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TORRANCE REFINERY
SAFETY ADVISOR PROJECT

EVALUATION OF MODIFIED HF ALKYLATION CATALYST

(In Support of Consent Decree Section 4)

Final Report, Rev. 1

Primary Contributors: Steven T. Maher

Dr. Geoffrey D. Kaiser

Approved:

S.T. Maher
Technical Manager

EQE International
18101 Von Karman, Suite 400
Irvine, California 92715

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EXECUTIVE SUMMARY

As a result of the settlement of a public-nuisance lawsuit filed by the City of Torrance against Mobil Oil Corporation in 1989, a Consent Decree (Reference 1) was entered into between the two Parties and was filed with the Superior Court of the State of California for the County of Los Angeles. One of the primary objectives of the Consent Decree was the establishment of a Safety Advisor (SA) for the Mobil Oil Corporation Refinery in Torrance, California. Among other responsibilities, the Safety Advisor has the authority to investigate and make recommendations on a wide range of safety-related issues for the refinery.

Section 4 of the Consent Decree permits Mobil "to commit to a modified HF catalyst by December 31, 1994 only if it has demonstrated to the satisfaction of the Safety Advisor that the catalyst as modified would not form an aerosol or dense vapor cloud upon release." A subsequent Stipulation and Order was filed in September 1994 (Reference 2) which allows the SA, as an alternative, to use risk criteria as a facet of its review, i.e., Mobil may demonstrate that "the modified HF catalyst (including mitigation) presents no greater risk than a sulfuric acid alkylation plant producing a comparable amount of alkylate." The Consent Decree and subsequent Stipulation and Order provide the objective, as well as the authority, for the Safety Advisor to evaluate and ascertain the basis and validity of both the phenomenological and quantitative risk comparisons provided by Mobil. This report is offered to address this objective and summarize the Safety Advisor's evaluation of the use of the Modified HF (MHF) catalyst at the Torrance Refinery (Task M of the Safety Advisor Project). The key activities involved in support of this evaluation effort included:

- Review of all information pertinent to the Torrance Refinery Alkylation Unit as well as key industry studies and test results cited as references in Section VIII,
- Performance of calculations to verify the adequacy of the analysis,
- Comparison with available risk assessment results for other refinery alkylation units,
- Comparison with other commercial and proposed alkylation technologies,
- Walkdown and discussion of operating history of the Paulsboro MHF Alkylation Demonstration Unit on November 8, 1994,
- Familiarity with the existing (late-1994) Torrance Refinery Alkylation Unit,
- Participation in a MHF Alkylation Catalyst Review Meeting in Paulsboro, New Jersey on November 7 and 8, 1994,
- Interaction with various Torrance Refinery, Mobil Engineering, and Torrance Fire Department personnel and participation in several meetings,
- Attendance at the October 31, 1994 and November 1, 1994 Alkylation Seminar, “The Role of Alkylation in the New Fuels Era,” sponsored by the Oil & Gas Journal, and

- Attendance at the December 20, 1994, “Synthetic Hydrocarbon Chemistry Seminar” sponsored by the Loker Hydrocarbon Research Institute.

The Consent Decree generally empowers the Safety Advisor to "conduct investigations" and "make recommendations". Thus, the Safety Advisor's results and conclusions focus on the ability to demonstrate safe operations by comparison with other available technologies as well as improvements in safety and operations for the existing facility. For this evaluation, the SA is empowered to determine if Mobil has demonstrated that it meets the specific, defined acceptance criteria identified in Reference 1 and Reference 2 for its proposed MHF alkylation technology. Recommendations may be provided for:

- specific changes which enable Mobil to meet the acceptance criteria
- any necessary verification items to validate the SA's conclusions
- any necessary follow-up SA actions

The recommendations identified within the report are summarized in Table ES-1, Summary of Specific Recommendations, and provide follow-up actions for Mobil, the Torrance Fire Department, or the Safety Advisor, necessary for closure of this Consent Decree activity.

Some elements, related to the Modified HF Alkylation Catalyst Evaluation, that are encompassed by other Safety Advisor Project evaluations include Refinery Chemical Monitoring/ Warning Systems and Emergency Response. The objectives of the Emergency Response Program Evaluation are to identify the adequacy of the existing Emergency Response Program (with any planned changes for the MHF conversion) in protecting “the environment and the health, safety, and welfare and property of all persons, both off-site and on-site.” The primary focus and criteria for this Emergency Response Program Evaluation are identified in Section IV.H and include the SA’s review of mitigation equipment, material characteristics, and emergency response timing assumptions. Subsections are included in this evaluation to address the above topics and identify any necessary follow-up actions for other evaluations conducted in support of the Consent Decree.

Discussion of Consent Decree Background and Objectives

The Consent Decree was originally crafted in 1990 prior to an improved understanding by industry of sulfuric acid release phenomenology, prior to significant progress in the development of HF catalyst vapor suppression additives, and prior to several regulatory initiatives in the field of process safety which increased the general understanding of risk and quantitative risk acceptance criteria. The September 1994 Stipulation and Order provided a vehicle for addressing many of these developments by making the Consent Decree criteria more contemporary and able to provide an improved perspective on one of the key Consent Decree objectives, the safety of the public and on-site personnel. In particular, the Stipulation and Order allowed for a comparative evaluation of alkylation processes as a way of more objectively assessing the risks to the off-site public and on-site personnel. Quantitative Risk Assessment (QRA) tools are frequently used for such comparative analyses and effective decision-making. However, for completeness, although the comparative risk criterion was the primary deciding factor, the Safety Advisor did address the first Consent Decree criterion as part of this evaluation. For simplicity, the SA's application of the first criterion is consistent with the most limiting interpretation of not forming "an aerosol or dense vapor cloud upon release."

Summary of Phenomenological Conclusions

The evaluation of phenomenological issues included a review of all information received from Mobil. The evaluation ascertained the validity and completeness of the data, and compared results against the criteria provided by the Consent Decree. Several key industry studies and test results were also used for reference and comparison and are identified in Section VIII. From this review, it was clear that Mobil's proposed alkylation technology offers dramatic and inherent improvements in properties that contribute to improved protection of "the environment and the health, safety, and welfare and property of all persons, both off-site and on-site," compared to Anhydrous HF (AHF), e.g.:

- Mobil has a) sponsored experiments on MHF releases, b) developed a theory of and a model for the behavior of fragmenting liquid MHF jets, and c) has sponsored experiments on the toxicological effects of HF as a function of exposure time. This work is scientifically defensible and has made it possible to perform credible analyses of MHF phenomenology and to perform a meaningful QRA. The SA considers this to be well beyond what a company would normally do for a new process design.
- The results of the theoretical models developed by Mobil and the experiments on MHF releases are consistent with no flash atomization of MHF upon release from the alkylation unit.

- This removal of flash atomization results in there being no evidence that the release mechanism causes the formation of an airborne aerosol. The subsequent formation of HF-water droplets, as the released HF mixes with moist air, is not considered to be a major contributor to risk. Therefore, the Consent Decree criteria for not forming an aerosol upon release has been explicitly met.
- Experimental data and modeling, support airborne HF release rates that are reduced by at least a factor of three from the equivalent AHF case.
- Consequences (i.e., health impact) when compared with an equivalent release of AHF are significantly reduced because the effective release rate is reduced.
- Reductions in cloud density are significant and immediate when compared with an equivalent AHF release (i.e., a reduction from more than 10kg/m^3 to 1.4kg/m^3). The resultant cloud density, while somewhat greater than air immediately after a release (and similar to the predicted density of an equivalent release from a sulfuric acid alkylation unit), is not a major factor in determining the impact on the community (e.g., 190th Street Community and Crenshaw boulevard) or on-site personnel. However, although significant and inherent improvements in safety are identified and vapor cloud density does not significantly affect community impact, Mobil is not able to demonstrate that "the catalyst as modified would not form ... [a] dense vapor cloud upon release" (Reference 1), assuming that “dense vapor cloud” means dense enough for there to be characteristic dense vapor cloud behavior. As identified above, this is the most limiting interpretation of this criteria.
- Inherent improvements in safety apply to all phases of MHF catalyst usage: transportation, storage, processing, and much of regeneration.
- Within the context of the uncertainties that exist in the modeling of both MHF and sulfuric acid releases, the consequences of equivalent releases (measured by accumulated dose) are approximately the same.

Summary of Quantitative Risk Comparison Conclusions

The evaluation of the quantitative risk comparison included a review of all information received from Mobil. The evaluation ascertained the validity and completeness of the data; compared key characteristics with available risk assessments from other alkylation units, other industrial facilities, and accepted practices; and compared results against criteria provided within the Stipulation and Order (Reference 2).

The Information received from Mobil was primarily in the form of Quantitative Risk Assessment (QRA) results and background information for:

- single event modeling of MHF and sulfuric acid releases

- comparative risks using ERPG-3 endpoints (Emergency Response Planning Guidelines are published by the American Industrial Hygiene Association to identify toxic dose endpoints. The ERPG-3 dose level corresponds to "the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for one hour without experiencing or developing life-threatening health effects.")

From this review, it is clear that the specific objectives of the Stipulation and Order will be met with a conversion to Mobil's stated MHF technology:

- The use of MHF would result in a significant reduction in the predicted risk to "the environment and the health, and safety, and welfare and property of all persons, both off-site and on-site," when compared to AHF.
- As a conservative comparison (Reference 511.02), the results of the "impact for a 2-inch settler leak" (i.e., assuming no active mitigation for MHF alkylation) showed fenceline doses to be approximately the same as those for a "sulfuric acid alkylation plant producing a comparable amount of alkylate."
- The specific criteria and objectives of the Stipulation and Order (Reference 2) (i.e., Torrance Refinery Alkylation Unit operation with the "modified HF catalyst (including mitigation)" presenting "no greater risk than a sulfuric acid alkylation plant producing a comparable amount of alkylate") have been explicitly met within the range of uncertainties that inevitably exists in the performance of QRAs.
- Significant and sufficient improvements have been achieved such that the use of commercially unproven and currently unavailable technologies (e.g., solid catalyst alkylation) to obtain further improvements need not be considered for the Torrance Refinery at this time.
- Significant layers of conservatism were included in the quantitative risk comparison that skew results to favor sulfuric acid alkylation and contribute to the expectation that there is an even further reduced contribution to risk of operations from a MHF alkylation unit beyond those identified by the Mobil risk assessment. Key conservatisms are identified in Section IV.E and include:
    - ♦ exclusion of assessment of transportation risks
    - ♦ exclusion of HF/moist air thermodynamics
    - ♦ exclusion of credit for additional HF rainout for impeded releases
    - ♦ including regeneration risks for MHF alkylation, but not for sulfuric acid alkylation
    - ♦ using a single, conservative airborne HF mass flux reduction fraction rather than a best estimate value

- ♦ use of a best estimate 2.8% airborne release fraction for sulfuric acid alkylation releases
- ♦ use of conservative HF toxicity data
- ♦ conservatively assuming a higher capacity MHF alkylation unit
- ♦ not taking into account the new information provided by Reference 523.00, which states that "occupational exposure to strong-inorganic-acid mists containing sulfuric acid is *carcinogenic to humans*..."

- Consistent with the spirit of the Consent Decree, a contemporary, commercial sulfuric acid alkylation unit was used as the reference point for the quantitative risk comparison. Since one specific engineering firm's sulfuric acid alkylation design is the most common technology in application, it was the appropriate basis for the reference sulfuric acid alkylation unit used by Mobil and the SA. In addition, a brief comparison, by the SA, of key safety features, identifies no significant differences in potential risk which would provide a compelling argument for the SA or Mobil to consider a different design for the reference sulfuric acid alkylation unit.
- There are many individuals with an understanding of QRA techniques, and some are experts in the field. There are also many specific approaches to QRA and certain topical QRA issues upon which experts would not likely reach agreement. For the quantitative risk comparisons performed by Mobil, issues associated with approach, level of detail, and completeness could be debated. It is clear to the SA, that one could likely find smaller contributors to risk that were not explicitly included in the quantitative risk comparison performed by Mobil, but which would not be expected to significantly impact the results. It is also clear that there are some areas in the risk comparison documentation that could be better explained or detailed to aid in understanding by interested non-experts. However, the dominant contributors to risk were reviewed by the SA along with the bases for key calculations and assumptions. These were compared with industry reference documents and accepted techniques. Debate over specific approaches or lesser contributors would not change fundamental conclusions:
  - ♦ The favorable comparison of the "impact for a 2-inch settler leak" (i.e., assuming no active mitigation for MHF alkylation) to a comparable sulfuric acid alkylation leak (see Section V.B) addresses the spirit of the original objectives of the Consent Decree, and shows that, even without active mitigation systems, the risk of MHF alkylation is comparable to that of sulfuric acid alkylation.
  - ♦ Significant layers of conservatism were included in the quantitative risk comparison which would be expected to skew results to favor sulfuric acid alkylation (see above). This further substantiates the conclusions drawn from this study regarding the acceptability of MHF alkylation.

- Although the original probabilities assumed for the successful actuation of mitigation systems in the MHF Alkylation Unit could be considered to be somewhat optimistic, sensitivity studies performed by the SA with more conservative choices of mitigation system availabilities showed MHF alkylation unit risk still smaller than the reference sulfuric acid alkylation unit.

Making Decisions on Issues Containing Inherent Uncertainties

The process of QRA deals with probabilistic and statistical issues which have inherent uncertainties. Although some QRA applications have included a detailed quantification of uncertainties, most effective decisions involve a numerical comparison of best estimate values with a clear identification, understanding, and consideration of the types and possible impact of uncertainties.

For the comparison which is the subject of this evaluation, the SA feels that uncertainty analyses at the detailed component level is unnecessary for making an effective comparative evaluation.

The best estimate risks and phenomenology results clearly identify MHF and sulfuric acid alkylation as being of comparable risk, with alkylation using a modified HF catalyst showing lower calculated best estimate risk values. Section IV.E identifies, characterizes, and discusses areas and simplifying assumptions which impose potential uncertainties. These areas of uncertainty which are inherent in the analyses are clearly designed to favor sulfuric acid alkylation which further supports the conclusion of the best estimate results identified above.

One of these areas of uncertainty is associated with the airborne release fraction for sulfuric acid from a sulfuric acid/hydrocarbon mixture. Previous estimates have ranged as high as 50%, more recent results identified in Section V.B indicate 2.4-3.2%, and the South Coast Air Quality Management District (AQMD) recommends a range of 4-7%. In Section V.B, the SA concluded that a best estimate value of a 2.8% airborne release fraction for sulfuric acid was appropriate for this quantitative risk comparison. It should be noted that this value, which is based on more up-to-date information, is significantly lower than what was used for some QRA applications even as recently as the early 1990's.

Even with potential uncertainties, the results clearly show that:

- The risks of both alkylation processes are comparable.
- For the Mobil Torrance Refinery, *both* processes represent a *significant* improvement in risk over the current alkylation process utilizing an anhydrous HF catalyst.

- Sulfuric acid alkylation does not present any demonstrable improvements in risk to on-site personnel or to the off-site public compared to alkylation with the subject modified HF catalyst. These conclusions are further supported via recent research that concludes "Occupational exposure to strong-inorganic-acid mists containing sulfuric acid is *carcinogenic to humans* ..." (Reference 521.00)

Summary

The SA concludes that:

- the scope and level of detail of this evaluation,
- the use of the subject HF additive at the Torrance Refinery,
- implementing the changes to unit design and operations associated with the MHF conversion,
- implementation of recommended actions precipitating from the SA's review, and
- the review of MHF conversion implementation at the Torrance Refinery by the SA

satisfy the stated requirements and objectives of the Consent Decree and subsequent Stipulation and Order.

Anhydrous hydrofluoric acid does have a significant potential for off-site impact. However, the EPA identified in Reference 15 that "The properties that make HF a potentially serious hazard are found individually or in combination in many other industrial chemicals..." The EPA concluded "...owners/operators (of facilities in which HF is used) can achieve an adequate margin of protection both for their workers and the surrounding community by assiduously applying existing industry standards and practices, existing regulations, and future guidance and regulations applicable to various classes of hazardous substances in various settings." Thus, the EPA clearly believes that even AHF can be safely used at a site such as Mobil's Torrance Refinery provided that regulations such as OSHA's Process Safety Management Standard and EPA's forthcoming Risk Management Program (40 CFR Part 68) are carefully implemented. The requirements of the Consent Decree associated with the use of modified hydrofluoric acid at the Torrance Refinery go beyond the EPA's "adequate margin of protection", in order to support the health and safety of the citizens of Torrance. A conversion to MHF at the Torrance Refinery takes a major additional step towards significantly reducing the inherent risks associated with the use of hydrofluoric acid catalysts within alkylation units, thus going beyond the letter of EPA's conclusions.

A conversion to MHF at the Torrance Refinery Alkylation Unit can provide a substantial reduction in the potential risk associated with releases of alkylation catalyst inventory. Mobil should be commended for its effort, the application of sound scientific and engineering principles in the development of the modified HF catalyst, the careful research and testing effort associated with this development, investments associated with any upcoming retrofit to the existing HF alkylation process, and its responsiveness to the requirements of the Consent Decree and to the safety of the Community.

Both Mobil and the City of Torrance have put forth significant effort and worked diligently, and with a spirit of cooperation, to support the requirements and schedule of the Consent Decree.

TABLE ES-1
SUMMARY OF SPECIFIC RECOMMENDATIONS

ACTION	CLASSIFICATION	IMPLEMENTATION RESPONSIBILITY
M-1) Mobil shall supply to the Court, the SA, and TFD, the anticipated schedule and flow chart setting forth the external permitting process for the MHF conversion. The schedule and flow chart shall identify the required permits, the agencies involved, and anticipated scheduling. Mobil shall also supply to the Court, the SA and TFD, the anticipated schedule for the physical design, construction, and implementation of the MHF conversion. The initial anticipated schedule shall be supplied by Mobil by March 31, 1995.	Recommendation	Mobil
M-2) Mobil shall implement the MHF conversion consistent with the projected schedule. After the MHF conversion has been constructed and implemented, Mobil (1) shall not transport AHF to or from the Torrance Refinery; (2) shall not store AHF at the Torrance Refinery; and (3) shall not use AHF at the Torrance Refinery, except as AHF is present in minor amounts as part of the alkylation unit process using MHF, as specified in the SA's MHF Report and February 7, 1995 letter, or an amount which would not affect the SA's conclusions. The SA's verification that its conclusions are not affected shall occur prior to testing and operation. The parties shall continue to support the Court's monthly monitoring of the project. At such conferences, Mobil shall keep the Court, the SA, and TFD apprised of the progress toward permitting and implementing the MHF conversion.	Recommendation	Mobil, TFD, & Safety Advisor
M-3) Mobil shall timely notify the Court, the SA, and TFD of technical or regulatory issues or problems that threaten Mobil's ability to meet the projected MHF conversion schedule. Further, Mobil shall timely notify the Court, the SA, and TFD of technical or regulatory issues or problems which make MHF conversion infeasible. In such an event, and in light of the requirement in paragraph four (4) of the Consent Decree that Mobil cease use of AHF at the Mobil Refinery by 12/31/97, Mobil shall advise the Court, the SA, and TFD, of its plan for fulfilling the requirements of the Consent Decree.	Recommendation	Mobil

M-4) In order to provide for effective monitoring of the recommendation closeout process, the SA will enclose a summary of the recommended schedule and status of implementation in the monthly project status reports to the Court, Mobil, and the City. As part of the monthly teleconferences, all parties will have the opportunity to comment or identify any potential issues regarding the schedule or implementation of recommendations.	Recommended SA Follow-up Action	Safety Advisor
M-5) Prior to testing and operation of the MHF unit (following conversion), the SA shall review the design and implementation of key equipment, review the ability of operating procedures to ensure adherence to key operating parameters, and verify key assumptions (e.g., additive concentration), including walkdowns as necessary.	Recommended SA Follow-up Action	Safety Advisor
M-6) Upon completion of the MHF conversion design, Process Hazard Analyses will be performed. These include Process Hazard Analyses consistent with Mobil PSM policy, OSHA PSM and California's RMPP process. Prior to testing and operation of the MHF Alkylation Unit, the SA shall verify that the results of these Process Hazard Analyses do not affect the conclusions of the SA's modified HF catalyst evaluation.	Recommended SA Follow-up Action	Safety Advisor
M-7) As part of the SA's seismic review under the Consent Decree, the SA shall analyze and report on the seismic safety of the MHF unit's final design and construction, including a walkdown prior to testing and operation. This seismic safety review will include a review of conclusions and recommendations resulting from any RMPP effort to verify that the conclusions of the SA's modified HF catalyst evaluation are not affected.	Recommended SA Follow-up Action	Safety Advisor
M-8) Prior to testing and operation of the MHF Alkylation Unit, the SA shall review and determine the acceptability of Mobil's operational practices and procedures for ensuring that additive concentrations remain within the predefined limits evaluated by the SA in the MHF report.	Recommended SA Follow-up Action	Safety Advisor
M-9) Mobil and TFD shall develop a mutually agreeable audit plan to monitor additive concentrations which will be reviewed by the SA, prior to testing and operation of the MHF Alkylation Unit. This plan shall include weekly transmittal of Mobil's audit documentation to TFD, or as otherwise requested by TFD, as well as periodic on-site auditing by TFD.	Recommendation	Mobil and TFD

M-10) Consistent with the SA task objectives specified in the Consent Decree and consistent with the scope of the ongoing Evaluation of Chemical Monitoring/Warning Systems and Evaluation of the Emergency Response Program, the SA shall investigate and make recommendations with respect to the following issues: HF warning systems; community notification, including but not limited to, notice to residents, schools and other institutions, and commercial and industrial entities; and emergency response programs in its pending reports on those subjects, and shall place a priority upon prompt completion of those reports and closure of those issues. In addition, Mobil is planning to participate in a Blue Ribbon Committee charged with addressing these issues.	Recommended SA Follow-up Action	Safety Advisor

NOTE

Specific suggestions for improving the phenomenological and risk analyses (which were provided by Mobil and evaluated by the SA) were considered inappropriate under the requirements of the Consent Decree. Of course, at Mobil's option, it may wish to consider updating its analyses to address some of the potential improvement areas identified in this evaluation.

TABLE OF CONTENTS

I. INTRODUCTION

A. BACKGROUND

With the objective of improving the environmental impact of fuel and combustion products, the Clean Air Act Amendments of 1990 and the California Air Resources Board (CARB) mandated stringent controls on motor fuel composition with respect to aromatics, benzene, oxygen, vapor pressure, olefins, and sulfur. Although there are other mechanisms for achieving these goals, the use of alkylate as a blending component for the mandated "reformulated gasoline" addresses many of these environmental issues. Reference 18 indicates that "Alkylate may be the ultimate hydrocarbon-based clean fuel. It has no benzene, no aromatics, no sulfur, no olefin, low RVP and good octane." Alkylate is an ideal, and valuable, blending component for helping refiners achieve the EPA and CARB objectives along with the octane requirements of premium, reformulated gasolines.

The two primary alkylation processes, for converting light olefins and isobutane to alkylate, utilize two different acid catalysts: hydrofluoric acid (HF) and sulfuric acid. In general, HF alkylation processes are considered more robust operationally, require significantly less acid consumption, and are less expensive to operate. Sulfuric acid alkylation processes, however, utilize a catalyst that typically has a lower associated airborne release fraction, higher inventories, and with a slightly higher toxicity. Alkylation units exist in most of the major refineries in the United States and internationally. "Of the two alkylation technologies that are being used commercially, HF acid alkylation has a larger total installed capacity" (Reference 19).

Anhydrous HF is widely recognized as having chemical characteristics that increase the potential severity of release events compared to sulfuric acid:

- higher volatility

- for certain types of releases, flash atomization can cause aerosolization and lead to the formation of a plume that contains both vapor and liquid droplets (i.e., the effective release rate to the atmosphere is increased relative to what it would be if the liquid fell to the ground).

On November 24, 1987, a fire at the Torrance Refinery HF Alkylation Unit resulted in a release of 165 pounds of HF (which was dispersed by the fire). Although there were no reported exposures to HF (there was one minor injury), this event occurred shortly after a significant release of 30,000-53,000 pounds of HF at the Marathon Texas City Refinery on October 30,

1987. These two events, along with spill tests by industry, are often cited as the key stimuli for focusing public and regulatory attention on the use of HF by industry (Reference 15). The November 24, 1987, event clearly heightened interest in the use of HF at the Torrance Refinery.

As a result of the settlement of a public-nuisance lawsuit filed by the City of Torrance against Mobil Oil Corporation in 1989, a Consent Decree (Reference 1) was entered into between the two Parties and was filed with the Superior Court of the State of California for the County of Los Angeles. The original criteria provided in the Consent Decree were subsequently augmented within the September 30, 1994, Stipulation and Order (Reference 2). The acceptance criteria provided by these two documents are designed to address safety concerns associated with the use of anhydrous HF within the Alkylation Unit at the Torrance Refinery and to identify whether the proposed, modified HF catalyst supports plant operation "in a manner that protects the environment and the health, safety, and welfare and property of all persons, both off-site and on-site."

This evaluation is offered to independently verify that Mobil has adequately demonstrated that it has met the acceptance criteria provided by these two documents.

B. CONSENT DECREE OBJECTIVES & EVALUATION SCOPE

The September 30, 1994, Stipulation and Order, agreed to by the Parties, provides the latitude of demonstrating "to the satisfaction of the Safety Advisor that its modified HF catalyst meets the phenomenological standard originally set forth in the Consent Decree *or* that the modified HF catalyst (including mitigation) presents no greater risk than a sulfuric acid alkylation plant producing a comparable amount of alkylate."

This evaluation focused on release characteristics, potential risks, and general safety issues associated with the use of a modified HF catalyst within the Alkylation Unit at the Torrance Refinery. In general, the scope of the SA review encompassed a review of all information (addressing both phenomenology and quantitative risk comparison) provided by Mobil as well as key industry studies and test results cited as references in Section VIII, to determine if Mobil:

a) "... has demonstrated to the satisfaction of the Safety Advisor that the catalyst as modified would not form an aerosol or dense vapor cloud upon release." (Reference 1)

- or -

b) has demonstrated to the satisfaction of the SA "... that the modified HF catalyst (including mitigation) presents no greater risk than a sulfuric acid alkylation plant producing a comparable amount of alkylate." (Reference 2)

Specific standards and resources used in the evaluation are listed in Section II, Evaluation Criteria, and Section VIII, References.

The above criteria do not require comparison of the quantitative results to any absolute risk acceptance criteria.

II. EVALUATION CRITERIA

This evaluation and the corresponding approach are unique. This evaluation focused on release characteristics, potential risks, and general safety issues associated with the use of a modified HF catalyst within the Alkylation Unit at the Torrance Refinery, and for comparison, a sulfuric acid alkylation unit of the same throughput, also assumed to be located at the Torrance Refinery. Methodologies for a phenomenological evaluation of an Anhydrous HF (AHF) release are well known and have been updated to reflect recent experimental results and new understandings of the phenomena associated with releases of AHF. Methodologies for the performance of specific QRA elements are also well known. However, definition of absolute risk acceptance criteria, application of Consent Decree acceptance criteria, and definition of an acceptable level of detail for this type of evaluation for a modified HF catalyst are not issues that are explicitly defined within the technical community or which have direct precedent.

The following criteria are considered to be reasonable, to be technically appropriate, and to address the key requirements and acceptance criteria of the Consent Decree and subsequent Stipulation and Order.

Some Specific Criteria for the SA QRA Evaluation

The SA reviewed Mobil's quantitative risk comparison to determine:

A) if the data used as a basis for the accident scenario frequencies is appropriate for use in a risk comparison with sulfuric acid alkylation units

B) Accident Scenario Validity:

- if all potentially significant accident scenarios have been identified, properly characterized, and quantified
- if any potential releases which are excluded have been evaluated to be highly unlikely or of low consequence
- if for credited mitigation features, defensible assumptions have been used for equipment reliability and human error probabilities

C) if the risk assessments supporting the results of the comparison between MHF and sulfuric acid alkylation units consistently compare the same phenomena and are sufficiently detailed to support conclusions

D) if consequence categories have been appropriately matched to the accident scenarios and have adequate supporting dispersion modeling -- Verifying the acceptability of the consequence modeling, e.g., release phenomenology and dispersion modeling, has been performed as part of the phenomenological review.

E) if probabilistic weather data was correctly incorporated into the QRA

F) if uncertainties are known, identified, and characterized (specific uncertainty calculations have not been deemed to be necessary)

G) if the characterization of off-site population and potentially sensitive receptors is appropriate

H) if identified accident scenarios correlate with historical events at the Torrance Refinery.

I) if comparisons with sulfuric acid alkylation have addressed transportation and regeneration risks (which are often considered areas of significant potential risk for sulfuric acid alkylation)

J) if dominant accident sequences appear sensible and complete (dominant sequences may be reviewed against similar evaluations through a comparison with other published and unpublished risk assessment results)

Some Specific Criteria for the SA Phenomenological Evaluation

The SA reviewed Mobil's phenomenological evaluation to determine:

K) if the estimates of the rates of release of MHF, the HF airborne release fraction, and the resulting HF cloud density are scientifically defensible

L) if appropriate dispersion models have been used

M) if pessimistic meteorological conditions have been considered for single event dispersion modeling

N) if sensitive receptors and vulnerability zones have been considered

O) if defensible health effects models have been used to determine defensible concentration limits for endpoints

P) if there are other viable alkylation technologies that are ready for commercialization and clearly safer than the MHF technology

Q) if the reliability and accuracy of HF monitors remains unaffected by the addition of the additive to the catalyst

III. SUMMARY OF EVALUATION METHODS UTILIZED

A. Key Activities

The following summarizes key activities involved in this evaluation of the use of the modified HF catalyst in the Torrance Refinery Alkylation Unit:

- Review of all information pertinent to the Torrance Refinery Alkylation Unit as well as key industry studies and test results cited as references in Section VIII,
- Performance of calculations to verify the adequacy of the analysis,
- Comparison with available risk assessment results for other refinery alkylation units,
- Comparison with other commercial and proposed alkylation technologies,
- Walkdown and discussion of operating history of the Paulsboro MHF Alkylation Demonstration Unit on November 8, 1994,
- Familiarity with the existing (late-1994) Torrance Refinery Alkylation Unit,
- Participation in a MHF Alkylation Catalyst Review Meeting in Paulsboro, New Jersey on November 7 and 8, 1994,
- Interaction with various Torrance Refinery, Mobil Engineering, and Torrance Fire Department personnel and participation in several meetings,
- Attendance at the October 31, 1994 and November 1, 1994 Alkylation Seminar, “The Role of Alkylation in the New Fuels Era,” sponsored by the Oil & Gas Journal, and
- Attendance at the December 20, 1994, “Synthetic Hydrocarbon Chemistry Seminar” sponsored by the Loker Hydrocarbon Research Institute.

