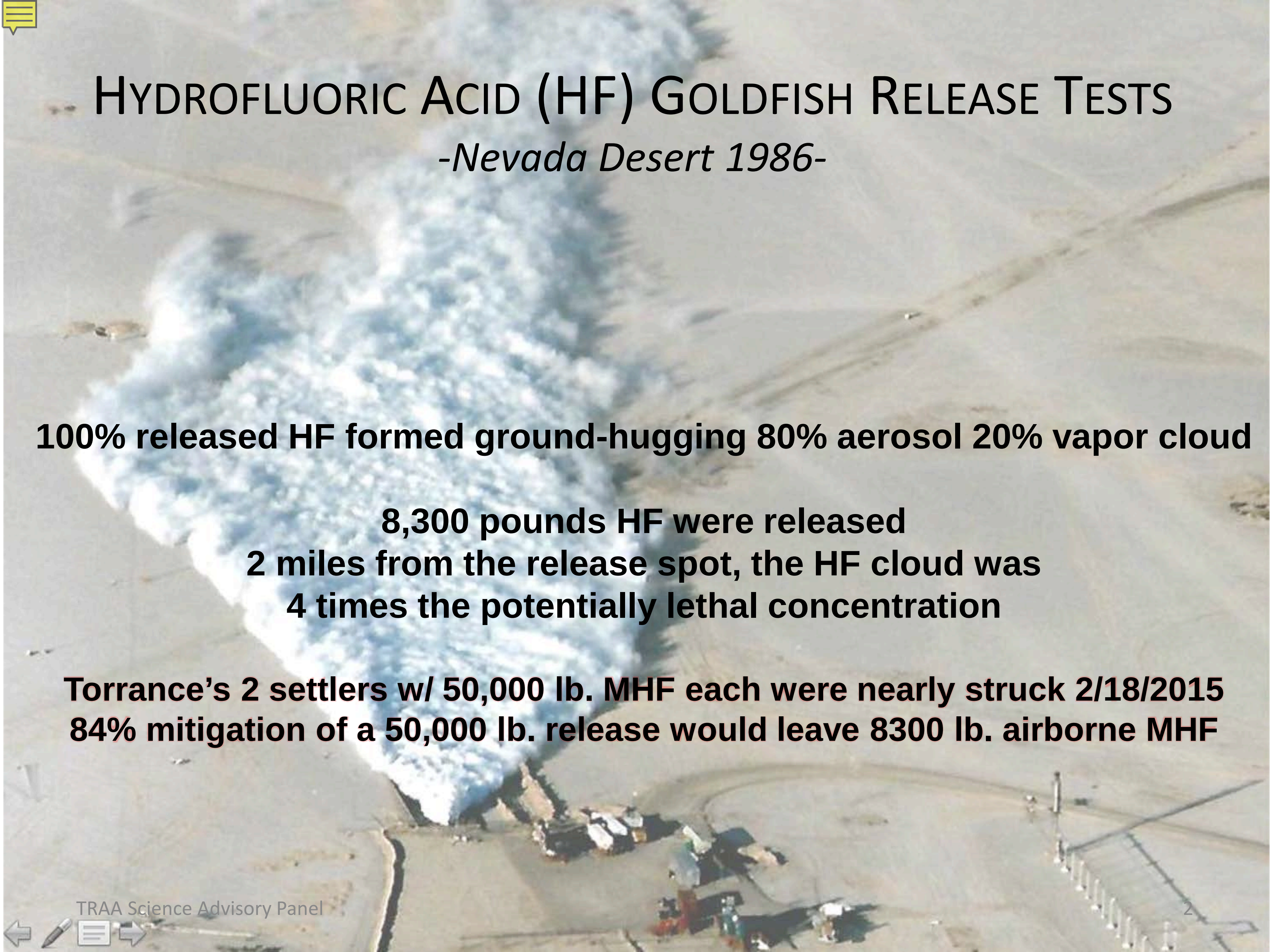
MHF and HF Alkylation Unit Dangers Are Equivalent

