VIA EMAIL: pfine@aqmd.gov, cc: SCAQMD Board members

August 22, 2017

Philip Fine, Ph.D.
Assistant Deputy Executive Officer, Planning and Rules
South Coast Air Quality Management District
21865 Copley Drive, Diamond Bar, CA 91765

Re: ToRC Comments on AQMD's July 28, 2017 presentation for the PR 1410 Working Group

Dear Dr. Fine:

The Torrance Refinery Action Alliance (TRAA) and the many thousands of community members we represent are supportive of and grateful for the SCAQMD staff's initial conclusion that it is necessary to phase out modified hydrofluoric acid (MHF) technology. The Torrance Refining Company's (ToRC) letter of August 1, 2017, on the contrary, expressed disappointment and dismay at what it calls a "premature position." But this position is long overdue.

The 1990 Torrance-Mobil Consent Decree was meant to eliminate the dangers of hydrofluoric acid (HF) alkylation at the Torrance refinery. But ever since its signing, the refinery has waged an effective campaign that, in Congressman Ted Lieu's words, "hoodwinked" the community, including the City of Torrance, residents, and yes, the SCAQMD, into believing false claims that an additive, along with other Band-Aid "safety" measures, made MHF alkylation "24-times safer than sulfuric acid," an HF alternative.

ToRC attempts to continue this false narrative. The SCAQMD staff has found that evidence does not support ToRC's MHF safety claims, and TRAA's eight-member Science Advisory Panel agrees. Based on information from the MHF industry and former Torrance City Councilman Don Lee's recollection, in 1990 Mobil pledged to use a MHF compound that was 50% HF and 50% vapor suppressant additive (Sulfolane) by weight. The actual concentration used hovers around 10% or less.

The SCAQMD foretold in 1991 why the MHF experiment ultimately failed.1 MHF cannot function in the alkylation unit as a catalyst if the vapor suppressant "additive" is kept at high enough levels to suppress airborne acid formation upon accidental release. Since HF concentration must be greater than 88% by weight in the unit, a maximum of 11% additive can be used. That is too little to matter as a safety measure at the high temperatures and pressures of refinery alkylation units.

Developers Mobil, Phillips, and ExxonMobil affirmed in multiple MHF patents that HF strength should be maintained at 88% - 94% by weight, [2,3,4,5,6] and that "loss of acid strength precipitate[s] immediate degradation in alkylate product quality."[7] Since water, an alky unit

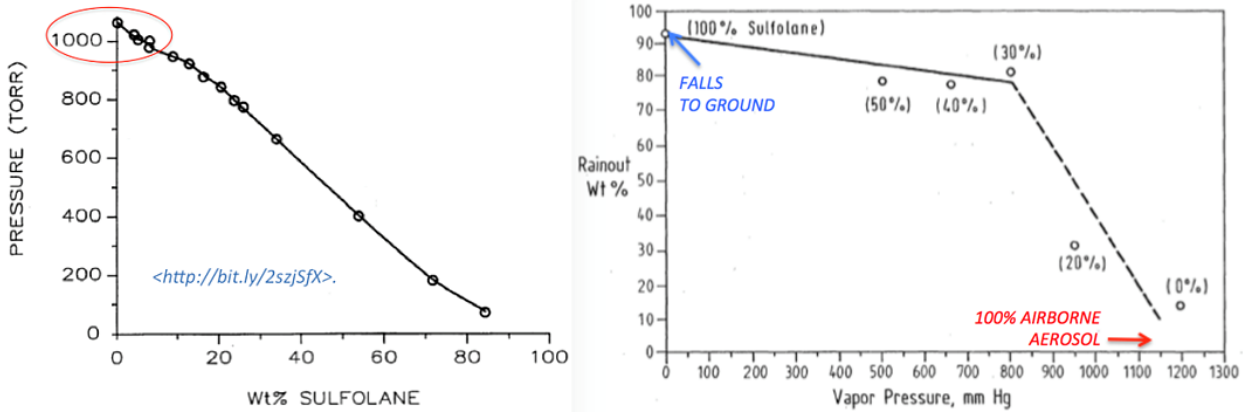
contaminant, and Acid Soluble Oil (ASO), an undesired byproduct, also reduce HF strength, *MHF additive needs to be kept even below 11% to avoid problems*.

When acid strength declines, undesirable side reactions can cascade into a "runaway" process.[8] When HF concentration dips towards 80%, the entire acid inventory can convert to ASO and organic fluorides.[9] PBF/ToRC reported HF concentration of 80% in one alky unit sample, using 8% additive.