B. Key Methods and Approaches

The following are some of the key methods and approaches that apply to both the SA phenomenological and quantitative risk comparison evaluation:

- Clearly define the importance of safety items to the QRA or phenomenology evaluation.
- Identify specific references.
- Correlate the review of the specific issues to specific criteria.
- Perform spot checks and calculations, as appropriate, to verify the adequacy of the analysis.
- Determine if the analytical models are sufficiently detailed and appropriate for their intended use, and for characterizing or comparing risk or phenomenological results.

- Review all information to determine if there is an adequate and appropriate basis for decision-making and demonstrating the acceptability of the use of the MHF catalyst in the Torrance Refinery Alkylation Unit.

C. Representative Review Activities

Some of the spot checks and check calculations performed to verify the adequacy of the analysis include the following:

- Comparisons were made with the results from select, published information regarding potential hazards and accident scenarios.
- SA calculations were performed to verify key MHF and sulfuric acid alkylation QRA release scenario frequencies. Release frequencies were calculated and compared with historical data from Reference 15.
- SA calculations were performed to ensure that there was a clear correlation between potential contributors to risk and the calculated risk values and to verify the risk assembly process.
- SA calculations to evaluate the sensitivity to key human error probability and mitigation system availability assumptions to MHF Alkylation Unit risk were performed.
- Comparisons were made between the results of the various sensitivity studies performed for the QRA and driving forces precipitating the differences between the sensitivity studies.
- Comparisons were made with results from select, published information regarding dominant sequences and contributors.
- Independent runs of different atmospheric dispersion models were performed.

D. Specific Information Reviewed by the Safety Advisor

All documents reviewed are explicitly identified in Section VIII, which lists all the salient references. Where non-written (e.g., verbal or visual) information was obtained, a reference to the date and source is provided.

IV. QUANTITATIVE RISK COMPARISON OBSERVATIONS

IV.A ACCIDENT SCENARIO IDENTIFICATION

IV.A.1 Importance to QRA/Phenomenology Review

Key elements of a QRA include:

- Accident Scenario Identification
- Accident Scenario Quantification to Determine Scenario Frequency
- Consequence Analysis
- Risk Assembly (combining the likelihood of a potential hazard with its consequences)

Just as hazard identification is the cornerstone of Process Safety Management (PSM), identification of potential hazards and accident scenarios, that could be key contributors to risk, is one of the first and most critical tasks of a QRA. The identification of accident scenarios not only entails using specific techniques designed to address root design and operations issues, but also addresses previous events which have occurred at the Torrance Refinery.

This section reviews the identified potential hazards and accident scenarios for the quantitative risk comparison and addresses:

- completeness
- correlation with applicable previous events
- consistency with other published results

IV.A.2 Key References Reviewed by SA

- 15
- 32
- 507.02
- 508.00
- 509.01

IV.A.3 Key Criteria Referenced

- II.B
- II.H

IV.A.4 Review Activity/SA Calculation Summary

No specific SA calculations were required to evaluate this specific issue. The SA's review focused on the above identified references. Comparisons were made with results from select published information regarding potential hazards and accident scenarios. Comparisons were also made with historical events at the Torrance Refinery.

IV.A.5 Results/Observations

Table IV.1 summarizes hazards identified and considered for the MHF alkylation QRA and various publicly available risk assessment studies for HF alkylation units. Table IV.2 summarizes hazards identified and considered for the reference sulfuric acid alkylation unit. Table IV.3 summarizes relevant significant accidental releases of HF at the Torrance Refinery from Reference 36 (through 31July1990), the HF Alkylation Unit Risk Management and Prevention Program (RMPP), and select events from the Safety Advisor files.

The following are some of the salient results/observations:

- The choice of the accident scenario for the single event modeling (i.e., a 2" orifice in the Acid Settler) was consistent with:
  - ♦ the SA's understanding of the design and operation of the HF and sulfuric acid alkylation systems
  - ♦ potential accident sequences identified in other published risk assessments
  - ♦ addressing key phenomenology issues for HF and sulfuric acid atmospheric dispersion for other scenarios
  - ♦ did not take into account the higher probability of sulfuric acid leaks

- The choice of the potential hazards and release scenarios for the QRA was consistent with:
  - the SA's understanding of the design and operation of the MHF and sulfuric acid alkylation systems
  - significant potential hazards and dominant accident sequences identified in other published risk assessments (see also Table IV.1) - Scenarios considered implausible due to the specific design of the Torrance Refinery Alkylation Unit or changes addressing previous difficulties were excluded.
  - relevant significant accidental releases of HF at the Torrance Refinery (see also Table IV.3) - Note that residual releases from equipment disassembly during maintenance were not appropriate for inclusion in the QRA due to their expected low contribution to risk.
- A quality QRA explicitly quantifies dominant scenarios but may exclude scenarios considered to be of low risk. In this manner, accuracy is achieved in a manageable fashion. Once a baseline is established, as additional hazards are considered and quantified, the calculated value of risk increases. Table IV.2 contains only those hazards identified for the reference sulfuric acid alkylation unit. Given that the MHF Alkylation Unit release hazard identification appears complete, a comparison with published studies is not necessary for sulfuric acid alkylation, since if there were any incompleteness in hazard identification for sulfuric acid alkylation, it would serve to skew results in favor of sulfuric acid alkylation for the quantitative risk comparison.
- The identified hazards and accident sequences have appropriately addressed key HF alkylation unit events and root causes which have occurred at the Torrance Refinery (See also Section IV.B.5.c):
  - KOH Treater Fire - November 24, 1987
  - Thermowell Breach - July 15, 1992
  - Coalescer Inlet Piping Hydrocarbon Release and Fire - October 19, 1994
- Root causes of other key industry events have been addressed as part of Mobil's design and operations practices at the Torrance Refinery and need not be explicitly quantified as hazard scenarios within this quantitative risk comparison:
  - Marathon, October 30, 1987
  - Great Lakes Chemical, June 27, 1989

- The QRA explicitly considered potential releases associated with the MHF unloading process.
- The QRA considered HF regeneration but not sulfuric acid regeneration. This skews results in favor of sulfuric acid alkylation in the quantitative risk comparison.
- Seismic hazards were not explicitly quantified. See Section IV.B.5.d for a discussion regarding the treatment of external events.
- A “What-if?” was used for the identification of potential release scenarios.
- Potential hazards due to chemical interactions, new equipment, and neutralization are accommodated by the QRA and supporting information (e.g., Reference 514.05). Reference 504.00 provided process design information sufficiently detailed to contrast the MHF process and the current AHF alkylation unit.

TABLE IV.1

HAZARDS IDENTIFIED AND CONSIDERED

FOR VARIOUS PUBLICLY AVAILABLE RISK ASSESSMENT STUDIES

FOR HF ALKYLATION UNITS

UOP MHF Alkylation Unit (Reference 508.00):

Reaction Section

- #1 Settler
- Pipe from #1 Settler to AES isolation valve
- #1 Reactor including pipes inside isolation valves
- Circulating Pumps
- Pipe from pump isolation valve to #1 Reactor isolation valve
- #2 Reactor including pipes inside isolation valves
- #2 Settler
- Pipe from #2 Settler to AES isolation valve
- Pipe from #2 Settler isolation valve to pump suction isolation valve
- Pipe to #2 Reactor

Storage Section

- Drum 5C-31
- Pipe to pump isolation
- Acid pumps inside isolation
- Pipe from acid pump isolation to Settlers
- Tank truck (including relief valves) or hose while unloading

Regeneration Section

- Pipe from acid pump to Regenerators including heaters and piping
- Regenerators (2)
- Vapor line from Regenerators to Isostripper Overhead Condensers
- Surge Drum and piping

Fractionation Section

- Pipe from fractionation to settler isolation valves and including Depropanizer Accumulator
- Isostripper overhead vapor system including condensers
- Isostripper condensers, pump, and piping
- Depropanizer overhead vapor piping
- Depropanizer condensers and piping to Accumulator
- Piping Reverse Flow from Reaction Section

Failure Types for Each Section (as appropriate)

- Pressure Vessels (sight glasses are implicit in the data; however, Reference 36 identified design changes to reduce the potential for this type of failure)
- Process Piping
- Flanges
- Pumps (includes gland and seal leaks)

HF Alkylation Unit Scenarios (Reference 15):

- Vessel Rupture - Bulk Storage
- Loading Hose Failure (w/ & w/o function of automatic shutoff valves)
- Settler Leak - Bottom
- Reactor Vessel Leak
- Settler Leak - Inlet Pipe
- Pump Seal Failure

UOP HF Alkylation Unit (Reference 509.01):

Scenarios Leading to Potential Releases (each of these was treated as a fault tree in Reference 509.01)

- Excess HF to propane treating unit
- Process leak into cooling water return
- Release of HF during truck unloading
- Release of HF to the environment (contains all releases of HF not covered in other fault trees)

- HF contamination of alkylate
- Excess HF to butane treating unit
- Hydrocarbon releases to the environment
- Wet feed upset to the alkylation unit
- Failure of acid gas relief system
- Upsets to neutralization unit

Release Categories

- accidents during truck unloading, in particular hose ruptures and releases through the relief valves
- major pump seal failures
- valve failures, gasket leaks, or pipe leaks
- failure of the storage vessel, including pipe ruptures in the liquid or vapor space
- large leaks or more severe failures in the reactors, settlers, or connecting pipework
- excess HF entering the propane or butane treating unit
- failure of the acid gas relief system
- earthquakes
- fires that cause a release of liquid HF
- miscellaneous, relatively small, liquid HF releases from points such as the boot of the depropanizer receiver
- minor releases with no off-site consequences

UOP HF Alkylation Unit RMPP Scenarios (Reference 36):

- HF Acid Unloading, Storage, and Transfer
  - ♦ Acid Transfer Pump Seal Failure
  - ♦ Hose Failure
  - ♦ Acid Truck Relief Valve
- Reaction Section
  - ♦ Sight Glass Failure
  - ♦ Small Piping/Tubing Connection Leaks
  - ♦ Flange/Gasket Failure
  - ♦ Pump Seal Failure

- Regeneration Section
  - Sight Glass Failure
  - Small Piping/Tubing Connection Leaks
  - Flange/Gasket Failure
- Fractionation Section
  - Small Piping/Tubing Connection Leaks
  - Flange/Gasket Failure
  - Sight Glass Failure
  - HF Carryover to KOH Treaters

UOP HF Alkylation Unit RMPP Scenarios (Reference 32):

- Truck unloading accident
- Acid Storage Drum - Bottom Line Rupture
- Acid Storage Drum - Top Rupture
- Isostripper - Top Rupture
- Acid Recirculation Pump Seal Failure

TABLE IV.2

HAZARDS IDENTIFIED AND CONSIDERED

FOR THE REFERENCE SULFURIC ACID ALKYLATION UNIT

(Reference 508.00)

Sulfuric Acid Reaction Section Release Scenarios

- Piping downstream of the feed flow control valve
- Significant breach of Reactors 1 or 2
- Leak in the mixers of Reactors 1 or 2
- Leak in Acid Downcomers
- Rupture of piping between the Settlers and flow control valve for the removal of spent sulfuric acid
- Breach at the bottom of the Settlers
- Piping leak in the top of the Settler to the pressure control valve
- Piping leak in the top of the Settler between the pressure control valve and the Flash Drum

Sulfuric Acid Flash Drum Release Scenarios

- Rupture of Flash Drum - bottom
- Piping leak

Sulfuric Acid Wash Drum Release Scenarios

- Acid Wash Drum rupture
- Piping or acid pump leakage

DATE	TIME	TAG #	RELEASE QUANTITY	RELEASE DURATION	SUBSTANCE & CONCENTRATION	ACTUAL OFF-SITE HEALTH/ENV IMPACT	POTENTIAL OFF-SITE HEALTH/ENV IMPACT	DESCRIPTION
SYSTEM: Alkylation					**SUBSYSTEM: N/A**			
FAILURE TYPE: Connection Leakage (non-flange)								
15 July 92	2240	Line between B Reactor and B Settler	32 lbm	10 minutes	HF / 1 0	Intentionally Blank	Intentionally Blank	Failure of the 16" thermowell in the 20" line between the B Reactor and B Settler resulted in a release of HF from the thermowell housing The identified root cause was vibration fatigue Corrective actions included a reduction in thermowell length
01 February 92	1625	Loose/Leaky Fitting	< 1 lbm	N/A	HF & Butane	Intentionally Blank	Intentionally Blank	Corrosion due to leaky fitting resulted in release of small amount of butane and HF
29 April 90	0900	5E-9F	Not Avail	Not Avail	HF	Intentionally Blank	Intentionally Blank	Evacuation line of 5E-9F was leaking at 1" union
12 April 89	0300	5C-4	Not Avail	Not Avail	HF	Intentionally Blank	Intentionally Blank	Leak of HF in a line to relief gas scrubber occurrred Leak was at weld joint
08 April 89	1020	5G-33A Evaculation Line	Not Avail	Not Avail	HF	Intentionally Blank	Intentionally Blank	Weld on 90 deg elbow failed resulting in a release of HF acid mixture
29 April 88	2000	5G-1	Not Avail	Not Avail	HF	Intentionally Blank	Intentionally Blank	Operator was pumping fresh acid when a leak developed on a pipe nipple located on inlet line
29 November 87	1040	Alky Evacuation Line	Not Avail	Not Avail	HF	Intentionally Blank	Intentionally Blank	Evacuation line leak resulted in HF release
10 September 87	0800	5C-8	Not Avail	Not Avail	HF	Intentionally Blank	Intentionally Blank	Overhead line thermocouple TI-5-1-38 developed a leak in the weld
FAILURE TYPE: Distillation Section								
24 November 87	1753	5C-15 & Associated Equipment	165#	Not Avail	HF	Intentionally Blank	Intentionally Blank	Operational upset in KOH Treater, 5C-15, resulted in subsequent explosion and fire
FAILURE TYPE: Flanges								
23 December 88	1025	5C-8	Not Avail	Not Avail	HF	Intentionally Blank	Intentionally Blank	Flange on inlet line for 5C-8 leaked
19 November 87	1045	Alky Flush Line	Not Avail	Not Avail	HF	Intentionally Blank	Intentionally Blank	A small flange leak occurred on flush line
04 September 87	1317	5G-8A	Not Avail	Not Avail	HF	Intentionally Blank	Intentionally Blank	Flange gasket on recycle intake on 5G-8A leaked

TABLE IV.3

HISTORY OF RELEVANT SIGNIFICANT ACCIDENTAL RELEASES

DATE	TIME	TAG #	RELEASE QUANTITY	RELEASE DURATION	SUBSTANCE & CONCENTRATION	ACTUAL OFF-SITE HEALTH/ENV IMPACT	POTENTIAL OFF-SITE HEALTH/ENV IMPACT	DESCRIPTION
FAILURE TYPE: Maintenance Error								
01 May 92		5G-33A	< 1 lbm	Not Avail	HF / 1 0	Intentionally Blank	Intentionally Blank	Failure of 5G-33A outboard pump seal during pump startup resulted in a small release of HF Root cause was identified as maintenance practices which were subsequently modified to address the particular failure mechanism involved
23 October 87	2100	Acid Relief Line	Not Avail	Not Avail	HF	Intentionally Blank	Intentionally Blank	Contractor making tie-in to acid line to 5C-4 relief line Pipe pressured up, forcing a temporary plug from flange opening Two contractors received minor burns from HF vapor
09 October 87	0825	5G-7A	Not Avail	Not Avail	HF	Intentionally Blank	Intentionally Blank	A maintenance activity was initiated without proper authorization Discharge flange on 5G-7A opened resulting in small vapor release
FAILURE TYPE: Sight Glass								
10 April 89	0045	5C-28	Not Avail	Not Avail	HF	Intentionally Blank	Intentionally Blank	HF leak on 2" gauge glass Employee reported throat irritation
25 September 88	0410	5C-37	Not Avail	Not Avail	HF	Intentionally Blank	Intentionally Blank	Sight glass started leaking, releasing HF vapors to atmosphere Three employees received minor injuries
28 August 88	1400	5G-33A	Not Avail	Not Avail	HF	Intentionally Blank	Intentionally Blank	Acid circulation pump seal pot gauge glass failed, causing HF release
FAILURE TYPE: Valve-Related Releases								
09 February 90	2130	LRC05080	Not Avail	Not Avail	HF	Intentionally Blank	Intentionally Blank	Packing gland leak on level controller
26 November 89	1830	LC05080	Not Avail	Not Avail	HF	Intentionally Blank	Intentionally Blank	Packing gland leak on level controller
23 November 89	2030	LRC05080	Not Avail	Not Avail	HF	Intentionally Blank	Intentionally Blank	Packing gland leak on level controller
05 September 89	0830	FIC95952	Not Avail	Not Avail	HF	Intentionally Blank	Intentionally Blank	Packing gland leak on flow indication controller
26 August 89	1115	LIC05070	Not Avail	Not Avail	HF	Intentionally Blank	Intentionally Blank	Packing gland leak on level indicator
30 December 88	2220	Fresh Acid Line	Not Avail	Not Avail	HF	Intentionally Blank	Intentionally Blank	HF release occurred because of faulty block valve upstream of blind location
20 November 87	1210	5C-25	Not Avail	Not Avail	HF	Intentionally Blank	Intentionally Blank	Evacuation line valve packing (and flange) developed leak

TABLE IV.3

HISTORY OF RELEVANT SIGNIFICANT ACCIDENTAL RELEASES

IV.A.6 Conclusions

The accident scenarios identified for sulfuric acid alkylation correlate well with an understanding of the reference sulfuric acid alkylation process and do not include any scenarios that should not be considered for a QRA.

The accident scenarios identified for the modified HF catalyst alkylation unit:

- are complete based on the SA's understanding of HF alkylation units
- correlate well with potentially significant accident scenarios identified for various publicly available risk assessment studies (see Table IV.1)
- address previous events at the Torrance Refinery

The identification of release scenarios utilizing a "What-if?" approach is suitable for the quantitative risk comparison.

There are no additional recommendations which precipitate from this review of accident scenario identification, other than those encompassed by Recommendation M-6 (see Table ES-1 and Section VII).

IV.B ACCIDENT SCENARIO FREQUENCIES

IV.B.1 Importance to QRA/Phenomenology Review

As identified in Section IV.A.1, the calculation of accident scenario frequencies is one of the key elements of a QRA. The likelihood of potential scenarios is combined with the calculated magnitude of the consequences to determine risk.

After they are identified (Section IV.A.1), calculating the frequency of accident scenarios entails consideration or quantification of several factors, e.g.:

- equipment failures
- human errors (e.g., diagnostic, commission, omission)
- common mode failures
- external events

This section reviews the determination of accident scenario frequencies within the quantitative risk comparison and addresses:

- completeness
- treatment of special issues (e.g., common mode failures)
- correlation to applicable previous events
- consistency with other published results

IV.B.2 Key References Reviewed by SA

- 15
- 33
- 35
- 508.00
- 510.08
- 512.05
- 514.01/.02/.03/.04/.06/.07

- 516.00

IV.B.3 Key Criteria Referenced

- II.A
- II.B
- II.H

IV.B.4 Review Activity/SA Calculation Summary

The SA's review focused on the above identified references. SA calculations to evaluate the sensitivity to key human error probability and mitigation system availability assumptions to MHF Alkylation Unit risk were performed. SA calculations were performed to verify key MHF and sulfuric acid alkylation QRA release scenario frequencies. Release frequencies were calculated and compared with historical data from Reference 15.

IV.B.5 Results/Observations

The following are some of the salient results/observations:

IV.B.5.a Equipment Failure Probabilities

- The failure probabilities used for breaches in Reference 508.00 are as follows:
  - ♦ Vessel Failure Frequency (per year)

    1.8E-5 (5 mm leak)
    8.25E-5 (25 mm leak)
    3.75E-5 (50 mm leak)
    5.55E-6 (100 mm leak)
    6.5E-6 (rupture)
  - ♦ Piping Failure Frequency (per meter year) (equivalent leak diameter in mm)

    1.9E-5 (25 mm leak)
    1.2E-5 (38 mm leak)
    9.3E-6 (50 mm leak)

6.3E-6 (75 mm leak)
4.6E-6 (100 mm leak)
3.1E-6 (150 mm leak)
2.3E-6 (200 mm leak)
1.9E-6 (250 mm leak)
1.5E-6 (300 mm leak)
1.3E-6 (350 mm leak)
1.2E-6 (400 mm leak)
1.0E-6 (450 mm leak)
7.9E-7 (600 mm leak)
5.2E-7 (900 mm leak)
3.9E-7 (1200 mm leak)

- The following hole size distributions for piping breaches were used:
  60% of piping failures - hole<22.4%
  25% of piping failures - 22.4%<hole<44.7% diameter
  10% of piping failures - 44.7%<hole<100% diameter
  5% of piping failures - hole = 100% diameter
- The following leak frequencies were assumed for the dominant scenarios for "Tank Truck or Hose while Unloading".
  50mm leak - 8.54E-03/yr
  25mm leak - 1.81E-02/yr
- Flanges - 1.0E-5/yr (if d <= 6", 5 mm equivalent diameter; if d > 6", 10% as 25 mm and 90% as 5 mm)
- Pump Seal Leak Frequency (per pump year) (equivalent diameter in mm)
  5 mm Single Seal - 2.5E-2/yr
  5 mm Double Seal - 2.5E-3/yr
  25 mm (10-50) - 6.6E-4/yr
  100 mm (50-150) - 6.6E-5/yr

are consistent with other literature sources:

- Total Vessel Failure Rate (Reference 33) = 9.6E-5/yr (1.09E-8/hr)
- Total Vessel Failure Rate (Reference 37, Table A10.3) = 1E-5/yr - 1E-4/yr
- Catastrophic Leakage (Reference 33, for large piping systems) = 1.5E-7/m-yr (2.68E-8/mile-hr)

- ♦ Catastrophic Leakage of Butane Pipeline (15/20" diameter) (Reference 37, Table A10.3) = 3E-7/m-yr
- ♦ Rupture of Pipe (<3") (Reference 37, Table A9.3) = 1E-9/hr-section = 2.9E-6/m-yr (assuming an average section length of 3 m)
- ♦ Rupture of Pipe (>3") (Reference 37, Table A9.3) = 1E-10/hr-section = 2.9E-7/m-yr (assuming an average section length of 3m)
- ♦ Rotating Seal Failure (Reference 37, Table A9.2) = 6.1E-2/yr (7E-6/hr) (assumed to be a relatively small leak rate)
- ♦ Catastrophic Pump Failure (Reference 37, Table A10.3) = 1E-4/yr (assumed to be a relatively large leak rate)
- ♦ Hose Failure (Reference 37, Table A9.2) = 3.5E-2/yr (4E-6/hr) - This was identified in Reference 522.00 as the root basis for the hose failure rates used for the MHF QRA.
- ♦ Hose Failure (Reference 33, 3.2.5, Rupture) = 5.0E-3/yr (5.7E-7/hr)

- The SA used some highly simplified assumptions regarding breach size (25mm equivalent diameter and 6" piping and flanges) and approximations for the number of components (Reference 508.00, Appendix 2.1), and contrasted them to the data for the observed release events in Exhibit 8-2 of Reference 15. The relative/fractional contributions of the release scenario types for the MHF QRA correlated well with the industry data considering that the industry data is derived from many sources, and an alkylation unit is likely to have more pumps and piping than other industrial sources (e.g., transportation). This reinforces the validity of the data used for the QRA.
- During the walkdown of the demonstration unit, it was identified that the operating history and lack of significant leakage problems correlated well with the low initiating frequencies for releases used in the QRA.
- Due to the simplicity of the release scenarios, site specific fault trees were not created, or necessary, for the determination of accident scenario frequencies.
- Sulfuric Acid QRA Scenarios 7T, 8T, and 9T are initiated by leaks in the mechanical seals of the mixers in Reactors 1 and 2. Although the breach frequency for a double seal is likely less than that of a single seal, the failure frequency for 7T, 8T and 9T is based on generic data for seal failure frequencies, which should conservatively underpredict the actual mixer seal failure frequency for contemporary sulfuric acid alkylation units.

IV.B.5.b Common Mode Failures

- For two coincident failures, common mode effects (e.g., common cause failures, common utility dependencies, human error, etc.) have the potential to result in the likelihood of a second, dependent event being significantly greater than the random event probability. For release events potentially mitigated by multiple systems, common mode failures are not only of acute interest, but can often dominate total risk. For this quantitative risk comparison, the sulfuric acid release scenarios do not take credit for mitigation, and therefore, are not as likely to be susceptible to common mode failure. For both the MHF and sulfuric acid alkylation QRAs, the simultaneous occurrence of multiple breaches is considered to be a very low probability event and should not be assumed.

- Common mode failures have the greatest potential impact on equipment failures, utility dependencies (e.g., firewater supply, electrical power), and human actions involved in the mitigation systems credited for the MHF QRA. For the MHF QRA, common mode failures were not modeled with the exception of a 5 mm leak in the double seal Acid Circulation Pumps where the conditional failure probability of the second seal was conservatively assumed to be 0.1. Since the Acid Evacuation System (AES), Acid Circulation Pump isolation/shutdown, and the water spray/deluge are functionally diverse, and human error probabilities dominate the net mitigation system failure rate; modeling common mode equipment failures is not required. Potential common mode human errors are considered to be more likely to impact the QRA results, but were not explicitly modeled in Reference 508.00. Please also see the human reliability analysis discussion below.

IV.B.5.c Previous Events

- Previous events at the Torrance Refinery correlate acceptably well with the data and results of the MHF alkylation QRA:
  - ♦ The QRA equipment failure rates were used to calculate the likelihood of a breach such as the thermowell failure event of 15Jul92. Although the calculated likelihood of a thermowell breach (Reference 514.06) was approximately a factor of 6 lower than that of the observed failure, this correlates acceptably well considering:

- The uncertainties involved in determining a leak frequency from a single data point are large (i.e., from a statistically insignificant sample).
- The event resulted from a specific and known cause (i.e., vibration fatigue) which was subsequently corrected.

♦ An accident scenario involving carryover of significant quantities of acid to the KOH Treater has not been explicitly considered by the MHF QRA; however, the following bases for this exclusion were provided in Reference 514.04 and are reasonable for use in the QRA:

- The need for neutralization for both the HF and sulfuric acid alkylation processes results in the expected incremental risk to be comparable for the two types of alkylation processes resulting in this event not being of importance for the quantitative risk comparison.
- The most likely scenario for this event is ignition. The resultant thermal draft would be expected to reduce the ground-level dispersion hazard, thereby reducing the total magnitude of the risk to the off-site public (and also on-site personnel).
- These considerations correlate well with toxicity concerns being of lesser importance for the event which occurred on 24Nov87.

IV.B.5.d External Events

The Torrance Refinery is located in a seismically active region. During the November 7 and 8 meetings in Paulsboro, a question was raised regarding the treatment of seismic events in the quantitative risk comparison, and a reply was provided in Reference 514.02. The SA's observations are as follows:

- It is reasonable to assume the same breach frequency for two general systems (not necessarily alkylation units) of similar complexity, built to similar design standards, operated similarly, and without any specific seismic vulnerabilities such as physical interaction of equipment during a seismic event. With respect to the breach frequency of alkylation units, the SA agrees that "the inclusion of external events may increase the overall" breach frequency "of both process units by a similar amount" (i.e., a proportional, incremental risk for each alkylation unit). However, the

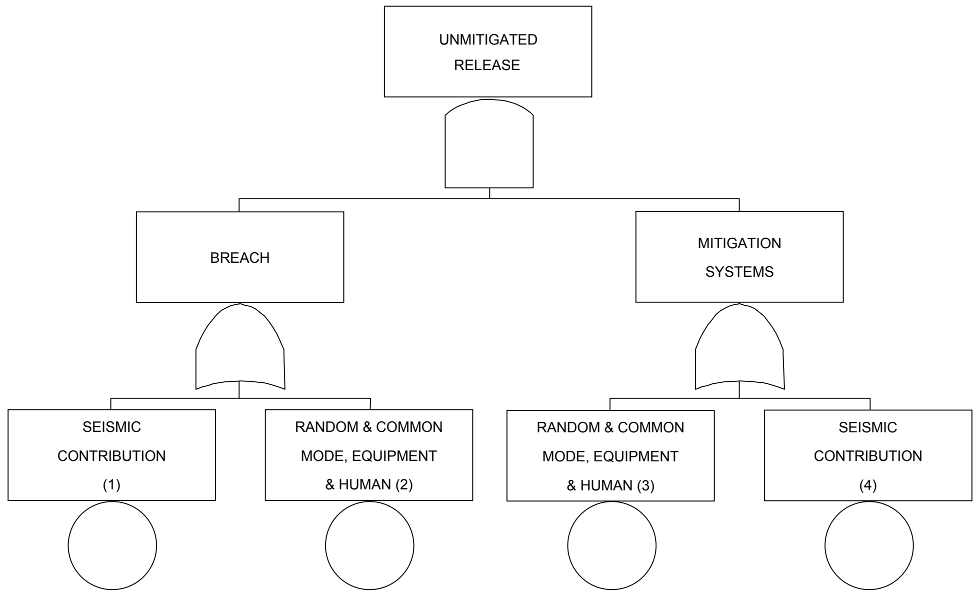
MHF QRA accident sequences take credit for several types of active mitigation systems, whereas the sulfuric acid alkylation QRA takes credit for only operator action in isolating the release.