AQMD Proposed Rule 1410 Working Group Meeting #3

Dr. S. Hayati and the TRAA Science Advisory Panel   June 15, 2017



Hydrofluoric Acid (HF) Goldfish Release Tests

-Nevada Desert 1986-

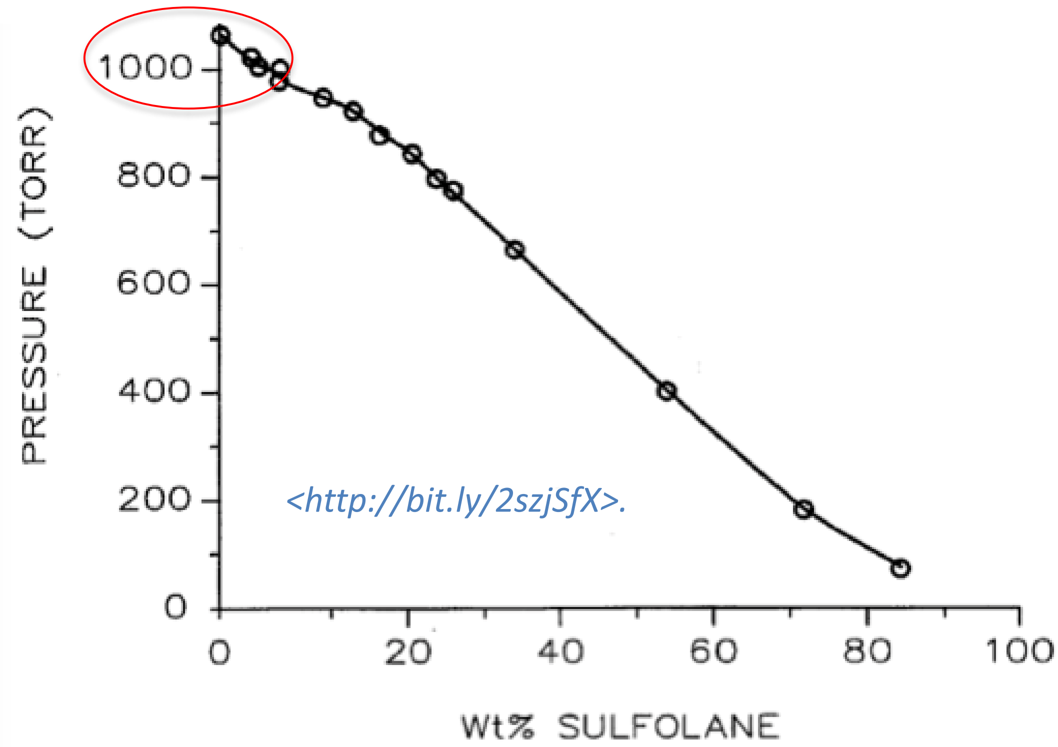
100% released HF formed ground-hugging 80% aerosol 20% vapor cloud

8,300 pounds HF were released
2 miles from the release spot, the HF cloud was
4 times the potentially lethal concentration

Torrance's 2 settlers w/ 50,000 lb. MHF each were nearly struck 2/18/2015
84% mitigation of a 50,000 lb. release would leave 8300 lb. airborne MHF

