U.S. Chemical Safety and Hazard Investigations Board

Business Meeting

April 13, 2017

CSB Headquarters Office - Washington, DC

U.S. CHEMICAL SAFETY BOARD MEMBERS PRESENT:

VANESSA ALLEN SUTHERLAND, CHAIR

MANNY EHRLICH, MEMBER

RICK ENGLER, MEMBER

KRISTEN KULINOWSKI, MEMBER [BY PHONE]

STAFF PRESENT:

KARA WENZEL, ACTING GENERAL COUNSEL

OPERATOR: Welcome to the business meeting. My name is Cammie and I will be your operator for today's call. At this time, all participants are in a listen only mode. Later we will conduct a question and answer session. During the question and answer session, if you have a question, please press * then 1 on your touchtone phone. Please note that this conference is being recorded. I would now like to turn the call over to Ms. Vanessa Allen Sutherland. Ms. Sutherland, the floor is yours.

VANESSA ALLEN SUTHERLAND: Thank you and good afternoon. Welcome to this business meeting of the U.S. Chemical Safety Board or CSB. Today, we meet in open session, as required by the Government Sunshine Act, and we will discuss the operations and agency activities of the CSB.

I am Vanessa Allen Sutherland, the Chairperson and CEO of the Chemical Safety Board and joining me today in person are Members Ehrlich and Engler and joining by phone is Dr. Kulinowski. Also joining us is Kara Wenzel and members of the staff.

The CSB is an independent, non-regulatory federal agency. We investigate major chemical accidents at fixed facilities. The investigations examine all aspects of chemical incidents, including physical causes related to equipment design as well as inadequacies in regulations, industry standards, safety management systems, or

other areas. Ultimately, we issue safety recommendations, which many are designed to prevent similar incidents in the future.

I will now share today's agenda. First, the Board will give an update on investigations, studies, recommendations, and current deployments. Next I will give an overview of ongoing Inspector General audits and I will provide a financial update. You will also hear the schedule for our upcoming news conference...new conferences to release final reports and preliminary findings for several investigations.

I am also pleased to announce that the CSB has released the 2016 Impact Report, which was then turned into a video. That twominute video is available on our homepage at csb.gov or on our YouTube channel. It's a really great... Our team did a really great job doing a two-minute video to just summarize the agency's accomplishments in FY2016.

If you are in the room and wish to make a public comment at the end of the meeting, please sign up by using the yellow sheets that were at the registration table. For those who are on the phone, please remember to submit your public comments by emailing them to <u>meeting@csb.gov</u>. That's meeting@csb.gov to be included in the official record.

Before we officially begin, I'd like to point out some brief safety information for our meeting room. Please take a moment to note the locations of the exits at the side and back of the room. There's a door to my left up front and an open hallway. When you get to the front, to the door through which you came for this meeting, you'll notice there are two stairwells that say exit, both to your left and right.

Also, I would also want you to mute your phone, vibrate, silence, turn them off, so that these proceedings will not be disturbed. Thank you for that.

So, again, I'd like to thank everyone for attending today. This is our third public business meeting for Fiscal Year 2017. I'm pleased I am pleased to share updates on the CSB's progress and its many activities.

I will now recognize my fellow Board Members for any opening statements. And Dr. Kulinowski, we recognize that you are on the phone in the muted scenario with everyone who dialed in. So I will assure that if you have comments at the end when we open the line, you will be the first to go.

But in the room, Member Ehrlich, any opening comments?

MEMBER EHRLICH: Thank you, Madam Chairperson. Only that I'd like to welcome you all to this meeting. I think we're making

tremendous progress in this agency and I want to say particularly thank you to the Chair for her tenacity in helping us move forward. Thank you for... Thank you all for coming.

VANESSA ALLEN SUTHERLAND: Thank you. Member Engler?

MEMBER ENGLER: Yes, thank you. Welcome to the meeting. I would just like to express my appreciation for the many expressions of support from very wide-ranging constituencies. As I think everyone knows, the CSB has been zeroed out of the proposed Fiscal Year 2018 budget. Many, many, many constituencies from business, from individual companies, professional organizations, to environmental, public health, and labor organizations have expressed support for the role, for the progress, and for the particular mission of the CSB. And I wanted to express my thanks and appreciation to those efforts on behalf of protecting the American public.

VANESSA ALLEN SUTHERLAND: Thank you. So at this time, our first item of business will be to talk about some of the work that you just heard us refer to that is a result of our mission. And that's all of our open investigations. I will acknowledge each Board Member, who will provide an update on various ongoing investigations. More information about those investigations can be found at our website which I mentioned before at csb.gov. We will

provide continual updates, particularly as it relates to deployment.

So first I will recognize Member Ehrlich, who will provide an update on the most recent deployment of the agency at Loy-Lange Box Company, the Packaging Corporation of American hot work explosion, and the Sunoco Logistics Partner hot work explosion.

MEMBER EHRLICH: Thank you, Madam Chairperson. According to initial reports, on April 3, 2017, an incident took place at the Loy-Lange Box Company, which is in St. Louis, Missouri, when a boiler exploded at the plant, where one worker was killed. The force of the explosion launched the boiler into the air where it flew approximately 500 feet before landing on a nearby laundry facility, unfortunately killing two members of the public.

Our current status is that we are investigating. We have a team deployed on Wednesday, April 5 to Saint Louis, and the field investigation is underway. More details about this investigation will be shared when available.

The second investigation involves Packaging Corporation of America in DeRidder, Louisiana. On February 8, 2017, three contractors were killed and seven contractors sustained injuries in an explosion at the Packing Corporation of America facility in DeRidder, Louisiana. The fatally injured contractors were

conducting hot work activities near a 100,000-gallon atmospheric storage tank which contained a flammable atmosphere and ultimately exploded.

Current status, the CSB investigation team has completed its initial deployment stage of the investigation and is currently drafting a report for internal review.

Lastly, on August 12, 2016, seven workers were injured, including three critically, at Sunoco Logistics Partners, a terminal facility in Nederland, Texas. The incident involved a flash fire during welding.

Current status is the CSB's DC investigation team is continuing their work on the draft report and has started to develop draft safety recommendations and key findings. As part of their analysis, they are reviewing applicable consensus standards and developing a timeline for the completion of the report. Thank you.

VANESSA ALLEN SUTHERLAND: Thank you, Member Ehrlich. Member Engler will now discuss the Enterprise Products investigation, the ExxonMobil Torrance refinery explosion and the ExxonMobil Baton Rouge explosion.

MEMBER ENGLER: Thank you. In chronological order, I'll start with the Torrance Refinery incident. On February 18, 2015, an

explosion occurred in the ExxonMobil Torrance, California refinery's electrostatic precipitator or ESP, a pollution control unit connected to the fluid catalytic cracking or FCC unit. The ESP removes catalyst particles using charged plates that produce sparks during normal operation. The incident occurred when ExxonMobil was attempting to isolate the FCC equipment for maintenance while the unit was in an idled mode of operation. Preparations for the maintenance activity caused a pressure deviation that allowed hydrocarbons to backflow through the process and ignite in the ESP.