For cases where active mitigation (typically considered less rugged than process unit equipment) is credited, a seismic event of sufficient magnitude could result in both a breach and a concurrent failure of one or more mitigation systems. In addition to physical damage, additional human stress factors or accessibility difficulties can affect the estimated mitigation system unavailabilities. Therefore, in general, consideration of seismic events could be necessary to provide “a valid basis for comparing the process risks” where one system is taking credit for mitigation systems and the other is not.

- For the quantitative risk comparison, boundary conditions for an entire spectrum of seismic events can be identified (see Figure IV.1). For very mild seismic events, the seismic contribution is minimal (i.e., events 1 and 4 are negligible) and the resultant breach frequency and mitigation system unavailabilities are nearly equal to the values calculated in the current quantitative risk comparison. For large seismic events exceeding the design basis, the seismic contribution *dominates* (i.e., events 2 and 3 are negligible by comparison), and the frequency of an event which *both* causes the breach and disables mitigation features asymptotically approaches that of a unit with no active mitigation. Between these boundary conditions for a seismic event, mitigation system availability could be adversely affected by:
    - ♦ human stress factors and additional response difficulties
    - ♦ potential support system failures (e.g., control power for mitigation features such as remotely-operated, elevated firewater monitors, and the AES)

FIGURE IV.1

Key Elements of Seismic Risk



- For facilities in seismically active regions, a seismic QRA is not uncommon. Just as accident scenarios are developed which consider and quantify random failures (appropriately adjusted with common mode or other conditional failures), a seismic QRA integrates the incremental seismic contribution to equipment failures and operator actions.

- The basic elements of a seismic QRA are described in Reference 5.

The quantitative risk comparison does not calculate incremental seismic risk (see Section IV.B.6 for conclusion); however, the following are noteworthy:

- Boundary conditions for an entire spectrum of seismic events are identified above. The most extreme case would still be expected to have consequences that are no more severe than the MHF “no-active-mitigation” case. See Section V.B.

- It is correct that, for process facilities, adherence to codes and standards are the typical mechanism for addressing seismic risks, both in Southern California and globally.

IV.B.5.e Human Reliability Analysis (HRA) and Mitigation System Availability

- For an independent QRA (i.e., not a quantitative risk comparison), HRA and the calculation of Human Error Probabilities (HEPs) can be critical in determining accurate values for risk. For this quantitative risk comparison, the information which would result from a detailed HRA is much less critical. For the sulfuric acid alkylation QRA, assumptions were used regarding accident scenario timing for when operators would be able to curtail the flow through a postulated breach by manually isolating portions of the system. The MHF alkylation QRA credited a more rapid response time from personnel actuating: pump isolation and shutdown, water spray/deluge systems, remotely-operated, elevated firewater monitors, and the AES.
- Response times assumed for the sulfuric acid alkylation QRA include:
    - ♦ 15 minutes for closure of the isolation valve downstream of the Settler nozzle
    - ♦ 5 minutes for termination of reactor feed flow
    - ♦ 5 minutes for closure of the flow valve between the pressure control valve and the Flash Drum
- Response times and associated HEPs for the MHF alkylation QRA (Reference 508.00) were based primarily on the judgment and experience of personnel at the Torrance Refinery (see Section IV.B.6 for SA conclusion), and are summarized in Table IV.4. Some values in this table were provided in the November 7 and 8 meetings in Paulsboro. It should be noted that the success probabilities in Table IV.4 implicitly include equipment failure probabilities, and for this time frame, human error would be expected to dominate. It was noted by the Safety Advisor that Figure 5 (also in Appendix 1.2) (Reference 508.00) identifies the following mitigation actions: 1 min water, 2 min water, 30 sec isolation, and 2 min isolation; and the calculation tables in Appendices 1.2, 1.4, and 3.1 consistently specify 30 sec water, 1 min water, 1 min isolation, and 2 min isolation. It is assumed that this is a consistent typo throughout the appendices. Although calculations were spot-checked by the Safety Advisor (see Table IV.6) according to the above assumptions, changing these definitions or values would not alter the Safety Advisor's conclusions.

TABLE IV.4

CONDITIONAL SUCCESS PROBABILITIES OF KEY MITIGATION FEATURES

(Equipment success probabilities are implicit in total probabilities)

Mitigation Feature / Time	**5 mm**	**25 mm**	**50 mm**	**100 mm**	**Rupture**
General MHF Process Release					
Water System Actuation	.95	.95	.95	.95	.95
Water System Actuation within 1 minute	.75	.95	.95	.95	.95
AES Actuation (if water system is actuated within 1 minute)	.001	.75	.95	.95	.95
AES Actuation (if water system is actuated within 5 minutes)	.05	.85	.95	.95	.95
AES Actuation (if water system is not actuated)	.25	.95	.95	.95	.95
AES Actuation within 2 minutes (if water system is actuated within 1 minute)	.001	.20	.95	.95	.95
AES Actuation within 2 minutes (if water system is actuated within 5 minutes)	.005	.80	.95	.95	.95
AES Actuation within 2 minutes (if water system is not actuated)	.01	.80	.95	.95	.95
Acid Circulating Pump Release					
Water System Actuation	.97	.97	.97	.97	.97
Water System Actuation within 1 minute	.90	.90	.97	.97	.97
Breach Isolation (if water system is actuated within 1 minute)	.95	.95	.95	.95	.95
Breach Isolation (if water system is actuated within 2 minutes)	.95	.95	.95	.95	.95
Breach Isolation (if water system is not actuated)	.95	.95	.95	.95	.95
Breach Isolation within 30 seconds (if water system is actuated within 1 minute)	.95	.95	.95	.95	.95
Breach Isolation within 30 seconds (if water system is actuated within 2 minutes)	.95	.95	.95	.95	.95
Breach Isolation within 30 seconds (if water system is not actuated)	.95	.95	.95	.95	.95

- The event tree values (Reference 508.00, Figures 4 & 5), which are summarized in Table IV.4, correctly reflect several phenomena associated with the anticipated response to a MHF release event:
  - lower success probabilities for shorter response times
  - higher success probabilities for larger releases (reflecting a clearer need for taking a more significant action)
  - higher success probabilities for AES Actuation if water systems are not available or actuated (reflecting a clearer need for taking a more significant action)

  - ♦ assumed constant success probability for isolation of all Acid Circulation Pump breach sizes (reflecting training, a clearer need for isolation in the event of a release, and minimal consequences to unit operation following pump isolation)
- Some of the key mitigation systems can or will be able to be actuated from multiple locations (Reference 510.08). These mitigation systems were not credited for the no-active-mitigation case.
  - ♦ (7) - 1000 gpm remote-controlled, elevated firewater monitors. The two monitors in the Settler/Reactor area can be actuated/controlled from two locations and control from other stations may be considered following review by operations personnel prior to the MHF conversion.
  - ♦ Firewater Deluge Systems - actuated and shut-off from multiple locations and CCB:
    - Acid Circulation Pumps, 5G-33A/B (6036 gpm)
    - Fresh Acid Pumps. 5G-41A/B (4100 gpm)
    - Depropanizer Feed Pumps, 5G-8A/B
    - AES Vessel, 5C-54
    - Acid Storage, 5C-31
  - ♦ Firewater Spray Systems - actuated from a single location at the north end of the unit:
    - Rerun Overhead Receiver, 5C-17
    - Depropanizer Overhead Receiver, 5C-10, 5C-12
    - Isostripper Overhead Receiver, 5C-6
    - Acid Storage, 5C-3 (not typically operating)
    - Overhead Pump Rows
  - ♦ AES - actuation from the Central Control Building
- The above mitigation features are comparable to the best combinations of mitigation features for other commercial alkylation units.
- Other locally-activated firewater monitors are available (Reference 510.08):
  - ♦ 17-500gpm fixed/foam firewater monitors
  - ♦ Portable:

    2-2500gpm (processing area)

    1-2000gpm (AES area, now a fixed monitor)
- Reference 508.00, Table 1 credits locally-controlled firewater monitors after 9 minutes for some scenarios. In general, the response times chosen in the QRA appear appropriate.

Response times correlate well with the 15Jul92 thermowell leak where refinery personnel indicated that two remotely-operated monitors were trained on the leak within two minutes of detection.

- Many of the dominant scenarios in Section 3.0 of Reference 508.00 involve shorter time frame response actions.
- The above HEPs were modeled as part of an event tree (Reference 508.00, Figures 4 & 5) which was used to determine the net success and failure probabilities of mitigation features for use in the quantification of accident scenario frequencies. Although many QRAs may explicitly quantify associated equipment failure probabilities and combine them with HEPs to determine the net mitigation feature unavailability, previous QRAs have shown that HEPs are typically much larger than the associated equipment failure probabilities and dominate the total unavailability of the mitigation feature. This was implicitly assumed for the MHF alkylation QRA, and the SA concurs that this is a reasonable and acceptable approach.
- In support of the judgment and experience-based response times and success probabilities, References 512.05 and 516.00 provided additional information. These references also identified several factors such as special training and awareness of potential HF releases which support rapid and effective response.
    - ♦ Implicitly including human-induced errors in the net frequency of a potential breach is acceptable and consistent with typical practice.
    - ♦ The conditional probabilities used for the event trees in Reference 508.00, Figures 4 & 5, are expected to be dominated by human error.
    - ♦ Absolute Probability Judgment (APJ) is a valid and frequently used expert judgment technique. The individuals involved in Reference 508.00, Section 4.10 are considered an appropriate group for the MHF QRA.
    - ♦ The use of field results and a 5 minute default for response times is considered appropriate.
    - ♦ A 95% success probability for “a critical action under conditions of moderately high stress” and a 75% success probability for “a critical action under conditions of extremely high stress” are identified in Reference 5. Reference 5 further clarifies that “Conditions of extremely high stress would occur when dealing with an abnormal event that could result in a ... toxic chemical release that could kill or seriously injure the operator or his friends.” “Conditions of extremely high stress”

would appear consistent with a situation that might exist during a major release of HF or MHF.

- ♦ Reference 5 does not clarify whether these suggested probabilities are appropriate for short- or long-duration recoveries.
- ♦ No reference was provided in the QRA for the 0.97 success probabilities used for Acid Circulating Pump release events.
- ♦ Reference 516.00 summarizes an apparently effective process for AES activation; however, a reference to specific plant operating procedures or training modules was not provided. General issues associated with training and emergency response will be evaluated as part of the SA's Evaluation of the Emergency Response Program.
- ♦ It is agreed that there are special factors which support rapid and effective response; however, it would be better substantiated if supported by references to authoritative sources that address the question of training effectiveness for "conditions of extremely high stress."

- Although the reference for the higher response action success probability values is valid, the choice could be considered to be somewhat optimistic. For example, other bases could have also been chosen for a single response to a potentially significant event, e.g.:
  - ♦ Reference 5, Figure 3.18: Diagnosis Failure Probability is > 0.5 for diagnosis times less than 10 minutes
  - ♦ Reference 35, Table 6.3: Failure Probability is 0.9 for "Operator fails to act correctly after the first 5 minutes after the onset of an extremely high stress condition"
  - ♦ Reference 35, Table 6.3: Failure Probability is 0.2-0.3 "... given very high stress levels where dangerous activities are occurring rapidly"
- Other references substantiate the above conservative choices, while others could be used to apply Performance Shaping Factors to properly account for quality training programs, ease of diagnosis for severe releases, conditional failure probabilities, etc.
- The SA did not attempt to correlate the chosen probabilities with the decision factors in not actuating the AES for the October 19, 1994 explosion/fire in the pipe rack immediately south of the Alkylation Unit.
- In summary, although judgment and experience are often used for the determination of HEPs (e.g., APJ method), and many important human factors considerations were addressed, Mobil non-conservatively did not explicitly address several key issues:
  - ♦ diagnostic error probabilities

- specific errors of omission and commission
- dependencies between multiple, sequential human actions (i.e., type of common mode failure)

However, the simplified HEP calculations (Section IV.B.5.f) and the mitigation system availability sensitivity study (Table IV.7) demonstrate that the above assumptions would not change the conclusions of the QRA or of the SA.

IV.B.5.f Simplified HEP Calculations for Mitigation System Availability Sensitivity Study

To address the sensitivity on the MHF QRA results to some of the issues raised above, the SA recalculated the risks of the dominant MHF release scenarios with more conservative HEPs. The objective was to perform straightforward HEP calculations based on common HRA approaches to characterize the impact on the dominant risk scenarios.

Consistent with the best estimate calculations originally performed by Mobil, equipment failures are typically dominated by HEPs, and therefore, are not explicitly calculated. In general, the likelihood of detection failure (i.e., detector equipment failure, video detection failure, operator visual detection), is considered implicit in the diagnostic failure probability. Since all mitigation functions can be performed remotely, equipment accessibility adjustments are not made. Literature data for diagnostic failure probabilities are not common and not directly applicable to the HF release diagnosis activities modeled for this QRA.

Elsewhere, detailed THERP analyses have been used to determine HEPs for some industrial facilities where the responses involved invoking detailed procedures from a central control room. Due to the straightforward nature of these postulated MHF releases and follow-up responses, the approach detailed in Reference 5 was used.

Appendix A details the simplified HEP calculations which were used to calculate probabilities for this mitigation system availability sensitivity study. The results of these calculations are as follows:

25-100mm Circulating Pump and Acid Truck Releases

Mitigation Event Tree Path 1 Probability	0.54
Mitigation Event Tree Path 2 Probability	0.038

Mitigation Event Tree Path 3 Probability	0.17
Mitigation Event Tree Path 9 Probability	0.091

25-100mm Other Releases

Mitigation Event Tree Path 1 Probability	0.49
Mitigation Event Tree Path 9 Probability	0.097

Results of this sensitivity study are presented in Tables IV.5 and IV.7, located in Section IV.D.

Although one could argue the exact HEP values utilized for the sensitivity study, they are clearly conservative and are based on relatively common HRA techniques. This approach is adequate for characterizing the dependency on the results of the MHF QRA on HEP assumptions. As expected, the risk results presented in the tables in Section IV.D from this sensitivity study fall between the active and no-active-mitigation QRA results; however, they are arithmetically closer to the original best estimate active mitigation case. This characterizes and validates the safety enhancements offered by mitigation features at the Torrance Refinery Alkylation Unit.

IV.B.5.g Other Issues

- Several areas in the MHF alkylation process contain high concentrations of HF without the vapor pressure and flash atomization suppressing additive. For the following locations, containing HF without the additive, the quantity of HF present does not represent a significant potential risk to the public (References 514.01 and 576.00):
    - Depropanizer Feed Settler Boot - 50 gal nominal
    - Depropanizer Receiver Boot - 50 gal nominal
    - Boot Return Piping - 15 gal
    - Acid Regenerator Vapor Phase (15 to 25 wt%) - 270 gal

IV.B.6 Conclusions

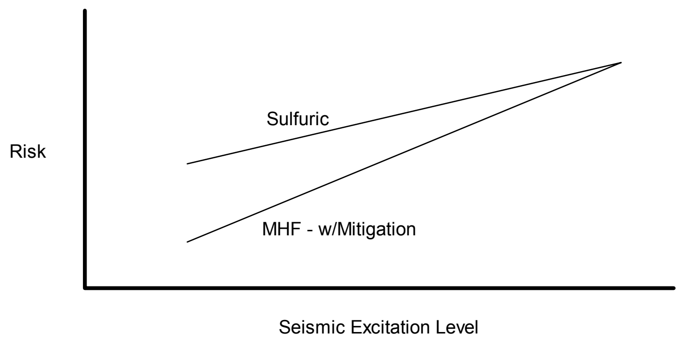
During the follow-up SA inquiries, responses to specific technical issues were complete, contained a firm technical basis, and reflected a robust QRA.

Key conclusions:

- Equipment failure probabilities were appropriate for use in the quantitative risk comparison, and correlate well to observations such as the 15Jul92 breach of the Torrance Refinery Alkylation Unit thermowell.
- The simplifying assumption that HEPs dominated the unavailability of mitigation systems was reasonable and acceptable.
- The treatment of response actions for both sulfuric acid and MHF alkylation QRAs were consistent, and Table IV.5 provides the calculated risk using a very conservative mitigation system modeling approach (i.e., no-active-mitigation). The calculated risk of the “no-active-mitigation” case for MHF is comparable to that of a sulfuric acid alkylation unit. Therefore, although the original modeling of mitigation systems and the associated HEPs could be considered to be optimistic, sensitivity studies performed by the SA with more conservative choices of mitigation system availabilities showed MHF alkylation unit risk still smaller than the reference sulfuric acid alkylation unit.
- It is clear that the incremental increase in breach frequency is proportional for both the MHF and the sulfuric acid alkylation units. Seismic events are expected to have a greater incremental impact on MHF alkylation unit risk (with credit for active mitigation for low excitation level seismic events) (compared to sulfuric acid alkylation unit risk) due to common mode effects on *both* the likelihood of the breach and the unavailability of key mitigation systems (see Figure IV.2). If active mitigation is not credited, the incremental risk due to seismic events would be expected to be proportional for both alkylation units. Therefore, for potential seismic events, the calculated risk of the MHF “no-active-mitigation” case would be expected to show that the risk of a “sulfuric acid alkylation plant producing a comparable amount of alkylate” is comparable, and the performance of a specific seismic QRA is not considered necessary. A seismic QRA would be expected, however, to show a significantly lower seismic risk for the MHF Alkylation Unit due to the availability of existing seismically-qualified mitigation systems.

FIGURE IV.2

Seismic Risk Characterization



- The required emergency response actions do not mandate the installation of automatic mitigation system actuation features (e.g., actuated from ambient HF concentrations higher than the current setpoints).
- The small quantities of HF (w/o additive) existing in the system do not represent a significant potential risk to the public.

The assumptions, models, and calculational basis for the quantification of accident scenario frequencies were appropriate for this quantitative risk comparison.

The SA can identify no additional accident scenario quantification requirements, to address Consent Decree issues, mandated as a result of using the modified HF catalyst. However, there are necessary follow-up actions:

- As part of the SA Project, the SA will be completing the previously identified Evaluation of the Emergency Response Program. As part of this evaluation, the SA will also review the procedures, training, and responsibilities for actuation of the firewater pumps, water spray systems, water deluge systems, remotely-operated firewater monitors, and the AES. Also to be considered for this evaluation is:
    - ♦ the adequacy of the AES test procedures to thoroughly verify functionality (as appropriate, a more complete test or complete system dump may precipitate from the SA's Evaluation of the Emergency Response Program)
    - ♦ the need for any specific training or drills for the actuation of Alkylation Unit mitigation systems

- Reference 516.00 specifies that the "Shift Supervisor should notify Fire and Safety, FCC/Alky Supervisors and the AQMD." Issues associated with the notification of the Torrance Fire Department (TFD) were raised and will be addressed through the implementation of Recommendation E from the Fire Fighting Capabilities and Procedures Evaluation.
- Verifying the capacity and location of key mitigation equipment will be performed as part of the SA's Evaluation of the Emergency Response Program.

The above tasks are important; however, these specific activities are either currently planned or included as part of existing refinery practices and procedures, or regulatory requirements. Therefore, there are no additional recommendations beyond those actions underway or planned by Mobil or the Safety Advisor.

IV.C CONSEQUENCE ANALYSIS

IV.C.1 Importance to QRA/Phenomenology Review

As identified in Section IV.A.1, the consequence analysis is one of the key elements of a QRA. The calculated magnitude of potential consequences is combined with the likelihood of potential accident scenarios to determine risk.

The consequence analysis entails consideration or quantification of many factors, e.g.:

- size and characteristics of release (e.g., materials, process conditions, mitigation system availability, direction, jet effects, etc.)
- flash atomization and aerosolization phenomenology
- dispersion physics
- dispersion modeling parameters such as surface roughness
- meteorological conditions
- concentration endpoints
- health effects models (e.g., probits)
- population profiles and potential sensitive receptors

IV.C.2 Key Criteria Referenced

- II.C
- II.E

IV.C.3 Summary

The following issues related to consequence analysis are addressed in the QRA sections of this evaluation:

- IV.B Accident Scenario Frequencies:
    - ♦ mitigation features credited

  - ♦ calculated/estimated equipment failure and human error probabilities for mitigation features
- IV.D Accident Scenario Quantification and Risk Assembly:
  - ♦ correlation of specific accident sequences to the appropriate consequence modeling results

The technical areas of interest for the consequence analysis for the QRA are also of concern for the phenomenological review conducted to address the first Consent Decree criteria. Therefore, key issues associated with the QRA Consequence Analysis are addressed in the following sections:

- V.A HF Release Rates and Aerosol Formation, e.g.:
  - ♦ flash atomization and aerosolization modeling
  - ♦ jet release modeling
  - ♦ HF oligomerization
  - ♦ MHF vapor pressure
  - ♦ process conditions
  - ♦ reduction in airborne mass flux for the modified HF catalyst
- V.B Dispersion Modeling Evaluation, e.g.:
  - ♦ key assumptions
  - ♦ release and source-term calculations
  - ♦ water spray efficiencies and comparison with results of industry test programs for HF
  - ♦ assumptions regarding the use of water sprays for sulfuric acid alkylation units
  - ♦ aerosolization and airborne release fractions for sulfuric acid
  - ♦ choice of dispersion models
  - ♦ comparison to single event modeling
- V.C Meteorological Assumptions, e.g.:
  - ♦ surface roughness
  - ♦ stability class assumptions
  - ♦ meteorological data sources
- V.D Consideration of Sensitive Receptors and Vulnerability Zones
  - ♦ key assumptions

    - ♦ location of sensitive receptors
    - ♦ modeling of sensitive receptors
    - ♦ impact on the quantitative risk comparison
- V.E Health Effects Models, e.g.:
    - ♦ use of ERPG-3 concentration endpoints
    - ♦ extrapolation of experimental data from animals to humans
    - ♦ extrapolation of experimental data over short time periods
- V.F Comparison with Other Alkylation Unit Technologies, e.g.:
    - ♦ commercially available technologies
    - ♦ technologies likely to become available in the near future
- V.G Refinery Chemical Monitoring/Warning Systems

IV.D ACCIDENT SCENARIO QUANTIFICATION AND RISK ASSEMBLY

IV.D.1 Importance to QRA/Phenomenology Review

For a Quantitative Risk Assessment (QRA), one way of expressing the overall calculated risk is the sum of the risks posed by the discrete scenarios:

$$\text{Risk} = \sum_{i=1}^{n} P_i * C_i \qquad \text{(Equation IV.D.1)}$$

where P_i is the scenario frequency and C_i is the magnitude of the consequences.

Thus, it is important to not only calculate accurate values for the likelihood and resultant consequences of a release event, but to also ensure that these values are appropriately combined and summed. A complete risk assessment includes the explicit quantification of at least key contributing scenarios. A comparative risk assessment must at least use a range of chosen scenarios which reflect the range of scenarios and consequences for the complete risk assessment.

This section reviews the overall quantification process for the QRA and addresses accurate combining of accident scenario frequencies with the calculated magnitude of the consequences (i.e., risk assembly).

Simplifying assumptions are addressed in Section IV.E. Correlation of the QRA results to other select, published results is addressed in Section IV.G.

IV.D.2 Key References Reviewed by SA

- 507.01
- 507.02
- 508.00
- 511.02
- 514.07
- 515.03
- 523.00

IV.D.3 Key Criteria Referenced

- II.B
- II.C
- II.D

IV.D.4 Review Activity/SA Calculation Summary

The SA's review focused on the above identified references. SA calculations were performed to ensure that there was a clear correlation between potential contributors to risk and the calculated risk values and to verify the risk assembly process. SA calculations were also performed to address the sensitivity of dominant MHF release scenarios on mitigation system success probabilities. Comparisons were made between the results of the various sensitivity studies performed for the QRA and driving forces precipitating the differences between the sensitivity studies.

IV.D.5 Results/Observations

Table IV.5 summarizes the results of various sensitivity studies which were performed in support of the quantitative risk comparison. Table IV.6 itemizes dominant MHF release accident scenarios, summarizes primary contributors, and correlates results with the risk scenario summaries in Appendix 3.1 of Reference 508.00. The driving factors for approximately 50% of the total risk are identified on this table.

To address the impact on the MHF QRA results of some of the Human Reliability Analysis (HRA) and Mitigation System Availability issues raised in Section IV.B.5.f, the SA recalculated the risks of the dominant MHF release scenarios with more conservative HEPs than were originally assumed for the active mitigation case. The objective was to perform straightforward HEP calculations based on common HRA approaches to characterize the impact on dominant risk scenarios.

Equation IV.D.1 illustrates the basis for overall calculated risk being the sum of the risks posed by discrete scenarios. Section IV.B.5.f and Appendix A describe the HEP calculations performed to determine mitigation path probabilities in support of the mitigation system availability sensitivity study. The resultant conservative mitigation path probabilities were used in Table IV.7 to calculate the “Sensitivity of Dominant MHF Release Scenarios on Mitigation System Success Probabilities”.

Using the same calculational approach as in Table IV.6, which verified risk calculations for dominant scenarios for the active mitigation case, Table IV.7 uses an “Updated Mitigation Path Probability”, based on the mitigation event tree path probabilities determined in Section IV.B.5.f, to calculate an “Updated Calculated Exposures Per Year”. This updated value is then compared to the original calculated exposures per year for *both* the active and no-active-mitigation case release scenarios. This results in the “Estimated Impact” on *both* the active and no-active-mitigation case results for each dominant scenario. These impacts were then summed to determine an upper and lower range for estimated total calculated exposures per year for the QRA. Although only the dominant scenarios were recalculated, the sensitivity of risk results to more conservative HEP values was adequately characterized for the purpose of this SA evaluation.

The following are some of the salient results/observations:

- As a conservative comparison (Reference 511.02), the results of the “impact for a 2-inch settler leak”, for the following appropriate comparative bases:
    - no-active-mitigation for the MHF alkylation (Table IV.5, Case b) and inventory-limited releases for 2.8% airborne-release-fraction sulfuric acid (Table IV.5, Case f) (i.e., no credit for response)
    - active mitigation (e.g., water spray, water deluge, pump isolation/shutdown, and firewater monitor application) for MHF (Table IV.5, Case a) and 15 minute-limited releases for 2.8% airborne-release-fraction sulfuric acid (Table IV.5, Case d) (i.e., reasonable emergency response actions)

  showed MHF fenceline doses to be approximately the same as for a “sulfuric acid alkylation plant producing a comparable amount of alkylate.”
- Comparison of the following, critical 2” release and risk results in Table IV.5 appropriately reflect comparative, expected doses and release frequencies:

    a) MHF - Active Mitigation

    b) MHF - No Active Mitigation -- Even without AES actuation, event duration would be inventory limited to 6.6 minutes.

c) Sulfuric - 2.8% Airborne Release Fraction, 15-minute limited for single event and varying operating response time and actions for QRA

- Although typos seem to exist within the QRA (e.g., Appendix 3.1, Scenarios PUMP59 and PUMP49 making reference to AES and 5 min water actuation, RX-76 and RX2-75 referencing isolation and not AES, etc.), these do not impact the calculational quality of the QRA and, correspondingly, the Safety Advisor's conclusions. In general, the numerical calculations and results appeared robust.
- The results of Table IV.6 are readily derivable from the scenario definitions and basic probabilities, AND correlate well with the risk results of the MHF QRA. This provides good substantiation of the dominant risk contributors.
- The values in Table IV.6 for the average number of individuals exposed to ERPG levels appear to be comparatively consistent, e.g.:
  - Impeded vs. unimpeded
  - Isolation vs. no isolation
  - Breach size
- Table IV.7 documents the calculations and results of the "Sensitivity of Dominant MHF Release Scenarios on Mitigation System Success Probabilities". The results showed that a better estimate using more conservative HEP calculations, but taking credit for active mitigation resulted in a characteristic value of approximately 0.04/yr with an "upper range" value (used in Table IV.5) of 0.064/yr. The calculations in Table IV.7 are based on conservative HEP calculations and more accurately reflect the contribution of the mitigation systems at the Torrance Refinery in protecting "the environment and the health, and safety, and welfare and property of all persons, both off-site and on-site."
- Another potential source of uncertainty (conservatively skewing results to favor sulfuric acid alkylation) is the use of the results of the DEGADIS model for the comparisons offered in Table IV.5. SLAB is considered a better model for the more likely horizontal jets resulting from a breach in the reference sulfuric acid alkylation unit.
- Section V.B compares the results of the SLAB and DEGADIS calculations for both sulfuric acid and MHF.