MHF Evaluated: Despite "Trade Secret" Rights

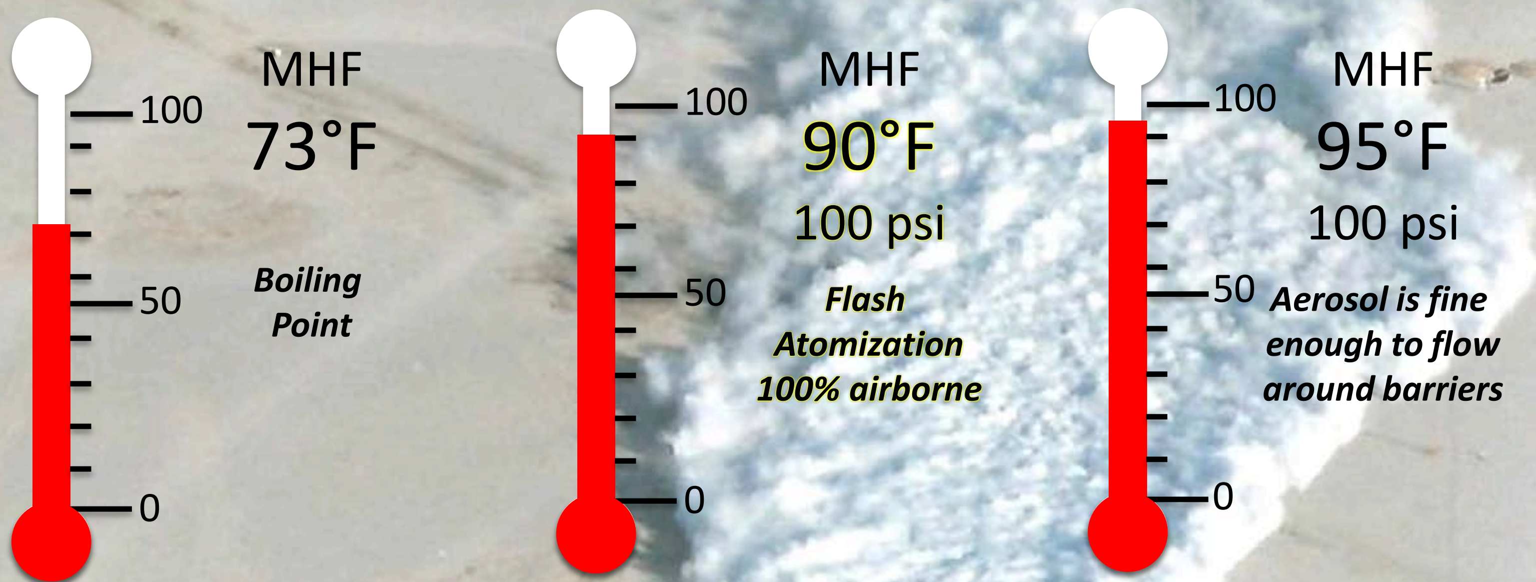
MHF solution by weight: HF 90 wt% + Sulfolane (additive) 10 wt% MAX
by molecule count: HF 98.4 mol% + Sulfolane (additive) 1.6 mol% MAX



George Harpole, Ph.D., Chief Engineer at Northrop Grumman Aerospace Systems in Redondo Beach.

1. *"HF and MHF – Equivalent Ground Hugging Fog Hazards." <http://bit.ly/2qoAfP0>.*
2. *"Flash Atomization of HF and MHF," <http://bit.ly/2jqBiGK>.*
3. *"Flash Atomization of MHF" <http://bit.ly/2pEt9FE>.*

MHF and HF Are Equivalent Hazards



Mobil's MHF & barrier ARF estimates are invalid for many reasons. Most significantly, with 10 wt% Sulfolane, MHF's critical superheat point is within alkyl unit parameters.

Misleading Arguments for MHF Safety Continue

(1) Industry claims MHF is 80% HF, not 98.2% HF

Industry won't concede (molecule) mole percent (mol%) is most relevant to vapor pressure

Component	CAS-No.	Weight %	Mole %
Hydrogen fluoride	7664-39-3	90.00%	98.2%
Sulfolane	126-33-0	10.00%	1.8%

Honeywell MHF SDS
http://bit.ly/21T6yAt

Industry conflates MHF w/ the contents of alky unit

Alky unit contents: 80% HF, 7% additive, 3% H_2O, 3% ASO, 7% other HC that are not soluble

- Note: 80% HF is at lowest edge of viable alkylation, near acid runaway
- 93.5 wt% of the *solution* is MHF, which is 8 wt% additive + 92 wt% HF

  Or by molecule count, 1.4 mol% additive + 98.6 mol% HF
- Hydrocarbons + H_2O (contaminant) + ASO (byproduct) can't stop HF or MHF flashing