On March 28, 2017, the Board unanimously approved the final investigation report on this incident. The report will be released at a news conference in Torrance, California, on May 3, 2017. Additional details will of course be added to the CSB website.

I would also like to note that this specific CSB report does not assess a potential near miss that occurred at the refinery alkylation unit involving hydrofluoric acid that has been reported on in prior public business meetings. The CSB has still not received adequate information about this potential near miss from ExxonMobil, which would be required to make such an assessment and we are continuing to seek this information.

Second investigation is at Enterprise Products in Moss Point, Louisiana. There, a flammable gas release with subsequent fire and explosions occurred at the Enterprise Products Pascagoula Gas Plant, in Moss Point, Mississippi, on June 27, 2016. The incident occurred in a cryogenic or cooling process line, which takes Deepwater natural gas received via pipeline from offshore and separates the gas into natural gas liquids, such as propane and butane, and residual natural gas, such as methane. Both the NGLs and natural gas products are either commercially sold or transferred through another pipeline for further processing at other facilities. Enterprise assumed full ownership of the site just four weeks prior to the incident. Before that time, the site was majority-owned by BP. There are numerous gas plant installations similar to this one in regions across the U.S. where oil and gas are produced and so we think that the findings and recommendations in the report may well have important implications for other facilities.

The investigation team will be reviewing results from metallurgical failure analysis testing of physical evidence, including brazed aluminum heat exchangers, and is drafting the investigation report.

Finally, on...the third and last incident that I'm reporting on. On November 22, 2016, an isobutane release and fire occurred in the sulfuric acid alkylation unit of the ExxonMobil Baton Rouge refinery in Louisiana. The fire seriously injured four workers. Flammable isobutane vapor released from process piping when a valve came apart valve following removal of an inoperable hand wheel and gearbox assembly. The isobutane reached an ignition source approximately one minute after the release, while workers were still in the vapor cloud. The fire burned for less than 20 minutes.

The CSB investigation team has completed its initial deployment stage of the investigation and is drafting a report for internal review. Thank you.

VANESSA ALLEN SUTHERLAND: Thank you, Member Engler. I would note very briefly that by email yesterday we did receive a comment from Dr. Tur[?] regarding the ExxonMobil Torrance Refinery incident that Member Engler just described from February 18, 2015, regarding comments about the near miss incident involving HF. Not going to read that in entirety but wanted to acknowledge that the comment has been received and will be reviewed, so thank you for that.

I will now provide updates on the CSB's MGPI investigation, Airgas, the Delaware City Refining Company, and DuPont LaPorte.

First, for MGPI, on October 21, 2016, a chemical release occurred at the MGPI Processing plant in Atchison, Kansas. MGPI Processing produces distilled spirits and specialty wheat proteins and starches. The release occurred when a chemical delivery truck, owned and operated by Harcros Chemicals, was inadvertently connected to a tank containing an incompatible material. The plume generated by that inadvertent mixing of sodium hydrochloride and sulfuric acid led to a shelter-in-place order for thousands of residents in the community. At least 140 employees and members of the public sought medical attention.

The CSB has completed that...its preliminary investigation, as a matter of fact, had a news conference yesterday to share six preliminary findings from that incident. We have completed analytical testing of samples and other evidence obtained from the incident site. And we'll continue to gather information, review findings, photos, and other evidence before completing a report sometime hopefully in the fall of 2017. An overview of our findings [inaudible] video can be found on the website also, csb.gov.

For Airgas, that occurred August 28, 2016, at approximately 12:00 noon. A nitrous oxide trailer truck exploded at the Airgas manufacturing facility in Florida. The explosion killed the only

Airgas employee present and heavily damaged the facility, which halted nitrous oxide manufacturing at the Cantonment indefinitely...facility indefinitely.

Our current status is that on March 16, 2017, the Board approved the final investigation report. That report will be released at a news conference in Pensacola, Florida, on April 20, which is next week. Additional details about the news conference can be found on the CSB's website. The final report and recommendations will be published on the website following the news conference.

On Sunday, November 29, 2015, an operator at the Delaware City Refining Company-I'm going to use DCRC-at their sulfuric acid alkylation unit suffered second-degree burns to the face and neck and third-degree burns to the wrist from a flash fire. The incident occurred when operations personnel were preparing equipment for maintenance work by deinventorying and draining vessels located between two isolation points. A single block valve isolated the vessels being decontaminated from a pressurized and inventoried depropanizer column containing hydrocarbons. Unknown to operations personnel, the valve leaked in the closed position, resulting in backflow of flammable material from the depropanizer. When an operator opened the vessel drain valve to empty what he assumed was

condensate water from the vessel to the oil water sewer, the hydrocarbons from the depropanizer also released to the sewer and ignited, resulting in a flash fire.

On April 11, 2017, the CSB Board approved a safety bulletin entitled "Key Lessons for Preventing Incidents When Preparing Process Equipment for Maintenance: Flash Fire at the Delaware City Refinery." The final report will be released at a news conference in Delaware in mid- to late-May. Additional details will be made available on the CSB's website when that date is confirmed.

Lastly, on November 15, 2014, nearly 24,000 pounds of methyl mercaptan was released at the DuPont Chemical manufacturing facility in La Porte, Texas. That release resulted in the deaths of three operators and of a shift supervisor inside an enclosed manufacturing building. Additionally, three workers...three other workers were injured from their exposure to the methyl mercaptan and at least three more workers experienced methyl mercaptan exposure symptoms.

Current status of that investigation is that with the announced closure of the La Porte facility, the final investigation report will evolve and will focus on broader lessons learned and identify corporate process safety management issues. DuPont has

completed production of responsive records and the final report is currently being drafted.

In addition to our investigation and deployment efforts, we like to share information about our recommendations, which many of you know are result of the investigative work that we do.

To date, the CSB has issued a total of 794 recommendations. Currently the agency has a ratio of 78%, which is 622, recommendations closed to 22%, which is 172, in an open status.

The status of all of our recommendations can be found on our website at www.csb.gov/recommendations. Recommendations that have been recently voted on can be found on the recommendations page under "Recent Recommendations Status Update". Each recommendation has a Status Change Summary that describes the rationale for the Board vote.

Since the last business meeting, the CSB has closed 14 recommendations, bringing the total closed in Fiscal Year 2017 to 30 recommendations. Of those 30 closed recommendations, I will provide a more specific breakdown. Three were closed exceeds recommended action. Six were closed unacceptably. Eleven were closed acceptably. Two were closed as reconsidered or superseded. And eight were closed as no longer applicable.