TABLE IV.5
SENSITIVITY STUDY RESULTS[(a), (c)]

Case		Fenceline Dose[(b)]	Risk (SRI)[(d)]
a	MHF - active mitigation DEGADIS & SAFETI (Refs. 507.02 and 508.00)	6.4	7.85E-3/yr
b	MHF - no-active-mitigation, DEGADIS & SAFETI (Refs. 511.02 and 514.07)	18.3	0.18/yr
c	MHF - active mitigation sensitivity study (conservative mitigation system availability assumptions are detailed in Section IV.B.5.f and Appendix A) - the SRI value reported here is conservatively the upper range of values calculated in Table IV.7	N/A	0.064/yr
d	Sulfuric Acid - 2.8% airborne release fraction, 15 minute limited for single event and 5 and 15 minute operator response time and actions for QRA, fenceline dose linearly extrapolated from the results below in (e). See (k). SRI was explicitly calculated by Mobil.	6.0	0.148/yr
e	Sulfuric Acid - 4% airborne release fraction, DEGADIS and SAFETI, 15 minute limited for single event and 5 and 15 minute operator response time and actions for QRA (Refs. 507.02 and 508.00)	8.6	0.24/yr
f	Sulfuric Acid - 2.8% airborne release fraction, inventory limited, linearly extrapolated from results in (g).	13.8	N/A
g	Sulfuric Acid - 4% airborne release fraction, inventory limited, DEGADIS (Ref. 507.02)	19.8	N/A
h	Sulfuric Acid, 3.75" Orifice - 2.8% airborne release fraction, DEGADIS, inventory limited, 10 minutes (Ref. 517.00)	10.9	N/A
i	MHF, SLAB - active mitigation (Ref. 515.03)	6.6	N/A
j	Sulfuric Acid, SLAB - 4% airborne release fraction, 15 minute limited (Ref. 515.03)	13.6	N/A
k	Sulfuric Acid - 2.8% airborne release fraction, 15 minute limited, linear extrapolation from SLAB results in (j).	9.5	N/A

(a) All fenceline results for a 2" orifice, unless otherwise indicated.

(b) Fenceline dose is expressed as a ratio to ERPG-3 for direct comparison, and the concentration is calculated for 190th street, unless otherwise indicated. 190th Street was chosen as a point of comparison and is not intended to be the closest or highest risk fenceline point.

(c) All results for 2.8% sulfuric acid release fraction obtained by linear ratio from Mobil's results for 4% except (h), extrapolated from the 3% results provided by Mobil. See Section V.B for a discussion regarding the basis for the sulfuric acid airborne release fraction.

(d) SRI = Societal Risk Index (using ERPG-3 reference) and consequence analyses performed for the risk assessment were performed using the SAFETI Software package.

Scenario	Risk Rank	Breach Freq (/yr) (App 1.3)	Impeded or Unimped'd Fraction (Pg 41)	Mitigation Path Probability (Fig 4 & 5)	Event Frequency	Avg. # Exp. to ERPG Lvl (App 3.1)	Calc. Exp. Per Year	% of Total	Correlation	Description
TOTAL EXPOSURES PER YEAR (Reference 508.00, App. 3.1)							7.85E-03	100.00		
CIRCULATING PUMPS (5G-33A/B inside isolation valves)										
PUMP75	1	1.00E-04	0.9	8.49E-01	7.64E-05	6.3	4.81E-04	6.13	Yes	100 mm leak on Circ Pump, 30s water, 1 min isol, impeded (2a)
		(1)								
PUMP61	3	2.50E-04	0.9	4.70E-02	1.06E-05	26	2.75E-04	3.51	OK	50 mm leak on Circ Pump, 30s water, no isol, impeded (2b)
PUMP43	8	7.50E-04	0.9	4.37E-02	2.95E-05	5.33	1.57E-04	2.00	Yes	25 mm leak on Circ Pump, 30s water, no isol, impeded (2b)
		(3)								
PUMP79	15	1.00E-04	0.9	4.70E-02	4.23E-06	29.6	1.25E-04	1.60	Yes	100 mm leak on Circ Pump, 30s water, no isol, impeded (2b)
PUMP77	16	1.00E-04	0.9	4.47E-02	4.02E-06	29.8	1.20E-04	1.53	Yes	100 mm leak on Circ Pump, 30s water, 2 min isol, impeded (2c)
						SUBTOTAL	1.16E-03	14.76		
Adding Other Key Circulating Pump Scenarios (Appendix 3.1)						PUMP76	1.12E-04	1.43		
						PUMP57	1.01E-04	1.28		
						PUMP59	5.26E-05	0.67		
						PUMP55	4.92E-05	0.63		
						PUMP62	4.23E-05	0.54		
						PUMP80	3.21E-05	0.41		
						PUMP44	3.20E-05	0.41		
						PUMP78	3.15E-05	0.40		
						SUBTOTAL	4.52E-04	5.76		
				TOTAL (Circulating Pump Check)			1.61E-03	20.52		
PIPE 5C-102-16" from pump isolation valve to #1 Reactor Isolation Valve and other lines										
C102-76	2	1.23E-05	0.5	8.15E-01	5.01E-06	68.1	3.41E-04	4.35	Yes	100 mm leak on Pipe C102, 1 min water, 2 min AES, unimpeded
C102-75	13	1.23E-05	0.5	8.15E-01	5.01E-06	28.3	1.42E-04	1.81	Yes	100 mm leak on Pipe C102, 1 min water, 2 min AES, impeded

TABLE IV.6

DOMINANT MHF RELEASE ACCIDENT SCENARIOS WITH PRIMARY CONTRIBUTORS IDENTIFIED

C102-58	14	3.04E-05	0.5	8.15E-01	1.24E-05	10.1	1.25E-04	1.59	Yes	50 mm leak on Pipe C102, 1 min water, 2 min AES, unimpeded
C102-57	26	3.04E-05	0.5	8.15E-01	1.24E-05	6.2	7.68E-05	0.98	Yes	50 mm leak on Pipe C102, 1 min water, 2 min AES, impeded
						SUBTOTAL	6.85E-04	8.72		
Adding Other Key Pipe 5C-102 Scenarios (Appendix 3.1)						C102-74	5.61E-05	0.71		
						C102-01	3.23E-05	0.41		
						C102-43	2.71E-05	0.35		
						C102-62	2.25E-05	0.29		
						C102-88	2.04E-05	0.26		
						C102-80	1.97E-05	0.25		
						SUBTOTAL	1.78E-04	2.27		
				TOTAL (Pipe 5C-102 Check)			8.63E-04	10.99		
PIPE 5C-103-18" from #1 Settler to AES Isolation Valve and including spool pieces										
SPOOL1-75	4	3.86E-06	0.75	8.15E-01	2.36E-06	99.1	2.34E-04	2.98	Yes	100 mm leak on #1 Settler Spool, 1 min water, 2 min AES, impeded
			(6)							
SPOOL1-57	5	9.51E-06	0.75	8.15E-01	5.81E-06	33.7	1.96E-04	2.49	Yes	50 mm leak on #1 Settler Spool, 1 min water, 2 min AES, impeded (assumed by SA)
(4)			(6)							
SPOOL1-76	6	3.86E-06	0.25	8.15E-01	7.86E-07	227	1.78E-04	2.27	Yes	100 mm leak on #1 Settler Spool, 1 min water, 2 min AES, unimpeded
			(6)							
SPOOL1-58	27	9.51E-06	0.25	8.15E-01	1.94E-06	38.6	7.47E-05	0.95	OK	50 mm leak on #1 Settler Spool, 1 min water, 2 min AES, unimpeded
			(6)							
						SUBTOTAL	6.83E-04	8.69		
Adding Other Key Spool-1 Scenarios (Appendix 3.1)						SPOOL1-61	4.48E-05	0.57		
						SPOOL1-43	3.61E-05	0.46		
						SPOOL1-69	2.58E-05	0.33		
						SPOOL1-59	2.47E-05	0.31		
						SPOOL1-44	1.84E-05	0.23		
						SUBTOTAL	1.50E-04	1.91		
				TOTAL (Spool-1 Check)			8.32E-04	10.60		
TANK TRUCK OR HOSE WHILE UNLOADING										

TABLE IV.6

DOMINANT MHF RELEASE ACCIDENT SCENARIOS WITH PRIMARY CONTRIBUTORS IDENTIFIED

TRUCK62	9	8.54E-03	0.5	4.51E-02	6.01E-06	26.1	1.57E-04	2.00	Yes	50 mm leak on Acid Truck, 1 min water, no isol, unimpeded
				(5)	(7)					
TRUCK61	17	8.54E-03	0.5	4.51E-02	6.01E-06	19.9	1.20E-04	1.52	Yes	50 mm leak on Acid Truck, 1 min water, no isol, impeded
				(5)	(7)					
TRUCK56	24	1.81E-02	0.5	2.50E-03	7.06E-07	115	8.12E-05	1.03	OK	25 mm leak on Acid Truck, no water, no isol, unimpeded (8)
				(5)	(7)					
TRUCK55	34	1.81E-02	0.5	2.50E-03	7.06E-07	80.9	5.71E-05	0.73	Yes	25 mm leak on Acid Truck, no water, no isol, impeded (9)
				(5)	(7)					
						SUBTOTAL	4.15E-04	5.28		
Adding Other Key Tank Truck or Hose Scenarios (Appendix 3.1)						TRUCK73	3.21E-05	0.41		
						TRUCK74	2.84E-05	0.36		
						TRUCK58	2.67E-05	0.34		
						TRUCK02	1.59E-05	0.20		
						TRUCK57	1.41E-05	0.18		
						SUBTOTAL	1.17E-04	1.49		
				TOTAL (Truck or Hose Check)			5.32E-04	6.78		
1. This is conservative w.r.t. the leak frequency of 6.6E-5/yr identified in Section 4.6.										
2a) It appears as if what was meant was 30s isolation, 1 min water, b) 30s isolation, no water, c) 30s isolation, 2 min water.										
3. This is conservative w.r.t. the leak frequency of 6.6E-4/yr identified in Section 4.6.										
4. This scenario did not materialize in the summary table in Appendix 3.1, but was located later in the QRA.										
5. Figure 4, Appendix 1.2, and Appendix 1.4 identify the scenarios as no AES; however, it is clear that the appropriate reference is for no isolation.										
6. Although impeded (low velocity) releases were identified as 50% or 90% in Section 4.10, Appendix 1.3 identifies 0.75 for relatively congested areas.										
7. A multiplier of 0.0312 was incorporated to address fractional Truck/Hose Service time. This is a reasonable value considering 24 deliveries per year (Reference 512.04).										
8. Appendix 3.1 identifies this as "impeded"; however, it was corrected here to correlate with the data.										
9. Appendix 3.1 identifies this as "unimpeded"; however, it was corrected here to correlate with the data.										
10. Valve reliability numbers in Section 4.6 and Appendix 2.1 do not appear to be used for the dominant scenarios for this QRA.										
General: Referenced pages, sections, and figures refer to Reference 508.00 unless otherwise indicated.										

TABLE IV.6

DOMINANT MHF RELEASE ACCIDENT SCENARIOS WITH PRIMARY CONTRIBUTORS IDENTIFIED

Scenario	Risk Rank	Breach Freq (/yr) (App 1.3)	Impeded or Unimped'd Fraction (Pg 41)	Mitigation Path Probability	Event Frequency	Avg. # Exp. to ERPG Lvl (App 3.1)	Calc. Exp. Per Year	% of Total	Original Mitigation Path Probability	Original Calculated Exposures Per Year	Updated Mitigation Path Probability	Updated Calculated Exposures Per Year	Estimated Impact on No-Active Mitigation Case	Estimated Impact on Active Mitigation Case	Mitigation Path	Description
TOTAL EXPOSURES PER YEAR (No-Active-Mitigation Case, Reference 514.07)							1.83E-01									
TOTAL EXPOSURES PER YEAR (Active Mitigation Case, Reference 508.00)							7.85E-03									
Dominant No-Active Mitigation Scenarios																
25003/04 - 35055	1	7.50E-04	0.9	1.00	6.75E-04	48.7	3.29E-02	18.00	0.0015	4.93E-05	9.70E-02	3.19E-03	-2.97E-02	3.14E-03	9	Reaction Section Scenario 4 (Pumps) - 25mm leak, no water, no isolation, impeded
25006/15 - 35056	2	1.81E-02	0.5	1.00	2.82E-04	115	3.25E-02	17.78	0.0025	8.12E-05	9.10E-02	2.95E-03	-2.95E-02	2.87E-03	9	Acid Truck Leak - 25mm leak, no water, no AES, unimpeded (3) - Note that this scenario is also a dominant scenario for the active mitigation case.
					(2)											
25006/15 - 35055	3	1.81E-02	0.5	1.00	2.82E-04	80.9	2.28E-02	12.51	0.0025	5.71E-05	9.10E-02	2.08E-03	-2.08E-02	2.02E-03	9	Acid Truck Leak - 25mm leak, no water, no AES, impeded (3) - Note that this scenario is also a dominant scenario for the active mitigation case.
					(2)											
25006/15 - 35055	4	8.54E-03	0.5	1.00	1.33E-04	96.3	1.28E-02	7.03	0.0025	3.21E-05	9.10E-02	1.17E-03	-1.17E-02	1.14E-03	9	Acid Truck Leak - 50mm leak, no water, no AES, unimpeded (3)
					(2)											
25006/15 - 35055	5	8.54E-03	0.5	1.00	1.33E-04	85.4	1.14E-02	6.23	0.0025	2.84E-05	9.10E-02	1.04E-03	-1.03E-02	1.01E-03	9	Acid Truck Leak - 50mm leak, no water, no AES, impeded (3)
					(2)											
25005/04 - 35073	6	2.50E-04	0.9	1.00	2.25E-04	46.9	1.06E-02	5.78	0.0015	1.58E-05	9.70E-02	3.19E-05	-1.05E-02	1.61E-05	9	Reaction Section Scenario 4 (Pumps) - 50mm leak, no water, no isolation, impeded
										(1)						
25007/02 - 35055	7	2.29E-05	0.75	1.00	1.72E-05	243	4.17E-03	2.29	0.0025	1.04E-05	9.70E-02	1.26E-05	-4.16E-03	2.20E-06	9	Reaction Section Scenario 2 (#1 Settler Spool) - 25mm leak, no water, no AES, impeded
										(1)						
25004/04 - 35056	8	7.50E-04	0.1	1.00	7.50E-05	53	3.98E-03	2.18	0.0015	5.96E-06	9.70E-02	1.20E-05	-3.96E-03	6.07E-06	9	Reaction Section Scenario 4 (Pumps) - 25mm leak, no water, no isolation, unimpeded
25007/04 - 35091	9	1.00E-04	0.9	1.00	9.00E-05	29.6	2.66E-03	1.46	0.0015	4.00E-06	9.70E-02	8.06E-06	-2.66E-03	4.07E-06	9	Reaction Section Scenario 4 (Pumps) - 100mm leak, no water, no isolation, impeded
										(1)						
						TOTALS	1.34E-01	73.25			Subtotal of Impact Sum		-1.23E-01	1.02E-02		
Dominant Active Mitigation Scenarios from Table IV.6 (See Table IV.6 for Clarifying Footnotes)																
PUMP75		1.00E-04	0.9	8.49E-01	7.64E-05	6.3	4.81E-04				5.40E-01	3.06E-04	3.06E-04	-1.75E-04	1	100 mm leak on Circ Pump, 30s water, 1 min isol, impeded
PUMP61		2.50E-04	0.9	4.70E-02	1.06E-05	26	2.75E-04				1.70E-01	9.95E-04	9.95E-04	7.19E-04	3	50 mm leak on Circ Pump, 30s water, no isol, impeded
PUMP43		7.50E-04	0.9	4.37E-02	2.95E-05	5.33	1.57E-04				1.70E-01	6.12E-04	6.12E-04	4.55E-04	3	25 mm leak on Circ Pump, 30s water, no isol, impeded
PUMP79		1.00E-04	0.9	4.70E-02	4.23E-06	29.6	1.25E-04				1.70E-01	4.53E-04	4.53E-04	3.28E-04	3	100 mm leak on Circ Pump, 30s water, no isol, impeded
PUMP77		1.00E-04	0.9	4.47E-02	4.02E-06	29.8	1.20E-04				3.80E-02	1.02E-04	1.02E-04	-1.79E-05	2	100 mm leak on Circ Pump, 30s water, 2 min isol, impeded
C102-76		1.23E-05	0.5	8.15E-01	5.01E-06	68.1	3.41E-04				4.90E-01	2.05E-04	2.05E-04	-1.36E-04	1	100 mm leak on Pipe C102, 1 min water, 2 min AES, unimpeded
C102-75		1.23E-05	0.5	8.15E-01	5.01E-06	28.3	1.42E-04				4.90E-01	8.53E-05	8.53E-05	-5.65E-05	1	100 mm leak on Pipe C102, 1 min water, 2 min AES, impeded
C102-58		3.04E-05	0.5	8.15E-01	1.24E-05	10.1	1.25E-04				4.90E-01	7.52E-05	7.52E-05	-4.98E-05	1	50 mm leak on Pipe C102, 1 min water, 2 min AES, unimpeded
C102-57		3.04E-05	0.5	8.15E-01	1.24E-05	6.2	7.68E-05				4.90E-01	4.62E-05	4.62E-05	-3.06E-05	1	50 mm leak on Pipe C102, 1 min water, 2 min AES, impeded
SPOOL1-75		3.86E-06	0.75	8.15E-01	2.36E-06	99.1	2.34E-04				4.90E-01	1.41E-04	1.41E-04	-9.31E-05	1	100 mm leak on #1 Settler Spool, 1 min water, 2 min AES, impeded
SPOOL1-57		9.51E-06	0.75	8.15E-01	5.81E-06	33.7	1.96E-04				4.90E-01	1.18E-04	1.18E-04	-7.80E-05	1	50 mm leak on #1 Settler Spool, 1 min water, 2 min AES, impeded (assumed by SA)
SPOOL1-76		3.86E-06	0.25	8.15E-01	7.86E-07	227	1.78E-04				4.90E-01	1.07E-04	1.07E-04	-7.11E-05	1	100 mm leak on #1 Settler Spool, 1 min water, 2 min AES, unimpeded
SPOOL1-58		9.51E-06	0.25	8.15E-01	1.94E-06	38.6	7.47E-05				4.90E-01	4.50E-05	4.50E-05	-2.98E-05	1	50 mm leak on #1 Settler Spool, 1 min water, 2 min AES, unimpeded
TRUCK62		8.54E-03	0.5	4.51E-02	6.01E-06	26.1	1.57E-04				1.70E-01	5.91E-04	5.91E-04	4.34E-04	3	50 mm leak on Acid Truck, 1 min water, no isol, unimpeded (2)
TRUCK61		8.54E-03	0.5	4.51E-02	6.01E-06	19.9	1.20E-04				1.70E-01	4.51E-04	4.51E-04	3.31E-04	3	50 mm leak on Acid Truck, 1 min water, no isol, impeded (2)
											Subtotal of Impact Sum		4.33E-03	1.53E-03		
											Impact Sum		-1.19E-01	1.17E-02		
											Sum of Total Exposures/yr		6.37E-02	1.17E-02		
1. These scenarios appear to have fallen below the original threshold value.											Characteristic Average		3.77E-02			
2. A multiplier of 0.0312 was incorporated to address fractional Truck/Hose Service time. This is a reasonable value considering 24 deliveries per year (Reference 512.04).																
3. These are identified in Reference 508.00 as "No AES"; however, it is clear that the appropriate reference is for no isolation.																

TABLE IV.7

SENSITIVITY OF DOMINANT MHF RELEASE SCENARIOS ON MITIGATION SYSTEM SUCCESS PROBABILITIES

IV.D.6 Conclusions

The risk assembly performed for the quantitative risk comparison properly considered the type and magnitude of the consequences coupled with the accident scenarios leading up to them.

The results of the sensitivity studies performed for the quantitative risk comparison:

- appropriately reflect changes in key assumptions regarding mitigation system availability and release phenomenology
- show MHF fenceline doses to be approximately the same as a "sulfuric acid alkylation plant producing a comparable amount of alkylate"
- reflect release consequences, for appropriate comparative cases for MHF and sulfuric acid, that are approximately the same, given modeling uncertainties and applied conservatisms

Table IV.6 itemizes dominant MHF release accident scenarios, summarizes primary contributors, and correlates results with the risk scenario summaries in Appendix 3.1 of Reference 508.00. Results correlate well. In addition, the dominant scenarios are consistent with the results of other risk assessments and appear to correlate well with potential hazards for the MHF Alkylation Unit.

Table IV.7 summarizes the results of the "Sensitivity of Dominant MHF Release Scenarios on Mitigation System Success Probabilities". Although one could argue the exact HEP values utilized for the sensitivity study, they are clearly conservative and are based on relatively common HRA techniques. This approach is adequate for characterizing the dependency on the results of the MHF QRA on HEP assumptions. As expected, the risk results presented in Table IV.7 are between the active and no-active-mitigation MHF QRA results; however, they are arithmetically closer to the original best estimate, active mitigation case. This characterizes and validates the safety enhancements offered by mitigation features at the Torrance Refinery Alkylation Unit and their application (with conservative HEP values) for this quantitative risk comparison.

One of the potential concerns previously identified for the quantitative risk comparison of MHF and sulfuric acid alkylation is that an MHF unit with favorable assumptions about mitigation availability was being compared with a sulfuric acid alkylation unit that could be provided with more effective mitigation (e.g., additional isolation valves to reduce the duration of release of some of the dominant scenarios). The sensitivity calculations in Table IV.7 partially address this concern by using more conservative and defensible assumptions about MHF mitigation system availabilities. This still leaves a margin of approximately a factor of three in favor of the MHF societal risk estimate compared with the sulfuric acid alkylation best estimate. This margin allows for potential improvements to the sulfuric acid alkylation unit design without altering the SA's conclusion about the acceptability of MHF at the Torrance Refinery. In addition, the margin is even greater due to the numerous conservative assumptions identified in Section IV.E.

Figures IV.3 and IV.4 illustrate the range of societal risk results for MHF and sulfuric acid alkylation from variations in airborne release fractions for sulfuric acid alkylation and treatment of mitigation systems for MHF alkylation. Both figures illustrate the calculated societal risks of sulfuric acid alkylation (4% and 2.8% airborne release cases) with available active mitigation (i.e., emergency response). Figure IV.3 also contains the best estimate active mitigation (i.e., emergency response) case for MHF alkylation, and Figure IV.4 also contains the no-active-mitigation (i.e., no emergency response) case for MHF alkylation. The extremely conservative case in Figure IV.4 shows the risks of both alkylation process to be comparable. The sensitivity study in Table IV.7, performed by the SA with more conservative choices of mitigation system availabilities shows MHF alkylation unit risk to be between the active and no-active-mitigation QRA results and arithmetically closer to the original best estimate, active mitigation case. If superimposed onto Figure IV.3, this would be graphically depicted between the lower and middle curves. Thus, the most appropriate MHF alkylation unit comparative risk results, show calculated MHF alkylation unit risk to be smaller than the reference sulfuric acid alkylation unit.

These quantitative comparisons illustrate the improvements in risk offered by conversion to MHF, satisfying the comparative risk criteria of the Stipulation and Order (Reference 2).

There are no recommendations precipitating from this review for additional QRA analyses to satisfy the quantitative risk comparison criteria of the Stipulation and Order.

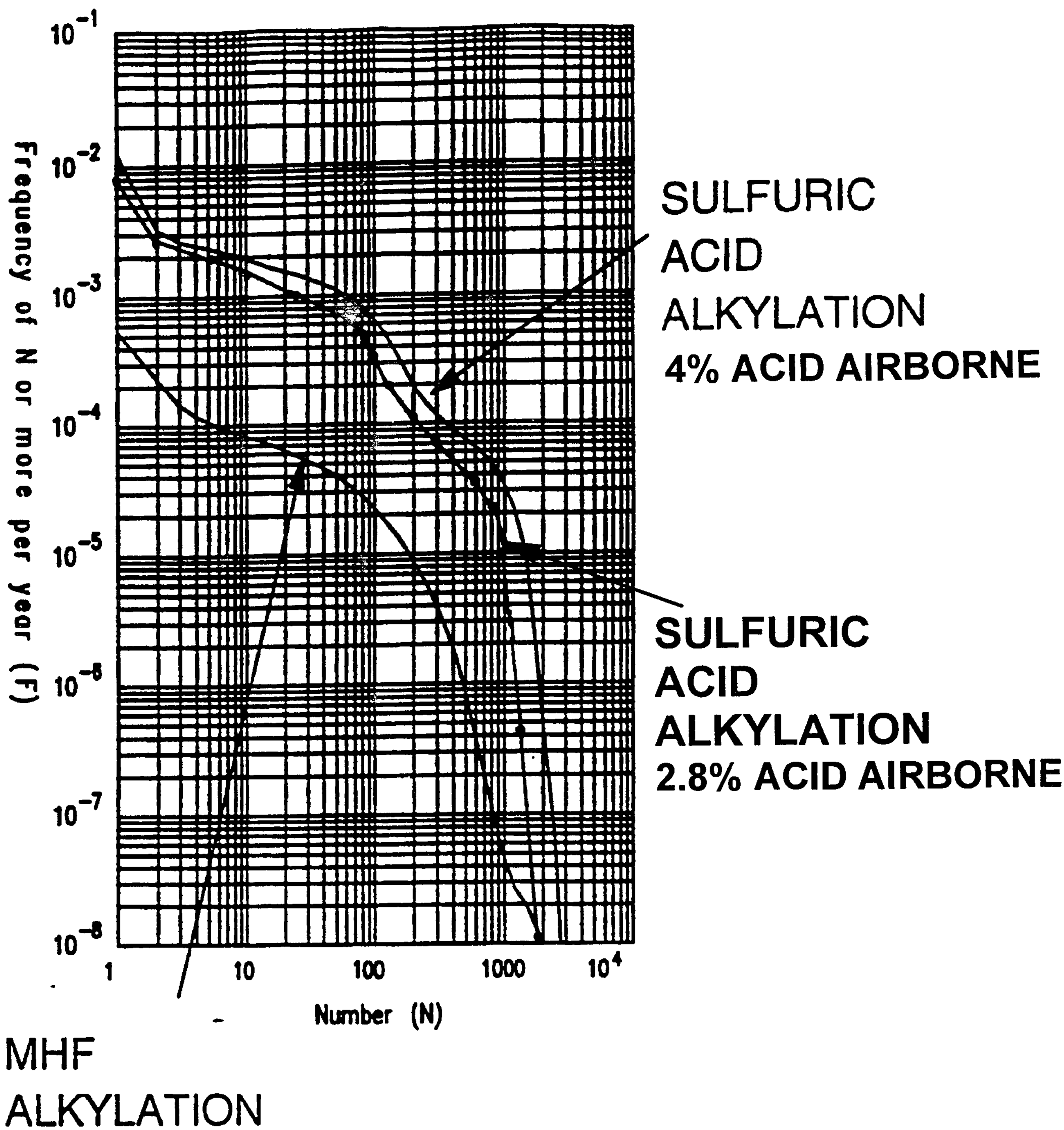


FIGURE IV.3

Societal Risks for MHF (with active mitigation) vs. Sulfuric Acid (4% and 2.8% acid airborne) for ERPG-3 Dose

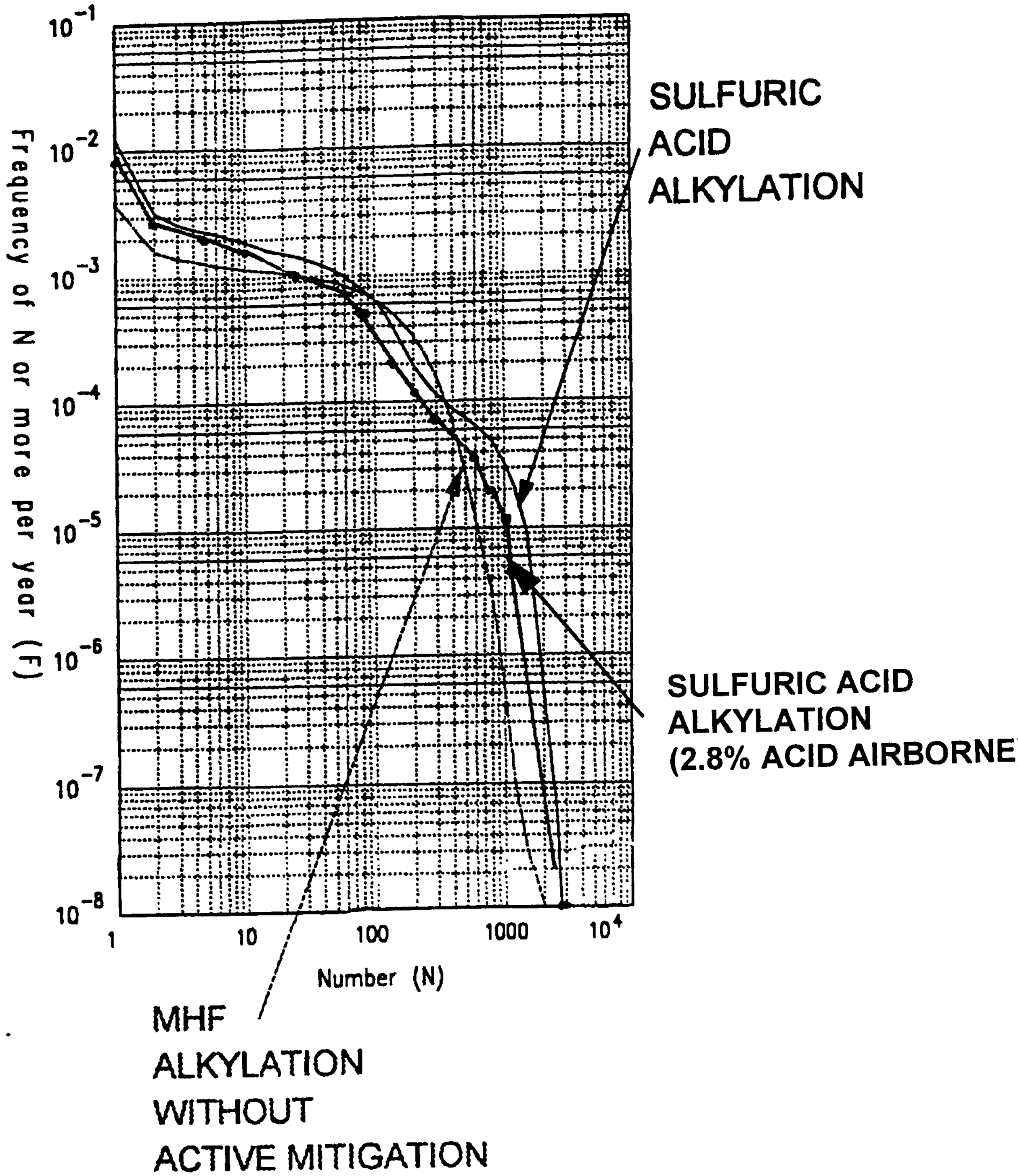


FIGURE IV.4

Societal Risks for MHF (without active mitigation) vs. Sulfuric Acid (4% and 2.8% acid airborne) for ERPG-3 Dose

IV.E UNCERTAINTY CHARACTERIZATION AND SIMPLIFYING ASSUMPTIONS

IV.E.1 Importance to QRA/Phenomenology Review

Any quantification of risk typically involves many potential uncertainties, e.g.:

- equipment failure and human error, probability and frequency assignments
- release phenomena
- dispersion phenomena
- meteorology
- human health effects
- analysis completeness and accuracy

Typically, these uncertainties are addressed by making the analysis as accurate as possible, and as necessary, applying simplifying assumptions which are conservative. A qualitative understanding of these uncertainties and the impact of simplifying assumptions is important for any quality risk assessment. Some QRAs have gone beyond this qualitative assessment and performed specific quantitative uncertainty calculations.