MISLEADING ARGUMENTS FOR MHF SAFETY CONTINUE

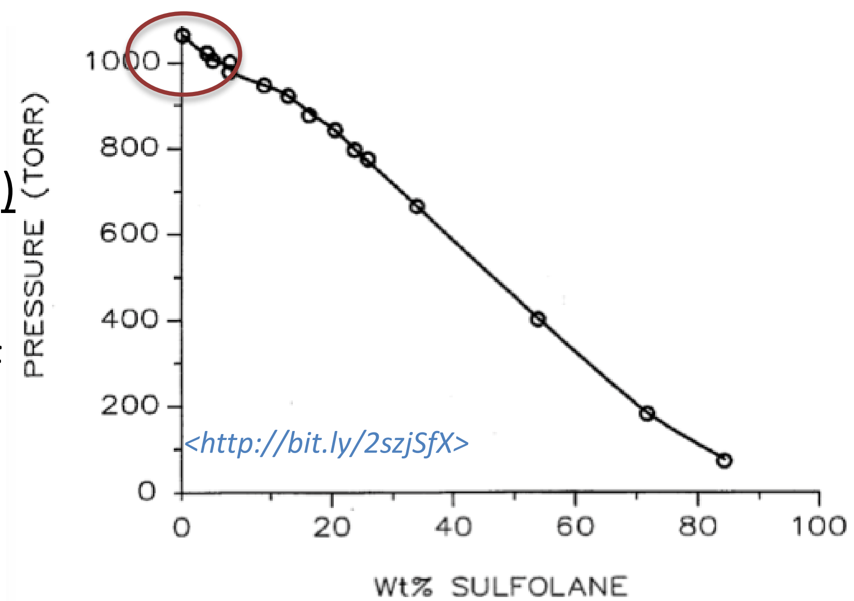
*(2) Industry claims H bonds with additive & water **prevent** MHF flash atomization*

- ***MHF Hydrogen bonds already accounted for in TRAA's MHF assessment***
- Raoult's Law ideal solns: vapor pressure (VP) α mol%, 10 wt% MHF VP = 98% HF VP
- But MHF has H bonding, an attractive force, ∴ MHF is not an "ideal solution"
- That's why we used this graph of MHF VP vs additive wt%, which reflects H bonding

10 wt% MHF VP = 89% HF VP

- 1 sulfolane molecule can't form H bonds with 60-70 HF molecules
- Parameters ↑: boiling pt, critical superheat
- MHF 10 wt% → 6˚F higher than for HF
- MHF 8 wt% → **5˚F** higher than pure HF (soln)

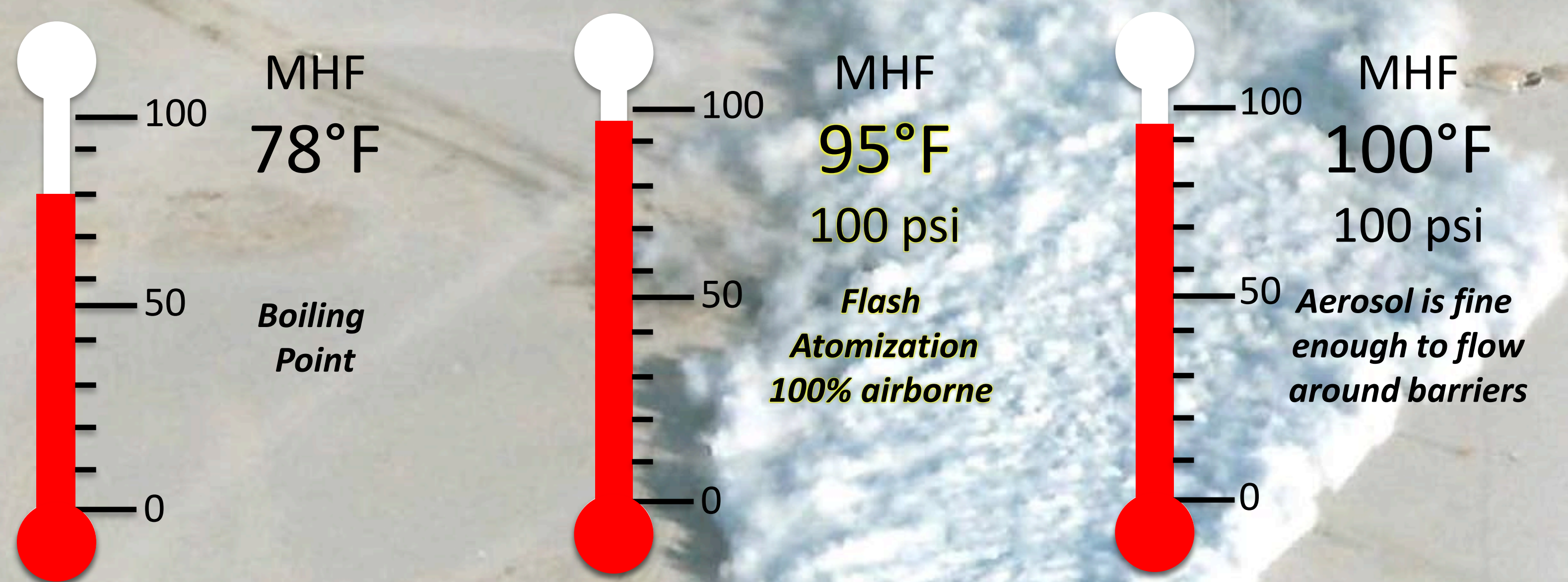
- ***H bonds from 3.2 wt% water, 3% ASO (soln)***
- VP 11% ↓ H_20/MHF VP ≈ 79% HF VP, extra 5˚F
- ASO effect is less than water, extra 1˚F
- H2O/ASO: parameters **6˚F** ↑ than MHF