Since the last business meeting, the CSB also has voted to change the status of 27 recommendations, meaning they are not closed but we have received information and the recipient is either working toward closure or providing us with additional feedback. The status of the 27 recommendations who have experienced a change brings the total number of status changes in Fiscal Year 2017 to 47 recommendations. These include eight were moved from open, awaiting a response to open acceptable. Three were moved from open, awaiting a response to open, unacceptable. And six new recommendations were issued with completion of the Airgas report.

Next, we spend much of our time making sure that we are engaged with the Inspector General in a productive and collaborative way.

The CSB recently completed three open recommendations due to the IG by March 31, 2017. With the completion of those open recommendations, the CSB has closed 36 of 37 recommendations from the Office of Inspector General. Currently, the CSB now only has one recommendation open related to future office leasing that will not occur until 2019 for the Denver Regional office and 2022 for the DC office.

To say that another way, in the last 18 months, we've closed 36 recommendations from the IG that have been open...some of them had

been open for quite some time. Our team worked really tirelessly, as did the EPA Inspector General, to really prioritize our response, [inaudible] give great feedback, and ultimately work to resolve some pretty complex recommendations. So it's not in my scripted materials, but I want to thank the EPIG and our team internally because that was truly a collective and collaborative effort. We could not have done that kind of work in the short of amount of time without everyone focusing on it and being extremely diligent and creative and focused on completion.

I would like to...you know, at the end of this, if you have questions about that in more detail, we can certainly discuss it but I would also like to move now to what we are currently working on with the Office of Inspector General and that includes four audits.

The first is our CSB Fiscal Year 2017 Purchase Card Risk Assessment. The CSB has provided all the requested documentation to the OIG and they will review that documentation.

Second, we are involved in an audit entitled Review to Identify Unimplemented Recommendations as of March 31, 2017. We have updated and provided the requested table and documentation to the OIG. So we currently only have one open recommendation.

Third, our annual Management Challenges and Internal Control Weaknesses audit is underway. The OIG is drafting the management challenges letter and expect to issue the final document by June 8, 2017.

And lastly but not leastly, we are working on the Financial Statement Audit. The OIG held their entrance meeting with us on April 6, 2017, but that audit will likely not be completed for a few months.

From a financial perspective, as many of you in the room and on the phone are aware, and as Member Engler alluded to a moment ago, about a month ago...actually just a little over three weeks ago, I was called over to the Office of Management and Budget, or OMB, to discuss the new Administration's FY18 budget proposal to Congress. Understanding that there was likely to, of course, be some discussion about reducing our spending, we started to go through very diligently and look at our current budget to figure out where we might be able to reduce line items or consolidate certain services. And the team did a very good job, despite the fact that our budget has been flat for the last several years. So even back in September we were fairly conservative when proposing yet another year at \$11 million. So our expectation was that we

would be discussing how we could potentially execute our mission at slightly less than \$11 million.

Unfortunately, as many know already, the CSB was informed that the President was proposing the CSB for elimination entirely, which would be effective as of FY18. So we would receive a budget but it would simply be to wind down the operations of the agency, if that budget were to be approved.

We remain committed, however, to the mission and to completing our open investigations, closing out recommendations, releasing our reports to the public and deploying to new incidents as they occur, like the multi-fatality explosion at the Packaging Corporation of America, PCA, that Member Ehrlich described, or the one at Loy-Lange Box Company in Saint Louis, to which we just recently deployed.

So with that, we will segue into new business, which is really more of a description of some of our activities related to the completion of many of the investigations that we just described.

The CSB has heard from many stakeholders that they would like our investigations completed a little bit more quickly so that the lessons learned can be shared more broadly and promptly to prevent future incidents or similar incidents. We've heard your comments, taken them to heart, and our staff has been working extremely

diligently to complete several open investigations, one of which was completed within six months of the incident date. As a result of this excellent work, the CSB has been focusing on the release of several investigations this spring.

As I mentioned, yesterday, we were in Kansas City, Missouri, at our MGPI news conference to share preliminary findings because, given the number of chemicals that are loaded and unloaded every day across the country, we felt that sharing our preliminary findings, photos, and a very brief video from laboratory testing would be helpful for those who are engaged in that activity on a daily basis. All of that information can be found on our website.

On April 20, as I mentioned, the Airgas investigation team will release the Board-approved final report at a news conference in Pensacola. That is the investigation to which I was referring, that was completed within six months of the incident date. On May 3, the CSB will hold a news conference in Torrance, California, to release the Board-approved final report into the February 2015 ExxonMobil explosion and chemical release. And, as I also mentioned, in mid- to late-May, we will be in Delaware to release the agency's Delaware City Refining Company Board-approved final report.

So that will all be updated and additional details will be provided on our website so that...in the event we have to tweak those dates and if you want specific information about the venue or the hotel, etc., at which we will be present, you can find it on csb.gov.

In addition to the investigations we are finalizing, the agency continues to conduct ongoing outreach and advocacy activities. We still think it's important to promote the Critical Drivers List, the CDL, and so you will continue to see us share information about past and current investigative work as part of our outreach activities.

So at this time, I would like to open the floor for public comment. Operator, if you could unmute the line so that I could inquire as to whether Dr. Kulinowski has any comments to make, that would be wonderful. If you're in the room, as I mentioned, please sign up and try to keep your comments to three minutes. Same request for those who are on the phone. If you are in the queue and recognized, please try to keep your comments to about three minutes. And if anyone has joined late, you can e-mail comments to us by...from your call by emailing meeting@csb.gov.

So with that, Operator, is the line unmuted for Dr. Kulinowski?

OPERATOR: At this time, opening up all lines.

MEMBER KULINOWSKI: Good afternoon, everyone. This is Member Kulinowski. I want to thank you all for attending and I do apologize for not being able to be there in person but I am there in spirit and just want to support the efforts of my fellow Board Members and Chair in bringing you the results of our latest activity. Thank you.

VANESSA ALLEN SUTHERLAND: Thank you, Member Kulinowski. Operator, at this time, if you could let us know if there are any other comments or questions in the queue, I will start in the room if you could key up the first caller's question or comment. Are there any comments in the room? Questions? All right. If not, do we have any questions on the phone?

[UNIDENTIFIED]: Can I ask a question? [inaudible]

VANESSA ALLEN SUTHERLAND: Talk a little louder.

[UNIDENTIFIED]: You talked about the budget proposal. Have you had any discussions yet with members of Congress about your budget for the upcoming fiscal year? And do you plan to work with them to secure a budget that wouldn't result in being zeroed out?

VANESSA ALLEN SUTHERLAND: The question, for those who are on the phone, is given the budget blueprint proposal, has the CSB met with members of Congress and do we anticipate working with them to

reach a resolution on this. On the first part, yes, we have engaged members of Congress, both on the House and Senate side, in part to express the value of what we do, our work, and to provide more context about our budget. And we do expect to continue to work with them and engage them to not only explain the work that we do and the mission that we do, but to submit a budget that we think would be able to allow us to operate effectively in FY18 to carry out the mission.