The MHF unit predictably failed upon startup in 1997, at an additive level of 19%.[10] The public was never informed. The unit produced little product of poor quality and was *dangerously unstable*, said the Consent Decree Safety Advisor (SA) in a report not made public until discovered by this author in 2015.[11] Recently, ToRC created an outrageous new story to explain the additive cut, claiming years of successful operation followed by new tests and optimization by the SA.[12] Yet Phillips and ExxonMobil patents issued after additive concentration was slashed to 10% or less in 1998, reveal that even these low additive levels interfere with alkylation.[13,14,15] Additive reductions throughout MHF's R&D phase reflect necessity, not optimization. Public safety has taken a back seat to expediency and profits.

The main safety claims for MHF with 7-10% additive is that upon accidental release, an aerosol will not form and 50% less acid will remain airborne than for HF. MHF industry tests show this claim is not credible, which is why SCAQMD experts act responsibly in coming to a decision now.

This data curve from a Phillips 1995 patent (below, L) shows MHF vapor pressure as a function of additive concentration.[16] The effects of Sulfolane's hydrogen bonding are reflected in this graph. With 10% or less additive (red ellipse), vapor pressure is nearly identical to HF. This is unsurprising. At 8% additive by weight, e.g., out of every 100 MHF molecules, 98.6 are HF and only 1.4 are additive.[17]



The MHF acid Airborne Reduction Factor (ARF) is also called acid *rainout*. The graph at right, from a Phillips 1992 patent, shows MHF rainout as a function of MHF vapor pressure.[18] MHF vapor pressure is a function of additive concentration, as discussed. Phillips labeled five vapor pressure points with the corresponding additive concentration. For additive levels below 30%, the acid rainout benefit plunges. MHF developers therefore admitted (pre-MHF startup failure) that barely modified HF is barely different from HF. Vapor pressure and rainout curves like these do not have an expiration date.

But even this sorry state of affairs overstates MHF's tiny "safety" advantage. Quest Consultants, the firm that did the MHF testing,[19] agrees. Quest published a peer-reviewed paper in 1995 stating that 100% of MHF will form an aerosol upon release when mixed with hydrocarbons in the alky unit, even with a very high 50% additive level.[20] Just like HF. But the HF alternative, *sulfuric acid,* forms no aerosol or persistent vapor cloud upon release at all, said Quest, even when mixed with hydrocarbons. These observations are the opposite of what the MHF industry has claimed since 1994.

Based on MHF industry data and standard chemistry, the TRAA Science Advisory Panel has calculated that MHF with 10% additive boils at 73ºF and flash atomizes at 90ºF and 100 psig. Released MHF becomes 100% airborne, like HF. MHF reactions take place in the alky unit at around 100ºF.[21] The MHF tank nearly struck on 2/18/2015, contains 50,000 lb. MHF under pressure at 105°F.

The reason ToRC has not been able to demonstrate MHF will not flash or form a dense HF cloud is because MHF will do both. ToRC's strategy is therefore to pile documents without end onto SCAQMD staff, insisting on a complete review of each page. This is a delay tactic only. Furthermore, post-failure safety claims that contradict years of MHF R&D are of dubious origin and questionable merit. One post-1997 graph shown to the public is clearly not lab test data, as claimed.

Unable to defend MHF on its scientific merits, ToRC's letter invokes the sanctity of the 1990 Mobil-Torrance Consent Decree. But one judge's recognition of a mutual agreement by parties bound by a Consent Decree is nothing more than that. Furthermore, the SA's 1999 report said decisions should be revisited if new technical information becomes available that puts in question the basis of the risk analysis.[22] Also the Decree clearly notes, "Nothing herein shall be construed to limit, preempt, or interfere with any regulatory action undertaken by Torrance… or other regulatory agencies."[23]

The sole value of MHF is the false perception of greater safety compared to HF. But MHF's drawbacks are many; it adversely impacts production and increases complexity. This creates a conflict of interest for the refinery. Under the Decree, only the Safety Advisor (SA) team was to have access to proprietary Mobil data. It alone could perform an independent evaluation of Mobil's performance and of MHF. Because Torrance and Mobil could not agree which entity should fill this role, it was up to retired Judge Harry V. Peetris, with a bachelor's degree in accounting and legal experience in personal injury, business law, traffic court, and mental health court. He chose to appoint the company selected by Mobil, industry consultant, Westinghouse. The city said it was like "a fox watching the chicken coop."[24]

Westinghouse's Project Manager Steve Maher hired theoretical elementary particle physicist Dr. Geoffrey Kaiser to act as his expert consultant. The year before, Allied Signal had hired Kaiser to protect its El Segundo refrigerant plant against SCAQMD's 1991 Rule 1410 banning HF use.[25] Kaiser authored Allied's report, "An Analysis of the Safe Use of Hydrogen Fluoride." He provided the same service to HF refineries Ultramar, Wilmington (Valero) and Golden West, Santa Fe Springs.[26,27] Thus, *two pro-industry HF advocates* acted as the sole evaluators of MHF and watchdogs for the public.

