In 12/16 (75%) of cases including the 2 workers with 70% HF splashes, there was no requirement for further treatment following initial Hexafluorine® decontamination. The mean lost work time was < 1 d (0.69 ± 0.95 d).

DISCUSSION

The severity of HF burns is due to its "double danger". The acid portion (due to the H^+ ion) is responsible for superficial tissue necrosis. This superficial acid injury allows the fluoride (F^-) ion to penetrate deeply into the tissues and to chelate calcium (Ca^{2+}) as calcium fluoride (CaF_2) (1). Calcium depletion can induce physiological perturbations, such as non-perfusing cardiac arrhythmias, cardiac conduction defects, and hypotensive shock. There is also liberation of potassium ions (K^+) which may be responsible in part for the sensation of intense pain with HF burns (2). The higher the HF concentration, the faster the onset and greater the severity of pain (3). With exposure to HF concentrations > 50%, onset of pain is nearly immediate, and tissue necrosis and depletion of serum Ca^{2+} and magnesium ions plus release of K^+ may occur. These electrolyte abnormalities can lead to cardiac arrest and death. With exposure to HF concentrations less than 20%, pain onset and tissue necrosis are delayed.

The problem of decontamination of HF eye and skin splashes is not simple. The development of water plus topical calcium gluconate decontamination/treatment protocols has allowed a decrease in the sequelae of HF splashes, but has not allowed prevention of burns (4-6).

The first emergency actions following a chemical splash are removing contaminated clothing as well as lavage. The quality and rapidity of the initial lavage following an HF splash determine whether or not burns and/or deleterious sequelae will develop (7).

Water decontamination has only the effects of mechanical rinsing and dilution of the chemical product on the surface of the exposed tissue. Being hypotonic, water may actually favor the penetration of the toxicant into the tissues. Water decontamination is therefore not optimal.

The use of water lavage followed by topical calcium gluconate has in general allowed a decrease in the severity of HF burns. However, with exposure to high concentrations of HF, despite treatment with water decontamination plus Ca^{2+} (even with iv injection of calcium gluconate or calcium chloride), the outcome can be fatal (8-10).

The case reported here of a 70% HF splash on the arms and abdomen clearly demonstrates that initial water decontamination followed by treatment with topical, sc and iv calcium preparations is not optimal. Cardiac arrest was only avoided by repeated defibrillations, intubation and other intensive care measures. Deep burns also developed which required skin grafting, and the victim lost 1 y of work as well as functional and psychological sequelae.

While the protocol of water + topical calcium gluconate has been used for dermal splashes, it is controversial for HF ocular splashes (11). The interest of an efficacious and single-agent emergent decontamination protocol that can be used regardless of the HF concentration, mixture with other acids, and tissue involved remains significant (12).

Hexafluorine® is an emergent lavage solution specifically designed for decontamination of eye and skin HF splashes. Because it is hypertonic, it prevents HF tissue penetration and establishes an osmotic gradient that can leach out some HF that has penetrated into the tissues but not yet bound to tissue receptors. Moreover, its strong affinity for both H^+ and F^- ions allows it to bind them both at the same time and prevents the development of deleterious sequelae. Hexafluorine®'s chemical reactions with these ions is not exothermic (does not release heat which could itself damage tissues).

The efficacy of Hexafluorine® has been previously demonstrated in vitro (3) and in the industrial setting (13, 14). In the 16 cases reported, initial Hexafluorine® decontamination was of interest regardless of the concentration of HF (alone or mixed with strong acids) or the location and extent of the splash. There were no sequelae or severe burns. In 12/16 cases (75%), there was no requirement for treatment other than initial Hexafluorine® decontamination, and the mean lost work time was < 1 d (due to the duration of hospital observation).

This study also demonstrates the interest of developing a policy of prevention for chemical splash risks and a systematic method of response. In the involved workplace, there was a hospital consultation in more than 60% of HF splash cases and in 75% of cases active decontamination began within 1 min. Decontaimination was delayed in 3 cases. These involved exposure to the dilute 6% HF/15% HNO_3 mixture, which likely explains the delayed decontamination as the sensation of pain was probably delayed in onset. Exposure to such dilute HF preparations, which are decontaminated only after a delay, can lead to development of burns and complications (15,16).

The dilute HF involved in the present study was mixed with nitric acid, a strong corrosive that can cause superficial tissue injury and increase the penetration of toxic fluoride ions. In 3 cases of exposure to dilute HF reported here, even delayed decontamination with Hexafluorine® allowed prevention of chemical burns.

Two workers splashed with 70% HF were efficaciously decontaminated with Hexafluorine®. The risks of systemic toxicity and prolonged further treatment were avoided. Burns did not develop, in contrast to the 70% HF exposure case reported here when treatment was with initial water decontamination followed by topical, sc and iv calcium salts.

The combination of establishing an effective chemical safety policy and the utilization of the active HF and other acids lavage solution, Hexafluorine®, has allowed maximal decontamination of HF splashes and avoidance of HF burns in the Avesta Polarit Group.

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