Any questions on the phone?

OPERATOR: At this time, I have no questions in the queue.

VANESSA ALLEN SUTHERLAND: Okay. We had one question come in by email. It's... It says one of... I'm going to have to do this. I hate to do this, but I have to, the font. One of the members gave [inaudible] on the CSB and the Trump budget blueprint upon introducing himself this afternoon. What is the Chair's or the CSB's position? In addition to the Impact Report, which efforts does the CSB plan to further illustrate its value and impact? And that comes from National Safety Council Associate Editor.

So, on the latter half, "In addition to the Impact Report, which efforts does the CSB plan to further illustrate its value and impact?" Well, we have...in addition to the impact, which is the impact video, which is more evenly distributed, there is in person

here and certainly if you email <u>public@csb.gov</u>, a larger packet which explains the states to which we have deployed for various incidents and the number of times to which we have deployed, a summary of our unique statutory mandates that we are, in fact, other than the NTSB, the only federal agency that has the role of being an independent, objective, non-regulatory safety agency to investigate the root causes of chemical accidents. We have, in that packet also, a summary of what was called the business case. Some of the more catastrophic events that we have investigated now have...enough time has passed that we can describe the economic impact, not only to the company but also to the community that was affected by that incident. So in monetary terms, we have that business case document.

We also continue to just publish great work. Our investigations are coming out. Most of those investigative products have an accompanying safety video which we all know people use very often in training. We plan to summarize our strategic plan which we just publishes, ironically, this year for 2017-2021. We plan to share that so people would know what our vision would be for five years.

And so, yes, we have a lot of information. In addition to the stakeholder support that we mentioned at the very beginning of this

meeting. The way in which they use our work and the way in which they use our products, I think illustrates our value and the impact that we've had.

On the first part, my perspective isn't any different than, I think, Member Engler's comments about the fact that we feel very encouraged by a lot of the stakeholder support that we have received following the draft budget, the budget blueprint proposal to eliminate the CSB. I think many of you have seen my statement on the website. I was very disappointed, as we all were. The staff was shocked and disappointed. The Board Members, in fact, were shocked as the staff were. Because we think we have a unique role and an important mission and we do that for a fairly consistently flat budget.

So I would say on behalf of the CSB, our goal is to make sure that we are communicating that value effectively and meaningfully because it is a truly impactful body of work that we've done. And I think it would be a shame if we didn't continue.

So this says, "Can you restate how many audits you are doing now and how much time is being allocated to them?" Well, we are currently involved in four Inspector General audits. They are routine. As I mentioned, the Purchase Card Risk Assessment, the Review and Identify Unimplemented Recommendations, Management

Challenges and Internal Control Weaknesses, and Financial Statement Audit. We have provided all requested information to the IG. So the amount of time we're spending on them right now is very little. The IG is reviewing our Purchase Card documentation and they will provide a report. We only have one unimplemented recommendation, as I mentioned, and we've provided all information in response to the IG's request. The IG is working on a letter, a document, for delivery to us around June 2017 on Management Challenges and Internal Control Weaknesses. And they held an entrance exam meeting with us but much of the work on the Financial Statement Audit will take place over the next several weeks.

So I hope that answers the question, Jeff, regarding the time being allocated towards those. I think the majority of our time right now is being allocated towards investigative recommendations and strategic outreach activities.

Next is a comment, "Thank you for your support with the 2015 accident at the ExxonMobil Refinery. Torrance Refinery Action Alliance, TRAA, offers all of our resources to support the CSB's ongoing work and hope you will continue these efforts." And thank you very much. That's from Melanie Cohen, Steering Committee Director at Torrance Refinery Action Alliance. Thanks for sending that in.

And I hope that I answered the other two questions adequately. If I didn't, please feel free to email a follow-up if you want additional information.

At this time I'll ask the operator are there any phone comments? Is anyone in the queue?

OPERATOR: At this time, we do have one person who queued up for questions. Our question comes, in fact, from Melanie Cohen. Ms. Cohen, you may begin.

MELANIE COHEN: Good afternoon. Again, I want to thank you for all your assistance in this matter. Despite the amount of publicity and work Torrance Refinery Action Alliance and local groups have been doing, a new refinery has taken over and we still have ongoing issues.

My question to you is, although this is not what you are investigating, how can we as citizens in and residents of Torrance, Redondo Beach, and the South Bay, continue to monitor and/or put pressure on this particular refinery because of unsafe practices, which we... It's all... There's many other groups. South Coast Air Quality Management is working on several regulations. There is bills putting forth on better refinery safety, which is all well and good and I'm...we're very, very pleased and this is all basically

because of CSB's participation. But how can we, as residents...what can we do immediately to impact what's going on?

VANESSA ALLEN SUTHERLAND: Well, first, thank you, Ms. Cohen, for the [inaudible] our team. I hope some of them were listening. The investigative team that spent a lot of time out in Torrance I know worked in getting a lot of information, worked very collaboratively with not only TRAA but a lot of other groups in the community. So, first, thank you for calling in and for all of the collaboration that you've shown our team as they've been physically out in the field.

I think Member Engler mentioned that the ESP, the electrostatic precipitator incident, is closed. The Board voted on that report and, as we've said in many, many previous business meetings, we were looking at the near miss incident as well and need additional documentation to move forward on that.

But on your broader question of what the communities can do, I think we tell everyone where we are during our public meeting that you are always free to engage not only the company who's there, whomever that ownership might be, and I know it's changed hands from Exxon to PBG, and engage your local representatives. I certainly know that having been out there a few times myself the local congressional delegation is very much aware of all of the

activities and incidents at the facility. So certainly continuing to engage them. We've also worked very closely with [inaudible], OSHA, and EPA, and I know that they are very immersed in these issues as well.

So, from what I can recall, I think you all are doing a lot of what, as citizens, you can do and should do in order to make your voices heard.

[multiple voices]

[UNIDENTIFIED]: Can you just repeat how to ... the instructions on how to make a comment for those online?

OPERATOR: Yes. As a reminder, if you do have a question, please press * then 1 on your touchtone phone. If you are using a speaker phone, you may need to pick up the handset first before pressing the numbers. Once again, if you do have a question, please press * then 1 on your touchtone phone.

Our next question comes from Nick Green. You may begin.

NICK GREEN: Yes, good morning. This is Nick Green with The Daily Breeze in Torrance. I was...have two questions. One, I was wondering if you could tell me the time and the place of the May 3 hearing and press conference in Torrance. I don't see that on your website. And I was wondering if the additional information you were still looking for from ExxonMobil related to the near miss and

the explosion itself had anything to do with the subpoenas that were issued to them requesting information. I was wondering if that's the case, if you can shed light on how many subpoenas remain unanswered out of however many you were...you did issue or the Department of Justice issued on the agency's behalf. Thank you.