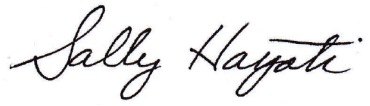
ToRC tries to shield MHF by quoting industry talking points delivered by SCAQMD when Valero switched to MHF. That decision relied upon the Consent Decree. The district, having

many battles to face and reassured by the Safety Advisor and Torrance, failed to make an independent MHF assessment. Now that the staff has had an opportunity to investigate, they understand MHF far better.

Note, however, Quest Consultants' conclusion in Valero's documents that MHF reduces toxic distances by only 7.9% compared to HF.[28] A path of death and injury 10-miles long would be reduced to 9.3-miles. Only those who don't live in the community could see this as "significant." This corresponds to about a 15% reduction in airborne acid (ARF), far less than the 50% claimed for MHF by ToRC.

If the industry had proof MHF was 50% less deadly than HF (which, incidentally, is not safe enough for the densely populated South Bay), and that simple impingement barriers achieved an additional 40% reduction in airborne acid, they would show it to the world. They have nothing to lose, since MHF and the barriers are patent protected. MHF is a failed R&D effort; but as a PR tool it's been a great success at saving HF alkylation from a ban in California, up to now. The community will not allow this deception to continue any longer. We appreciate the SCAQMD's efforts to get the facts on MHF.

Sincerely,



Sally Hayati, Ph.D.
President, TRAA

ENDNOTES

[1] Rule 1410, Resolution Number 90, South Coast Air Quality Management District, April 1991, <https://goo.gl/JbgQZX> [I. Executive Summary – page 4, Document stamp page 00023, .pdf p. 31.] The importance of HF strength in alky units for alkylate quality and to avoid corrosion in the unit is universally recognized: "Acid strength …normally ranges between 83% and 90%. *Components that reduce acid strength are water, ASO and dissolved reactants.* [note: this doesn't include the MHF additive, which is an additional component that reduces acid strength] Low acid strength contributes to further formation of acid ASO and organic fluorides. From a corrosion standpoint, it is preferable to operate in the higher end of the range at all times, preferably above 88%. Operation below 80% can result in an acid runaway in which the entire acid inventory converts to ASO and organic fluorides." The 1997 MHF unit predictably failed operations and became "dangerously unstable" because of just 19% additive. Having operated HF units since the 1960s, how could Mobil not have known of this problem earlier? FROM: The Effect of Operating Conditions on Corrosion in HF Alkylation Units, Johnathan Dobis, Inspectioneering, 2004-05. <https://inspectioneering.com/journal/2004-05-01/312/the-effect-of-operating-condit#>. Note the additive causes problems even at 10% concentration, because water, ASO, and dissolved reactants cause additional reductions in acid strength, bringing it below 88%. See: HF alkylation process with acid regeneration, US Patent 7847142 B2, ExxonMobil Research and Engineering Company, 2007 (filing date), <http://www.google.com/patents/US7847142>.

[2] 1991-06-21, US Patent 5196628, Liquid Acid Alkylation Catalyst and Isoparaffin: Olefin Alkylation Process, Mobil Oil Corporation, Rossi. <https://www.google.com.au/patents/US5196628>. This is another form of MHF that uses a nitroalkane additive plus the sulfonic additive. This patent explores nitromethane and similar "nitrogen containing additives [that] surprisingly have only minor effects" on alkylation. "The mechanism underlying the unusual behavior of the nitroalkanes is not well understood; indeed, this development contradicts the reasonable expectation that dilution would degrade HF catalyst performance." But this avenue was apparently abandoned, possibly because the mystery meant Mobil hadn't understood it yet, or because nitroalkanes needed lower alky unit temperatures and very low water contaminant levels.

[3] 1992-12-17, US 5264652 A, Mobil Oil Corporation, Method for separating conjunct polymeric byproducts from mixture containing hydrofluoric acid and a sulfone, <https://www.google.com/patents/US5264652>.