MHF/H_2O/ASO: parameters **11˚F** ↑ than pure HF

Dr. George Harpole, "Flash Atomization of MHF," <http://bit.ly/2pEt9FE>.

MHF and HF Are Equivalent Hazards



Mobil's MHF & barrier ARF estimates are invalid for many reasons. Most significantly, 8 wt% Sulfolane, 3.5% H_2O, 3% ASO, MHF's critical superheat point w/in unit params

Misleading Arguments for MHF Safety Continue

(3) Industry claims pressure & temp can be flexibly manipulated to increase ARF

Pressure & Temp: set by processing parameters of alkylation unit
too little variability to make a difference

How Does ARF Protect Me

- MHF (1994) Original Additive Concentration

  MHF + Pressure + Temp = 65% ARF

- MHF (1998) Revised Additive Concentration (unbarriered)

  8 wt% additive

  MHF + Pressure + Temp = 50% ARF

- MHF (1998) Revised Additive Concentration with Barriers

  MHF + Pressure + Temp = 89% ARF

Torrance Public Workshop, Quarterly Refinery Update, 2017-02-28. http://bit.ly/2rplhVF

<u>1999: Consent Decree Safety Advisor S. Maher, "Evaluation of MHF Alky Catalyst"</u>

- **Unit pressure has no measurable effect** [on ARF] over operating range of Alky Unit.
- **ARF varies little with temperature change** between MHF's boiling & flash points

"There are no data on the value of the critical superheat for MHF."

Consent Decree Safety Advisor 1995 Report

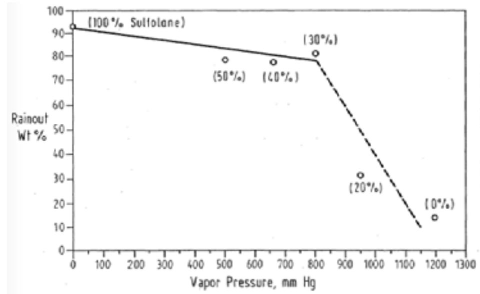
Misleading Arguments for MHF Safety Continue

(4) 8 wt% sulfolane delivers 50% ARF

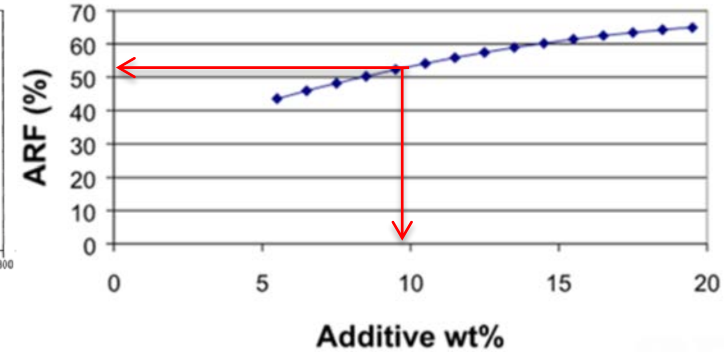
Original MHF developers data, testing done early 90s

HF/Additive Tests Pressure: 140 psig

Additive wt %	Temperature °F.	Impact Plate & Pad Yes/No	Rainout wt %
50	110	N	64
50	110	Y	99
34	90	N	53