This section identifies and examines the expected impact of key simplifying assumptions and other potential uncertainties, addresses the defensibility of the quantitative results, and ascertains the need for specific quantitative uncertainty analysis.

IV.E.2 Key References Reviewed by SA

- 507.02
- 508.00
- 517.00
- 518.01
- 522.00
- 523.00

IV.E.3 Key Criteria Referenced

- II.F

IV.E.4 Review Activity/SA Calculation Summary

No specific SA calculations were required to evaluate this specific issue. The SA's review focused on the above identified references.

IV.E.5 Results/Observations

The following tables list key uncertainties and simplifying assumptions:

Table IV.8 - skewing results in favor of sulfuric acid alkylation, applied to one or both of the:

- MHF alkylation QRA
- Sulfuric acid alkylation QRA

Table IV.9 - skewing results in favor of MHF alkylation:

- MHF alkylation QRA
- Sulfuric acid alkylation QRA

Table IV.10 identifies uncertainties and simplifying assumptions which may impact the absolute value of the quantitative risk results of the QRA, but do not impact the conclusions of the quantitative risk comparison.

TABLE IV.8
KEY UNCERTAINTIES AND SIMPLIFYING ASSUMPTIONS
SKEWING RESULTS TO FAVOR SULFURIC ACID ALKYLATION

APPLIED TO BOTH THE MHF AND SULFURIC ACID ALKYLATION QRAs

- Transportation risks are excluded from the quantitative risk comparison. See also Section IV.F for a more detailed discussion of this topic.
- Both sulfuric and hydrofluoric acid are considered highly corrosive. For alkylation unit operation, both acids present corrosion challenges which are addressed via thorough maintenance practices and proper choice of materials. Due to heightened toxicity and risk concerns, it is generally considered that there is greater attention focused on maintenance practices for HF alkylation units. Thus, the use of generic equipment failure rates would be expected to skew results to favor sulfuric acid alkylation.
- As discussed in Section V.B, the use of the SLAB model yields sulfuric acid dose results which are approximately a factor of 1.5-2 higher than does DEGADIS. Thus, the use of the DEGADIS model skews results to favor sulfuric acid alkylation.
- The atmospheric dispersion model used for the QRA (SAFETI) does not contain HF/moist air thermodynamics (Section V.B). The new version of PHAST, which does contain HF/moist air thermodynamics, gives lower atmospheric concentrations for identical releases.

MHF ALKYLATION QRA

- For cases where a jet release would be expected to be impeded, credit for momentum (velocity) reduction is taken, but credit for additional expected rainout is not. Additional rainout would improve the airborne reduction percentage on several dominant scenarios.
- Regeneration risks are included for the MHF alkylation QRA but not for the sulfuric acid alkylation QRA.
- A single 65% value for the reduction in the airborne HF mass flux was chosen for all MHF releases. Whereas, the 2.8% airborne release fraction dose for sulfuric acid is a “best estimate” value; the 65% value for the reduction in airborne HF mass flux is one of the more limiting which could be chosen. Since a “best estimate” for HF mass flux could have been justifiably used, this use of a single conservative value skews results in favor of sulfuric acid alkylation.

- The single-event calculation for MHF assumed unimpeded release from the bottom of the settler for a 45 ft jet distance. In actuality, the bottom of the settler is 16 ft above ground and a release at the bottom of the settler would not travel 45 ft unimpeded. This significantly overestimates the impact for MHF since a reduction of 77% would be achieved, instead of 65% due to the impeded jet. This has the effect of reducing the average airborne HF rate by up to a factor of 2, when mitigation systems are considered, compared to a 65% reduction case. This affects MHF only, and therefore, overestimates the risk of MHF relative to sulfuric.
- Reference 518.01 describes the basis for the use of toxicity data obtained through "mouth-breathing" experiments as conservative.
- No credit was taken (Reference 522.00) for MHF hoses "designed, tested and maintained to higher standards than typical hoses".

SULFURIC ACID ALKYLATION QRA

- The reference sulfuric acid alkylation unit capacity assumed for the QRA was 20.6 TBD (compared to 22 TBD for the reference MHF alkylation unit).
- In general, the sulfuric acid alkylation unit QRA used a less complete set of accident scenarios. This underpredicts the risk and favors sulfuric acid alkylation, further substantiating the conclusions of this evaluation which demonstrate the comparative acceptability of MHF Alkylation.
- Section 3.2 of Reference 508.00 identifies that, for the sulfuric acid QRA, "acid loading-unloading facilities are not included in the scope of the risk assessment." Sections IV.D and IV.G of this document identify the Acid Truck/Hose as a dominant contributor for MHF alkylation risk.
- The initial single event comparisons did not address the higher frequency of release (for the same size breach) which would be expected (due to the larger number of vessels and piping) for a sulfuric acid alkylation unit. This higher likelihood was addressed later (Reference 517.00) through a comparison of the 2" breach for MHF and a 3.75" breach (considered comparable probability as the 2" MHF breach), Table IV.5, case h.
- The 2.8% best estimate airborne release fraction for sulfuric acid alkylation represents a significant reduction compared to values previously used for sulfuric acid releases and is the lower average value identified by Quest (Reference 523.00).
- No adjustments are made to the results of the QRA or the single event modeling to address the new information provided in Reference 523.00, which states that

"occupational exposure to strong-inorganic-acid mists containing sulfuric acid is *carcinogenic to humans...*".

TABLE IV.9

KEY UNCERTAINTIES AND SIMPLIFYING ASSUMPTIONS SKEWING RESULTS TO FAVOR MHF ALKYLATION

MHF ALKYLATION QRA

- For the MHF alkylation QRA (Reference 508.00), actuation of various mitigation systems within a short time frame was credited. See Sections IV.B and IV.D for a more detailed discussion of this topic. Although mitigation system success probability assumptions were “best estimates”, it should be noted that the no-active-mitigation case for MHF alkylation, still supported the conclusion that the operational risk of the MHF Alkylation Unit presented “no greater risk than a sulfuric acid alkylation plant producing a comparable amount of alkylate.”[1] In addition, the SA performed a sensitivity study utilizing more conservative HEP values for the probability of successful actuation of MHF mitigation systems and found results that were still relatively low.

SULFURIC ACID ALKYLATION QRA

- Credit is not taken for firewater monitor knockdown of sulfuric acid vapors in the event of a release. Some mitigation, however, would be expected from significant quantities of water spray (possibly more than a contemporary sulfuric acid alkylation unit would be expected to contain) directed at a sulfuric acid release.

[1]As identified in Section IV.B.6 as part of the upcoming SA evaluation of the Emergency Response Program, the SA will also review the procedures, training, and responsibilities for actuation of the firewater pumps, water spray systems, water deluge systems, remotely-operated firewater monitors, and the AES (including test procedures and the need for emergency drills).

TABLE IV.10
KEY UNCERTAINTIES AND SIMPLIFYING ASSUMPTIONS
THAT DO NOT IMPACT
THE CONCLUSIONS OF THE QUANTITATIVE RISK COMPARISON

- Simplifying meteorological conditions are applied equally to the QRAs for both alkylation catalysts.
- Off-site population profiles are applied equally to the QRAs for both alkylation catalysts. It should be noted that, although the calculations performed focus on off-site population, comparative results using off-site population profiles, implicitly compare potential impacts to on-site personnel, and address the requirement of the Consent Decree for protecting "the environment and the health, and safety, and welfare and property of all persons, both off-site and on-site."
- ERPG-3 endpoint concentrations are used for the risk assessment for both alkylation catalysts. This would be expected to generally overpredict risk for both alkylation catalysts, as a significant health impact for most individuals would be expected to occur at higher concentrations than this threshold value.
- Conservative surface roughness factors are applied equally to the QRAs for both alkylation catalysts.
- Ignition can help reduce toxic risk potential. The following conservative assumptions were used in both the MHF and sulfuric acid alkylation QRAs for the probability of ignition:
  - 0% for ruptures 4" and smaller
  - 85% for impeded ruptures greater than 4"
  - 95% for unimpeded ruptures greater than 4"
- Single-event calculations used rural conditions in DEGADIS which will overpredict the impact at fenceline (applies to both MHF and sulfuric acid alkylation)

IV.E.6 Conclusions

The uncertainties and simplifying assumptions identified in Table IV.10 that apply to both HF and sulfuric acid alkylation are appropriate for the quantitative risk comparison.

The simplifying assumptions and areas of uncertainty identified in Tables IV.8 and IV.9 were typically chosen to favor sulfuric acid alkylation, and therefore, are generally conservative with respect to use for the quantitative risk comparison. This approach ensures that the analysis is more robust, provides margin for uncertainty, and further supports the conclusions of the quantitative risk comparison. The impact of simplifying assumptions identified in Table IV.9 which skew results in favor of MHF alkylation is discussed in Sections IV.B and V.B.

Although significant differences exist, from a QRA perspective, sulfuric acid and HF alkylation units have much in common. Given the similarity between the two processes for the areas of potential uncertainty identified in Section IV.E.1, the SA feels that a detailed uncertainty analysis would not provide any additional basis for decision-making in support of the acceptance criteria identified in Section II.B. See also the discussion in the Executive Summary.

There are no additional recommendations which precipitate from this review of potential uncertainties and simplifying assumptions.

IV.F TRANSPORTATION AND REGENERATION RISKS

IV.F.1 Importance to QRA/Phenomenology Review

It is generally recognized that a potentially significant portion of alkylation unit risk is associated with transportation and regeneration. Transportation of AHF clearly has significant potential risks, should a release event occur. However, proponents of HF alkylation often cite the quantities of sulfuric acid needed to maintain the alkylation process (a factor of 280 greater than HF, Reference 509.01) as a potentially significant contributor to environmental and health risk. The basis for these additional potential risks associated with sulfuric acid catalyst usage is increased transportation requirements and the additional processing required for regeneration. Increased transportation requirements for the sulfuric acid catalyst may also impact traffic volume, the quality of life for some citizens, and the need for TFD's and other emergency response agency capabilities.

Thus, modeling transportation and regeneration risks would complete the characterization of the comparative risks associated with MHF and sulfuric acid alkylation. Manufacturing risks (i.e., production of HF or sulfuric acid) are not within the scope of the evaluations performed for the Consent Decree.

As identified in Section IV.F.6, the introduction of the additive prior to transportation offers a significant improvement in risk compared to both the current transport of AHF and transport of sulfuric acid to the Torrance Refinery (primarily due to the decreased frequency of transport.

IV.F.2 Key References Reviewed by SA

- 20
- 30
- 31
- 508.00
- 509.01
- 512.03
- 512.04

IV.F.3 Key Criteria Referenced

- II.I

IV.F.4 Review Activity/SA Calculation Summary

Some simple numerical verifications were performed and are identified below in the Results/Observations subsection. The SA's review focused on the above identified references which appropriately considered the site characteristics and transportation requirements of the Torrance Refinery.

IV.F.5 Results/Observations

The following are some of the salient results/observations:

- Section 3.3 of Reference 508.00, concluded that "the potential toxic plus collision risks of sulfuric acid transportation would be expected to exceed that of the MHF process." Therefore, transportation risks were conservatively not credited in the comparative risk assessment. In addition, sulfuric acid regeneration risks were *not* and MHF regeneration risks were included in the quantitative risk comparison. All of these simplifying assumptions are expected to skew QRA results in favor of sulfuric acid alkylation.
- Reference 512.04 calculated sulfuric acid and HF transportation risks (both collision and chemical) and identified the sulfuric acid transportation risk as being significantly higher. Reference 20 also calculated transportation risk estimates (based on frequency) which showed sulfuric acid risks to be "significantly higher".
- The key conclusions of the identified references are:
    - A fatality due to the truck collision itself (irrespective of truck contents) is identified as dominating risk for HF. This result would be expected to be even more robust for MHF which has a significantly lower vapor pressure than AHF. Although "risk aversion" considerations (i.e., heightened concerns due to the number of individuals affected) could more heavily weight MHF truck chemical hazards (compared to sulfuric acid transportation), "risk aversion" weightings are:
        - outside the scope of the Consent Decree, and
        - not as significant for MHF which has a much smaller inherent risk of toxic exposure than AHF.

  - The number of shipments, which is much larger for sulfuric acid, is the most relevant comparative risk parameter.
- For the collision risk calculation provided in Reference 512.03, a collision fatality rate of 3.5E-08/mile-vehicle was assumed. Reference 30 provides a slightly higher value for hazardous materials trucks. This further validates the value chosen by Mobil as appropriate and conservative. The straightforward collision risk assumptions, bases, and calculations in Reference 512.03 were also checked by the SA and deemed appropriate for the comparison of collision risks.
- Mobil's calculation conservatively assumed that the toxic risk of sulfuric acid during transport was negligible. Per the Quest experiments (Reference 10), there will be no airborne sulfuric acid particles generated following an accident during transportation.
- It was noted by the SA that, for transportation and storage, it is planned that the MHF will have an additive concentration { } sufficient to minimize vapor pressure, minimize the potential for flash atomization and aerosolization, and reduce the release rate of HF by 75%.
- The SA recognizes that the additive concentration necessary to achieve a 75% reduction in the airborne release rate for transportation and storage is less than that required to achieve the target 65% reduction for the process. The specific target operating concentrations reproduced in Figure V.1 provide the vehicle for achieving this 65% target. The operating specifications in Figure V.1 are also similar to the Composition 3 used for the release tests. Although this already acceptable comparative risk could be further reduced by increasing additive concentration during transportation and storage, comparative risk acceptance criteria have been met and any further reduction in risk would be optional.

IV.F.6 Conclusions

The introduction of the additive prior to transportation offers a significant improvement in risk compared to both the current transport of AHF and transport of sulfuric acid to the Torrance Refinery (primarily due to the decreased frequency of transport). The QRA has conservatively:

- included regeneration hazards as part of the MHF risk assessment
- not included the incremental risk of sulfuric acid regeneration
- not credited incremental transportation risks (favoring sulfuric acid alkylation)

Regarding transportation and regeneration risks, the SA can identify no additional requirements mandated as a result of using the modified HF catalyst. However, there is a necessary follow-up action:

- The modified HF catalyst will be significantly less volatile than AHF. Quality control of materials entering the Torrance Refinery will meet the criteria established for airborne release fractions. For the MHF catalyst, Mobil will be verifying the adequacy of its existing practices for quality control of materials used in the process (e.g., update of Procedure 5.3 of Reference 31) for the MHF catalyst.

The above task is important; however, the specific activity is either currently planned or included as part of existing refinery practices and procedures. Therefore, there are no additional recommendations beyond those actions already underway or planned by Mobil.

IV.G COMPARISON WITH OTHER PUBLISHED AND UNPUBLISHED RISK RESULTS

IV.G.1 Importance to QRA/Phenomenology Review

The specific approaches and level of detail for any QRA vary significantly with:

- techniques used
- individual analysts
- critical simplifying assumptions

However, these complexities and the results of the QRA typically distill to a relatively short (10-100) set of dominant sequences of events. When using a QRA to optimize design or operations by eliminating potential system weaknesses, improvements typically focus on these dominant events. For some QRAs, “importance” calculations are performed to identify dominant contributors (i.e., specific failures that have the most direct impact on the quantitative outcome).

Although each plant has unique design and operations features, there are many characteristics which are common to the main types of sulfuric acid and HF alkylation units. Comparison of results with other risk studies can identify potential discrepancies in the quantitative results and dominant contributors for the MHF Alkylation Unit and reference sulfuric acid alkylation unit QRAs.

Section IV.A reviews the identification of potential hazards and accident scenarios, focusing on:

- numerical risk results
- dominant sequences
- dominant contributors

and addresses:

- completeness
- consistency with other published results

IV.G.2 Key References Reviewed by SA

- 15
- 508.00
- 509.01
- 512.04

IV.G.3 Key Criteria Referenced

- II.J

IV.G.4 Review Activity/SA Calculation Summary

No specific SA calculations were required to evaluate this specific issue. The SA's review focused on the above identified references. Comparisons were made with results from select, published information regarding dominant sequences and contributors.

IV.G.5 Results/Observations

Tables IV.11 and IV.12 summarize dominant sequences or contributors from select risk assessment studies for HF and sulfuric acid alkylation units.

The following are some of the salient results/observations:

- Characteristics of previous alkylation unit risk assessments include:
  - ♦ Large airborne release fractions for sulfuric acid and HF were used.
  - ♦ Concentration endpoints and risk calculations were based on a determination of the potential for fatalities.
- Characteristics of the current alkylation unit quantitative risk comparison include:
  - ♦ Lower airborne release fractions for sulfuric acid were used based on an improved understanding of release characteristics (References 10 and 523.00).

- ♦ A lower airborne release fraction for HF was used, based on the use of the additive.
- ♦ Concentration endpoints and risk calculations were based on ERPG-3 dose limits.

- Given the decrease in expected airborne release fractions for both MHF (compared to AHF) and sulfuric acid, calculated values for risk would be expected to be correspondingly lower. Because of these improvements and the difference in endpoints for previous studies, comparison of the absolute risk values calculated from this study to previous studies offers few insights. Therefore, Tables IV.11 and IV.12 are most useful for comparing the dominant contributors to risk, and a comparison of quantitative results does not provide any useful conclusions.
- The dominant contributors identified by the Mobil Risk Assessment compare well to dominant risk contributors in other HF alkylation unit risk assessments; e.g., Reference 15 for Ultramar, "The types of releases found to represent the highest risk were rupture of acid settlers, serious leakage from settlers, and serious leakage as a result of fire or explosion." The impact of not explicitly modeling fires and explosions is discussed in Section IV.E.
- The resultant dominant sequences/contributors from the QRA were generally consistent with:
  - ♦ the SA's understanding of the design and operation of MHF and sulfuric acid alkylation systems
  - ♦ dominant sequences/contributors identified in other risk assessments (see also Tables IV.11 and IV.12)

TABLE IV.11

DOMINANT SEQUENCES/CONTRIBUTORS FROM RISK STUDIES

HYDROFLUORIC ACID ALKYLATION UNITS

	UOP MHF Alkylation Unit Quantitative Risk Comparison (Ref. 508.00)	**UOP HF Alkylation Unit (Ref. 509.01)**	**Phillips HF Alkylation Unit (Ref. 512.04) (excluding transportation)**
Dominant Sequences/ Contributors	• Circulating Pumps (24.3%) • Piping from Pumps to #1 Reactor (14.4%) • #1 Settler Pipe Spool (11.0%) • Acid Truck/Hose (7.8%) • Piping from Reaction to Regeneration (6.6%) • Acid Pump Suction Piping (5.9%) • Piping from #1 Settler to #2 Reactor (4.6%) • #1 Settler (4.5%) • Acid Storage Tank (4.4%) • Piping from Fractionation to Reaction (3.3%) • Circulating Pump Suction Piping (2.7%) • #2 Settler Pipe Spool (2.2%)	In order of contribution: • Holes of diameter 1-2" from the settlers, reactors, and connecting pipework • Major ruptures of the same equipment leading to the rapid loss of contents • Causes range from corrosion to external events such as fires and explosions	• Reaction Section (primarily acid coolers) (64%) • On-Site HF Acid Regeneration (primarily acid pump) (34%) • Hydrocarbon Feedstock Storage (2%) • Lower Contributors: Acid Unloading Operation, HF Storage, Fractionation

Quantitative Results	Using ERPG-3 Dose Endpoint:
	♦ Societal Risk Index (SRI) = 7.85E-3/yr
	♦ Societal Risk Points:
	  • < 1 exposure @ 1.0E-3/yr
	  • 6 exposures @ 1.0E-04/yr
	  • 180 exposures @ 1.0E-5/yr
	  • 475 exposures @ 1.0E-6/yr
	♦ Distance to ERPG-3 Dose Endpoint:
	  • 656 ft @ 1.0E-4/yr
	  • 4264 ft @ 1.0E-5/yr
	  • 6560 ft @ 1.0E-6/yr
			Distances for Individual Risk Contours:
			• site boundary @ 1.0E-4/yr
			• 5 miles @ 1.0E-8/yr

TABLE IV.12

DOMINANT SEQUENCES/CONTRIBUTORS FROM RISK STUDIES

SULFURIC ACID ALKYLATION UNITS

	Sulfuric Acid Alkylation Quantitative Risk Comparison (Reference 508.00):	**Reference 512.04 (excluding transportation):**
Dominant Sequences/ Contributors	• 25 mm, 100 mm, or 5 mm Leak from Reactor Mixer (35.7 + 9.5 + 2.8%) • 100 mm Leak, 25 mm Leak, or Rupture in Reactor #1, #2, or Pipe 2 (27.2+5.5+2.9%) • 5 mm Leak in Acid Wash Drum or Pipe AW1 (4.8%) • 100 mm Leak in Acid Downcomer (3.9%)	• Releases of Emulsive Mixtures from the Reaction Section • Hydrocarbon Feedstock Storage (small contribution)
Quantitative Results	Using ERPG-3 Dose Endpoint (and 4% airborne release fraction): ♦ Societal Risk Index (SRI) = .24/yr ♦ Societal Risk Points: • 55 exposures @ 1.0E-3/yr • 340 exposures @ 1.0E-04/yr • 1600 exposures @ 1.0E-5/yr • 1850 exposures @ 1.0E-6/yr ♦ Distance to ERPG-3 Dose Endpoint: • 3505 ft @ 1.0E-4/yr • 7349 ft @ 1.0E-5/yr • 9966 ft @ 1.0E-6/yr	Distances for Individual Risk Contours: • site boundary @ 1.0E-4/yr • 2 miles @ 1.08E-8/yr

IV.G.6 Conclusions

As stated above, although the main types of alkylation units have the majority of key characteristics in common, differences in unit design and operation do exist. With due consideration to these design and operations differences, as well as differences which could result from the scope of this QRA (i.e., a quantitative risk *comparison)* and advances in technology, the results of the quantitative risk comparison:

- are complete based on the SA's understanding of alkylation units
- correlate well to other risk assessment studies (see Tables IV.11 and IV.12)

There are no additional recommendations which precipitate from this comparison.

IV.H EMERGENCY RESPONSE

IV.H.1 Importance to QRA/Phenomenology Review

Even with the inherent safety improvements associated with the use of the proposed modified HF catalyst at the Torrance Refinery, the potential for an emergency still exists. In fact, the most likely emergencies involve hydrocarbons and are relatively independent of the catalyst used within the unit. To verify that Mobil successfully demonstrated that it met the comparative risk criteria specified by the Stipulation and Order, the SA reviewed assumptions regarding mitigation equipment, material characteristics, and emergency response timing to determine if:

- Requirements were met by the current emergency response program or additional needs accommodated by proposed improvements, and
- Emergency response to potential releases was appropriately modeled (if mitigation features were credited within the quantitative risk comparison)

For any refinery, effective emergency response can help insure that incidents do not propagate into more serious accidents. For a QRA, the modeling of accident progression is predicated on key assumptions regarding the training and abilities of the emergency responders, reflex time, available equipment and resources, and the general effectiveness of the emergency response program. Reflex time refers to the time interval between the initiation of an event and the initiation of emergency response.

IV.H.2 Key References Reviewed by SA

- 15
- 501.01
- 501.02
- 503.00
- 504.00
- 507.01
- 507.02
- 508.00

- 510.08

IV.H.3 Key Criteria Referenced

- II.A
- II.B
- II.D

IV.H.4 Review Activity/SA Calculation Summary

No specific SA calculations were required to evaluate this specific issue. The SA's review focused on the above identified references.

IV.H.5 Results/Observations

The following are some of the salient results/observations:

- The results of the QRA demonstrate that the "modified HF catalyst (including mitigation)" presents "no greater risk than a sulfuric acid alkylation plant producing a comparable amount of alkylate.
- No specific changes to the Torrance Refinery emergency response procedures have been identified by Mobil, as necessary.
- Mitigation features for the Torrance Refinery Alkylation Unit are comparable to those generally identified for refineries in Reference 15.
- The most important material characteristics for emergency response are: toxicity, flammability, reactivity (especially with water), quantity, volatility, decomposition and combustion products, and process conditions. Comparing MHF to AHF (References 15, 501.01, 501.02):
  - ♦ *Toxicity*: The additive is considered "essentially inert and devoid of physiological activity." Although handling precautions should be taken, data clearly indicates that the additive is significantly less toxic than HF. Neither the additive or HF is considered carcinogenic. It may be noted that Reference 521.00 concludes that "occupational exposure to strong-inorganic-acid mists containing sulfuric acid is *carcinogenic to*

humans...". In general, having an understanding of the Material Safety Data Sheet (MSDS) for the additive is the key additional need for the emergency responder. The emergency response to a catalyst or catalyst/ hydrocarbon release for the MHF conversion imposes no new practical requirements or toxicity issues for emergency responders.

- *Flammability*: HF is nonflammable; however, contact with metals can produce hydrogen gas. The flashpoint of the additive is 330° F, and it is not considered a significant flammability hazard.
- *Reactivity*: The heat of reaction with water for the additive is negligible and significantly less than HF. Water application is a recommended response agent for both chemicals.
- *Quantity*: There are no significant increases in stored quantities of catalyst for MHF.
- *Volatility*: MHF is significantly less volatile.
- *Decomposition and Combustion Products*: Under fire conditions, the additive may emit toxic fumes of carbon monoxide, carbon dioxide, and sulfur oxides.
- *Process Conditions*: The pressures and temperatures for the process are similar for MHF vs. AHF.

All of these differences between MHF and AHF are manifested as significant safety improvements (which also facilitate emergency response). The key safety improvements result from the lower volatility of the proposed modified HF catalyst compared to a standard AHF catalyst.

- Although one change in emergency response may be an increased need for spill cleanup due to the lower volatility of the modified HF catalyst, this would not be expected to significantly impact emergency response requirements. Compared to AHF, the increased need for spill cleanup for MHF may more closely resemble spill cleanup requirements for a sulfuric acid alkylation unit catalyst release event.
- For the above emergency response considerations, the number of Mobil emergency response personnel at the facility during different shifts (part of the SA's Evaluation of the Emergency Response Program) does not generate any new issues for MHF.
- Section IV.B addresses the mitigation system modeling for the QRA performed for the quantitative risk comparison.

IV.H.6 Conclusions

With respect to emergency response, use of the proposed modified HF catalyst:

- represents a significant improvement compared to the existing AHF catalyst
- would be expected to have emergency response requirements significantly less than those for the existing anhydrous HF catalyst and be similar to a sulfuric acid catalyst for some releases

The SA can identify no additional emergency response requirements mandated as a result of using the modified HF catalyst. However, there are several necessary follow-up actions:

- As part of the SA Project, the SA will be completing the previously identified Evaluation of the Emergency Response Program. This evaluation will also compare the spray and fire water capacities of the Torrance Refinery Alkylation Unit to applications at other U.S. refineries as well as address the adequacy of the number of emergency response personnel for various shifts.
- Mobil will be making additive MSDS accessible to refinery personnel and potential emergency responders as a normal part of its safety program implementation. As appropriate, TFD will be involved.
- As part of its existing training program, Mobil will train plant operations personnel and emergency responders in the use of any new mitigation systems planned for the Alkylation Unit. As appropriate, TFD will be involved.

The above tasks are important; however, these specific activities are either currently planned or included as part of existing refinery practices and procedures. Therefore, there are no additional recommendations beyond those actions already underway or planned by Mobil or the Safety Advisor.

V.A HF RELEASE RATES AND AEROSOL FORMATION

V.A.1 Importance to QRA/Phenomenology Review

The amount of aerosolization and the release rates are critical to both the phenomenology of HF releases and to the consequence modeling portion of the QRA. These characteristics have a direct impact on the risk to the public, on-site personnel and the environment.

Using existing Anhydrous Hydrogen Fluoride (AHF) alkylation technology, AHF can be present in the process at temperatures in excess of 100^{o}F and pressures in excess of 100 psig. In these circumstances, liquid HF released to the atmosphere will partly vaporize (20% being typical, see Reference 22). The remaining 80% will be broken into very fine particles by a process known as flash atomization. These particles will remain airborne as has been conclusively demonstrated in the "Goldfish" series of large scale AHF experiments (Reference 22).

If it can be proved that the new MHF technology significantly reduces or eliminates aerosolized HF (i.e. that any droplets produced fall to the ground), then there is immediate potential for a large reduction in the initial airborne mass flux of HF (the effective release rate to the atmosphere). The intent of the new MHF technology is to achieve this by mixing HF and an additive so that the resulting mixture has a vapor pressure that is never high enough to allow flash atomization to occur. In addition, the initial dilution of HF with additive also contributes to a reduction in the effective release rate of HF to the atmosphere.

