3/13/18 AGENDA, ITEM 6A - CONSIDERATION OF THE SUBMITTAL OF A RESOLUTION OR LETTER SUPPORTING A REQUIREMENT TO IMPROVE SAFETY AT THE TORRANCE REFINERY BY THE SCAQMD THROUGH THE RULE 1410 PROCESS AND OPPOSING TO THE USE OF MODIFIED HYDROFLUORIC ACID AT THE REFINERY. SUPPLEMENTAL LETTER AND ATTACHMENTS FROM GEORGE HARPOLE SUBMITTED TO THE CITY COUNCIL ON 3/11/18 AT 10:40 P.M.

From: g.harpole@verizon.net [mailto:g.harpole@verizon.net]
Sent: Sunday, March 11, 2018 10:40 PM
To: City Council <citycouncil@hermosabch.org>
Subject: Refinery MHF (3/13/2018 agenda item)

To: Hermosa Beach City Council

Attached is a short rebuttal to the Torrance Refining Company "Setting the Record Straight", Chapter 6.

My article on hazard of MHF (modified hydrofluoric acid) and HF (hydrogen fluoride) -- also attached -- was falsely and incompetently attacked (my name was used 11 times).

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George Harpole, Comment on MHF at Refineries, Rebuttal to ToRC Document

Hermosa Beach City Council Meeting, March 13, 2018

I'm George Harpole, PhD in Engineering from UCLA, specialty areas Heat and Mass Transfer and Fluid Mechanics, PhD dissertation on droplet evaporation – all directly relevant to HF releases, as are my subsequent decades of experience.

My findings were falsely and incompetently attacked, numerous times, in the Torrance Refining Company "Setting the Record Straight" package, chapter 6. The Modified Hydrofluoric Acid (MHF) with 10% by weight sulfolane additive vapor pressure curve in my article is based on actual data at 75°F, 86°F, and 100°F from a Honeywell patent and the material safety data sheet (MSDS). Boiling point is where vapor pressure is 1 atmosphere – 67°F for hydrogen fluoride (HF) and 73°F for MHF. MHF is proven to be very nearly as volatile as pure HF. This is far too elementary to send to a professional, peer reviewed journal. It is disturbing that refinery engineers refuse to understand such basics.

The HF compound is not modified in MHF. MHF is trucked to the refinery as a mixture with less than 3 molecules sulfolane additive per 100 molecules HF (15% by weight additive, 2.9% by molecule count). The refinery then removes half the sulfolane. HF properties are not altered much by the then 1.4% sulfolane molecules. And, the water and acid soluble oil (ASO) would be the same with or without this additive, so are not MHF vs. pure HF distinguishers.

Hydrogen bonding is ubiquitous to many fluids, not special to sulfolane, and it is not a separate, quantifiable fluid property. Hydrogen bonding is important both for pure HF and for MHF. But it is important only for its impact on vapor pressure. The data-based vapor pressure curve already includes and accounts for the hydrogen bonding effect.

Flash boiling occurs at a critical temperature difference above the boiling point. I wrote a separate article on that. It relates to the fraction evaporated before evaporative cooling brings the liquid back to the boiling point. MHF will flash evaporate with similar critical temperature difference to that for HF.

MHF is HF. Both are very dangerous. Refinery operators have admitted the danger of pure HF. MHF a few degrees warmer than HF will act identically.

HF and MHF – Equivalent Ground Hugging Fog Hazards

George Harpole, Ph.D., 10/21/2016 (3/11/2018 further Fig. 1 annotation)

MHF (modified hydrogen fluoride) with 10% additive (10% by weight sulfolane)[1] is almost the same as pure, anhydrous hydrogen fluoride (HF). Only 1.8% of the moles or molecules are sulfolane, and 98.2% are HF. The molecular weight of HF is 20 g/mol, and that of sulfolane is 120 g/mol – so molecules of sulfolane weigh 6 times as much. Adding sulfolane to HF increases the mixture molecular weight, so increases the gas density when it evaporates in a release. Still, to exceed the effective density of air (molecular weight 29 g/mol), at least 37% by weight sulfolane (9% mole fraction) would be needed – if evaporation resulted in only pure gas. Instead, when liquid HF (or MHF) is released and mixed with air, there is substantial cooling by evaporation and by depolymerization, such as $(HF)_6 \rightarrow 6HF$ [2]. The air/HF mixture temperature drops below the dew point, and a fog is formed by condensation of water vapor in the air. Then, the effective density exceeds that of air, so this becomes a ground hugging fog. The water aerosol warms up again as it absorbs the HF. But, water has low volatility, so the fog persists.