1999 SA report graph, redacted



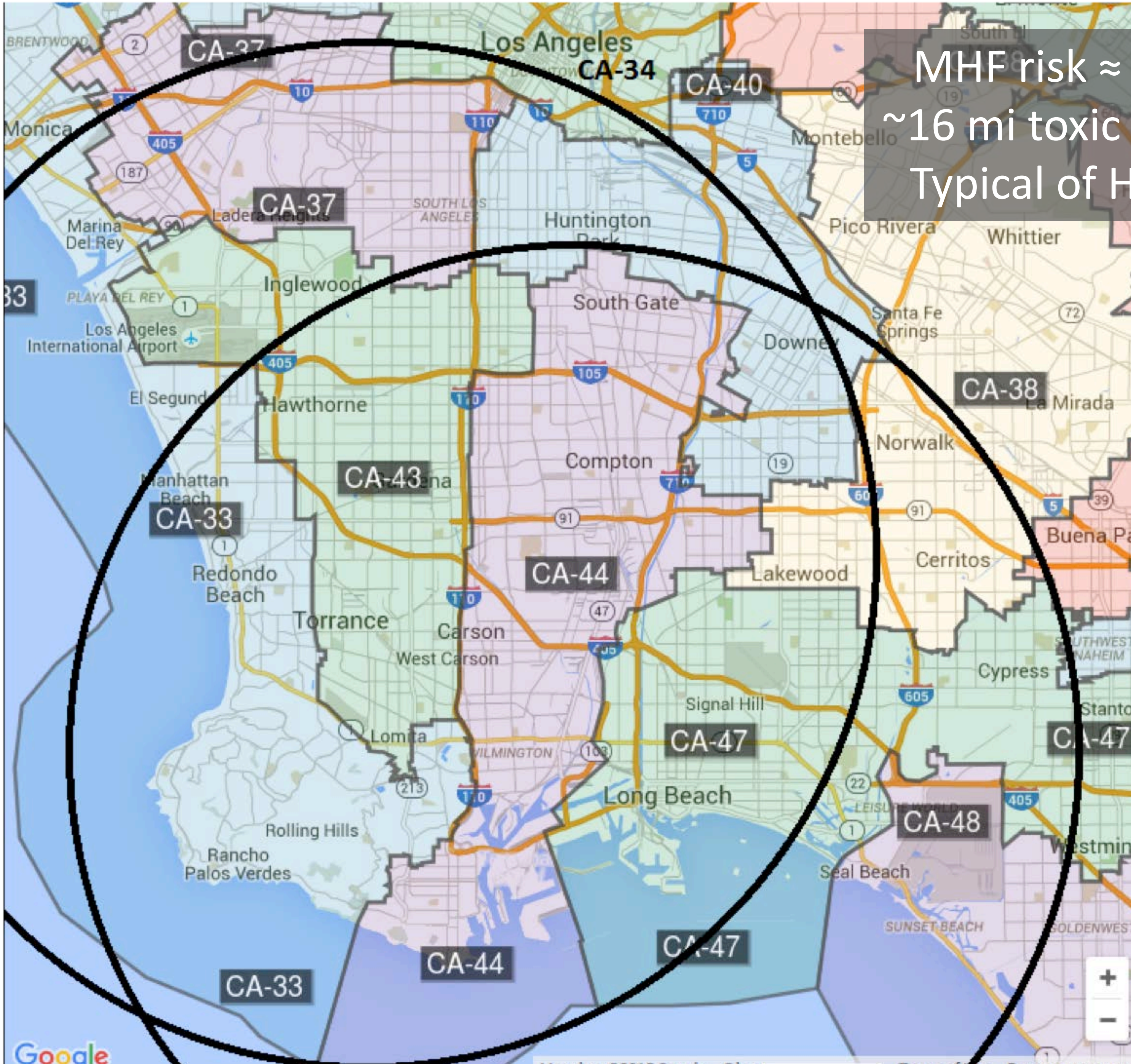
Post MHF 1997 unit failure: a little (additive) goes a long way

- 8% sulfolane credited with 50% ARF at --/--. 100ºF/100 psig std alky unit

Original R&D: preferred MHF composition 20–40% additive.[2] ARF ↓ if add wt% < 30%.