V.A.2 Key References Reviewed by SA

- Reference 22 (Blewitt et al., 1987) "Goldfish" experiments.
- Reference 9 (Jersey et al., 1993)
- Reference 510.05 (Muralidhar et al., 1994)
- Reference 501.00 (Schatz et al., 1993)
- Reference 507.01 (Krambeck, 1994)
- Reference 507.02 (MRDC,1994)
- Reference 28 (Spicer and Havens, 1989)
- Reference 26 (Schotte, 1987)
- Reference 510.04 (Viewgraph Presentation, 11/7/94)
- Reference 520.00 (12/12/94 Response to questions from Safety Advisor)

V.A.3 Key Criteria Referenced

- II.K

V.A.4 Review Activity/SA Calculation Summary

No specific SA calculations were required to evaluate this issue. The SA's review focused on the above identified references.

V.A.5 Results/Observations

Mobil has approached this issue in a scientifically defensible manner using a parallel path of theory/model development and experimental work.

(1) Experimental Work

The experimental work was performed at the Quest Consultant's test site near Norman, OK (Reference 9). In these experiments, approximately 150 - 500 pounds of MHF were released per test through a circular orifice into a specially designed flow chamber. The amount of airborne HF and the amount of HF falling downward into collection pans to form a liquid pool (rainout) were measured. Tests were conducted for a range of compositions, temperatures, pressures and orifice sizes.

The attached Table V.1, taken from Reference 9, summarizes the experimental tests and shows airborne HF reduction percentages in the range 62.8% to nearly 100%, depending on the conditions of release. The "proprietary mitigation technologies" that are mentioned in the table are (1) water in the collection trays acting as a liquid pool evaporation suppressant and (2) physical obstructions (which lead to enhanced droplet fallout and smaller amounts of HF remaining airborne) together with evaporation suppression.

Comment - the definition of the airborne reduction potential used by Mobil is not the simplest that could be used, which would be as follows: the total mass of additive and AHF released is x lb of which y lb is HF ($y<x$). z lb of HF falls to the ground ($z<y$). The airborne reduction percentage is then $100z/y$. However, Mobil makes an allowance for the initial dilution of HF by the additive so that Mobil's definition of the airborne reduction percentage is $100\,(z+x-y)/x = 100\,(1-W_{HF}(1-C_{HF}))$ (the same formula as is in Reference 9) where W_{HF} is the weight fraction of HF in the release mix and C_{HF} is the fraction of the released HF that is collected as liquid rainout. Thus, the airborne release reduction is expressed as if the whole of the original release were AHF rather than a mixture of HF and additive, and is larger than just $100z/y$. However, this

somewhat counterintuitive definition does not affect any later results or conclusions and is consistent with the reduction definitions used in the QRA and dispersion modeling comparisons.

Comment - in subsequent atmospheric dispersion studies (Reference 507.02) and in the QRA, Mobil has used an airborne release reduction factor of 65%. As can be seen from Table V.1, this chosen value is at the low end of the range of experimental results. Mobil could have plausibly selected a higher value for the reduction percentage from the experimental results. Conservatively choosing this more limiting airborne release reduction factor provides more conservative results and makes the conclusions that the new technology reduces risk more robust and defensible.

The choice of a 65% reduction level is expected to facilitate the control of operating conditions in the alkylation unit reactor and settler while ensuring that this reduction factor will be the minimum achieved, should there be a release. This is illustrated by the attached Figure V.1, which was provided by Mobil on November 7 in a viewgraph presentation entitled "Airborne HF reduction for MHF Process" (Reference 510.04). Figure V.1 shows how the temperature can be varied as a function of AHF percentage in the MHF to maintain a constant 65% passive airborne reduction factor. (The assumptions used in deriving Figure V.1 are a release of MHF through a 2" orifice driven by a pressure of 225 psig and assuming a jet length of 45 feet before the jet strikes the ground.) The SA considers that it is acceptable for Mobil to consider the range of possible additive concentrations within the context of operating requirements.

Comment - a question arose as to why Quest did not perform any release tests in which MHF was mixed with hydrocarbons. This question is pertinent for two reasons. First, such a mixture corresponds to the actual conditions expected in certain parts of the alkylation unit, such as the reactor. Second, as is discussed in detail in Section V.B, the presence of hydrocarbons in the sulfuric acid case is a necessary condition for there being any airborne sulfuric acid at all, so it is pertinent to ask whether hydrocarbons can have a similar effect on the amount of HF that remains airborne.

Quest did not use hydrocarbons because, unlike in the sulfuric acid experiments (see below), the MHF experimental releases were confined to a closed system (Reference 9). There was therefore concern about the potential for confined vapor cloud explosions. Instead of hydrocarbons, a refrigerant (G-124) with similar flashing properties was used (References 510.02, 520.00).

The crux of the matter is that mixtures of MHF and hydrocarbons behave in very different ways from mixtures of sulfuric acid and hydrocarbons. In the sulfuric acid case, one possible explanation for the observed phenomenon is hydrocarbon flashing, atomizing sulfuric acid into droplets that are potentially small enough to remain airborne. In addition, the presence of surfactants in the sulfuric acid promotes the formation of small bubbles of acid surrounding hydrocarbon vapor, and these bubbles remain airborne. The collapse of these bubbles could potentially leave an airborne sulfuric acid mist. By contrast, it is known that the same surfactant phenomenon does not exist in HF/hydrocarbon mixtures, nor does it exist in the HF/hydrocarbon simulant mixture that was used in the experiments. The primary mechanism for the appearance of an airborne HF vapor phase is evaporation from large MHF droplets as they fall to the ground. Thus, the explicit use of hydrocarbons for the MHF release tests was not necessary.

Comment - It is also pertinent to consider whether, once the jet of MHF has fallen to the ground, there can be significant subsequent evaporation from the resultant pool. First, the pool has a lower concentration of HF than does the original jet (because some of the HF has evaporated as droplets fall to the ground) and it has also cooled (because of the same evaporation). Mobil has confirmed by direct calculation (Reference 520.00) that a typical value of the vapor pressure of MHF immediately upon release is 1100 mm Hg. After a path length of 45 feet, the vapor pressure upon hitting the ground is only 50 mm Hg. Therefore, the partial vapor pressure of HF over the pool is low and the rate of evaporation per unit area is small. Second, the surface area available for evaporation is much greater while the material is in trajectory because the surface area of the many small droplets far exceeds the area of the flat surface where the liquid impacts the ground. It is estimated that the difference in these areas is as large as a factor of 30. Third, looking at Table V.1, the airborne HF reduction percentages for the cases with water in the collection pans are not significantly different from those cases without water in the collection pans. If evaporation from the pool on the ground were a large component of the total airborne amount of HF, the existence of water in the collection pans would be expected to make a much larger difference.

(2) Release Model

Mobil has developed a two-phase release model (Reference 510.05) that is intended to provide the initial conditions and release for subsequent runs of atmospheric dispersion models such as DEGADIS (Reference 28). During the first phases of the release, a liquid MHF stream fragments into droplets. However, the process is not flash atomization but rather breakup due to the action of hydrodynamic forces that are generated by the difference in velocity between the stream and its surroundings. Such mechanical breakup leads to the formation of much larger droplets than does flash atomization and these droplets fall to the ground. As they are falling, HF evaporates from them. Mobil's model predicts the pathway of the liquid droplets and the amount of evaporation that occurs before the droplets hit the ground.

The evaporation model incorporates those features of HF/moist air interactions that have previously been demonstrated to be important in explaining the behavior of AHF in air, namely HF oligomerization (the tendency of AHF to form larger molecules such as $(HF)_2$ and $(HF)_6$) and the exothermic interaction of HF with water vapor, which can lead to the formation of small droplets of aqueous HF (Reference 26).

Figure V.2 (Reference 510.05) gives an example of how the model agrees with the large scale experiments described above. It is the judgment of the Safety Advisor that this demonstrates that the model adequately accounts for the physical phenomena that control the behavior of fragmenting liquid streams of MHF. Note that Figure V.2 also shows that some experiments were performed at 225 psig (experiments not reported in the paper presented to the AIChE (Reference 9) from which Table V.1 was taken). Figure V.2 therefore shows that the model is valid at the highest expected operating pressures of the MHF alkylation unit reactors and settlers, which are approximately 225 psig.

The Safety Advisor asked a number of questions to clarify whether there can be circumstances in which there could be flash atomization of MHF, leading to airborne particles that are so small that they will not fall to the ground. This question was prompted by information provided by Mobil that showed that at least one potential MHF composition has an atmospheric boiling point of about 88^{o}F and a vapor pressure of about 1,000 mm of mercury (about 1.3 atmospheres) at a plausible alkylation unit operating temperature of 105^{o}F.

Mobil responded by providing information on further experiments that have been performed at higher temperatures using MHF compositions that have boiling points that are less than 100^{o}F up to temperatures of 140^{o}F. The results are presented on Figure V.3 (Reference 507.01) and show that the model (which does not include flash atomization) adequately reproduces the experimental results - that is, it is not necessary to postulate flash atomization to account for the experimental observations.

The explanation for this phenomenon (Reference 507.01) is reproduced here because the absence of flash atomization is critical to the judgment that the use of MHF provides a substantial reduction in the risks associated with the operation of the alkylation unit at the Torrance refinery:

> "As the temperature of a pressurized liquid is increased above its boiling point, the fraction of material that falls to the ground as liquid rainout upon release to the atmosphere does not decrease abruptly. Rather, the liquid rainout decreases slowly with increasing temperature until a critical superheat (defined as the difference between the storage temperature and boiling point) is exceeded. Up to this temperature, the released jet hydrodynamically breaks into drops and flash vaporization of HF occurs from the surface of the drops. If the critical superheat is exceeded, the flashing of the released liquid creates sufficient vapor to cause the jet to disintegrate into very small droplets, a phenomenon referred to as flash atomization. In this regime, the liquid rainout decreases abruptly and much of the released material becomes airborne."
>
> "Experiments on pure liquids indicate that the critical superheat may be between 5 and 40K (9 and 72^{o}F) depending on the released material". In summary, the liquid capture or rainout is not strongly impacted by temperature associated with vapor pressures above atmospheric as long as the critical superheat is not exceeded."

In conclusion, although there are no data on the value of the critical superheat for MHF, the modeling and experiments summarized on Figure V.3 clearly show that, up to 140^{o}F, the critical superheat has not been exceeded (because the model reproduces the experimental data without needing to invoke flash atomization).

The Safety Advisor also asked about the justification for scaling up model predictions from the largest experimental cases (500 lb of MHF released through a 3/4" orifice) to the larger releases that are hypothetically possible in an alkylation unit (e.g. many tons released through a 2" orifice or larger). Mobil responded by providing Figure V.4, which shows the airborne HF reduction percentage for (1) small scale laboratory tests; (2) the large scale experiments at the Quest Consultant's facility and (3) the predictions of the model. The experiments in Figure V.4 span a range of orifice diameters from 0.025" to 0.75", a factor of 30 on diameter and a factor of at least 900 on release rate (which is proportional to orifice diameter). Further extrapolation to an orifice diameter of 2" represents only an increase of a factor of 2.7 in diameter or about 7 in release rate. The demonstration that the model satisfactorily accounts for a factor of 900 in release rate gives confidence that it can also adequately represent the further extrapolation by a factor of 7 in release rate.

Finally, it should be noted that the model is sensitive to path length (i.e., the distance that a released jet of MHF travels before it impinges onto the ground). Therefore, the model is able to distinguish between impeded and unimpeded releases and also between releases from different heights. For the QRA, Mobil assumed a path length of 45', which is conservative for the most critical risk contributors such as releases from the acid circulation pump at ground level.

V.A.6 Conclusions

Mobil has performed experimental work and model development that is sound and scientifically defensible and can be used as the basis for the calculation of meaningful release rates and airborne HF fractions. The new aerosol model does an excellent job of reproducing the experimental data. The assumption that a 65% reduction in the airborne HF mass flux can be achieved using the proposed relationships between temperature and composition as shown in Figure V.1 is both defensible and conservative.

Test No.	Release Composition	P (psig)	T (F)	Orfice (inch.)	Ambient T (F)	Rel. hum.	% Airborne HF reduction	HF MB Closure %	Additive MB Closure %
16	Composition 1	50	90	0.125	80.8	80	92.1	93.7	85.9
17	Composition 1	140	90	0.25	84.0	83	92.0	96.7	95.4
18	Composition 1	140	55	0.25	85.2	65	93.0	98.0	99.7
19	Composition 2	50	90	0.125	86.0	66	77.5	88.7	104.8
20	Composition 2	50	90	0.25	92.1	60	85.6	93.4	88.3
21	Composition 2	140	90	0.25	87.5	68	79.7	101.4	95.2
22	Composition 2	50	90	0.5	94.9	56	87.0	97.6	94.8
23+	Composition 2	50	90	0.5	91.0	57	90.8	-	-
24	Composition 3	50	90	0.25	82.4	46	72.3	96.3	101.0
25	Composition 3	140	90	0.25	76.5	57	62.8	95.9	101.9
26+	Composition 3	140	80	0.25	88.8	44	66.8	104.5	108.9
27+	Composition 3	50	77	0.125	86.7	53	73.6	98.9	157.9
28	Composition 3	140	78	0.5	84.1	59	67.8	96.8	117.2
29	Composition 3	100	88	0.25	89.0	48	65.2	98.3	101.4
30	Composition 2	140	110	0.5	86.0	52	82.0	93.8	94.2
31	Composition 2	100	110	0.5	89.6	42	84.5	88.3	107.6
32	Composition 2	50	90	0.75	92.0	39	89.8	97.8	105.3
33	Composition 3	140	93	0.5	80.7	69	68.0	101.0	91.7
34	Composition 2	140	108	0.5	83.8	73	81.4	104.5	90.5
35 *	Composition 2	50	90	0.25	88.4	58	99+	101.2	82.6
36 *	Composition 2	140	110	0.75	81.0	70	98.3	105.6	99.3
37 *	Composition 3	140	90	0.75	87.5	59	94.1	101.5	107.5
38 *	Composition 3	140	90	0.75	83.2	67	89.5	100.7	106.0

\+ Tests with proprietary mitigation technology 1

* Tests with proprietary mitigation technology 2

Note :- Tests 1 - 15 are shakedown tests

TABLE V.1

MHF RELEASE EXPERIMENTAL TEST SUMMARY

{FIGURE V.1}

MHF Percentage as a Function of Temperature

to Maintain a 65% Passive Airborne Reduction Factor

{FIGURE V.2}

Measured vs. Predicted HF Capture

{FIGURE V.3}

Effect of Temperature on Airborne HF Reduction

{FIGURE V.4}

Predicted vs. Measured HF Airborne Reduction

V.B DISPERSION MODEL EVALUATION

V.B.1 Importance to QRA/Phenomenology Review

Clearly, the atmospheric dispersion modeling is critical in making judgments about risk. Quantitative risk is a function of both the frequency of occurrence of accidents and the magnitude of the consequences. It is the atmospheric dispersion modeling that provides an estimate of those magnitudes considering factors such as the weather conditions and the wind direction. In addition, the dispersion modeling enables estimates to be made of concentrations and doses at fencelines or at sensitive populations. The accuracy and adequacy of the atmospheric dispersion modeling affects both the phenomenology review and the quantitative risk comparison.

V.B.2 Key References Reviewed by SA

- Reference 507.02 (MRDC, 1994)
- Reference 28 (Spicer and Havens, 1989)
- Reference 26 (Schotte, 1987)
- Reference 512.03 (Mobil Oil Corporation, 1994)
- Reference 27 (SCAQMD, 1991)
- Reference 20 (PLG, 1990)
- Reference 23 (ICHMAP, 1989)
- Reference 511.03 (Quest, 1992a)
- Reference 21 (AIHA, 1990)
- Reference 507.01 (Krambeck, 1994a)
- Reference 513.01 (Krambeck, 1994b)
- Reference 5 (CCPS, 1989)
- Reference 25 (PERF, 1992)
- Reference 508.00 (The Risk Assessment)
- Reference 7 (DNV Technica, 1994)
- Reference 6 (DNV Technica, 1993)
- Reference 8 (Hanna et al., 1991)
- Reference 523.00 (Quest Consultants, 1994)

V.B.3 Key Criteria Referenced

- II.K
- II.L
- II.M

V.B.4 Review Activity/SA Calculation Summary

Independent runs of different atmospheric dispersion models were performed as a check. In addition, the SA reviewed the references cited above. Discussions were also held with Quest consultants concerning the potential magnitude of airborne releases of sulfuric acid.

V.B.5 Results/Observations

Mobil has performed a stand-alone comparison of the consequences of equivalent large scale releases of MHF and sulfuric acid from the settlers in alkylation units (Reference 507.02). In addition, Mobil has performed dispersion calculations as part of a quantitative risk comparison of an MHF alkylation unit and a comparable sulfuric acid alkylation unit (Reference 508.00). These two studies are reviewed separately below.

(1) Single Event Modeling of MHF and Sulfuric Acid Releases Using the SCAQMD Rule 1410 Methodology (Reference 507.02)

a. *Choice of Model*

The model selected for use by Mobil was DEGADIS (Reference 28). This is a well established, public domain model that is available on the Environmental Protection Agency's Electronic Bulletin Board. The principal reason why Mobil selected this model is that it is the one specified by the South Coast Air Quality Management District's Rule 1410. Other models could have been selected, such as the HGSYSTEM or SLAB models that have been shown to compare well with large scale experimental data on HF (the “Goldfish" experiments). Mobil considers that the choice of a model is not particularly critical because the purpose of the work was to make comparisons between the two alkylation catalysts and not to produce absolute values of the predicted airborne concentrations or doses for comparison with a standard.

One of the key criteria for the choice of a dispersion model is whether it can accept the source term. DEGADIS allows the user to choose between three source terms: (1) a puff release; (2) a low momentum release at ground level such as from an evaporating pool and (3) a vertically oriented jet. The release in question is a horizontal jet with substantial initial horizontal momentum so, therefore, it would appear that DEGADIS is not the best model. Mobil recognizes this and gives qualitative reasons why neglecting these initial momentum effects does not matter when predicting the concentrations and doses at an effective fenceline distance of 400 meters, (Reference 507.2). Nevertheless, the Safety Advisor recommended using SLAB, which does allow the user to choose a horizontal jet. Mobil performed follow-up SLAB calculations (Reference 513.01).

The SA also considered whether the chosen dispersion models are suitable for use with plumes or puffs that contain suspended liquid droplets -- for example, a sulfuric acid mist. The answer is that they are suitable. For example, both SLAB and DEGADIS have been used to simulate the AHF "Goldfish" experiments (Reference 39). The initial plume in these experiments contained about 80% liquid droplets (Reference 22).

Regarding the use of these models (and SAFETI/PHAST) for plumes that contain suspended sulfuric acid as fine liquid droplets or mist, the only question that has to be asked is whether the suspended droplets are large enough to fall out of the plume under the influence of gravity. In the text below, there is an extended discussion about how much sulfuric acid is expected to remain airborne beyond the first few hundred feet (2.8 - 3.0%). The experimental results upon which this observation is based (Reference 25) give relatively little information about the particle size distribution. However, in some of the experimental runs, flat glass squares were placed on 25-foot centers over a 100' by 100' area downwind of the capture pans. At the end of the runs, the plates were observed and sometimes photographed. The photographs were used to determine the quantity and size of drops on the plates. After one of the runs, careful analysis of the glass plates showed that the mass mean particle diameter of the droplets ranged from 32 to 65 microns. The total mass deposited on the plates represented only a small fraction of the material not collected in the capture plans. From this, it is reasonable to deduce that a) most all of the sulfuric acid not collected in the capture pans remained airborne beyond the glass plates (i.e., at least 175 feet downwind), and b) 32 to 65 microns represents an upper bound on the mass mean diameter of any liquid droplets that remain airborne.

In order to determine whether such droplets will remain airborne or will fall out of the cloud within a further short distance, it is pertinent to discuss the deposition velocity. Figure V.5 is a summary of a comprehensive review of deposition velocities (Reference 41). Figure V.5 contains the particle density (~ 1.8 for sulfuric acid, with unity corresponding to water). As can be seen, for high roughness lengths of greater than 10 cm (as is the case at the Torrance site), gravitational settling ceases to be the dominant component of the dry deposition velocity at a diameter of several tens of microns. For example, at a roughness length of 10 cm (less than that at Torrance) and a density of about unity, the deposition velocity is about one cm/sec.

Deposition velocities of this order are well within the range that can be accepted by atmospheric dispersion models that basically ignore the gravitational settling of the particulate matter that is contained within the plume. For example, many nuclear QRAs have been carried out in which the Gaussian model has been used with dry deposition velocities of the order of one cm/sec (Reference 52). As noted above, it is reasonable to assume that the remaining airborne sulfuric acid droplets have diameters of 30 microns or less and would have deposition velocities of the order of one cm/sec.

Note that hydrogen fluoride is an extremely reactive vapor. Hanna and Hosker (Reference 43) show that a chemically active gas is likely to have dry deposition velocities in the range of 0.5 to 3 cm/sec, of the same order of magnitude as that deduced above for small sulfuric acid droplets. Therefore, neglecting dry deposition in the MHF and sulfuric acid QRAs should introduce similar conservatisms into both sets of calculations.

b. *Source Term*

<u>MHF Release</u>

For the modified HF catalyst release, Mobil has selected a hole of 2" diameter in the acid settler of the alkylation unit (Reference 507.02). The initial release rate of MHF out of this orifice is 63.7 kg/s as predicted by Bernoulli's formula (Reference 5). The SA performed a hand calculation that confirms this value. As discussed above in Section V.A, 65% of this falls to the ground, leaving only 22.3 kg/s of HF airborne. Mobil assumes that 3,000 gpm of water sprays becomes available after 1 minute and 6,000 gpm after 2 minutes. The Acid Evacuation System is also assumed to be activated after 2 minutes. This would lead to a reduction in driving pressure that would somewhat reduce the release rate. In addition, based on previous experiments on the effectiveness of water sprays (Reference 23), Mobil assumed that spray efficiency would be 32% between minute 1 and minute 2 and 64% thereafter. Based on the two minute activation assumption, after 287 seconds, the AES will have removed practically all of the MHF and no more will be released.

Other than questions about activation timing, which are addressed in Section IV.B, the SA feels that the above are valid assumptions. However as is discussed below, Mobil also performed analyses assuming that none of these mitigation systems work, and these analyses demonstrate an adequate comparison with comparable sulfuric acid releases. Based on this demonstration, along with the results of the mitigation system sensitivity study summarized in Table IV.7, the details of the timing and of the quantity of water available and of the effectiveness of the sprays are not critical to conclusions about the relative risks of sulfuric acid and MHF alkylation.

The Safety Advisor asked for the basis for the assumption that the water sprays would be as effective on MHF releases as it was on the AHF releases that were studied during the Industry Cooperative HF Mitigation/Assessment Program (ICHMAP). The response was provided in Reference 507.07. In principle, the large scale experiments carried out by Quest Consultants show that virtually all of the additive drops out of a pressurized MHF release so that only HF is left airborne. There is no reason to doubt that water sprays would act any differently on this HF than was demonstrated to be the case by ICHMAP. In addition, Quest Consultants installed water sprays at the end of the experimental chamber. The spray configuration was similar to that used in the ICHMAP experiments. Therefore, it was possible to estimate the efficiency of water sprays during the Quest tests. The results are summarized on Figure V.6, which also displays the ICHMAP data. As can be seen, the Quest results are consistent with, or even perhaps marginally better than, the ICHMAP results.

Finally, one result of the source term analysis is that Mobil predicts that the initial density of the HF vapor cloud that is used as input to the DEGADIS model is 1.4 kg/m^3. One of the tasks of the SA is to determine whether Mobil "...has demonstrated to the satisfaction of the Safety Advisor that the catalyst as modified would not form a dense vapor cloud upon release." However, the Consent Decree does not give a criterion for determining whether a vapor cloud is dense or not. For example, a density of 1.4 kg/m^3 is significantly less than the density of AHF vapor/droplet mixtures, such as those observed in the "Goldfish" experiments, in which initial densities can exceed 10 kg/m^3. From the above perspective, Mobil has achieved a considerable reduction in the density of the initial airborne cloud and it could be argued that the spirit of the Consent Decree has been met.

From a different perspective, the density of air at about 70^{0}F is about 1.2 kg/m^3. When input into heavy vapor dispersion models such as DEGADIS, SLAB, or PHAST, such a density is sufficient to ensure that the phenomena characteristic of heavy vapor dispersion will be predicted by the computer programs. In this sense, the vapor cloud is still denser than air.

The implication of this is that the letter of one of the requirements of the Consent Decree has not been met, namely that Mobil "... has demonstrated to the satisfaction of the Safety Advisor that the catalyst as modified would not form a dense vapor cloud upon release." For an additional perspective, as discussed below, a sulfuric acid release would have an initial density of 1.3 kg/m^3, which is also denser than air. Therefore, it does not appear to the SA that the fact that the vapor cloud is initially denser than air is in itself a reason why the safety impact would be significantly larger than if the release had the same density as air, or a reason that would tend to make the results of HF dispersion analyses less favorable relative to the results of comparable sulfuric acid analyses.

Sulfuric Acid

A 2" leak from the bottom of a sulfuric acid settler was used as a near worst-case scenario for comparison with the above described MHF release. The basic data in support of this scenario was taken from Reference 20, which was performed on behalf of SCAQMD, with the exception of airborne release fractions. For SCAQMD, PLG assumed that 20-50% of the sulfuric acid released from the settler would become and remain airborne. Recent experiments sponsored by the Petroleum Environmental Resource Forum (PERF; Quest, Reference 511.04) have shown that this airborne percentage will be much smaller than 20%. Mobil has performed the single event analyses assuming airborne percentages in the range 4-7%. The predicted airborne sulfuric acid mass fluxes are then in the range 1.89-3.31 kg/s for 35 minutes (inventory limited) or 15 minutes (some unspecified action is assumed to stop the release).

The prediction that as much as 4-7% of the sulfuric acid would remain airborne has a direct impact on the results presented below and their use for the phenomenological and quantitative risk comparison. Sulfuric acid, like the MHF, has a very low vapor pressure at typical alkylation unit operating temperatures and would intuitively be expected to fall out of liquid jets in the same way, leading to very small source terms and predictions of very small airborne concentrations from the dispersion model. Indeed, the PERF experiments show that, **for pure sulfuric acid, no aerosol is formed or becomes airborne**. This means that there will be no aerosol source term from the sulfuric acid storage vessel or if an accident should occur during transportation.

It is only if sulfuric acid is mixed with hydrocarbons, as within a sulfuric acid alkylation unit, that sulfuric acid can become and remain airborne. The Quest sulfuric acid experiments demonstrate convincingly that this phenomenon does occur.

The Safety Advisor questioned whether the 4%-7% range chosen by Mobil for the single event modeling is a valid interpretation of the results of the experiments. Figure V.7 is taken from the Quest summary that was presented at the NPRA conference in March, 1994 (Johnson, 1994; 511.03). Figure V.7 shows that the majority of the results lie in the recovery range 96-100% (airborne fraction 0-4%). The average is 97.6% (2.4% airborne). Note that Quest established that there is a systematic experimental bias of 0.6% so that the average is in fact about 3% airborne.

There is one result on Figure V.7 that is at 92.7% recovery (T34 -7.3% airborne). However, the original Quest report (Reference 511.03) states that "the validity of the (92.7) percent capture is suspect because there was significant overspray beyond the end and sides of the capture system." It appears to the SA that there is a case to be made that the best estimate (i.e., data point average) release is about 3% airborne and that the upper bound may be approximately 5% (note that there several data points at about 5%). The SA requested Quest to provide its own independent assessment of what would be the best estimate airborne release fraction for sulfuric acid, based on the experimental evidence. Quest provided that assessment (in the range of 2.8 to 3.0% of the released acid) in Reference 523.00, which states:

> “while an argument may be made that some of the uncaptured acid would fall to the ground within a short distance of the capture equipment, there is no experimental evidence to support this conclusion. The acid deposited on the glass plate array (see below) would change the results an average of about 0.1 percentage points. Any factor applied to reduce the value of 2.8 to 3.0 percent airborne material could not be supported by the data obtained in our experiments.”

The strongest support for the continuation of airborne sulfuric acid beyond the Quest site boundary was that there is little evidence of deposition beyond the end of the collection pans into which the sulfuric acid fell. During several runs, flat glass squares were placed on 25 foot centers over a 100’ X 100’ area downwind of the collection pans. The total mass of sulfuric acid deposited on the plates was measured after each experiment. Extrapolating the measurements to the 100’ X 100’ area showed that the total mass deposited represented “only a small portion of the material not collected in the capture pans.” (Reference 25). This was further reinforced by Reference 523.00, which states, “The acid deposited on the glass plate array would change the results an average of about 0.1 percentage points.”

It is also pertinent to note that wet pH strips placed at a distance of 300' evidenced a uniform color change, and indicate that sulfuric acid, or an acid cloud, was still airborne at this distance (Reference 25).

In addition, because there is no evidence of any dependence on any of the experimental variables, it is reasonable to assume that the observed variability in the experimental results is the result of random experimental error. In that case, it is possible to establish a statistical confidence interval around the best estimate of the mean. This can be done using standard statistical formulae such as those described in Perry's Chemical Engineer's Handbook (5th Edition), p. 2-66. The 90% confidence intervals for the best estimate are 2.4 - 3.2% with a mean of 2.8% (excluding the run mentioned above where there appeared to be considerable splashing outside the collection pans). That is, it is possible to establish a narrow range on the best estimate such that sensitivity studies to the extremes of that range would not be expected to greatly affect the magnitude of the risk results or of the single event dispersion analyses.

