

A review of the taking up of hydrofluoric acid burns: two cases reported

C.L. Siéwél, J. Nehles², J. Blomet³, M. Gross⁴

¹ Prévior Toxicologie Laboratory F-95760 VALMONDOIS ² MD. Occupational physician.Mannesmann Hoesch PräzisrohrGmbH.BliedinghausserStraBe 21/23.D-42859 REMSCHEID
³ Chemist engineer.Scientific Director.Prevor. Laboratory F-95760 VALMONDOIS. ⁴ Safety & Product Responsible, Krupp Edelstahlprofil GmbH, UterlinsersraBe-1.G-58849 Werdohl

INTRODUCTION

Hydrofluoric acid (HF) has been used in glass-making to make engravings and/or polish glass at least since 1670. It was only in 1809 that Thenard and Gay-Lussac described its exact clinical characteristics¹. Several cases have been described in the literature but the treatment need further documentation^{2,3,4}.

The two cases reported are observations concerning a cleanse with Hexafluorine[®]. Those accidents occurred in two different factories in Germany. The first accident occurred in a company specialised in the manufacture of precision pipes which are used in the automobile industry. After annealing the steel the scale is removed by picking, depending on the quantity of the steel, nitric, sulphuric and hydrofluoric acid are used in different concentrations. The second occurred in a company specialised in the dipping and the galvanisation. The table contains stainless steel for construction and machine tools. Those materials are treated before in a bath in order to draw. They are chemically dipped and laminated with a mixture of nitric and hydrofluoric acid solution.

OBSERVATIONS

Observations 1

August 1995: a worker, 43 years old, pumping 40% hydrofluoric acid (HF) from a container, using a submersible pump with a flexible tube connection. The flexible tube connection had loose from the pump and the HF sprayed into a worker's eyes, face and the upper of his body. His colleagues standing nearby switched immediately the pump off and rinse the worker with Hexafluorine[®]. The clothes completely wet with HF were torn from his body and immediately afterwards his eyes were washed once again with Hexafluorine[®]. In the hospital, he was examined thoroughly by a surgeon, a dermatologist and an ophthalmologist. No damage found by none of the doctors. The worker left the hospital and returned to work the following day.

Observations 2

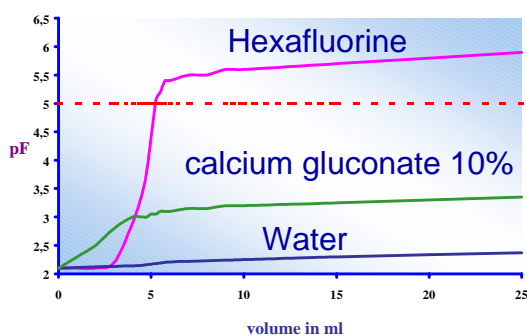
July 1995, a 55 years old worker, when using the acid bath, approached the dipping bath, filled up with nitric and hydrofluoric acid through a pipe. He became an ocular splash of 38% concentrated hydrofluoric acid from a defective pipe. The worker rinsed his eye with the Hexafluorine[®]. After the ophthalmologic control, there was no injury found and he took up his work the next day.

COMMENTS

In those companies, employees directly subjected to the risk of hydrofluoric acid spattering are sensitised to the risk linked to their use and workplaces are respectively equipped by Hexafluorine[®] body showers and eyewash solution since 1985 and 1995 on workplaces. Highly concentrated solutions inflict immediate caustic burns. Whereas the diluted solutions cause late lesions. Linked to the penetration of histoxic fluorides ion. In mineral industry, hydrofluoric acid is used to produce fluorides. In metallurgy for metal stripping and cleaning, as a catalyst in the organic industry, in the paper industry and in analytical chemistry. Hydrofluoric acid is corrosive and toxic. The skin and eye splashes with hydrofluoric acid are always fearsome accidents. The consequences, sometimes dramatic, constitute real alerts.

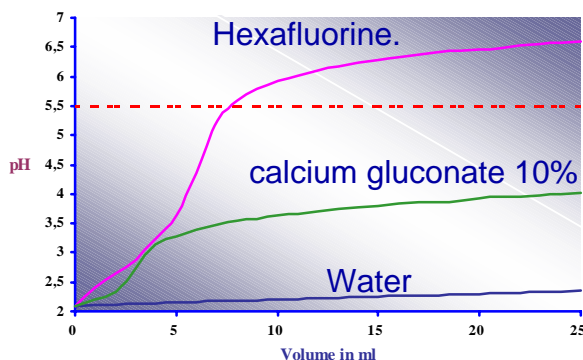
MECHANISM OF THE ACTION OF WATER AND CALCIUM GLUCONATE GEL

The first-aid treatment in case of a chemical burn must be the cleanse. This bathing has to be able to remove the product that has not yet reacted and to neutralise the part of the product already in contact with the skin. and as for the treatment. has to be started without delay. HF is toxic due to the fluoride anion (F^-). and corrosive because of the presence of the hydrogen ion (H^+) Blinking has a rinsing effect dilutes the toxic agent and reduces its concentration, but not sufficient to reduce the residual toxic rate and the progression of the burn⁶⁻⁸ We can note that the procedure water/calcium gluconate is the most routinely used². Some authors propose between 15 and 20 minutes in case of the washing with water⁷. This duration is sufficient to favour the destruction of the tissues and the penetration of the fluorides^{2,6,8}. The Ca^{++} ions from calcium gluconate precipitate the F^- anions. giving an insoluble compound. and decrease the pain^{2,6} Calcium gluconate has indeed a certain effect on the toxic content, inducing the tmprovement of the hypocalcemia observed after its application. However. it does not have any effect on the corrosive agent⁹.