VANESSA ALLEN SUTHERLAND: Thank you, Mr. Green, for that. The time and place will be emailed out to everyone, as I mentioned. For some of these events, as we're continuing to work on logistics and get the space and rent space, whatever... If it's a conference center or hotel, etc., that will...the specific time and location will be available. We know it's going to be May 3 because we want to make sure we block out that week. But we can certainly make sure that when we have nailed down the specific logistical agenda and calendar, that we place that on the website.

On the near miss, I will ask Ms. Wenzel to talk about the specificity of the number [inaudible] for the subpoenas. But, yes, to answer your question broadly, those are the documents that relate to the near miss and so we…in order to move forward with analysis on the near miss incident, we would need the documents that were the subject of those subpoenas. Do you have anything to add?

KARA WENZEL: Yeah, there were mere five total subpoenas but each one sought a number of items. Some of those, ExxonMobil has complied with through a long, protracted series of discussions with them. They have agreed to produce some of those items so we have stricken them from the list. But there still remain several...several dozen actually documents relating to the alkylation unit and the near miss that they have declined to produce.

VANESSA ALLEN SUTHERLAND: We also have a comment for meeting...from <u>meeting@csb.gov</u>. "With the loss of the CSB, what would be the impact of investigations of these...of any future tragedies, the data loss...I think it's, okay, loss of life, and recommendations? Who would tell us the truth?"

I'm not sure that I could answer that. As I mentioned, the CSB is the only agency in the federal government that has this particular mission to investigate incidents with the primary purpose of preventing them in the future. And we didn't get any additional budget information about if and when we were to be eliminated, what the proposal or alternative would be to place that independent, non-regulatory role into another agency.

So I...unfortunately, I apologize to Ms. Gonzalez. I don't have an answer to who might perform it if we were not performing that

work. I think we are the only ones currently performing this type of activity. Oh, sure.

MEMBER ENGLER: Yeah, just... It's relevant to understand the history of the CSB in this regard. Because in fact, in the early years of the CSB, after the Clean Air Act Amendments of 1990 established the Board, that the Board was not funded because of opposition from two presidents, Clinton and Bush. And what the position of those administrations was at the time was that OSHA and EPA should be able to carry out the function of the CSB. And, in fact, special funds were allocated in the budget, limited funds, to OSHA and EPA to do a joint investigation.

And one of those investigations...there were only one or two, in fact, I believe, was of Napp Chemical in Lodi, New Jersey, which had an explosion in 1995, killed five workers, polluted the environment, led to exposures for firefighters and other emergency responders. And that investigation was not a comprehensive investigation. It was not an all cause investigation. Did not fully look at the variety of factors that led to the Lodi Napp Chemical disaster. And at that point, after waiting and waiting for that inadequate report, Senator Lautenberg looked at this administration's position and said it was unacceptable and pursued

vigorously with industry support, with support of broad public constituencies, actual funding for the CSB and that happened.

So I think it's interesting to note that the same…and to some extent we're speculating here because we haven't been told exactly why the CSB does not perform a necessary function. But if it can be anticipated that it is somehow duplicative, this is the same exact historical dynamic that played out in the late 1990s that led to CSB's initial funding and the work that followed since then.

VANESSA ALLEN SUTHERLAND: Are there other comments in the queue, on the phone, or questions?

OPERATOR: We do have another question. Our next question comes from John Morvid[?]. You may begin.

JOHN MORVID[?]: Yes, again, thanks to Chairwoman Sutherland as well as all the members of the board and the staff. As everybody has said, CSB really performs a really invaluable service. It's a unique service and we much appreciate it, not just the facilities where tragedy has struck or that we may represent workers. It's the hazard analysis but most especially the recommendations that Chairwoman Sutherland mentioned that are extremely valuable, broad recommendations.

And I would just add beyond that, I would hope and I don't know whether the recommendations beyond the numbers that Chairwoman

presented, whether they're separated out by the types of recommendations. I think some of them are to county organizations, state organizations, volunteer associations. Some are particularly to individual companies. But I think they each serve different purposes. And I think it might be interesting to see which...how each...all of them play out.

The other comment on recommendations is it sounds like the metric is has the recommendation been closed. I would just suggest that sometimes closing a recommendation is beyond...often beyond the CSB's control. And I don't think it's necessarily a negative aspect if it is not closed. And it sounded like that was the implication. So that's all I had to comment and ask a question.

VANESSA ALLEN SUTHERLAND: First, thanks for calling in. and those are both good points. On the type of recommendation, we do have the ability to segment what type of recommendation. For example, we can tell you if we have recommendations made to a specific entity or based on specific types of incidents. So we do actually track that. We do look at that internally.

Part of the reason we present at a summary level the recommendations by number and closure is that's a metric that Congress shared with us and then reiterated with me specifically. They wanted to know how many we were closing. So even if they were

closed unacceptably, they simply wanted to know were we making movement, were we engaging with the recommendation recipient. So that's part of the answer as to why we use the total number that we've issued and then look at the closing.

But it is an absolute legitimate point that sometimes keeping it open can be as meaningful or impactful as closing it out and, you know, not having movement. I think our team does a really great job of assessing when a recipient may need more time or when a recipient is working towards closure, that we have the flexibility and option to keep something open a little bit longer if we are continuing to engage in a collaboration with the recipient.

But to answer that question, no, just closing it or the number of closures is not the sole metric that we...that we look at. We do slice the data in other ways to look at certain areas of interest.

MEMBER ENGLER: And if I can add, I believe we're going to do a new publication on impact of types of specific safety improvements. It may highlight a number [multiple voices] that are from around the country but it's a pretty powerful record.

I mean in New Jersey, for example, fire code officials are being trained about the hazards of combustible stuff as a result of our investigation at the US Ink plant. Gas, using gas... One of

those things that should be obvious but using natural gas for cleaning piping. You'd think that might not be a good idea when there are substitutes for doing that. Well, workers died in Connecticut. The CSB investigated gas...using gas for pipe cleaning piping systems is banned in Connecticut. The New York City Fire Code was revised as a result of CSB work to address incidents there. And even though they're not industrial facilities that are so much associated with the work of this agency, I think it could be credibly argued that chemistry labs in schools across the country are safer as a result of CSB's work and our investigation, our video and our outreach around it.

So I think that...that CSB will be further illustrating some of the very concrete impacts that have made a difference in protecting people in the coming weeks.

VANESSA ALLEN SUTHERLAND: Yeah, I think our team has done a great job of proposing how to illustrate that and then distilling it into a way that it's digestible. The fact that their creativity is how do we take all of the work that we've done, even the business case, showing the impact on the other side, what happens when these facilities have catastrophic failures. What's the cost to California consumers on gasoline when the refinery that supplied

10% of all gasoline is shut down for a long period of time? That's a real impact.