Vapor pressure is the only fluid property related to the claimed relative safety of MHF. Added sulfolane reduces the MHF vapor pressure relative to that of pure HF. Raoult's law for ideal liquids estimates the vapor pressure as proportional to mole fraction, so about 98% that of pure HF. However, the mixture is not an ideal liquid. Data show the vapor pressure of MHF (with 10% by weight sulfolane) to be 90% of that for pure HF [1,3]. Vapor pressures of HF [4] and MHF are shown in Figure 1 as functions of temperature. HF (boiling point 67°F) and MHF (boiling point 73°F) are both very volatile. If the MHF were 6°F (3.3°C) warmer, its vapor pressure would equal that of HF.

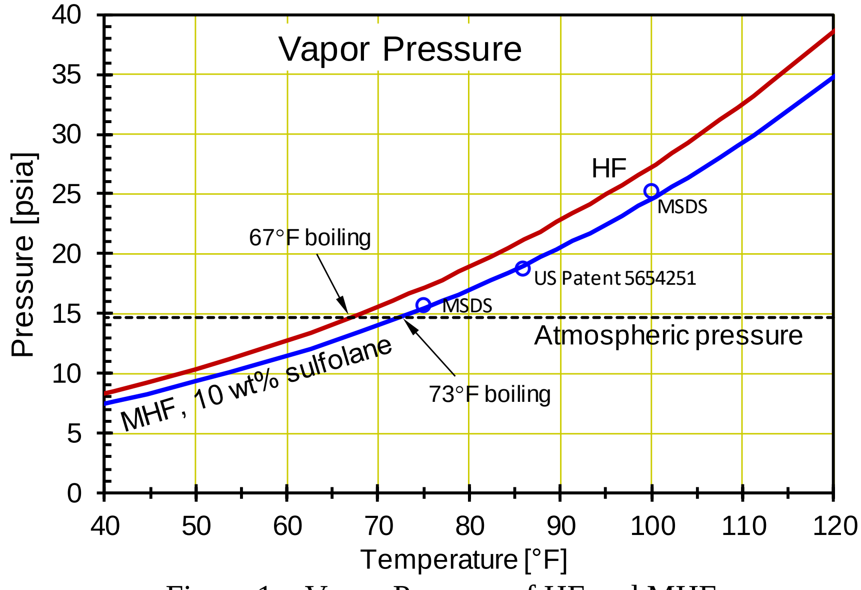


Figure 1 – Vapor Pressure of HF and MHF

In 1986, Lawrence Livermore and Amoco Oil Company conducted what has become known as the Goldfish tests. In each test, 8,300 lb of 104°F (40°C) HF was released in the Nevada desert on a smooth, dry lake bed with about a 10 mph wind. Nitrogen gas above the HF liquid pressurized the tank to about 130 psia. These conditions were selected to match what exists at refineries[5]. However, single vessels at the Torrance refinery, for example, hold six times as much HF (50,000 lb).

The Goldfish tests were alarming, due to the ground hugging fog that formed, with all of the HF participating. The complete and rapid mixing of all HF with air was due to the initial fine aerosol that was formed. Mobil research engineers attributed this complete aerosol to flash atomization [6]. Flash atomization is fragmentation of liquid that is initially superheated significantly above its boiling point when it is suddenly released to lower (atmospheric) pressure. But, MHF, with only 10% by weight sulfolane, would flash atomize over most of the same temperature range as would pure HF. MHF flash atomization characteristics would be identical to those of HF that is just a few degrees C colder. Moreover, atomization occurs by other mechanisms as well, such as from the kinetic energy of a pressurized liquid flowing out of an orifice. The claims of MHF being safer due to vapor pressure must relate to much higher sulfolane fractions than what is in use today.