COMPARED RESULT OF THE ASSOCIATION WATER/CALCIUM GLUCONATE AND HEXAFLUORINE®

Manv therapeutic procedures had been used such as washing with water. washing with water followed by calcium gluconate local application or injection/infiltration. Application of ammonium quaternary salts, and more recently. the mathematical approach. Know as the algorithmic approach, was proposed by Kirkpatrick and coll. (1995)¹⁰. The historical record of these methods shows that they are developing and becoming more and more complex. Bracken et coll. (1985)¹¹ showed the efficacy of the procedure water/calcium gluconate on rats. but there is still a controversy concerning the real efficacy on the human being^{2,6,8}. The early rinsing with water followed by the treatment with gluconate gives in certain cases acceptable results if the problem concerns skin spattering with concentrations in HF lower than 5%^{1,11,15}. Brown (1974) obtained good results by using 2.5% calcium gluconate for the treatment of ten buns due to a 40% concentration of HF. Since this period. many authors have used this method⁷. Mark Upfall and coll. (1990) note a considerable improvement in the water/gluconate procedure: they propose a local anaesthetic. followed by an injection of an analgesic in IV. and a local application of calcium gluconate. The calcium gluconate gel. while being easy to use. has a low efficacy on finger¹⁶ and ocular burns. and it has to be applied for several days or even several weeks^{6,8,17}. Furthermore. the application or injection of calcium gluconate is inadvisable for ocular solutions. the latter for which it is preferable to prescribe there being much widely directed to a 30 minute irrigation with water or $MgCl_2$. $MgSO_4$. MgO . $LaCl_3$ solution... It is moreover known that there procedure are long and often have aker-effects^{7,11}. According to a recent study. a subconjunctival application of calcium gluconate would induce toxic effects. with poor clinical results⁸.



INTEREST OF HEXAFLUORINE®

Hexafluorine® is a solution that has chelating and amphoteric properties used for the first-aid washing of HF splashes. Being aware of the mechanism of the reaction we combined the chelating power concept to the amphoteric molecule concept¹⁸. This double concept constitutes the main properties of Hexafluorine®. Each Hexafluorine® molecule can due to its chelating properties capture 6 fluoride ions (F^-) and 3 H^+ ions. The fluoride chelation is not a new concept but the innovative idea lies in the association of the neutralising power on the acid and the chelating effect on fluoride. This double concept makes it possible to avoid any skin application or injection after the accident. There is therefore a noticeable improvement in the comfort of the casualty and his medical follow up. In the water/gluconate procedure. The gluconate acts by precipitation of the fluoride. The action of water does not prevent the penetration of the toxic content this explains the importance of the effect of gluconate that has already penetrated into the skin. A quick bathing with Hexafluorine® neutralises all the HF whatever its concentration. Hexafluorine® has even an attraction force on toxic contents. Thanks to this energy the interaction between its molecule and the toxic one is greater than the attracting power between the toxic content and the skin. Hexafluorine® also has the advantage of being as well adapted to eye as to skin accidents. The experimental studies of various first-aid proceedings on animals, with 40% concentrated HF, show that the use of Hexafluorine® as an immediate cleanse solution allows a sufficient decontamination to decrease the necessity of secondary treatment with calcium gluconate. These studies were carried out on rabbits, showing the drawing power and the efficacy of Hexafluorine®. The comparison was made between rinsing with Hexafluorine® and rinsing with water, then between Hexafluorine® and the washing with water, followed by the application of calcium gluconate.

DISCUSSION

40% concentrated hydrofluoric acid entails a burn sensation and visible tissue destruction often characterised by blanching in the place. The penetration speed of the F^- ions is proportional to the concentration of the product. The fluoride, when it has penetrated deep, causes calcium imbalances, which even if they are not major on a chemical point of view, will start very important modifications in the physiological cycles, H^+ ion coming from the acid attacks and destroys the superficial layers of the skin. and the F^- ions come in direct contact with the cellular components and can react with the calcium that is there. Like water, Hexafluorine® allows a rinsing by sweeping effect. The experiments showed that the sweeping effect of water removes only 95% of the product, but the 5% that get through the skin barrier are sufficient to induce baneful effects for the organism, the chelating and amphoteric properties of Hexafluorine® allows it to stop quickly the action of the H^+ ion and the progression of the F^- ion. The quick action allows to decrease the length of the contact with the aggressive product.

CONCLUSION

Large progress was obtained thanks to the water rinsing followed by the treatment with calcium gluconate in solution or with triethanolamine. The calcium aggressivity and the impossibility to apply the gel on the eye limits the efficacy and the use of this method. In the case of an extensive burn, the hypocalcemia set off by fluoride is not easily reversible. Now a rinsing with Hexafluorine® which is a solution with amphoteric and chelating properties, can prevent the penetration and the tissue destruction induced by the toxic agent, as well as the appearance of the invalidating after-effects.