And so I think, even though we talk about them in isolated incidents...just for the last year we've been talking about West Fertilizer and how much of a coup it was to get FEMA, another federal agency, to work on our recommendation and issue emergency training grants, a \$1 million each, I might add. But I think we can name a lot of individual successful. I think the point is that we have to figure out how to do that in a more sort of easily distilled way. And I...I... I don't know that it's always as a result of our recommendations. Sometimes the work that we do is just that good that even if no recommendation has been made, people take the lessons. We share them broadly. And a recommendation may or may not have been attached to a case study or safety bulletin. But the fact that we told people what went wrong and we looked systemically at contributing causes, that's why we need to stay around. Because we do that. And others may be more narrowly focused on regulatory non-compliance.

Amy, I'm looking at your computer, but I want you to know it's just because comments have come in. Like the mention I gave to Dr. Tur[?] submitting comments to us for HF interest in California, I also wanted to acknowledge that Fred Millar also submitted written

comments just now. We haven't had a chance to read those two pages regarding Pamphlet 74 update which is...I think it's a request to review March 27th Revision 1 of Edition 6 of Pamphlet 74, which is Guidance on Estimating the Area Affected by a Chlorine Release. So wanted to acknowledge that and thank Mr. Millar for submitting that as well. We will read that also.

Scroll up. Okay, and that's just a duplicate of how to read the question. So, Operator, being mindful of time, I will ask that if you have any last callers in the queue, that this be the last caller. We'll see how many others we may have but we have about four more minutes. Are there any callers in the queue?

OPERATOR: We do have another question. Our next question comes from Tim Wagner. You may begin.

TIM WAGNER: Yes, good afternoon. Thanks for taking my call. I am calling representing Utah Physicians for Health & Environment in Salt Lake City. And speaking as…on behalf of an advocacy organization for healthy air and a clean environment for our constituents, and recognizing the importance of…of the CSB, I am wondering about the opportunity for our membership to make calls and emails to our members of Congress to reject the budget that would effectively eliminate this very critical program. And if…if

we do so, are there some talking points on your website that we could find that would help us reach out to our members?

VANESSA ALLEN SUTHERLAND: Well, there... No, there really aren't talking points or, you know, sort of guidance points of what someone would or could say if they called their member of Congress on our behalf. What... What I have said to people is, as a citizen, we certainly... I personally and I know the entire team appreciates that kind of feedback. And, yes, if you were to call your Representative and express how important the CSB's work is to you or your community, you have absolutely the right to do that. We don't have...I guess when you're saying like a script or talking points or the like, that we would tell you. I mean I would simply say that you sound like you are very familiar with us and our unique role and the, you know, importance of our mission. And so simply sharing that passion, sharing your perspective with your member of Congress is something that you absolutely can do as a citizen so that people understand that this work is valued and that people out in the community and in associations and in industry welcome and rely on the work that we do.

And I will ask Member Engler and Ehrlich if you have other comments, but certainly, you know, we are in a tricky position because we don't provide information or documentation as a federal

agency that, you know, encourages or directs people to go out to lobby on our behalf. But it's very encouraging to hear that people value the work and want to continue to see the mission and the investigative products of the CSB continue.

So, yes, as a citizen, you can always call your member of Congress and the oversight committee.

MEMBER EHRLICH: Yeah, I do have something to say. It was announced yesterday or perhaps the day before that on Whitehouse.gov there is a section now where the administration has asked the public for...

VANESSA ALLEN SUTHERLAND: Its comments.

MEMBER EHRLICH: Pardon? For its comments, which agencies they want. We're on there. That's on Whitehouse.gov. Tom, is that the right URL?

TOM[?]: Mm-hm.

MEMBER EHRLICH: Okay. And there's a section on there that goes through the... I'm sorry, Tom, can you refresh my memory on the name of that particular activity? Is it improving the...

VANESSA ALLEN SUTHERLAND: It's the broader administration's effort on improving or restructuring the executive branch. It was the... The Executive Order was originally out about a month ago and they recently updated it. And now the Whitehouse has opened up its

website for public comment for any agency that you would like to say should have more money, less money, stay the same. But it's allowing the public an opportunity to comment on not just the blueprint, but I suspect the larger, more detailed budget that is supposed to be coming out in the middle of May.

MEMBER EHRLICH: Thank you.

VANESSA ALLEN SUTHERLAND: Operator, we have time for, I think, one more question. Is there anyone in the queue?

OPERATOR: We do have one more question. Our next question comes from Richard Rusarra. You may begin, sir.

RICHARD RUSARRA: Yes, this is Richard Rusarra. Actually some of what you said is...is what I was going to ask about. Are there particular committees of Congress which you would like to...to highlight as being very important in the budget process? For instance, the Appropriations Committee in the House or the Senate?

VANESSA ALLEN SUTHERLAND: Yeah, I mean, all of those committees are certainly going to be evaluating the budget blueprint and our budget, our future. I don't know that everyone knows but we are...our oversight committees are the Senate EPW, Environment and Public Works Committee. Certainly Energy and Commerce has some interest, a lot of interest in what we do. The House Oversight and Government Reform, the House Appropriations,

Senate Appropriations. All of those…there are lots of different subcommittees. But broadly, the CSB, like many other federal agencies, are overseen by a variety of House and Senate committees. And so the ones that I just mentioned would…would be the most familiar with our work, our budget, what we do, how we do it. And they are also going to be the likely reviewers and decision makers on our budget, whether that is to eliminate it or to reduce it or to keep it the same.

RICHARD RUSARRA: Okay, thanks very much.

VANESSA ALLEN SUTHERLAND: You're welcome. Thank you for that question.

MEMBER ENGLER: This is Member Engler. Just...in terms of who does the actual marking up on the House side, the committee with jurisdiction is the Appropriations Committee but they have a subcommittee on Interior and Environment.

VANESSA ALLEN SUTHERLAND: So, Operator, I'm not sure if there are other questions in the queue. I see no others on my email or in the email list that we send out to people at <u>meeting@csb.gov</u>. However, I appreciate everyone's feedback and certainly we will continue to take suggestions, compliments, constructive criticism, feedback, all of the above at <u>public@csb.gov</u>. So if you happen to have a question or a comment after today's public business meeting,

please submit to <u>public@csb.gov</u> and we'd be happy to get back to you.

Is there a final question in the queue? I said that was the last one but then Richard's question was just a follow-up or refinement.

OPERATOR: At this time, we have no further questions in the queue.

VANESSA ALLEN SUTHERLAND: Great. Then I would like to thank everybody, those in the room and on the phone, for participating, listening, and sharing your questions and thoughts. I would also like to thank the staff, who some of them have gone off to meetings at 2:00, for their stamina, their teamwork, and ongoing dedication in the face of, you know, very challenging times. They continue to focus on the very important work of the agency and can do that is a very focused, undistracted way.

I'd also like to thank my fellow Board Members, including Member Kulinowski in absentia, on the phone, for their numerous contributions during this period, as well as at today's meeting. We all share a strong interest in trying to prevent chemical incidents or serious accidents in the future. And I hope that we can continue to work collaboratively with our stakeholders to make

sure that we're doing that in a way that's impactful and [inaudible].

