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Deputy Executive Officer
Planning and Rules
South Coast Air Quality Management District
21865 Copley Drive
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Re: Torrance Refinery Company LLC's Response to Questions Raised about the Torrance Refinery MHF Alkylation Unit Based on the QUEST 1995 Paper

Dear Dr. Fine,

This letter refers specifically to statements made during several Proposed Rule 1410, "Hydrogen Fluoride Storage and Use at Petroleum Refineries" ("PR 1410") meetings, most recently on August 23, 2017. During the public comment period on that date, Mr. James Eninger, a member of the ad hoc Torrance Refinery Action Alliance ("TRAA") Science Advisory Panel ("SAP"), expressed his opinion on the 1995 Quest research paper entitled "Effectiveness of Mitigation Systems in Reducing Hazards of Hydrogen Fluoride Leaks" by John B. Cornwell and David W. Johnson.

Mr. Eninger and other members of the TRAA SAP have repeatedly tried to cast doubt on the comprehensive, historic Modified Hydrofluoric Acid ("MHF") testing and modeling results that proved the efficacy of the MHF catalyst that has been safely and reliably used in the Torrance Refinery MHF Alkylation unit without any offsite release since 1997, when the unit was converted to MHF use. We note for the record that SAP members have no experience in or education related to refining or alkylation. Despite this and consistent with their history of misrepresenting facts associated with the Torrance Refinery MHF Alkylation unit, SAP members continue to opine that the 1995 Quest paper is proof that MHF would be unable to suppress flash atomization of hydrofluoric acid ("HF") if a release were to occur.

In response, Torrance Refining Company LLC ("TORC") offers the following supporting information and clarifications. To begin, the 1995 Quest paper refers to an Alkylation unit that differs fundamentally from the Torrance Refinery MHF Alkylation Unit's design, configuration and operations. In addition, we previously provided District staff with research and other evidence that MHF is a proven, inherently safe Alkylation technology that represents the latest commercially proven advance in alkylation catalyst, which is supported by District research, decisions, and permits issued in 199(6/7) for the Torrance Refinery and in 2003 for the Wilmington Refinery.

1. <u>The referenced 1995 Quest paper is inconsistent with Quest's 1996 Analysis of the Use of MHF at the Torrance Refinery developed for the District.</u>

Quest's 1996 Hazards Analysis conducted for the South Coast Air Quality Management District ("District") California Environmental Quality Act ("CEQA") analysis was specifically authored for the District's permitting of the Torrance Refinery's MHF Alkylation Unit and is the authoritative source for information on our MHF Alkylation unit. In their 1996 analysis, authored by John B. Cornwell, co-author of the 1995 paper, Quest states the following regarding MHF:

> "Quest has been active since 1991 in the modified hydrofluoric acid (MHF) project that Mobil Research and Development Corporation (MRDC) has undertaken. Quest performed MRDC's large-scale outdoor testing work that was completed in 1993. During the course of the testing, we measured the release behavior of anhydrous hydrofluoric acid; hydrofluoric acid with additive; and additive alone."
>
> "During the experimental testing, we observed that the addition of Mobil additive to HF was an effective method of reducing or eliminating the amount of aerosol formed during a release …"
>
> "The additive also has an obvious – dilution of the HF concentration in the liquid. Any amount of additive reduces the mass flow of HF from a given size hole when compared to pure HF release."

See District's "Addendum, Mitigated Negative Declaration, Mobil Modified Hydrogen Fluoride Conversion Project" (July 9, 1997), Appendix A, Quest Hazards Analysis, pp. 1-2 (June 16, 1996).

2. <u>The Alkylation Unit referenced in the 1995 Quest paper differs fundamentally from the Torrance Refinery's MHF Alkylation Unit design, configuration and operation.</u>

Specifically, the 1995 paper written by Quest Consultants was an early attempt to quantify the effect of mitigation systems on HF leak hazard reduction. A great deal of subsequent testing served to prove that many of the assumptions Quest used in this paper are inapplicable and irrelevant to the design, configuration, and operation of the Torrance Refinery MHF Alkylation Unit. Additionally, this 1995 paper disregards and omits key physical properties of the HF, additive and hydrocarbon mixtures that play a critical role in release phenomenology. This response describes some of the key oversights and omissions made in the 1995 paper, looking at the overall picture and then continuing the discussion for each release case.

a. <u>Alkylation Unit Details</u>

The unit configuration used as the basis for the theoretical analysis in the 1995 Quest paper differs fundamentally from the Torrance Refinery MHF Alkylation Unit process flow. In addition, there have been many engineering and mitigation design enhancements discovered and implemented on TORC's unit since this paper was written, which was before the unit was converted to utilize MHF. Key differences in design have significant effects on the dynamics of any potential release.