- 10% sulfolane extrapolated to 18% ARF at 86ºF/-- psig (not tested)[2,3]
- 20% sulfolane credited with 32% ARF at 90ºF/50 psig. Described as "fuming"[2]
- 34% sulfolane credited with 53% ARF at 90ºF/140 psig[1, 4] Described as liquid[2]

[1] Mobil, Containment of an Aerosolable liquid jet, US5286456, 1992. <http://bit.ly/2lmsmnx>.
[2] Phillips, Alky catalyst containing hydrofluoric acid & a sulfone, 1992, <http://bit.ly/2hPLiNr>.
[3] Phillips, Isoparaffin-olefin alkylation, US5534657, 1995, < http://bit.ly/2iWPonl>. Fig. 7
[4] Mobil, Containment of an Aerosolable liquid jet, 1992, <http://bit.ly/2lmsmnx>.



MHF risk ≈ HF risk
~16 mi toxic distance
Typical of HF units

HF Alkylation: Rejected Years Ago in So CA

1990 Torrance-Mobil Consent Decree

- MHF would not form aerosol or dense vapor cloud upon release

1991 AQMD Rule 1410

- MHF release would not result in atmospheric concentrations ≥ 20 ppm for 5 min & 120 ppm for one min at or outside facility boundary

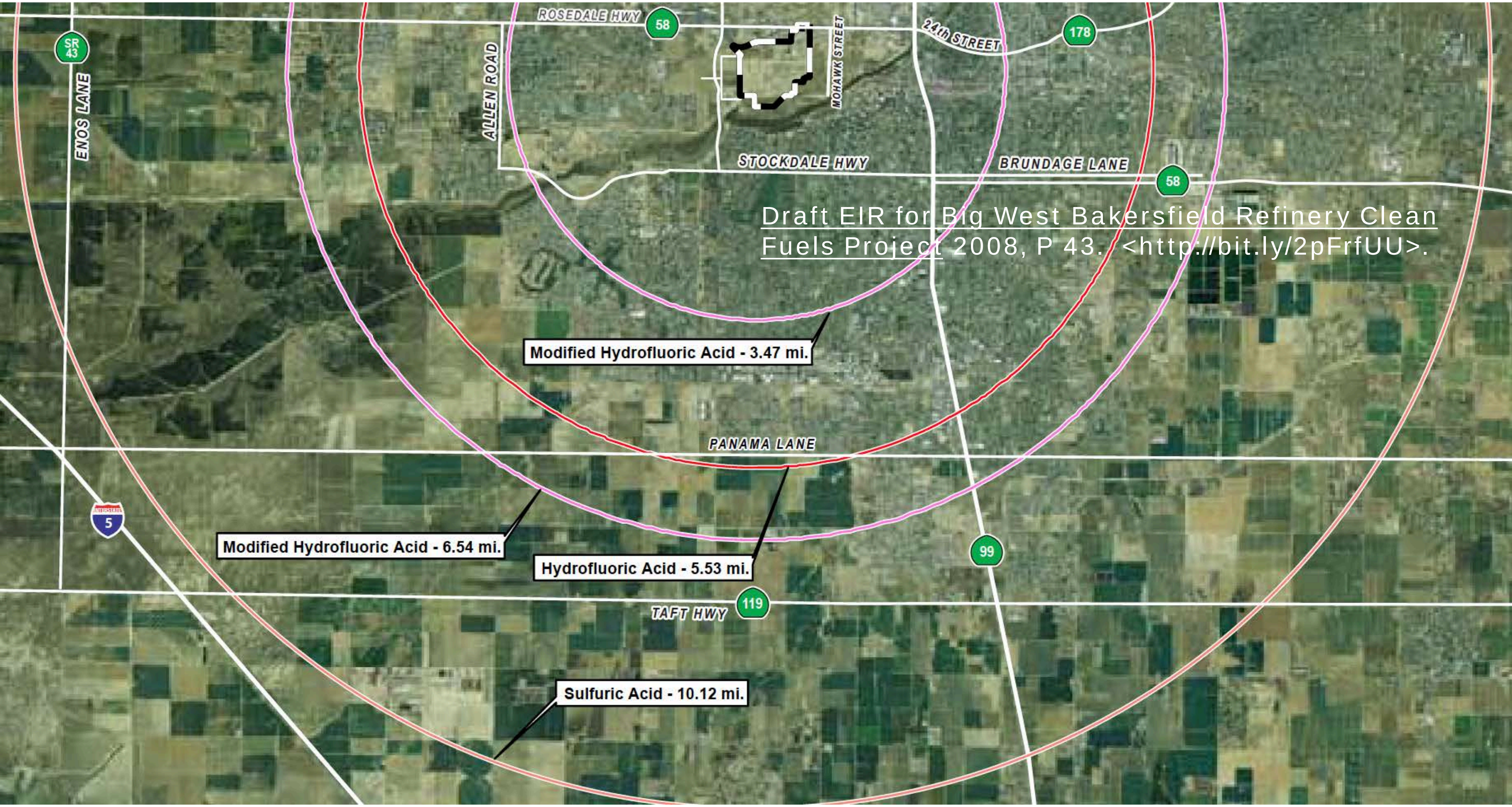
2003 SCAQMD Environmental Justice MOU

- Termination of storage and use of concentrated HF

LOWBALL OFFICIAL EPA MHF RMP WCSs show a dense vapor cloud forms & HF ≥ 20 ppm exist for miles around each refinery. ~1M people.

If not for false claims re: MHF & H_2SO_4, HF would've been gone years ago.

DENY MHF FLASHING; INVENT H_2SO_4 FLASHING



2008: Safety Advisor Maher hired by Big West Refinery to sell Bakersfield on MHF by claiming a 10-mile toxic distance for an H_2SO_4 alkylation unit vs 6.5-mi for MHF. Mobil & its hand picked Safety Advisor did the same under Consent Decree in '94. This rural area decided MHF was too dangerous and rejected the permit.

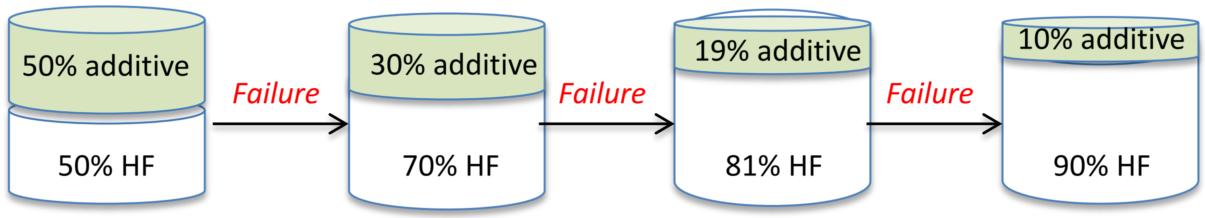
MHF Failure as Alkylation Catalyst Was Predictable & Predicted

- HF strength must be kept above 88% by weight [in the alky unit] to prevent undesired reaction products[1]
- [MHF] additives… reduce the catalytic performance of HF for alkylation[1]
