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Comite Technique Europeen du Fluor

Working Group Storage, Transport and Safety

HF NEUTRALIZATION TABLE

1st Edition

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PREFACE

Hydrogen Fluoride (HF) is essential in the chemical industry and there is a need for HF to be produced, transported, stored and used.

The HF industry has a very good safety record; nevertheless, the European HF producers, acting within CTEF have drawn up this document to promote continuous improvement in the standards of safety associated with HF handling.

This Recommendation is based on the various measures taken by member companies of the CTEF. These recommendations are of voluntary nature each company deciding individually either to apply (in full or partially) or not.

It in no way is intended as a substitute for the various national or international regulations, which should be respected in an integral manner.

It results from the understanding and many years experience of the HF producers in their respective countries at the date of issue of this particular document.

Established in good faith, this recommendation should not be used as a standard or a comprehensive specification, but rather as a guide which should, in each particular case, be adapted and utilised in consultation with an HF manufacturer, supplier or user, or other experts in the field.

It has been assumed in the preparation of this publication that the user will ensure that the contents are relevant to the application selected and are correctly applied by appropriately qualified and experienced people for whose guidance it has been prepared.

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The contents of this recommendation are based on the most authoritative information available at the time of writing and on good engineering practice, but it is essential to take account of appropriate subsequent technical developments or legislative changes. It is the intent of the CTEF that this guideline be periodically reviewed and updated to reflect developments in industry practices and evolution of technology. Users of this guideline are urged to use the most recent edition of it, and to consult with an HF manufacturer before implementing it in detail.

This edition of the document has been drawn up by a Working Group "Storage, Transport and Safety" to whom all suggestions concerning possible revision should be addressed through the offices of CTEF. It may not be reproduced in whole or in part without the authorisation of CTEF or of members companies.

NOTES TO NEUTRALIZATION CHART:

1. Any alkaline material may be used for HF neutralization. The chart above lists those most commonly used to mitigate spills. Others, such as Ammonium Hydroxide (NH_4OH) may be used but may have inherent deterrent factors (e.g. odor).

2. The common neutralizing materials are listed alphabetically (Column 1). The emergency responder must consider many factors when choosing the appropriate alkaline material including:
   - Cost
   - Availability and Ease of Acquisition
   - Physical Form and Ease of Handling
   - Ultimate Disposal of the Neutral Salt or Salt Solution (Column 6)

     - Calcium based materials yield non-hazardous but very insoluble Calcium Fluoride

     - Materials yielding salts, which may be classified as POISON but with high water solubility, may be preferable for scrubbing applications

3. The amount of alkaline material required for neutralization (Column 5) is based on Kg of equivalent 100% Alkali per Kg of 100% HF. The factor will have to be adjusted based on the Alkaline form used (Column 3)

4. Responders must take care to control the chemical reactions. For example, to better control the Heat of Neutralization, the HF Spill and Neutralizing Alkaline Solution should be diluted as much as practical, considering the need to contain and control all effluents.

5. When using carbonates (e.g. Soda Ash), the rate of Carbon Dioxide gas evolution must be controlled from upwind of the containment area.

TYPICAL ALKALINE MATERIALS (BASES) FOR NEUTRALIZATION OF HF

ALKALINE MATERIAL	COMMON NAMES	FORM AVAILABLE	HAZARDS + REACTION	Kg.100% BASE per Kg. 100% HF	SALT PROPERTIES
CALCIUM CARBONATE ($CaCO_3$)	LIMESTONE	PEBBLES	Slow reaction Slow evolution of carbon dioxide gas (CO_2) Pebble surface can become passivated	2.50 Kg / Kg HF	Calcium Fluoride (CaF_2) Non-hazardous Sol. In Water = 0.004%
CALCIUM HYDROXIDE [$Ca(OH)_2$]	HYDRATED LIME	DRY POWDER SLURRY IN WATER	High heat of neutralization Slippery when wet	1.85 Kg / Kg HF	Calcium Fluoride (CaF_2) Non-hazardous Sol. In Water = 0.004%
CALCIUM OXIDE (CaO)	QUICKLIME	DRY POWDER	Danger / UNO : -- / 1910 Very high heat of hydration & neutralization	1.40 Kg / Kg HF	Calcium Fluoride (CaF2) Non-hazardous Sol. In Water = 0.004%
POTASSIUM HYDROXIDE (KOH)	CAUSTIC POTASH	85% SOLID BEADS or FLAKE <45 % SOLUTION	Danger / UNO : 80 / 1813 Danger / UNO : 80 / 1814 Very high heat of hydration & neutralization	2.80 Kg / Kg HF	Potassium Fluoride (KF) Danger / UNO : 60 / 1812 Sol. in Water >40%
SODIUM BICARBONATE ($NaHCO_3$)	BICARB BAKING SODA	DRY POWDER	Rapid evolution of carbon dioxide gas (CO_2)	4.20 Kg / Kg HF	Sodium Fluoride (NaF) Danger / UNO : 60 / 1690 Sol. in Water = 4.0%
SODIUM CARBONATE (Na_2CO_3)	SODA ASH	DRY POWDER	Rapid evolution of carbon dioxide gas (CO_2)	2.65 Kg / Kg HF	Sodium Fluoride (NaF) Danger / UNO : 60 / 1690 Sol. in Water = 4.0%
SODIUM HYDROXIDE (NaOH)	CAUSTIC SODA	100% SOLID BEADS or FLAKE <50% SOLUTION	Danger / UNO : 80 / 1823 Danger / UNO : 80 / 1824 Very high heat of hydration & neutralization	2.00 Kg / Kg HF	Sodium Fluoride (NaF) Danger / UNO : 60 / 1690 Sol. in Water = 4.0%

TABLE OF DECISION FOR NEUTRALIZATION OF HF

ALKALINE MATERIAL / SITUATION	$CaCO_3$ pebbles	$Ca(OH)_2$ powder	KOH	$NaHCO_3$	Na_2CO_3	NaOH	water	comments
contaminated PPE					Spray or wash with solution		Flush with large quantities	Carefully inspect PPE after rinsing, search for potential damage
contaminated pipes, tools, valves, …				Soaked In tank			Flush with large quantities	
contaminated railcar or road tank	Avoid (not efficient)	Fill the tank with water and ad lime – stir with air	Fill the tank with water	Be careful with CO2 generation	Be careful with CO2 generation	Fill the tank with water		1 – Fill with water at least twice (pay attention to the temperature rise !). Beware of the risks of diluted HF solutions 2 – Then use neutralizing agent 3 - Repeat until pH paper indicates no remaining acidity
continuous leak	Dyke around the leak							Other adsorbent products can be used
traces of HF on the ground		Spread powder on the contaminated areas						Other adsorbent products can be used
small pool of HF (<0,5 m²)	Dyke around the leak							1- Contain HF by dyking with solid agent 2 – Then spread very slowly any neutralizing agent (beware the reaction with water)
large pool of HF (>0,5 m²)	Dyke around the leak							1- Contain HF by dyking with solid agent 2 – Then cover the pool by using polyacrylamide foam to stop HF evaporation 3 – Ask for advice of HF specialist to recover or to neutralize residual HF
spillage of HF to river / lake / pond / sewers								Warn the local authorities to stop all the pumping stations and prevent any public access to the river in the concerned area