[4] 1992, MHF Patent, European, EP 0796657 B1, "Alkylation catalyst containing hydrofluoric acid and a sulfone," Phillips Petroleum Company. <https://encrypted.google.com/patents/EP0796657B1>

[5] 2007-07-27, ExxonMobil, HF alkylation process with acid regeneration, US Patent 7847142 B2, 2007 (filing date). < http://www.google.com/patents/US7847142>.

[6] 2009-01-26, ExxonMobil, HF akylation process, US Patent 20090221863 A1 <https://www.google.com/patents/US20090221863>.

[7] 1991-06-21, US Patent 5196628, Liquid Acid Alkylation Catalyst and Isoparaffin: Olefin Alkylation Process, Mobil Oil Corporation, Rossi. <https://www.google.com.au/patents/US5196628>. This is another form of MHF that uses a nitroalkane additive plus the sulfonic additive. This patent explores nitromethane and similar "nitrogen containing additives [that] surprisingly have only minor effects" on alkylation. "The mechanism underlying the unusual behavior of the nitroalkanes is not well understood; indeed, this development contradicts the reasonable expectation that dilution would degrade HF catalyst performance." But this avenue was apparently abandoned, possibly because the mystery meant Mobil hadn't understood it yet, or because nitroalkanes needed lower alky unit temperatures and very low water contaminant levels.

[8] Refinery Alkylation Basics, <http://www.refinerlink.com/blog/liquid_gold_black_box>.

[9] The Effect of Operating Conditions on Corrosion in HF Alkylation Units, Johnathan Dobis, Inspectioneering, 2004-05. "Operation below 80% [HF strength] can result in an acid runaway in which the entire acid inventory converts to ASO and organic fluorides."<https://inspectioneering.com/journal/2004-05-01/312/the-effect-of-operating-condit>.

[10] According to the ToRC representative to the PR 1410 Working Group at Working Group Meeting #3 on June 15, 2017.

[11] Consent Decree 1999-10, Safety Advisor Report, Steve Maher, "Evaluation of Modified HF Alkylation Catalyst (Analysis of proposed additive concentration changes)." <https://drive.google.com/file/d/0B0sm-0cQ1vDqYzVITi1ibzFrNU0/view>. Read the Executive Summary from this report, annotated by Hayati, here: <https://drive.google.com/file/d/0B0sm-0cQ1vDqek5ScVkxWTVqVnM/view>. This author requested this document from the City of Torrance. Safety Advisor Steve Maher sent it by email to City Councilman Tim Goodrich, who forwarded to me.

[12] Sally Hayati, 2016-08-01, "The Torrance Refining Company Ad: Toxic Lies about MHF." <https://drive.google.com/file/d/0B0sm-0cQ1vDqNjR5X3BKc3dpT28/view>.

[13] 1999-09-27, US 6114593, Phillips, Method for reducing organic fluoride levels in hydrocarbons. (for MHF) <https://www.google.com/patents/US6114593>.

[14] 2007-07-27, US 7847142 B2, ExxonMobil, HF alkylation process with acid regeneration, <http://www.google.com/patents/US7847142>.

[15] 2009-01-26, US 20090221863 A1, ExxonMobil, HF alkylation process, <https://www.google.com/patents/US20090221863>.

[16] Red ellipse added to show relevant graph area (additive concentration ≤ 10%) 1995-06-02, US 5654251, Phillips Petroleum Company, Isoparaffin-olefin alkylation, <https://www.google.com/patents/US5654251>. Phillips was Mobil's partner in developing the ReVAP brand of MHF, used at Torrance and Valero, Wilmington.

[17] Physical chemists use not weight, but molar concentration (based on molecule count) to calculate vapor pressures for compounds like MHF. Sulfolane is much heavier than HF. So MHF with just 8% additive by weight consists mostly of HF molecules: 98.6 mol% HF and 1.4 mol% additive.

[18] Red and blue labels added for clarity. European Patent EP 0796657 B1, "Alkylation catalyst containing hydrofluoric acid and a sulfone," Phillips Petroleum Company, 1992, <https://encrypted.google.com/patents/EP0796657B1>.

[19] Consent Decree 1995-05-17 Safety Advisor Report, Steve Maher, "Evaluation of Modified HF Alkylation Catalyst (in Support of Decree Section 4)," Final Report, Rev 1, <http://psbweb.co.kern.ca.us/UtilityPages/Planning/EIRS/clean_fuels/Appendices/Appendix%20H_Torrance%20Report%2017May95FinalR1_PUB.pdf >. [Quest did MHF release tests (Page 92)]

[20] Quest Consultants, Inc., 1995, David W. Johnson, "Effectiveness of Mitigation Systems in Reducing Hazards of Hydrogen Fluoride Leaks," First Risk Control Engineering Seminar; Maracaibo, Venezuela; October 19-20, 1995. <http://www.questconsult.com/papers/mitigation-systems-hydrogen-fluoride-leaks/>.