- Components that reduce acid strength are water, acid soluble oil (ASO), dissolved reactants, organic fluorides,[2] and MHF additive
- Alky unit operation below 80% HF strength can result in an acid runaway in which the entire acid inventory converts to ASO and organic fluorides[2]
- Acid acts as a catalyst in a refinery alky reaction, and requires a minimal amount to enable the reaction to occur. As acid strength declines, undesirable side reactions occur, and can cascade on itself in a "runaway" manner that consumes all of the acid in the unit[3]
- If there is a build up of ASO by- product and HF acid is consumed (thereby reducing acid strength), the process can fail, with the resulting rapid consumption of the remaining acid – a so-called acid runaway event. Such an event is extremely costly[4]

1. *SCAQMD, Rule 1410, Resolution #90, April 1991, <http://bit.ly/2p0Wwla>.*
2. *Effect of Operating Conditions on Corrosion in HF Alkylation Units, Johnathan Dobis, Inspectioneering, <http://bit.ly/2rLKD1I>.*
3. *Refinery Alkylation Basics, <http://www.refinerlink.com/blog/liquid_gold_black_box>.*
4. *HF Alkylation, <https://library.e.abb.com/public/1b9c3c80511554ef8325734b004198cf/22-26%203M774_ENG72dpi.pdf>.*

MHF: Nothing but Failures & Broken Promises

Promised:
falls to ground upon release



Delivered:
100% airborne upon release

1990
Consent Decree

1994
Stipulation & Order

1997
MHF unit op failure

1998
secret modifications

MHF unit was dangerously unstable upon startup at end of '97 at just 19% additive. Unit filled w/ polymer gunk & produced small quantities of lousy alkylate.

The public was never told

The "safety conferring" additive was secretly slashed again.

The public was never told

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2nd proprietary "safety technology," physical barriers, added to "cover up" missing additive

The public was never told

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