Note that the SA also looked at the results on Figure V.7 in the context of orifice size, temperature and pressure and found no correlation with any of these variables (within the ranges considered in the experiments). Therefore, the SA concurs with Mobil's judgment that the same release fraction should be used for all potential conditions of release from the sulfuric acid alkylation unit reactors or settlers.

One other important assumption that Mobil has made in the QRA and the single event modeling is that there are no water sprays to mitigate the sulfuric acid release because "it would be expected that water would not be very effective in mitigating a sulfuric acid leak, since it was found by the ICHMAP study that the primary mechanism for the removal of HF by water sprays was the water-HF vapor interaction. Since there would be little or no sulfuric acid vapor associated with a sulfuric acid leak , it would not be expected that water sprays would be particularly effective." Note that Quest experiments on sulfuric acid aerosolization do not contain information on the effectiveness of water sprays, unlike the experiments on MHF. However, since existing commercial sulfuric acid alkylation units do not have water deluge systems, the SA considers that the assumption that there are no such sprays in the sulfuric acid modeling is a valid one. See Section IV.E for further comments.

Note also that, with this near worst-case sulfuric acid scenario, the initial density used by Mobil as input to DEGADIS is 1.3 kg/m^3, which is also denser than the surrounding atmosphere. To the extent that being denser than air is perceived (rightly or wrongly) to be a contributor towards greater risk (which appears to be implied by the fact that, for HF, the initial density is a prominent matter of concern in the Consent Decree), the sulfuric acid alkylation scenario has similar characteristics to those of the MHF alkylation scenario.

c. *Health Effects*

Mobil chose to use a comparison of HF and sulfuric acid Emergency Response Planning Guidelines (ERPGs), which have been promulgated by the American Industrial Hygiene Association. The basic assumption is that the dose, expressed in mg/m^3-min., is a suitable basis for comparison, irrespective of the exposure time, because the ERPGs are expressed as a dose in mg/m^3-min. The validity of this approach is discussed in Section V.E.

d. *Results of the Single Event Modeling*

(A) <u>Review of Results of Analyses Performed by Mobil</u>

Mobil performed a worst-case analysis assuming Stability Category F and windspeed 1 m/s. For the sulfuric acid releases discussed below, Mobil performed analyses with 4% or 7% airborne release fractions, which accounts for the range in Tables V.2 and V.3. For a discussion of the use of the best estimate 2.8% case, see Section d(B) below. The results are as follows, where the fenceline is assumed to be at a distance of 400m - the distance to 190th street to the north of the unit:

TABLE V.2

WORST CASE FENCELINE DOSE RATIO FOR 2-INCH SETTLER LEAK

	Sulfuric Acid	
MHF	Inventory Limited	15-Minute Limited
6.4	19.75 - 29.48	8.57 - 12.07

(Note - the Safety Advisor has converted the results given by Mobil in ppmv-min. in MRDC (1994) to a ratio between the predicted results and the ERPG-3.) Based on the above results, the consequences of a 2" leak in the MHF acid settler are comparable to or less than those for a 2" leak in the sulfuric acid settler.

Although this is not strictly a risk calculation, the Safety Advisor believes that it is worthwhile to perform these single event calculations because they demonstrate clearly that the consequences of a major leak in the MHF acid settler are comparable to or less than the consequences of a similar leak in the sulfuric acid settler.

Note that the predicted frequency of occurrence of a 2" leak in an MHF settler is less than in a sulfuric acid settler because a sulfuric acid unit contains more vessels and piping than does a comparable MHF unit (Reference 508.00). Therefore, if the consequences are comparable, the MHF risk will be smaller than the sulfuric acid risk for this case.

The meetings held at Paulsboro on November 7 and 8 discussed whether the times given above (1 minute for 3,000 gpm from the deluge system and 2 minutes for 6,000 gpm plus activation of the AES) are defensible. The SA asked Mobil to perform single event calculations assuming that there is no active mitigation of the MHF release. The results of this analysis were provided in Ref. 511.02, using DEGADIS. These results show that the predicted HF dose ratio at 400 meters for MHF increases to about 18.3. Conservatively comparing this result with the results above for the inventory limited sulfuric acid case, 19.75 - 29.48, shows that the MHF results are still within the range for sulfuric acid even with no mitigation being assumed.

As noted above, the Safety Advisor also asked Mobil to repeat the runs using SLAB rather than DEGADIS, because SLAB has an explicit horizontal jet option, whereas DEGADIS does not. These results show that, for the fully mitigated MHF case, SLAB predicts an MHF dose ratio of 6.64, to be compared with 6.4 from the DEGADIS runs in Table V.2. For the sulfuric acid case terminated after 15 minutes, SLAB predicts a sulfuric acid dose ratio at 190th street in the range 13.63 - 24.07. This compares with the DEGADIS prediction in the range 8.57 - 12.07 from Table V.2. Thus, for MHF, the DEGADIS and SLAB results are very close, whereas for sulfuric acid the SLAB results are a factor of 1.5-2 higher than the DEGADIS results. This kind of superficially odd result is not unusual when using heavy vapor dispersion models in which there are many subtle non-linear effects. The difference is within the range of uncertainty to be expected when applying such models.

The above results are based on a fenceline at a distance of 400 m, which is the distance to the nearest road/housing to the north of the facility. However, Crenshaw Boulevard runs directly through the site in a north-south direction and, at its closest point, is only about 135 m west of the settlers. The Safety Advisor recommended that a single event calculation be performed for this distance and using SLAB, because DEGADIS may not be valid for horizontal jet releases at such close distances. The results of this analysis show that the predicted HF dose ratio at Crenshaw Boulevard is 23.63, while that for sulfuric acid is in the range 34.67 - 60.67. These results again show that the consequences of the single event MHF release are comparable to or less than those of the comparable single event sulfuric acid release.

For the convenience of the reader, all of the above results are summarized in Table V.3.

TABLE V.3

SUMMARY OF RESULTS OF DOSE RATIO CALCULATIONS FOR 2-INCH SETTLER LEAK

			Sulfuric Acid	
		MHF	Inventory Limited	15-Minute Limited
(a)	DEGADIS, 400 m, mitigated MHF release	6.4	19.76 - 29.48	8.57 - 12.07
(b)	DEGADIS, 400 m, unmitigated MHF release	18.33	19.76 - 29.48	8.57 - 12.07
(c)	SLAB, 400 m, mitigated MHF release	6.64	-	14.19 - 24.07
(d)	SLAB, 135 m, mitigated MHF release	23.63	-	34.67 - 60.67

The SA carried out some independent confirmatory runs with SACRUNCH (Reference 519.00). These runs relate to line (a) in the above table. For the mitigated MHF release, the SACRUNCH dose ratio results lie in the range of 3.92 - 26.0. The range corresponds to the difference between a fully urban or fully rural representation of the turbulence in the atmosphere at the site, and predictions towards the lower end of the range are appropriate for the Torrance site. This range compares to Mobil's 6.4. For a 4%, inventory limited sulfuric acid release fraction, the SACRUNCH dose ratio results span the range 6.32 - 61.1. This is to be compared to Mobil's prediction of 19.76.

d (B) Use of Best Estimate Sulfuric Acid Release Fractions of 2.8%

As noted above, the best estimate release fraction, as confirmed by Quest, is 2.8% - 3%, with a fairly narrow range of ± 0.4% on the 2.8% estimate. This confirmation from Quest was obtained very close to the court-ordered deadline of December 31, 1994. Rather than require Mobil to perform additional runs of DEGADIS and/or SLAB, the SA ratioed some of the results in the above table to gain an approximate understanding of how the reduction from 4% to 2.8% might affect the conclusions of the study. These extrapolations are summarized in Table IV.5.

For example, comparing an unmitigated MHF release with an "unmitigated" (i.e., inventory limited) sulfuric acid release with a 2.8% airborne release fraction gives respective dose ratios of 18.3 and 13.8, respectively. Comparing a mitigated MHF release with a "mitigated" (i.e., 15-minute limited) sulfuric acid release gives dose ratios of 6.4 (DEGADIS) and 6.6 (SLAB) for MHF and 6.0 (DEGADIS) or 9.5 (SLAB) for sulfuric acid.

In summary, the above results illustrate that, within the uncertainties that exist on atmospheric dispersion modeling results, the consequences of the worst case MHF release are comparable to those of the equivalent sulfuric acid release.

Comment - A comparison was attempted between the dispersion model results for single MHF release cases and AHF releases evaluated in the RMPP (Reference 36). The single MHF release scenarios which are identified as dominating risk involve much larger rupture sizes than do the RMPP release cases (5mm cross-section, except for storage/loading releases which were of short duration). Thus, a direct comparison is not practical.

(2) Modified Hydrofluoric Acid and Sulfuric Acid Alkylation Risk Assessments

The risk assessment models used DNV Technica's integrated computer risk program SAFETI (Reference 7). The dispersion models in SAFETI are the same as those in DNV Technica's PHAST (Reference 8). PHAST was part of an extensive comparative study (Reference 8) that showed that it reproduces field data on ammonia and hydrogen fluoride with an accuracy comparable to that of many other models, including DEGADIS and SLAB. The SAFETI dispersion models do not contain HF/moist air thermodynamics. A new version of PHAST (4.2) does contain this thermodynamics and, according to Mobil, gives lower atmospheric concentrations for identical releases, so that the model used for the MHF QRA is conservative.

From the perspective of the Safety Advisor, the user of SAFETI/PHAST seems to have to accept several artificialities in the source term in order to get it to simulate the releases of MHF. For example, the aerosol model discussed above in Section V.A shows that all of the additive rains out and what is left is largely HF vapor with some very fine droplets of HF/water. It is this material that remains airborne that is assumed to be the source term for subsequent atmospheric dispersion. However, the initial source term for SAFETI/PHAST is sometimes almost entirely liquid. A good example of this is the input data to the dispersion model that is described on page 1 of Section 3.2 of the Appendix to Mobil's QRA (Reference 508.00). This PHAST case models a 4" leak in acid circulating PUMP75, with water sprays being activated after 30 seconds. According to the data given on p.1 of Section 3.2, the release is initially 95% liquid with drop diameter $7.08x10^{-8}$ m = 0.07 microns. These droplets do not fall out, but evaporate - in the example given, after the plume has traveled more than 120 m. These droplets are purely artificial - Mobil's aerosol model does not require them and they cannot represent HF/water droplets because SAFETI/PHAST does not have HF/moist air thermodynamics. Mobil told the Safety Advisor that this initial artificiality has no effect at concentration levels as low as the ERPGs. After detailed technical questioning, the SA concurs with this judgment. Similar comments apply to the sulfuric acid SAFETI/PHAST modeling.

Apart from the choice of the dispersion model SAFETI/PHAST, a significant driver of the results is the release durations assumed for the sulfuric acid release scenarios. For example, Scenario 8T, which contributes 36% of the total risk, has a release duration of one hour (see QRA Risk Assessment Appendix 4.4). Scenario 8T consists of a 25 mm leak in the mechanical seal of the mixers in reactors 1 or 2. In the sulfuric acid alkylation unit used as a model by Mobil, the reactors cannot be isolated from the settlers (see Figure 10 of the QRA for a schematic which is consistent with the sulfuric acid unit that Mobil operates at Beamont, Texas) so that a long duration of release is inevitable. The SA recognizes that it would be possible to design an alkylation unit so that shorter isolation times are possible for some of the sulfuric acid scenarios. However, the SA judges that it is reasonable to use sulfuric acid units that are typical of those being built and in actual operation in the USA rather than some hypothetical design which is not consistent with a contemporary operating sulfuric acid alkylation unit.

To summarize, the assumptions and inputs that drive the results of the consequence modeling part of the QRA are as follows:

- that the airborne reduction fraction is 65% for MHF released from the settler/reactor area and 75% from storage or other areas containing fresh acid. This assumption is acceptable to the SA and is well founded in Mobil's aerosol modeling and experiments

- that the airborne sulfuric acid fraction is 2.8%. As has been described above, this assumption is the best estimate from Quest's experimental results.

- that the ERPG-3 is a suitable measure to use as a basis for the comparative effects of airborne HF and sulfuric acid. The SA agrees that this is a valid assumption.

- that the ERPG-3 can be expressed in terms of dose (ppmv-min. or mg/m^3-min.) and that a given dose causes the same health effect, no matter what the exposure time. The SA concurs with this assumption, except at very low exposure times of less than 5 minutes, see Section V.E. However, Section V.E also shows that the uncertainties in the extrapolation of health effects to small exposure times does not affect the overall conclusion that MHF alkylation is no more risky than sulfuric acid alkylation.

V.B.6 Conclusions

The atmospheric dispersion and consequence modeling for the single event and for the QRA is adequate to support the conclusion that MHF alkylation is no more risky than sulfuric acid alkylation.

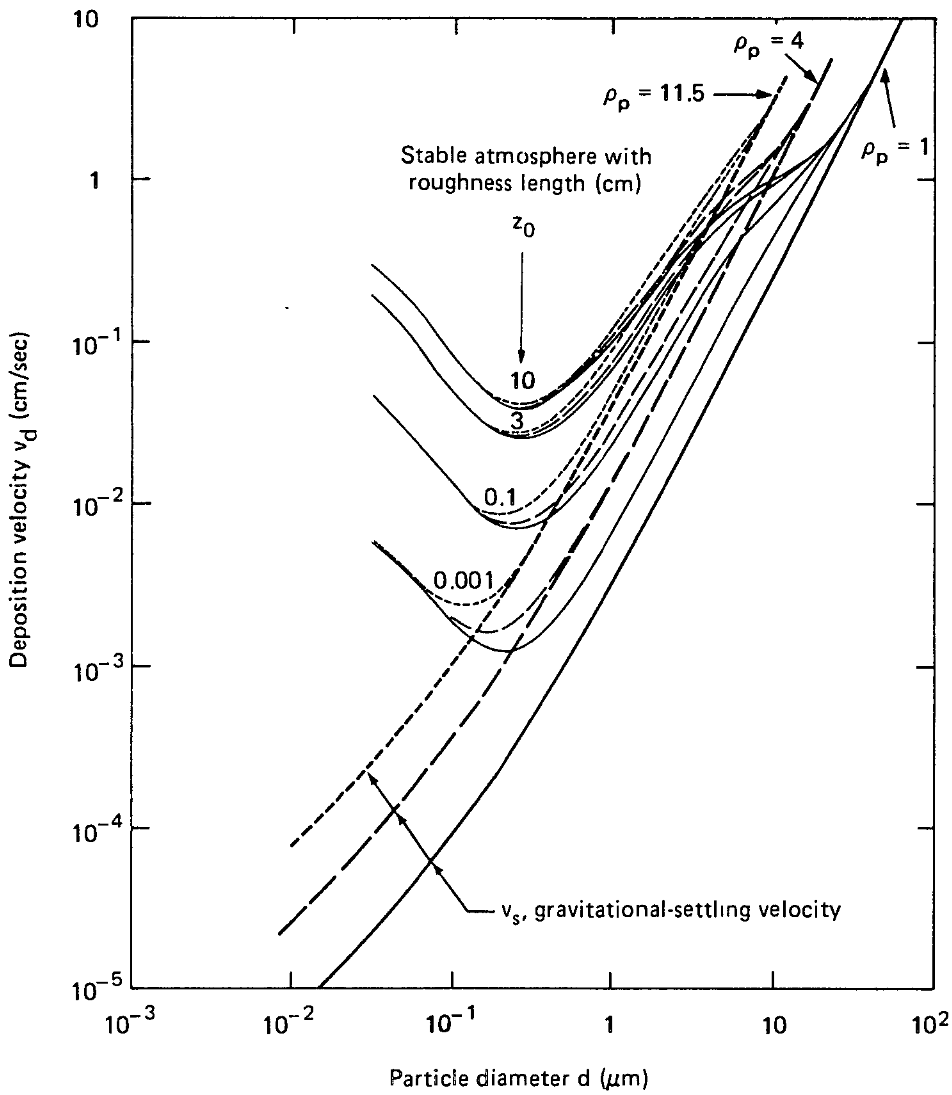


FIGURE V.5

Effect of the Meteorological Roughness Length Z_0 and Particle Density P_p on Deposition Velocity

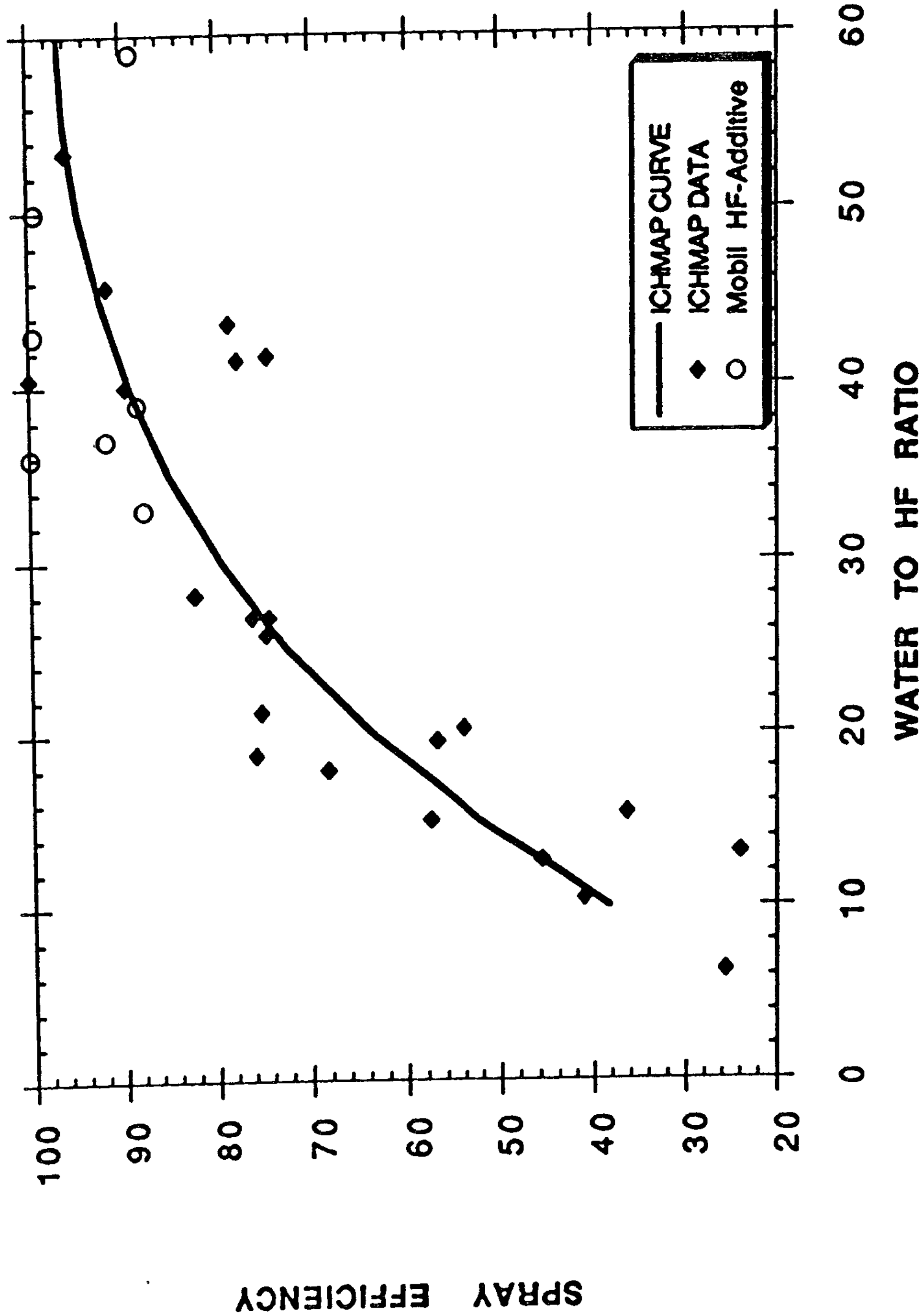


FIGURE V.6
Spray Efficiencies Compared to ICHMAP Results

{FIGURE V.7}

Summary of Acid Recovery Results

V.C METEOROLOGICAL ASSUMPTIONS

V.C.1 Importance to QRA/Phenomenology Review

For a comprehensive QRA, it is important to perform calculations for a full range of weather conditions that span the full range of expectations at the site, so that the full range of potential consequences and their associated probabilities can be factored into the results.

V.C.2 Key References Reviewed by the SA

- Reference 508.00 (Mobil Oil Corporation, 1994 - the QRA)
- Reference 4 (Briggs, 1973)
- Reference 11 (McElroy and Pooler, 1968)
- Reference 29 (USEPA, 1987)

V.C.3 Key Criteria Referenced

- II.E
- II.M

V.C.4 Review Activity/SA Calculation Summary

No specific SA calculations were required to evaluate this issue. The SA's review focused on the above identified references.

V.C.5 Results/Observations

The meteorology data used for the MHF QRA was prepared by Technica Ltd. in 1989 based on the 1981 King Harbor directions and windspeeds and on the Long Beach airport cloud cover. These data were supplied to Mobil by the South Coast Air Quality Management District (SCAQMD) and were used in the MHF QRA for consistency with prior work.

The US EPA (Reference 43), in "Technical Guidance for Hazards Analysis," has recommended the use of urban dispersion models in urban locations. In Appendix G of that reference, EPA presents two sets of parametrizations of the standard deviations in the basic Gaussian dispersion model, based on the work of Briggs (Reference 4); one for open-country or rural conditions and one for urban conditions. Briggs' parametrization of the urban conditions takes into account the enhanced surface roughness and additional thermal turbulence over an urban area (leading to more rapid dilution of a plume than is the case in a rural environment). It is based on experiments carried out in St. Louis (Reference 11). These EPA models apply to the passive phase of the dispersion history of a plume or puff - that is, after the models have evolved out of the initial heavy vapor dispersion phase. However, for HF (based on the SA's extensive experience in the atmospheric dispersion modeling of HF), HF plumes in air with humidities consistent with those found in Southern California evolve out of the heavy phase within a few hundred meters of the source of the release. When diluting to small concentrations such as the ERPG-3 (50 ppm), most of the plume's dispersion history is in the passive phase and discussion of whether urban or rural passive phase models should be applied is relevant.

In Mobil's atmospheric dispersion modeling, specifically the use of SAFETI/PHAST in the QRA, the Briggs' approach is not used. Instead, the E and F stability classes were converted to D stability to approximate urban dispersion in the SAFETI model. This is a common approach to taking account of urban dispersion when using models like SAFETI that strictly should only be applied over open country because they do not have any specific urban modeling in them. Although specific urban modeling would have been preferable for all stability categories, including E and F, the SA considers that, because the study is a comparative one and absolute results are not required, this simplified approach to urban sites in the QRA dispersion modeling is adequate.

In the QRA, the meteorological data was simplified to only 6 weather conditions with the following atmospheric stability categories/windspeeds: A-B/3.0 m/s, C/2.5 m/s, C/4.3 m/s, D/2.0 m/s, D/5.0 m/s and D/10 m/s. This is a coarser representation of the meteorological data than is normally used in QRAs, but it is the judgment of the Safety Advisor that there will be little effect on the accuracy of the comparative QRA.

It should be noted that, in the single event modeling, Mobil has used DEGADIS in Stability Category F with a windspeed of 1 m/s. DEGADIS is a model that, when it is used in its usual way, has a set of rural parametrizations of the standard deviations in the passive/Gaussian model. It follows that the dispersion modeling for the single event case is conservative compared with even the worst case in the QRA. However, as noted above, this discrepancy is not particularly significant because a comparative study is being undertaken and conservatism's will propagate equally to the MHF and sulfuric acid release event calculations.

V.C.6 Conclusions

Mobil has obtained its meteorological data from a suitable local source and has used it in a simplified but defensible way in the quantitative risk comparison and the single event dispersion modeling. The simplifying assumptions and approach are acceptable because this is a *comparison* between MHF and sulfuric acid alkylation

V.D CONSIDERATION OF SENSITIVE RECEPTORS AND VULNERABILITY ZONES

V.D.1 Importance to QRA/Phenomenology Review

For the comparative risk assessment it is important to ensure that nearby populations are adequately accounted for in the estimates of the number of people exposed to doses that equal or exceed the ERPG-3. These populations should include, for example, nearby hospitals and schools and heavily traveled nearby roads. For the single event modeling, it is important to ensure that the results of calculations are presented at meaningful locations, such as Crenshaw Boulevard or 190th Street.

V.D.2 Key References Reviewed by the SA

- Reference 508.00 (Mobil Oil Corporation, 1994 - the QRA)
- Reference 511.02 (Jersey, 1994)
- Reference 513.01 (Krambeck, 1994b)
- Reference 515.03 (Krambeck, 1994c)
- Reference 518.03 (Krambeck, 1994)

V.D.3 Key Criteria Referenced

- II.G
- II.N

V.D.4 Review Activity/SA Calculation Summary

No specific SA calculations were required to evaluate this issue. The SA's review focused on the above identified references.

V.D.5 Results/Observations

In the QRA, the population distribution is discussed in Section 2 of Risk Assessment Appendix 2.3. The population distribution used is one that was prepared in 1989, except that nighttime population distributions were increased by 5% to allow for growth.

The QRA contains a table of the number of people at schools, office blocks and shopping centers. These people were assumed to be present during the daytime, which was assumed to last for 50 hours per week (30%). Data on hospitals is also presented.

Reference 518.03 provides information on the traffic rates along various roads near the refinery. For example, Crenshaw Boulevard, which approaches to within 135m of the HF alkylation unit settlers, has an average of 1900 cars/hr. SAFETI requires population input in hectare (100m x 100m) blocks. For Crenshaw Boulevard, the daytime population has been represented by hectare blocks, aligned along the boulevard, containing 4-5 people. This appears reasonable - a hand calculation shows that 1900 cars/hr. moving at 30 mph would be spread out so that there are approximately 4 cars per 100m length of road. For all other locations, the density of population in adjacent dwellings and other buildings considerably exceeds 4-5 people/hectare, and the QRA is not sensitive to assumptions about-traffic densities on these roads. Note that the QRA does not take account of the way that cars move through the cloud. The people in the cars are assumed to be affected in the same way as other members of the population. This simplifying assumption would not impact the QRA results.

For the single event modeling, Mobil presented results at 190th Street (400 m N) and Crenshaw Boulevard (135 m E). These are the closest points at which members of the public are likely to be.

V.D.6 Conclusions

Mobil has used local population distributions that take account of the difference between day and night and include sensitive populations. Traffic densities have been considered. For the single event modeling, Mobil has chosen meaningful locations for which to present results. The modeling used for the QRA to address sensitive receptors and potential vulnerability zones adequately reflects appropriate population distribution. Thus, there are no additional recommendations which arise from this review.

V.E HEALTH EFFECTS MODELS

V.E.1 Importance to QRA/Phenomenology Review

In order to assess the magnitude of the consequences of an accidental release of MHF or sulfuric acid and/or to estimate the magnitude of the risk, it is necessary to understand how toxic vapors relate airborne vapor concentrations and exposure times to human health effects - that is, it is necessary to have a health effects model. The SA review focused on concentration endpoints and the extrapolation of experimental data for doses to short exposure times.

V.E.2 Key References Reviewed by SA

- Reference 21 (AIHA, 1990)
- Reference 29 (USEPA, 1987)
- Reference 512.01 (Dalbey, 1994)
- Reference 511.02 (Jersey, 1994)
- Reference 507.02 (Mobil Oil Corporation, 1994a)
- Reference 514.07 (Mobil Oil Corporation, 1994b)
- Reference 34 (Mudan, 1990)
- Reference 12 (Rusch, 1994)
- Reference 521.00 (IARC, 1994)

V.E.3 Key Criteria Referenced

- II.O

V.E.4 Review Activity/SA Calculation Summary

No specific SA calculations were required to evaluate this issue. The SA's review focused on the above identified references.

V.E.5 Results/Observations

The quantitative risk comparison was based on HF and sulfuric acid ERPGs (which have been promulgated by the AIHA (Reference 21). The ERPGs are intended to provide estimates of the airborne concentration which, for an exposure time of one hour, would be expected to lead to the following effects:

> ERPG-1: *the maximum airborne concentration below which nearly all individuals could be exposed for up to one hour without experiencing other than mild, transient adverse health effects or perceiving a clearly defined objectionable odor.*

ERPG-2: *the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action.*

ERPG-3: *the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing life-threatening health effects.*

The ERPG values for HF and sulfuric acid are given in the following table:

TABLE V.4

ERPG VALUES FOR HF AND SULFURIC ACID

	HF	Sulfuric Acid
ERPG-3	41 mg/m^3 (50 ppmv)	30 mg/m^3 (7.5 ppmv)
ERPG-2	16 mg/m^3 (20 ppmv)	10 mg/m^3 (2.5 ppmv)
ERPG-1	4 mg/m^3 (5 ppmv)	2 mg/m^3 (0.5 ppmv)

In the above table, ppmv stands for "Parts per million by volume." In the following, it will be taken as synonymous with ppm. Note that, in both the single event dispersion modeling and the QRA, comparisons with ERPG-3 are always consistent with the use of mg/m^3

Note - the AIHA is expected to change the ERPG-1 for HF to 2 ppmv (Reference 12). However, this change will not affect any of Mobil's conclusions, which are based on the ERPG-3.

It can be seen that, when compared on a mg/m^3 basis, HF and sulfuric acid are quite close, with the ERPG-3's differing only by about 30% and with the difference being conservative with respect to a HF/sulfuric acid comparison. The quantitative risk comparison uses ERPG-3's, which can be regarded as thresholds for potentially fatal effects, as a basis for comparison of the two substances. The Safety Advisor considers that this is a reasonable choice because the ERPG's have been carefully developed and peer reviewed. As summarized in Technical Guidance for Hazards Analysis (Reference 29), a consortium of 25 chemical firms has developed a uniform protocol for the development of ERPGs, based upon the National Research Council/National Academy of Science Guidelines known as Emergency Exposure

Guidance Levels (EEGLs) and Short Term Public Exposure Guideline Levels (SPEGLs). The AIHA then provides technical review and publishes the ERPGs.