So we appreciate your comments. As I mentioned, please feel free to submit additional follow-up at <u>public@csb.gov</u>. Our next public business meeting will be in July 2017. We will have additional details about that date and time in the upcoming weeks and will post that on our website. It will be in D.C. in our headquarters location on Pennsylvania Avenue.

But with that, thank you for your attention and attendance today. Your thoughts and contributions are appreciated. I don't have a gavel so the meeting is adjourned.

OPERATOR: Thank you, ladies and gentlemen. This concludes today's conference. Thank you for participating. You may now disconnect.

Reverse-engineering the oil industry's analysis of MHF, part 1, Antonie K. Churg, Ph.D. (Physical Chemistry), resident of Torrance, CA

This paper is offered to help the US Chemical Safety Board (CSB) assess how effective the additive in "modified" hydrogen fluoride (MHF) really is in suppressing HF volatility and aerosol formation. The independent investigation of industry claims is in the public-interest. Here, we are reverse-engineering the oil industry's analysis of the properties of MHF. Sally Hayati, Ph.D.¹ (Computer Engineering), lead researcher for the Torrance Refinery Action Alliance, asked me to assess some of the chemical aspects of this issue.

Apart from secrecy about "proprietary" information, the published reports about MHF are deceptive. The most glaring (and embarrassingly trivial) deception is that the oil companies describe the additive concentration in units of *weight percent*. The concentration units required for meaningful analysis and understanding of the physical chemical behavior are *mole fraction* or *mole percent*. When the additive concentration is given in the correct units, the inconsequential benefit of small amounts of additive is evident.

Exxon Mobil's safety rationale for accepting HF over sulfuric acid (H_2SO_4) is also critiqued, and the critique is damning. The Torrance Refinery Safety Advisor² claimed that MHF is slightly better than H_2SO_4 with regard to not forming an aerosol. This is shown to be dubious, because the "tests" of MHF aerosol formation substituted a refrigerant for the alkylation hydrocarbons, and that refrigerant is 4.74 times as dense as air and 2-4 times as dense as the alkylation reactants. No wonder the HF mixture travelled close to ground and fell in the water pools where it was collected! I also comment on the reasons that Refinery Manager Brian Ablett gave (during the CSB's January 13 report-back) for using HF rather than H_2SO_4 . I organize the presentation as a sequence of questions:

- That is the additive?
- The work of the sulfolane reduce the volatility of HF?
- How does MHF perform with respect to suppression of aerosol formation on release of HF in the atmosphere?
- The Torrance Refinery Safety Advisor claims that airborne release of MHF beyond the refinery fence line is *less probable* than escape of H₂SO₄. Why is this dubious?
- How do the reasons for choosing HF over H₂SO₄ given by Torrance Refinery Manager Brian Ablett (at the January 13, 2016 CSB report-back) square with other known facts?
- The well do existing models predict and quantify airborne release and dispersion?

What is the additive?

The mysterious additive in MHF is Sulfolane,³ or 2,3,4,5-tetrahydrothiophene-1,1-dioxide. The structural formula is:



We know this, because the Valero Refinery in Wilmington states that it is using "ReVAP".⁴ ReVAP stands for "Reduced Volatility Alkylation Process".⁵ ReVAP was patented by Phillips.^{6,7} Phillips had patented Sulfolane in 1951 for use as a selective solvent for liquid-vapor extractions.⁸ Shell used Sulfolane for extraction of butadiene. This affinity for butadiene suggests that Sulfolane might interfere with the alkylation reaction of propene, butene and pentene with isobutane. The degradation of Sulfolane in the harsh conditions of the alkylation unit should also be problematical. That was the case, and the amount of additive had to be reduced in order to keep MHF viable.

How much does Sulfolane reduce the volatility of HF?

Briefly: With 30% by weight Sulfolane, there is about 30% or 35% reduction in vapor pressure, compared to the vapor pressure of pure HF. With 10% by weight Sulfolane, *there is at most 15% reduction*. 10% Sulfolane is the formulation documented by the Valero refinery in Wilmington.⁹ 10% by weight is really 2% by moles. But use of weight percent hides the fact that Sulfolane cannot be doing its job!

Figure 1 shows the HF vapor pressure suppression by the additive, as displayed in Phillips' US patent. Presumably, Phillips measured the HF vapor pressure for a set of additive concentrations and drew a curve through the observed data points. The percent additive that is admitted [endnote 9] to be in use, 10% by weight, is the 6^{th} point from the left.



Figure 1: The diagram in Phillips' US patent [endnote 6] showing measured vapor pressure of HF (in millimeters Hg) vs. Sulfolane additive concentration in weight percent. The percent additive that is admitted [endnote 9] to be in use, 10% by weight, is the 6th point from the left.

The same empirical data are displayed in Figure 2, with Sulfolane concentration in units that are routinely used in physical chemistry: mole percent or mole fraction. Mole fraction and mole percent accurately reflect the *relative numbers of molecules*; lead pellets and jelly-beans are counted equally. If the weight percent of Sulfolane is w, the mole *fraction* of Sulfolane, f_S , is

$$f_{\rm S} = \frac{\frac{w}{120}}{\frac{w}{120} + \frac{100 - w}{20}} \,.$$
 Equation (1)

(The molecular weight of Sulfolane is 120, while the molecular weight of HF is 20). The corresponding mole fraction of HF is, of course, $1-f_S$. In Figure 2, the empirical data are compared with the vapor pressure predicted by Raoult's Law. Raoult's Law represents an "ideal" or "placebo" effect in which the additive is miscible with HF, but has no suppressive effect (other than dilution). Under Raoult's Law, the HF vapor pressure would be:

$$p_{\text{Raoult}} = (1 - f_{\text{S}}) p_{\text{HF}}$$
.¹⁰

Sulfolane does have a suppressant effect, compared to Raoult's law. However, the vapor pressure suppression is only appreciable for the four highest Sulfolane concentrations that Phillips reports.



Figure 2: Phillips data plotted *vs. mole percent* of Sulfolane, and a comparison with what would be observed if Sulfolane had no suppressive effect (other than dilution), i.e. an "ideal" or "placebo" effect described by Raoult's Law. The mole percent is equal to the *mole fraction* times 100. If the weight percent of is *w*, the mole *fraction* is the quantity (w/120)/(w/120 + (100 - w)/20). In the "ideal" model, the HF vapor pressure equals the mole fraction of HF times the vapor pressure of pure HF. [see also endnote 10]

The raw vapor pressure data in Figure 2 are suggestive of an exponential fall-off:

$$\frac{P_{\text{observed}}}{p_{\text{HF}}} \propto \exp(-\lambda X_{\text{S}}) ;$$

Equation (4a)

Equation (2)

$$\log_{e}\left(\frac{p_{\text{observed}}}{p_{\text{HF}}}\right) = -\lambda X_{\text{S}} + const \quad .$$
 Equation (4b)

In Equations (4a) and (4b), $p_{observed}$ is the observed vapor pressure of HF, p_{HF} is the vapor pressure of pure HF, X_s is the mole fraction of Sulfolane (mole fraction is more convenient than mole percent for the subsequent discussion), log_e denotes the logarithm to the base e, the natural logarithm. λ is a thermodynamic parameter that will be discussed in a moment. If the fall-off is exponential, then a plot of the logarithm of the *relative vapor pressure* ($p_{observed}/p_{HF}$) vs. mole percent Sulfolane will be a straight line.

