Decontamination of Hydrofluoric Acid Splashes (HF)

+How HF burns function + Review of handling effectiveness + Feedback

from Hexafluorine in the workplace



HYDROFLUORIQUE ACID A DOUBLE RISK

- a corrosive attack due to H⁺ ions
- penetration of F⁻ ions : a systemic effect



HF : a small weak acid



EFFECTS OF THE HF BURN

Segal EB Chemical Health and Safety, 2000, 18-23

- Concentration > 50% : immediate pain and fast necrosis
- Concentration 20%-50% : burn delayed from 1h to 8 h
- Concentration < 20% : pain and necrose delayed by more than 24h



HF burns with a lethal risk

Means of entry 9	6 affected surface	HF Concentration
Burn by contact	1	anhydrous
Burn by contact	5	> 70%
Burn by contact	7	50-70%
Burn by contact	10	20-50%
Burn by contact	20	<20%
Prolonged exposure or	minor HF burr	18
long delay before treatm	nent	
Ingestion of HF		>5%
Inhalation of HF		>5%

Dunser MW, Burns, 2004, 391-398



Evolution of a burn by 49% HF

in pigs

10 s exposure + 30 s contact



15 min



30 min



1 hour



2 hours



4 hours



TO DECONTAMINATE HF SPLASHES

- Wash and undress as quickly as possible
- Take immediate action against the double risk : H+ and F- ions
- Use a single protocol for eye-related and skin-related acid splashes.



HYDROFLUORIC ACID

Examples of cutaneous burns

Dr O. GOUET, La Baule, France, Oct.1997

Case: Cutaneous contact with 70% HF, immediate rinsing with water, the necrosis appears after 2 minutes. Hospitalisation many hours later with acute pain, extensive necrosis, necessity of surgery with discharge incisions and iterative excisions followed by amputation.





Photo 1 : Case n°1 : Hydrofluoric acid 70% initially



Photo 2: Case n°1 - Hydrofluoric Acid 70% 4 days later after excision and discharge





Photos 3 and 4:Case N°1-Hydrofluoric Acid 70% 1 year later after surgical flaps, skin grafts, and physical therapy

A CASE REPORT

AVESTA (Outokumpu Stainless AB) with water + calcium gluconate



A 45 year old employee

@ HF 70%

- valve checking
- immediate rinsing with water
 (15 min) then saline solution in the ambulance
- Hospital : Ca IV injection
- and Mg + Ca-Glu gel
 - I year off work



Published cases with very concentrated HF

Mayer (in 1985) 70% HF (water)

➤ 10% of body surface affected - death

- Mullet (in 1996) 70% HF (water + GluCa) ≥8% of body surface affected - death
- Ger Tepperman (in 1980) 100% HF (water + GluCa)
 ≥2.5% of body surface affected death
- Camarasa (in 1983) 100% HF (water + GluCa)
 - Partial permanent incapacity, on sick leave for 1 year
 - After effects = wearing of mittens, sensitiveness to the cold
- G→ Dunser (in 2004) 70% HF (water + GluCa)
 > 30% of body surface, improvement of the handling of the situation
 > no death, 25 day hospital stay



CLASSIC RINSING SOLUTIONS Evolution of protocols

Rinsing methods	Advantages	Disadvantages
Water	 External surface rinsing Dilution effect 	 Long rinsing time (20mn) Passive rinsing : no effect on H⁺ et F⁻ Hypotonicity : favours the penetration of F⁻ of H⁺ ions Risk of hypothermia
Water (Passive rinsing)	 External surface rinsing Dilution effect 	 Long rinsing time (20mn) Passive rinsing : no effect on H⁺ et F⁻ Hypotonicity : penetration of F⁻ of H⁺ ions Risk of hypothermia
+ calcium Gluconate (Secondary treatment)	 Chelation of fluoride ions that have already penetrated the deep layers 	 Weak action on the corrosiveness (H+) Multiple applications are necessary Factor depending on the pain sensation of the patient



Different treatments with water decontamination

- ✓ calcium gluconate
- ✓ local application
- injection IV + DMSO to help the penetration of Glu Ca in fingernails and toenails
- ✓ Zephiran salts (benzalkonium chloride) ou Hyamine salts (benzethonium chloride)
- \checkmark application of compresses in ice (not easy to do)
- ✓ lodine based mixtures
- \checkmark inhibition of apoptosis and of proteinase activity



