

HF and MHF – Equivalent Ground Hugging Fog Hazards

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MHF (modified hydrofluoric acid) with 90% by weight HF (hydrogen fluoride) mixed with 10 wt% additive (10% by weight sulfolane)¹ is almost the same as pure, anhydrous hydrogen fluoride (HF). The molecular weight of HF is 20 g/mol, and that of sulfolane is 120 g/mol. Only 1.8% of the molecules (or moles) are sulfolane, and 98.2% are HF, due to the six times larger molecular weight of sulfolane. HF is volatile, while sulfolane is a non-volatile organic solvent. When MHF evaporates, the vapor is essentially all HF. When liquid HF (or MHF) is released and mixed with air, there is substantial cooling by evaporation and by depolymerization, such as $(\text{HF})_6 \rightarrow 6\text{HF}$ 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 it would be about 98% that of pure HF. However, MHF is not an ideal liquid, so Raoult's law is not used here. Instead, data show the vapor pressure of MHF with 10 wt% sulfolane to be 90% of that for pure HF^{1,3}. Vapor pressures of HF⁴ 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.

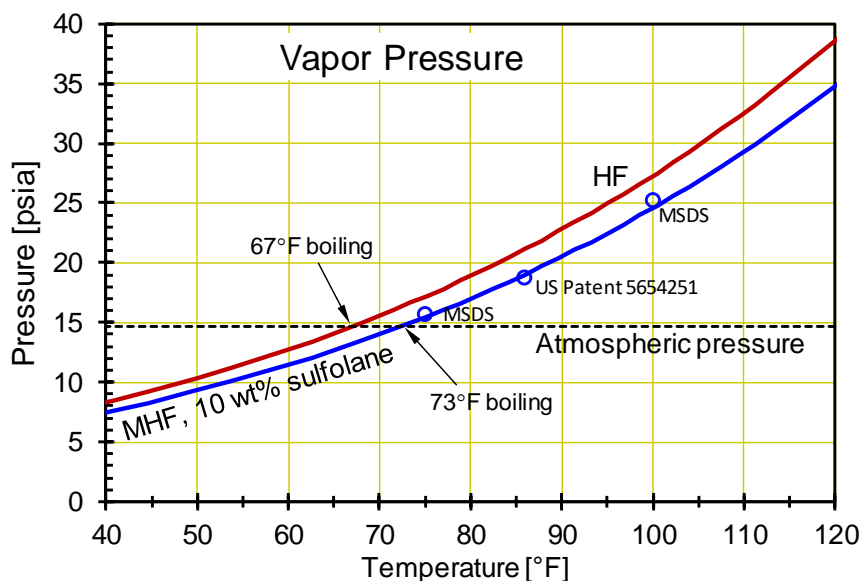


Figure 1 – Vapor Pressure of HF and MHF

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 refineries⁵. 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 atomization⁶. 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.