In addition, the quantitative risk comparisons are based on dose, i.e. the product of concentration and exposure time. For the ERPG-3, the dose for HF is 41mg/m^{3}x60 min. ~ 2,400 mg/m^3-min. (3,000 ppm-min.) and that for sulfuric acid is 30x60 ~ 1,800 mg/m^3-min. (450 ppm-min.).

The assumption that doses can be compared at widely differing exposure times to give a meaningful comparison of the relative harm caused by sulfuric acid and HF is an expression of Haber's Law (Reference 29). Whether or not Haber's law is valid can only be determined on a substance by substance basis. The Safety Advisor requested Mobil to provide the basis for the assumption that Haber's law is valid down to durations of cloud passage that, for some of the MHF scenarios in the QRA, can be less than a minute.

Mobil provided a "Short Status Report on 2-Minute Laboratory Exposures to HF" (Dalbey, November 1994, 512.01). In this experiment, rats were exposed to airborne HF for periods of 2, 10 and 60 minutes, during which they inhaled through the mouth. For the two minute exposure times, the inhaled dose in ppm-min varied from 1,186 to 17,242 (the ERPG-3 is 3,000 for humans ppm-min.). The results are summarized in Table V.5:

TABLE V.5

DOSES AND CONCENTRATIONS OF HF DURING EXPOSURES OF GROUPS OF RATS TO HF

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The results in this table seem to support the view that doses of 3,000 ppm-min (the ERPG-3), extrapolated to 2 minutes, do not cause fatality - i.e. that the ERPG-3 can be extrapolated using Haber's law to a time as small as 2 minutes, as is stated by Dalbey (1994; 512.01):

> "What information do these data provide regarding the extrapolation of the ERPG-3 of 50 ppm for HF from 60 minutes (a Ct of 3,000 ppm-min) to shorter exposure times? Although we cannot address directly the question of linearity of the Ct relationship from 60 to 2 minutes, our data are consistent with the concept that the ERPG value is valid at exposure times in the range of 2 minutes."

Some of the scenarios in the QRA have durations of release of only 30 seconds. Reference 512.01 contains the following pertinent observations:

> "Extrapolation from our data at 2 minutes to times as short as 30 seconds is more uncertain; any such extrapolation beyond available data points is indefinite. Our data show that no mortality would be expected with nose-breathing, but results with mouth breathing are less predictable. Within that context, our data from 2-minute exposures

add support to the premise that mortality might not occur with 30-second exposure to a Ct of 3,000 ppm-min."

Thus, the basis for extrapolation using Haber's law to 30 second exposure times, as is the case for some scenarios in the QRA, is based primarily on engineering judgment and not on actual experimental results. However, for the single event modeling, where the exposure times for HF are of the order of 5 minutes (References 507.02 and 511.02) the experimental results in 512.01 give support to the Haber's law extrapolation.

The Safety Advisor considered the following three additional questions: (1) is it legitimate to extrapolate HF data from rats to humans without any scaling factor?; (2) how would the results of the comparative risk assessment differ if extrapolation by Haber's law were valid only to (say) 5 minutes, with a constant concentration extrapolation for smaller exposure times? and (3) what is the evidence that a Haber's law-like extrapolation is valid for sulfuric acid?

1. The question of the extrapolation of health effects data from animals to humans has been considered in many publications. An example is the work of Mudan (Reference 34), who developed a probit equation for fatalities due to exposure to HF. Specifically, Mudan looked at the LC_{50}, which is the airborne dose that would prove fatal to 50% of those exposed to it. In order of increasing body weight, the mean LC_{50} in ppm-minutes is 26,800 for mice, 46,900 for small rats, 84,000 for large rats, 64,900 for guinea pigs and 106,440 ppm for monkeys. Mudan established that this represents a statistically meaningful increasing trend by body weight. Therefore, the available evidence shows that, by not introducing a scaling effect between rats and humans, Dalbey is being conservative in his use of experimental data.

2. The question of the validity of using Haber's law to extrapolate MHF doses to very small exposure times has been shown to be moot as a result of a sensitivity study performed by Mobil on the QRA assuming no active mitigation of MHF releases (Reference 514.07). The results show that the calculated risks of unmitigated MHF alkylation are still comparable to those of a comparable sulfuric acid alkylation unit. In considering MHF without mitigation, no scenario has a duration of release of less than five minutes, so that application of Haber's law remains comfortably within the range that has been validated by Dalbey's experiments.

3. In a telecon with Mobil personnel on 11/21/94, the SA learned that Mobil has conducted a review on the available evidence for how potentially fatal doses vary with

exposure time. This information was made available in Reference 518.22, which consists of a review of the available animal data in sulfuric acid mist inhalation. There are far fewer data sets available for sulfuric acid than for HF. However, it can be concluded that the available data are consistent with a Haber's Law approach to the ERPG-3 for sulfuric acid, albeit within a large range of uncertainty.

Finally, during the course of the project, the SA was provided with a copy of a report entitled "Occupational Exposures to Mists and Vapors from Sulfuric Acid and Other Strong Inorganic Acids," published by the International Agency for Research on Cancer (IARC) (Reference 521.00). The IARC is sponsored by the World Health Organization (WHO). This report states that "There is sufficient evidence that occupational exposure to strong-inorganic-acid mists containing sulfuric acid is carcinogenic," and "Occupational exposure to strong-inorganic-acid mists containing sulfuric acid is *carcinogenic to humans* (Group 1)."

V.E.6 Conclusions

Mobil is to be commended for funding a useful series of experiments on HF toxicity (Reference 512.01). These experiments greatly enhance the confidence with which the relationship between dose and health effects can be extrapolated to small exposure times.
The SA feels that the health effects modeling assumptions and their use in the quantitative risk comparison and single event scenario are appropriate and defensible:

- ERPG-3 is a suitable endpoint to use as a basis for the comparative effects of airborne HF and sulfuric acid

- ERPG-3 can be expressed in terms of dose (ppmv-min. or mg/m^3-min.) and a given dose causes the same health effect, no matter what the exposure time. Uncertainties in the validity of this statement for small exposure times do not affect the overall conclusion that the risks of MHF alkylation are comparable to or less than those of sulfuric acid alkylation.

There are no recommendations which follow from this review. However, the SA would encourage Mobil to have the HF toxicity experimental work published in the open literature.

V.F COMPARISON WITH OTHER ALKYLATION UNIT TECHNOLOGIES

V.F.1 Importance to QRA/Phenomenology Review

The MHF alkylation technology has been selected because it provides a significant reduction in risk compared to AHF technology.

Although it is clear that a review of alternate alkylation technologies is not mandated by the Consent Decree and subsequent Stipulation and Order, an understanding of the potential merits of alternate alkylation technologies by the Safety Advisor is consistent with the spirit of the Consent Decree and helps ascertain if the MHF technology proposed by Mobil is the best choice of all available technologies.

V.F.2 Key References Reviewed by the SA

- Reference 16 (O&GJ, 1994)
- Reference 44 (Sheckler et al., 1994)
- Reference 45 (Comey et al., 1994)

V.F.3 Key Criteria Referenced

- II.P

V.F.4 Review Activity/Check Calculation Summary

No specific check calculations were required to evaluate this issue. The SA's review focused on the above identified reference.

V.F.5 Results/Observations

The latest information on alternative alkylation technologies has been conveniently summarized in the proceedings of a recent conference that was organized by the Oil & Gas Journal (Reference 16) entitled "The Role of Alkylation in the New Fuels Era." The potential new technologies considered were:

- Haldor Topsoe has developed a fixed bed alkylation process which is based on a liquid acid catalyst supported on a solid medium. The process is being commercialized in a collaboration with the M.W. Kellogg Company. A pilot plant was constructed in 1991 which has generated about 9,000 hours of operation. Haldor Topsoe and the M.W. Kellogg company are currently preparing a feasibility study for a company which contemplates employing the process in the first commercial scale application (over 2,000 barrels per day of alkylate product).

- Catalytica Inc., Conoco Inc. and Neste Oy have joined together for the development of a solid acid catalyst process which uses an alumina/zirconia halide catalyst. This process is not available for license.

- Chemical Research and Licensing (CR & L) has developed a process that utilizes a slurry catalyst system and a 10 bpd pilot plant unit started up earlier this year at a Chevron refinery. The process may be available for licensing in 1995.

- Texaco and UOP are developing an HF ALKylation ADditive Technology that has been named Alkad^{TM}. The key to this technology is a class of additives that forms a stable complex with HF. The HF-complex significantly reduces the aerosol forming tendency of the circulating acid. The first commercial application of this technology started in September, 1994 at Texaco's Alkylation Unit in the El Dorado Refinery. This technology is similar to Mobil's in that it works by effectively reducing the vapor pressure of HF and its tendency to aerosolize.

  Experiments carried out at the Quest facility in Norman, OK using the same test facility as the one that was used for MHF have shown that an aerosol reduction of 60-83% was achieved (Reference 44). This aerosol reduction percentage was defined in exactly the same way as for MHF - that is, taking account of the diluent effect of the additive as well as the amount of HF that actually rains out onto the ground (Reference 45). The analysis of liquid rainout showed that essentially all of the additive released went into the liquid phase - that is, within a short distance from the source, the airborne cloud consisted entirely of anhydrous HF in the same way as was found in the MHF experiments that are discussed in Section V.A. Therefore, comparison between the aerosol reduction percentages of the Alkad^{TM} and MHF experiments is legitimate - like is being compared with like and the percentages achieved in the two technologies are approximately the same.

- Kerr-McGee is promoting a soluble catalyst in its HAT^{TM} (Homogenous Alkylation Technology). Kerr-McGee is currently considering the development of a pilot plant.

V.F.6 Conclusions

Representatives of the Safety Advisor attended the above referenced conference and became familiar with literature on the possible alternative alkylation technologies and concluded that none of the technologies discussed above is sufficiently far advanced and/or demonstrated to be clearly safer than the use of MHF to warrant a recommendation that Mobil should seek an alternative to MHF technology at the present time.

V.G REFINERY CHEMICAL MONITORING/WARNING SYSTEMS

V.G.1 Importance to QRA/Phenomenology Review

The reliable operation of HF monitoring/warning systems in the Torrance Refinery Alkylation Unit is necessary for an effective and timely response to a potential emergency which can help ensure that incidents do not propagate into more serious accidents. If released to the atmosphere, MHF should not adversely affect the operation of HF detectors in the alkylation unit.

V.G.2 Key References Reviewed by the SA

- Reference 503.00

V.G.3 Key Criteria Referenced

- II.Q

V.G.4 Review Activity/SA Calculation Summary

No specific SA calculations were required to evaluate this issue. The SA's review focused on the above identified reference.

V.G.5 Results/Observations

The refinery currently uses video cameras and a network of 27 Sensidyne HF detectors for detection, monitoring and warning. If an accidental release of MHF should occur, almost all of the additive (98% or more) will rain out after it has been effective at reducing the airborne HF mass flux. Only evaporated HF will remain airborne. Therefore, the detectors will see HF as they would if the release were from an AHF alkylation unit.

V.G.6 Conclusions

The Safety Advisor concurs with the conclusions provided in Reference 503.00 and their bases. The SA would not expect the very small quantities of additive to impact the accuracy or adequacy of the electrochemical detectors used for the Torrance Refinery HF detection/monitoring/warning systems. There are no SA recommendations related to refinery chemical monitoring/warning systems associated with conversion to a MHF catalyst.

VI. CONCLUSIONS

The conclusions resulting from this evaluation are provided in the following subsections within the Executive Summary and are not repeated here:

- Summary of Phenomenological Conclusions
- Summary of Quantitative Risk Comparison Conclusions
- Making Decisions on Issues Containing Inherent Uncertainties
- Summary

VII. RECOMMENDATIONS

The SA reviewed relevant Mobil and Industry information which provided a basis for the observations in the previous sections and the recommendations below. The nature of this SA evaluation was to determine if Mobil has satisfactorily demonstrated that it has met the criteria defined in the Consent Decree (Reference 1) and the subsequent Stipulation and Order (Reference 2). The SA evaluation focuses on Mobil's demonstration of the specific criteria. These follow-up items are primarily associated with:

- Mobil, TFD, or SA actions necessary for validating the implementation of select, key MHF conversion attributes
- Issues, peripheral to the MHF conversion, to be addressed as part of other SA evaluations which are identified in Section IV or V of this evaluation
- Items added following the issuance of the Revision 0 Final Report and pursuant to the requirements of References 596.00 and 597.00

The following are programmatic issues to support the achievement of the objectives of References 1 and 2:

M-1) Mobil shall supply to the Court, the SA, and TFD, the anticipated schedule and flow chart setting forth the external permitting process for the MHF conversion. The schedule and flow chart shall identify the required permits, the agencies involved, and anticipated scheduling. Mobil shall also supply to the Court, the SA and TFD, the anticipated schedule for the physical design, construction, and implementation of the MHF conversion. The initial anticipated schedule shall be supplied by Mobil by March 31, 1995.

M-2) Mobil shall implement the MHF conversion consistent with the projected schedule. After the MHF conversion has been constructed and implemented, Mobil (1) shall not transport AHF to or from the Torrance Refinery; (2) shall not store AHF at the Torrance Refinery; and (3) shall not use AHF at the Torrance Refinery, except as AHF is present in minor amounts as part of the alkylation unit process using MHF, as specified in the SA's MHF Report and February 7, 1995 letter, or an amount which would not affect the SA's conclusions. The SA's verification that its conclusions are not affected shall occur prior to testing and operation. The parties shall continue to support the Court's monthly monitoring of the project. At such conferences, Mobil shall keep the Court, the SA, and TFD apprised of the progress toward permitting and implementing the MHF conversion.

M-3) Mobil shall timely notify the Court, the SA, and TFD of technical or regulatory issues or problems that threaten Mobil's ability to meet the projected MHF conversion schedule. Further, Mobil shall timely notify the Court, the SA, and TFD of technical or regulatory issues or problems which make MHF conversion infeasible. In such an event, and in light of the requirement in paragraph four (4) of the Consent Decree that Mobil cease use of AHF at the Mobil Refinery by 12/31/97, Mobil shall advise the Court, the SA, and TFD, of its plan for fulfilling the requirements of the Consent Decree.

M-4) In order to provide for effective monitoring of the recommendation closeout process, the SA will enclose a summary of the recommended schedule and status of implementation in the monthly project status reports to the Court, Mobil, and the City. As part of the monthly teleconferences, all parties will have the opportunity to comment or identify any potential issues regarding the schedule or implementation of recommendations.

The following are specific recommendations necessary to validate the implementation of select, key MHF conversion attributes:

M-5) Prior to testing and operation of the MHF unit (following conversion), the SA shall review the design and implementation of key equipment, review the ability of operating procedures to ensure adherence to key operating parameters, and verify key assumptions (e.g., additive concentration), including walkdowns as necessary.

M-6) Upon completion of the MHF conversion design, Process Hazard Analyses will be performed. These include Process Hazard Analyses consistent with Mobil PSM policy, OSHA PSM and California's RMPP process. Prior to testing and operation of the MHF Alkylation Unit, the SA shall verify that the results of these Process Hazard Analyses do not affect the conclusions of the SA's modified HF catalyst evaluation.

M-7) As part of the SA's seismic review under the Consent Decree, the SA shall analyze and report on the seismic safety of the MHF unit's final design and construction, including a walkdown prior to testing and operation. This seismic safety review will include a review of conclusions and recommendations resulting from any RMPP effort to verify that the conclusions of the SA's modified HF catalyst evaluation are not affected.

The HF mass flux following a release of MHF is a key factor in the results and conclusions of the quantitative risk and the single event release comparisons. The additive concentration has a very direct impact on the HF mass flux reduction assumptions. The additive concentration will be manually controlled by the plant operator who will maintain process parameters within a target range which is a function of unit temperature (See Figure V.1).

Thus, one of the key process variables which influences the acceptable results and conclusions of this SA evaluation, is maintained through operating procedures and not through an intrinsic property of the modified HF catalyst. Although maintaining a safe operating configuration through adherence to operating limits and operating procedures is considered a standard practice for refinery processes, the critical dependence on additive concentration to the conclusions of this evaluation and demonstrating that Consent Decree criteria are met, warrant the implementation of effective measures to ensure maintenance of the appropriate additive concentration.

Therefore,

M-8) Prior to testing and operation of the MHF Alkylation Unit, the SA shall review and determine the acceptability of Mobil's operational practices and procedures for ensuring that additive concentrations remain within the predefined limits evaluated by the SA in the MHF report.

M-9) Mobil and TFD shall develop a mutually agreeable audit plan to monitor additive concentrations which will be reviewed by the SA, prior to testing and operation of the MHF Alkylation Unit. This plan shall include weekly transmittal of Mobil's audit documentation to TFD, or as otherwise requested by TFD, as well as periodic on-site auditing by TFD.

The following is a specific stipulation contained within References 596.00 and 597.00:

M-10) Consistent with the SA task objectives specified in the Consent Decree and consistent with the scope of the ongoing Evaluation of Chemical Monitoring/Warning Systems and Evaluation of the Emergency Response Program, the SA shall investigate and make recommendations with respect to the following issues: HF warning systems; community notification, including but not limited to, notice to residents, schools and other institutions, and commercial and industrial entities; and emergency response programs in its pending reports on those subjects, and shall place a priority upon prompt completion of those reports and closure of those issues. In addition, Mobil is planning to participate in a Blue Ribbon Committee charged with addressing these issues.

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APPENDIX A

SIMPLIFIED HEP CALCULATIONS FOR MITIGATION SYSTEM AVAILABILITY SENSITIVITY STUDY

The following supports the text in Section IV.B.5.f and the sensitivity study depicted on Table IV.7. Unless otherwise specified, the following are failure probabilities. PSF refers to Performance Shaping Factor.

Mitigation Path 9 (25-100mm releases for Circulating Pump and Acid Truck Leak)

Water application (failure of diagnosis and action within 2 min):

Diagnosis (recognition of event and identifying the appropriate corrective action)

Reference 5 identifies a value of	0.8
PSF for training	0.5
PSF for straightforward nature of diagnosing an alkylation unit breach and determining proper response	0.25
Net Diagnostic Failure Probability	0.1

Action

Reference 5 identifies a value of for a critical action under extremely high stress	0.25
PSF for training & clarity of action	0.5
Net Action Failure Probability	0.125

Net conservative failure probability for water application within 2 minutes	0.225

Isolation (failure of diagnosis and action within 2 min) - Note that this is a failure conditional on non-successful water application:

Diagnosis (recognition of event and identifying the appropriate corrective action) - partial credit is applied due to dependency on previous failure

Net Diagnostic Failure Probability	
Conditional on Previous Diagnosis Failure	0.5
Non-Conditional	0.1

Action (this is considered independent due to the likelihood for multiple individuals involved)

Reference 5 identifies a value for a critical action under extremely high stress of	0.25
PSF for training & clarity of action	0.5
Net Action Failure Probability	0.125

Net conservative and CONDITIONAL failure probability for isolation within 2 minutes is a Boolean combination of the above (i.e., total path 9 probability, (Dw+Aw)*(Di+Ai), 0.091 divided by the water application failure probability of 0.225) 0.40

Note that these values are consistent with the range identified in Reference 35 for error rates "... given very high stress levels where dangerous activities are occurring rapidly".

Mitigation Path 9 (other 25-100mm releases)

Water application (failure of diagnosis and action within 5 min):

Diagnosis (recognition of event and identifying the appropriate corrective action)

Reference 5 identifies a value of	0.6
PSF for training	0.5
PSF for straightforward nature of diagnosing an alkylation unit breach and determining proper response	0.25
Net Diagnostic Failure Probability	0.075

Action (note credit for additional time compared to the Circulation Pump and Acid Truck response is not taken)

Reference 5 identifies a value for a critical action under extremely high stress of	0.25
PSF for training & clarity of action	0.5
Net Action Failure Probability	0.125

Net conservative failure probability for water application within 5 minutes 0.2

It should be noted that this activity was carried out successfully for the previous thermowell leak.

AES Actuation (failure of diagnosis & action within 5 min) - Note that this is a failure conditional on non-successful water application:

Diagnosis (recognition of event and identifying the appropriate corrective action) - partial credit is applied due to dependency on previous failure

Net Diagnostic Failure Probability

Conditional on Previous Diagnosis Failure	0.5
Non-Conditional	0.075

Action (this is considered independent due to the likelihood for multiple individuals involved)

Reference 5 identifies a value of for a critical action under extremely high stress 0.25

PSF for training & clarity of action (credit removed for AES

Actuation due to likely process disruption)
Net Action Failure Probability 0.25

Net conservative and CONDITIONAL failure probability for AES actuation within 5 minutes is a Boolean combination of the above (i.e., total path 9 probability, (Dw+Aw)*(Di+Ai), 0.097 divided by the water application failure probability of 0.2) 0.30

Mitigation Path 1 (25-100mm releases for Circulating Pump)

Water application (failure of diagnosis and action within 1 min):

Diagnosis (recognition of event and identifying the appropriate corrective action)

Reference 5 identifies a conservative value of	1.0
PSF for training	0.5
PSF for straightforward nature of diagnosing an alkylation unit breach and determining proper response	0.25
Net Diagnostic Failure Probability	0.125

Action

Reference 5 identifies a value for a critical action under extremely high stress of	0.25
PSF for training & clarity of action	0.5
Net Action Failure Probability	0.125

Net conservative failure probability for water application within 1 minute 0.25

Isolation (failure of diagnosis and action within 30 sec) - Note that a conditional failure probability for non-successful water application would not apply:

Diagnosis (recognition of event and identifying the appropriate corrective action) -
Net Diagnostic Failure Probability 0.15

Action (this is considered independent due to the likelihood for multiple individuals involved)

Reference 5 identifies a value for a critical action under extremely high stress of	0.25
PSF for training & clarity of action	0.5
Net Action Failure Probability	0.125

Net conservative failure probability for isolation within 1 minute is the sum of the diagnostic and action failure probabilities 0.275

Mitigation Path 1 (other 25-100mm releases)

Water application (failure of diagnosis and action within 1 min) - as above

0.25

AES Actuation (failure of diagnosis & action within 2 min) - Note that a conditional failure probability for non-successful water application would not apply:

Diagnosis (recognition of event and identifying the appropriate corrective action) -
Net Diagnostic Failure Probability 0.1

Action (this is considered independent due to the likelihood for multiple individuals involved)
Reference 5 identifies a value for a critical action under extremely high stress of 0.25
PSF for training & clarity of action (credit removed for AES Actuation due to likely process disruption)
Net Action Failure Probability 0.25

Net conservative failure probability for AES Actuation within 2 minutes is the sum of the diagnostic and action failure probabilities
0.35

Mitigation Path 3 (25-100mm releases for Circulating Pump)

Water application (failure of diagnosis and action within 1 min)
- same as above 0.25

Isolation (failure of diagnosis and action within 2 min) - Note that a conditional failure probability for non-successful water application would not apply:

Diagnosis (recognition of event and identifying the appropriate corrective action) -
Net Diagnostic Failure Probability 0.1

Action (this is considered independent due to the likelihood for multiple individuals involved)
Reference 5 identifies a value for a critical action under extremely high stress of 0.25
PSF for training & clarity of action 0.5
Net Action Failure Probability 0.125

Net conservative failure probability for isolation within 2 minutes is the sum of the diagnostic and action failure probabilities
0.225

Mitigation Path 2 (25-100mm releases for Circulating Pump)

Water application (failure of diagnosis and action within 1 min)
- same as above 0.25

The net conservative failure probability for isolation (failure of diagnosis and action within 30 sec but within 2 min) is 0.05. - Note that this is simply 1.0-P(failure to isolate within 2 min)-P(successful isolation within 30 sec) = 1.0-0.225-0.725

APPENDIX B

GLOSSARY OF TERMS

ACRONYM	**MEANING**
AES	ACID EVACUATION SYSTEM (A SYSTEM TO DEINVENTORY HF FROM THE ALKYLATION UNIT AT THE TORRANCE REFINERY)
AHF	ANHYDROUS HYDROGEN FLUORIDE
AIChE	AMERICAN INSTITUTE OF CHEMICAL ENGINEERS
AIHA	AMERICAN INDUSTRIAL HYGIENE ASSOCIATION
Alkad™	ALKYLATION ADDITIVE TECHNOLOGY (A MODIFIED HF ALKYLATION TECHNOLOGY DEVELOPED BY TEXACO AND UOP)
API	AMERICAN PETROLEUM INSTITUTE
APJ	ABSOLUTE PROBABILITY JUDGMENT (EXPERT JUDGMENT TECHNIQUE FOR HUMAN ERROR PROBABILITIES)
AQMD	AIR QUALITY MANAGEMENT DISTRICT
CARB	CALIFORNIA AIR RESOURCES BOARD
CCPS	CENTER FOR CHEMICAL PROCESS SAFETY (AN INDUSTRY ASSOCIATION OF THE AICHE)
CR&L	CHEMICAL RESEARCH AND LICENSING (A COMPANY WHICH IS DEVELOPING A SLURRY CATALYST SYSTEM FOR ALKYLATION)
DNV Technica	(A RISK ASSESSMENT CONSULTING FIRM)
DOT	DEPARTMENT OF TRANSPORTATION
EEGLs	EMERGENCY EXPOSURE GUIDANCE LEVELS (THRESHOLD LIMITS FOR HUMAN EXPOSURE TO CHEMICALS)
EPA	ENVIRONMENTAL PROTECTION AGENCY
ERPG	EMERGENCY RESPONSE PLANNING GUIDELINE (THRESHOLD LIMIT FOR HUMAN EXPOSURE TO CHEMICALS DEVELOPED BY THE AIHA)
FEMA	FEDERAL EMERGENCY MANAGEMENT AGENCY
HAT™	HOMOGENOUS ALKYLATION TECHNOLOGY (A MODIFIED HF ALKYLATION TECHNOLOGY DEVELOPED BY KERR-MCGEE)
HEPs	HUMAN ERROR PROBABILITIES
HF	HYDROGEN FLUORIDE (ALSO USED TO REFER TO HYDROFLUORIC ACID)
HRA	HUMAN RELIABILITY ANALYSIS

ACRONYM	MEANING
IARC	INTERNATIONAL AGENCY FOR RESEARCH ON CANCER
ICHMAP	INDUSTRY COOPERATIVE HF MITIGATION/ASSESSMENT PROGRAM (AN INDUSTRY TEST PROGRAM THAT STUDIED RELEASES OF AHF AND WATER SPRAY EFFECTIVENESS.)
KOH	POTASSIUM HYDROXIDE (USED FOR NEUTRALIZATION OF ACIDS)
MHF	MODIFIED HYDROGEN FLUORIDE (REFERS TO THE ADDITIVE/HF SOLUTION USED FOR MOBIL'S NEW ALKYLATION TECHNOLOGY)
MRDC	MOBIL RESEARCH AND DEVELOPMENT CORPORATION
MSDS	MATERIAL SAFETY DATA SHEET (CONTAINS SAFETY INFORMATION FOR A PARTICULAR CHEMICAL)
NPRA	NATIONAL PETROLEUM REFINERS ASSOCIATION (AN INDUSTRY ASSOCIATION)
OG&J	OIL & GAS JOURNAL
PERF	PETROLEUM ENVIRONMENTAL RESOURCE FORUM
PHA	PROCESS HAZARD ANALYSIS (A TECHNIQUE FOR IDENTIFYING AND ASSESSING POTENTIAL HAZARDS IN PROCESS FACILITIES, E.G., REFINERIES)
PLG	PICKARD, LOWE, GARRICK (A RISK ASSESSMENT CONSULTING FIRM)
PSF	PERFORMANCE SHAPING FACTOR (A MULTIPLIER APPLIED TO A STANDARD HUMAN ERROR PROBABILITY TO ADAPT IT TO THE SPECIFIC SITUATION)
PSM	PROCESS SAFETY MANAGEMENT (A SYSTEM FOR MANAGING POTENTIAL HAZARDS AT PROCESS FACILITIES, E.G., REFINERIES)
QRA	QUANTITATIVE RISK ASSESSMENT (ONE EXAMPLE APPLICATION OF QRA IS TO MEASURE THE POTENTIAL CONSEQUENCES OF A RELEASE OF TOXIC MATERIAL AND THE LIKELIHOOD OF THE RELEASE IN THE FIRST PLACE.)
RMP	RISK MANAGEMENT PROGRAM (A SAFETY INITIATIVE PROPOSED BY THE U.S. EPA)
RMPP	RISK MANAGEMENT AND PREVENTION PROGRAM (A SAFETY INITIATIVE MANAGED BY CALIFORNIA ADMINISTERING AGENCIES, E.G., TORRANCE FIRE DEPARTMENT)
RVP	REID VAPOR PRESSURE (A MEASURE OF GASOLINE VOLATILITY)
SA	SAFETY ADVISOR
SCAQMD	SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT
SPEGLs	SHORT-TERM PUBLIC EXPOSURE GUIDELINE LEVELS (THRESHOLD LIMITS FOR HUMAN EXPOSURE TO CHEMICALS)
SRI	SOCIETAL RISK INDEX

ACRONYM	**MEANING**
	(FOR THIS REPORT, THE SRI IS THE SUM OF ALL THE INDIVIDUAL, NUMERICAL RISK VALUES FOR EACH DISCRETE RELEASE SCENARIO.)
TBD	THOUSAND BARRELS PER DAY (ONE BARREL IS 42 GALLONS)
TFD	TORRANCE FIRE DEPARTMENT
THERP	TECHNIQUE FOR HUMAN ERROR RATE PREDICTION (ONE HUMAN RELIABILITY ANALYSIS TECHNIQUE)
UOP	UNION OIL PRODUCTS (A COMPANY THAT PRODUCES VARIOUS REFINING TECHNOLOGIES)
WHO	WORLD HEALTH ORGANIZATION