- First aid washing solution in cases of eye and skin HF splashes
 - ✓ deactivates H⁺ ions
 - ✓ chelates F⁻ ions
 - ✓ hypertonic
 - ✓ rapid return to a physiological state



Innocuousness and properties

- \checkmark Non irritating for eyes and skin
- \checkmark Non toxic (LD₅₀ > 2000 mg/kg)
- ✓ Non sensitizing
- No side effects detected by the PREVOR medical devices vigilance system
- ✓ Immediate disappearance of pain
- ✓ Acts on all fluorides in an acidic environment (HF, BF₃, ...)



↔ WOESTE in Germany in 1997

Bath of hydrofluoric acid and hydrochloric acid

Dap Hexafluorine for body : no burns

>Water rinsing of eyes : severe burns

KRUPP in Germany in 1996

≻38% HF

>On the eye : no burns with Hexafluorine

ALCAN in Germany in 1993

>2 workers with 5% HF : no burns with Hexafluorine

ARC INTERNATIONAL in France in 1996
 HF Vapours 70% face : no burns with Hexafluorine
 (gluconate gel 1 day after)

Hall AH et al, SSA J, 2000, 14, 30-33



Mannesmann Series (1994-98)

Mathieu L et al, Vet Hum toxicol 2001, 43(5), 263-265

Ocular splashes	40%HF	6%HF /15%HNO ₃
Number	1	1
Surface	1 eye	1 eye
First rinsing	Hexafluorine®	Hexafluorine®
Second rinsing	Hexafluorine®	Hexafluorine®
After effects	0	0
Secondary treatment	0	0
Sick leave	0	0



Mannesmann Series (1994-98)

Mathieu L et al, Vet Hum toxicol 2001, 43(5), 263-265

Cutaneous splashes	40%HF	6%HF /15%HNO3
Number	5	5
% body surface	0.2 - 1 - 4.5 - 4.5 - 16.5	0.2 - 2.25 - 4 - 4.5 - 10.5
First rinsing	Hexafluorine ®	Hexafluorine ®
Second rinsing	Hexafluorine ®	Hexafluorine ®
After effects	0	0
Secondary treatment	0	0
Sick leave	0	0



Avesta (Outokumpu Sweden) Series (1998-99)

Soderberg K et al, Vet Hum toxicol 2004, 46(4), 216-218

Case N°	Exposure	Cutaneous splashes	Contact time
2	70% HF	Left forearm – oral cavity	< 1 min
1	HF/HNO ₃ pH=1	One thigh	< 1 min
2	HF/HNO ₃ pH=1	Two thighs	1h–1h 30
2	HF/HNO ₃ pH=1	Face + oral cavity – Forehead	< 1 min
3	HF/HNO ₃ pH=1	Forearm – arm + hand – elbows	< 1 min
1	HF/HNO ₃ pH=1	wrist	2 h



Avesta Series(Outokumpu Sweden) (1998-99)

Soderberg K et al, Vet Hum toxicol 2004, 46(4), 216-218

Case N°	Exposure	Ocular splashes	Contact time
1	HF (unknown concentration)	One eye	< 1 min
2	HF/HNO ₃ pH=1	One eye	< 1 min
1	HF/HNO ₃ pH=1	Two eyes	< 1 min
1	HF/HNO ₃ /H ₂ SO ₄ pH=1	One eye + face	3 to 5 min



Results of the Avesta Series Sweden (1998-99)

Soderberg K et al, Vet Hum toxicol 2004, 46(4), 216-218

- No immediate pain sensation,
- No after effects,
- No secondary treatment (75% of cases),
- An average of one day of sick leave ($\sigma = 1.1$)



Conclusion

- Hexafluorine constitutes an improvement of water rinsing in the treatment of hydrofluoric acid splashes.
- In addition to the effects of surface washing, it acts both:
- on the H⁺ corrosive ions
- and the F⁻ toxic ions
- Used as a first aid treatment, Hexafluorine allows the prevention or minimisation
- of the appearance of hydrofluoric acid burns of the eyes and the skin.
- When the duration of the contact is prolonged, Hexafluorine can be used to stop the evolution of chemical burns. A treatment allowing the chelation of calcium may then be put into effect.



PRFVOR