Goldfish test HF concentrations were measured at 0.3, 1, and 3 km (0.19, 0.62, and 1.86 miles) downstream, on the plume centerline, at ground level (see Table 1) [7]. The plume is in a turbulent boundary layer, and entrains more air and spreads as it moves downstream. HF gets more dilute further downstream from the source.

Table 1 – Goldfish Test Results

Test	Spill rate [gal/min]	Duration [minutes]	HF Concentration at 0.3 km (984 feet) [ppm]	HF Concentration at 1 km (0.62 mile) [ppm]	HF Concentration at 3 km (1.86 mile) [ppm]
1	469	2.1	25,473	3,098	411
2	175	6	19,396	2,392	N/A
3	172	6	18,596	2,492	224

The Goldfish test HF concentrations (Table 1) greatly exceed the 50 ppm ERPG-3 levels beyond 3 km (1.86 miles). ERPG-3 is the maximum airborne concentration below which nearly all individuals could be exposed for up to 1 hour without experiencing or developing life-threatening health effects.

In conclusion, MHF used at the Torrance refinery (with only 10% by weight sulfolane) can form a fine aerosol, with all MHF participating in the cloud, under realistic conditions. The additive (sulfolane) offers very little protection at the 10% by weight level (1.8% by mole). Until there is a repeat of the Goldfish tests, but with MHF, the results will have to be assumed similar. If the full 50,000 lb of MHF from a single vessel were released, the HF concentrations could be six times higher than those from the Goldfish tests.

Dangerous concentrations of HF could persist miles away from the refinery. The typical layers of protection approach (barriers, water sprays, pumps to spare vessels, etc.) may save lives for certain smaller leaks. However, a more catastrophic rupture, simultaneous with failure or bypass of the protection systems, is easy to imagine – in large earthquakes, accidental or deliberate explosions, or fire. Moreover, the delivery trucks traveling to the refinery carry MHF in similar quantities, and are even more vulnerable. They have no spare vessel or water spray system. They are exposed to the public and subject to crashes. There is clear danger to the community in the use of MHF at refineries in urban settings.

References and Notes

1. Honeywell MSDS 14512, Modified Hydrofluoric Acid – 90%

2. W. Schotte, "Fog formation of hydrogen fluoride in air," Ind. Eng. Chem. Res., 26, 300-306 (1987).

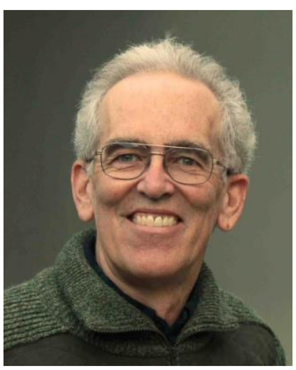
3. U.S. Patent 5,654,251, Figure 1.

4. Lange's Handbook of Chemistry

5. The temperature of the 50,000 lb of MHF in the Torrance refinery's Acid Settler Tank is nearly identical, at 105°F. Consent Decree Safety Advisor Steve Maher presented a chart titled "AHF/MHF" which listed "Typical settler temperature 105°F" at the 10/13/2015 City of Torrance Workshop regarding ExxonMobil's use of MHF catalyst.

6. R. Muralidhar, G.R. Jersey, F.J. Krambeck, S. Sundaresan, "A two-phase release model for quantifying risk reduction for modified HF alkylation catalysts," J. Hazardous Materials, 44, 141-183 (1995).

7. D. Blewitt, J. Yohn, R. Koopman, and T.C. Brown, 1987, "Conduct of Anhydrous Hydrofluoric Acid". International Conference on Vapor Cloud Modeling, Boston MA, Nov 2-4, (1987).



George Harpole holds a Ph.D. in Engineering from the U.C.L.A. School of Engineering, Chemical, Nuclear, and Thermal Engineering Department. He has been Chief Engineer of two chemical laser systems at Northrop Grumman Corporation. His current assignment is thermal analysis for the James Webb Space Telescope. He is the inventor, or co-inventor, of 14 U.S. Patents. He received two TRW Chairman's Awards. George Harpole lives in Torrance.