[21] US PIRG Education Fund, "Needless Risk: Oil Refineries and Hazard Reduction," August 2005, <http://www.uspirg.org/sites/pirg/files/reports/Needless_Risk_USPIRG.pdf>

[22] See page 7: Consent Decree 1999-10, Safety Advisor Report, Steve Maher, "Evaluation of Modified HF Alkylation Catalyst (Analysis of proposed additive concentration changes)." <https://drive.google.com/file/d/0B0sm-0cQ1vDqYzVITi1ibzFrNU0/view>.

[23] City of Torrance-Mobil Consent Decree, 1990-10-09, Filed with the Superior Court of the State of California for the County of LA, Case No. C719 953. <https://drive.google.com/file/d/0B0sm-0cQ1vDqYUFBYkNFN3NSdWM/view?usp=sharing>.

[24] 1991-06-06, "The 'Even-Handed' Judge in Mobil Case: Torrance: Retired Superior Court Judge Harry V. Peetris," Deborah Schoch, LA Times, < http://articles.latimes.com/1991-06-02/local/me-374_1_superior-court-judge >

[25] Rule 1410 was overturned on a technicality in 1993. SCAQMD hopes to revive Rule 1410 by the end of 2017. Kaiser, Geoffrey D., "Quantitative Risk Assessment of the Use of Hydrogen Fluoride at Allied-Signal's El Segundo Facility" (August 1990). Reference from Allied-Signal's October 1990 report to the SCAQMD, "An Analysis of the Safe Use of Hydrogen Fluoride at the Allied-Signal Facility in El Segundo." Kaiser was hired by Allied Signal to defend them against Rule 1410. REF: PAGE 249 of *Rule 1410, South Coast Air Quality Management District, "Draft Environment Assessment (EA) for proposed Rule 1410, Hydrogen Fluoride Storage and Use," February 22, 1991, Director of Planning Barry Wallerstein, D. Env.,* <*ftp://ftp.aqmd.gov/outgoing/R1410/*>.

[26] Kaiser Publications: Risk Assessment HF Use (Genetron Unit), (Project Manager and Principal Author). Prepared for AlliedSignal, El Segundo, CA, December 1990. Updated February 1995; Risk Assessment HF; Alkylation Unit, (Project Manager and Principal Author). Prepared for Ultramar Refining, Wilmington, CA, November 1990. Ultramar Refining Risk Management and Prevention Program for the HF Alkylation Unit, (Project Manager and Principal Author). Prepared for Ultramar Refining, Wilmington, CA, February 1990. Du Pont and the nuclear energy and weapons industries also employed Kaiser's assistance selling high-risk technology. FROM: Geoffrey D. Kaiser Biography, 2007-10. Pages 83-90: Science Applications International Corporation, "Relocation of Non-Nuclear Production to an Alternate Location," October 18, 2007. Prepared for the U.S. DoE, National Nuclear Security Administration, Defense Programs, Office of Transformation. <https://www.gsa.gov/portal/mediaId/137266/fileName/Business_Case_Relocation_Non_Nuclear_Production.action>.

[27] Kaiser's firm, Science Applications International Corporation (SAIC) was founded in 1969 by J. Robert Beyster "and a small group of scientists ... as a scientific consulting firm with a handful of government contracts for nuclear power and nuclear weapons effects study programs. In 1990 SAIC was indicted and pled guilty to 10 felony counts of fraud on a Superfund site, called "one of the largest (cases) of environmental fraud" in Los Angeles history. Sourcewatch.org, "SAIC," <http://www.sourcewatch.org/index.php/Science_Applications_International_Corporation>.

[28] 2004-12, Final Environmental Impact Report for: Ultramar Inc. - Valero Wilmington Refinery Alkylation Improvement Project, App. C. Hazard Analysis, December 2004, <http://www.aqmd.gov/docs/default-source/ceqa/documents/permit-projects/2004/ultramar-valero/appc252.pdf> [Document page 5-2/ .pdf page 31] "The implementation of the ReVAP process, with its use of the acid additive which reduces the volatility of the acid phase, results in an 7.9% reduction in the maximum hazard distance."