For example, the settler reactor configuration referenced in the 1995 paper is a Phillips design. The Torrance Refinery utilizes a UOP system, which is completely different in design, configuration, and operation from the Phillips system. Additionally, the Torrance MHF Alkylation Unit utilizes a pumped acid circulation system with isolation and segregation capability, whereas the 1995 paper references the Phillips' gravity-circulated system.

The Phillips design is used in about half of all HF units and contains 4-5 times more acid inventory than a comparable UOP designed alkylation unit, so Quest's claim that this is a "typical configuration" is inaccurate and misleading to uninformed readers.

Using a Phillips design instead of the UOP model used at the Torrance Refinery causes the potential height of a release and the distance to existing physical barriers such as the ground, process equipment, infrastructure, etc., to be dramatically overstated when compared to the Torrance Alkylation unit. In addition to these examples, various engineered barriers were incorporated in the MHF design at Torrance after the 1995 paper was published. These barriers have a significant, positive impact on the rainout of any release at the Torrance Refinery.

The Torrance Refinery MHF Alkylation Unit is designed to direct an acid release from the main settler system downwards from the bottom of the settler and ultimately to the ground. Time to hit grade would be minimal, causing the MHF to pool on the ground, where it would quickly mix with water discharged by nearly automated cannons. Additionally, the 1995 paper fails to take into account the Torrance Refinery's settler belly pan barriers, which are similar to the physical barriers mentioned previously that would dramatically improve rainout if an MHF release occurred.

b. <u>Emulsion Considerations</u>

The presence of an acid/Additive/hydrocarbon mixture that could be released after 17 minutes as described in release Case #2 is a non-credible scenario for Torrance. After initial onset of a release from the Torrance Refinery MHF Alkylation Unit, acid circulation in the affected area would be immediately stopped by remotely operated isolation valves.

As soon as acid circulation or hydrocarbon feed is stopped, the emulsion layer breaks and the density differences work almost instantaneously to separate hydrocarbons from the acid/Additive phase. This has been demonstrated in the Torrance Refinery Alkylation unit and documented to occur in less than one minute, well before the 17 minutes noted in the 1995 paper's Case #2 model, and referenced later in this letter.

Due to this quick separation, the mixture layer described in the 1995 Quest paper would have never reached the release orifice. Hydrocarbons would remain in the upper section of the settler while acid would settle to the bottom.

After the acid phase is released, only a hydrocarbon phase would remain within the 17 minute window noted in Case #2. This is dramatically different than the hydrocarbon/Additive/HF mixture assumed in the 1995 paper, invalidates the modeling of the second part of the release for scenario Case #2 and could potentially mislead someone without knowledge of Alkylation and the differences in unit designs, configurations and operations.

c. Pooling and Weathering

The assumption by the paper's authors that nothing will be done to disperse the pool of released HF/Additive mixture as HF weathers off the Additive is incorrect and again, misunderstood and misleading. The weathering effect is very slow and would take hours or perhaps days if nothing else is done to stimulate the pool, as described in the 1993 EPA "Hydrogen Fluoride Study Report to Congress", which states on page 13 that while "HF will vaporize quickly from a pool for the first few minutes..." the "...pool temperature will drop as HF vaporizes causing a corresponding decrease in evaporation rate." For the Torrance Refinery MHF Alkylation Unit, the hypothetical released pool of MHF would be flushed with water from nearby water cannons almost immediately, compounding with any free acid and allowing safe routing to the process sewer.

d. Dispersion Modeling

The dispersion model used in the 1995 Quest paper has many missing assumptions that limit the robustness of the conclusions that can be drawn. For example, the model fails to account for HF/water thermodynamics, which greatly reduces dispersion distances in release monitoring. The authors' choice of measuring dispersion to just the concentration end-point also seems deliberate. A statement on page 17 shows that if the results were taken into a risk assessment and a probit equation used, the model would have shown a significant risk reduction for the Rapid De-inventory System. A risk-based approach would have likely resulted in conclusions different from those presented by the authors.

3. Case by Case Analysis of the 1995 Quest Paper Scenarios

Release Case #1 addresses a non-additized unit. For a two-inch hole there would be rainout due to the presence of polymers and water in the acid phase that the paper fails to recognize. This would increase the percentage of acid that reaches the ground above the 3% cited in the 1995 paper.

Release Case #2 describes a non-additized HF/hydrocarbon mixture. As discussed above in the "Emulsion Considerations" section, the assumption that a mixed acid/hydrocarbon phase could leave the hole together is physically impossible due to density differences. Settling for a full 17 minutes would ensure the phases separate. For the Torrance Refinery MHF Alkylation Unit, this separation has been shown to occur in less than one minute. The release in the Phillips system would instead be an anhydrous HF release, described in release Case #1, followed by a hydrocarbon release.

Release Case #3 describes a 2,000 gpm de-inventory rate. At this rate, the acid would be drained from the Phillips unit in 7.5 minutes. The Torrance Refinery MHF Alkylation Unit completes a total de-inventory in seven minutes, with 80% of the acid volume transferred to the unit's Acid Evacuation System ("AES") in the first two minutes due to its staged system, which was successfully tested in 2015.

Release Case #3 incorrectly assumes, once again, that the acid emulsion never breaks. Even though that cannot happen because the emulsion will break, the acid cooler would become a manometer and the emulsion would be pushed up and displaced by the acid in the settler. This makes Figure 3/4 meaningless and irrelevant because the event in the 1995 Quest paper is calculated to be over in 8.5 minutes, assuming a one minute response time. TORC has proven in a real-life situation that transfer of the acid in unit to the AES can be triggered in less than 10 seconds.

Release Case #4 severely underestimates the effectiveness of water mitigation on HF acid releases. The proven efficiency of water mitigation is closer to 90% and higher with a well-designed system, not 50% as assumed or even 80% noted in Quest 1995 paper, especially at a 50:1 water to acid ratio. The distance of the water curtain from the release point is also much further in this scenario than for any potential release scenario associated with the Torrance Refinery MHF Alkylation Unit.

Release Case #5 correctly states that the Additive is a passive mitigation. Rainout would occur for the full acid/Additive phase. As the 1995 Quest paper describes, an HF aerosol does not form, instead only vaporizing from HF droplets as they fall to the ground. The paper states "... when HF is released with the additive, the HF remaining airborne is a vapor, not an aerosol." This is a key, correct statement from this paper, as HF remaining airborne as a vapor is lighter than air and thus cannot form a dense ground-hugging cloud.

Release Case #6 again incorrectly assumes the mixed acid and hydrocarbon phase are released from the hole together, which is physically impossible due to density differences. The aerosol the 1995 Quest paper contends forms with the hydrocarbon phase cannot occur as the two-phase acid complex with hydrocarbon would not exist due to the phase separation previously discussed. There is no shattering of the release and the small droplets do not form.

* * *

In closing, TORC trusts District staff finds our detailed response to Mr. Eninger's and the TRAA SAP's misunderstanding and subsequent misrepresentation of the 1995 Quest Paper to be respectful, enlightening, and of value to the proceedings associated with the PR 1410 rulemaking. We recognize the data supporting the efficacy, safety, and reliability of MHF Alkylation can be difficult to analyze correctly without comprehensive knowledge of and experience with the processes, designs, and operations of Alkylation units. Thorough examination and analysis requires access to and understanding of relevant technical information and broad experience in refining and alkylation, which Mr. Eninger and other members of TRAA SAP lack.

Frankly, we view this misrepresentation of the 1995 Quest Paper as yet another example in a long line of TRAA SAP's attempts to discredit MHF technology by presenting myths camouflaged as facts. Similarly, they have continually tried to discredit the court-appointed Safety Advisor, Superior Court judge who oversaw the Consent Decree process, Torrance City Council members and Fire Department, and anyone else associated with this issue, while we note again that SAP members have no experience in or education related to refining or alkylation.

Contrasting the allegations asserted by TRAA, developed without understanding that Quest's 1995 paper analyzes a Phillips unit, we carefully outlined the practical and design differences between the Alkylation unit that is the subject of Quest's 1995 Paper and our Alkylation unit. We again note the 1996 report Quest was commissioned by the District for the CEQA document that supports the current operating permit for Torrance Refinery's MHF Alkylation unit.

We plan to continue working collaboratively and openly with the District to conclude the PR 1410 rulemaking based on sound science and technology, including the current state of Alkylation technologies. We note for the record and as an indicator of our collaborative intent, that we have previously provided the District with test results, modeling, and other research and interpretative data, as well as explanatory letters and responses to District presentations, all of which support the efficacy of MHF, including historic District documents. We see this response as another step in setting the record straight and welcome District staff's comments, feedback, and/or questions on this and/or any other materials we have submitted to the District.

We look forward to working collaboratively and openly with the District to get the PR 1410 rulemaking back on a track, based on sound science and technology and the current state of Alkylation technologies.

Please note that in submitting this letter, TORC reserves the right to supplement its responses and comments as it deems necessary, especially if additional or different information is made available to the public regarding the PR 1410 rulemaking process.

Sincerely,

Steve Steach
Refinery Manager

cc: Wayne Nastri, via e-mail
Susan Nakamura, via e-mail and hand delivery
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