The exponential fall-off is confirmed in Figure 3. The slope of the line is a measure of the interaction between HF and Sulfolane, and we can estimate the enthalpy of solution of HF in Sulfolane, and compare that with the enthalpy of solution of HF and water.



Figure 3: The logarithm (base e) of the relative vapor pressure of HF, that is $\log_e(p_{observed}/p_{HF})$, vs. mole percent Sulfolane, and a least squares fit of the logarithmic data to a straight line. The slope of the line allows us to estimate the enthalpy of solvation of HF in Sulfolane.

I estimate of the enthalpy (heat) of solvation of HF in Sulfolane using the following argument: The free energy change ΔG when a liquid in equilibrium with its vapor goes from configuration *A* to *B* is given by:

$$\Delta G_{A \to B} = RT \log_{e} \left(\frac{p_{B}}{p_{A}} \right), \qquad \text{Equation (5)}$$

where *R* is the universal gas constant, 1.98717 calories ${}^{\circ}K^{-1}$ mole⁻¹ or 8.31431 joule ${}^{\circ}K^{-1}$ mole⁻¹, and *T* is the temperature in degrees Kelvin. (In the present problem "configuration *A*" refers to pure HF and "configuration *B*" to HF in Sulfolane.) It is thus quite reasonable to identify $RT\log_e(p_{observed}/p_{HF})$ with ΔG for dissolving HF in Sulfolane. When the mole fraction of

Sulfolane $X_s = 1$, we have the ΔG at "infinite dilution", call it ΔG_{∞} . The slope of the line in Figure 2 thus corresponds to the parameter λ of Equations (4a) and (4b); λ is thus interpreted as

$$\lambda \leftrightarrow \Delta G_{\infty}/RT.$$

The slope of the line in Figure 3 has the value is -0.06. To make the correspondence with λ in Equations (4a) and (4b), we need to multiply this by 100, because ΔG_{∞} is defined for $X_{\rm S}$ =1, not $X_{\rm S}$ =100.¹¹ This gives the free energy of solution of HF in Sulfolane (at infinite dilution) as ΔG_{∞} = -3.473 kcal mole⁻¹ = -14.53 kJ mole⁻¹. Equation (7) The thermodynamic parameter that is usually reported for solutes is the enthalpy of solvation, ΔH , where

$$\Delta G = \Delta H - T \Delta S.$$
 Equation (8)

The entropy of mixing contribution to ΔG is

$$\Delta S_{\text{mix}} = -R(X_1 \log_e X_1 + X_2 \log_e X_2), \qquad \text{Equation (9a)}$$

where¹²

$$-(X_1 \log_e X_1 + X_2 \log_e X_2) \le \log_e(2) = 0.6931.$$
 Equation (9b)

Therefore, the $-T\Delta S_{\text{mix}}$ contribution to ΔG at 303 °K is between -0.417 kcal mole⁻¹ (or -1.746 kJ mole⁻¹) and zero. At infinite dilution the entropy function is zero. So we can ignore the entropy of mixing, and ΔG_{∞} from Equation (7) serves as an estimate of ΔH_{∞} , the enthalpy of solution of HF in Sulfolane at infinite dilution of HF.

$$\Delta H_{\infty} \approx -3.5 \text{ kcal mole}^{-1} \approx -14.5 \text{ kJ mole}^{-1}$$
. Equation (10)

How does this result compare with the solvation enthalpy of HF in water? The enthalpy of solution of HF in water is^{13, 14, 15}

$$\Delta H_{\infty}^{\text{H}_2\text{O}} = -14.7 \pm 0.1 \text{ kcal mole}^{-1} = -61.5 \pm 0.42 \text{ kJ mole}^{-1}.$$
 Equation (11)

Equations (10) and (11) indicate that water is a substantially "better" solvent for HF than Sulfolane. This comparison is not surprising, but water is unsuitable for the alkylation reactions.¹⁶ One might still question whether water sprays can "soak up" the HF emitted from a large opening, and thereby prevent dispersion beyond the fence line. This concern motivated the "Goldfish" tests as early as 1986. [Please see endnote 22 discussed below.]

How does MHF perform with respect to suppression of aerosol formation on release of HF in the atmosphere?

Two claims were made for Sulfolane: (1) it reduces the HF vapor pressure; (2) it suppresses aerosol formation by promoting condensation, or "rain-out" of HF when the pressurized alkylation unit breaks open to the air. Reducing the vapor pressure of HF should reduce aerosol formation and increase rain-out,¹⁷ but the dynamics are complicated to model.¹⁸ Phillips'

Equation (6)

European patent [endnote 7] diagrams the percent rain-out of escaped fluid *vs*. the vapor pressure in the test vessel, and indicates the weight percent of Sulfolane in the test mixtures. The diagram from the patent is shown in Figure 4. Notice how the four data points (30%, 40%, 50%, 100%) with high rain-out in Figure 4 correspond to the four data points with appreciably lower vapor pressure than the "ideal" in Figures 1 to 3. But for mixtures with less than 30 weight % Sulfolane, the rain-out drops off sharply toward zero. Measuring the percent rain-out entails collecting dangerously toxic acid droplets around an exhaust hole/jet. This would not be reproducible from one pilot-project to another, and it affords poor prediction of what would happen in an explosion or accident.



Figure 4: Rainout percent of escaped HF-Sulfolane fluid mixtures *vs*. vapor pressure, as diagramed in Phillips' European patent [endnote 7].

It should also be mentioned that the Princeton model [endnote 18] for HF-"additive" rain-out uses the mole fraction of the "additive" as a parameter, but *the published paper does not provide analytical expressions or calculated results describing how the rainout depends on the mole fraction of additive*. Any reasonable mechanism for aerosol suppression would have to show how the suppressor molecule (Sulfolane) breaks up the polymerized HF molecules clustered in the aerosol. *Sulfolane is non-volatile*; Sulfolane will tend to rain out, and if the liquid starts as 2 mole percent Sulfolane, the percent of Sulfolane molecules in the vapor will be even lower. Aerosol suppression ought to be even less than the suppression of evaporation.

The Torrance Refinery Safety Advisor claims that airborne release of MHF beyond the refinery fence line is *less probable* than escape of H_2SO_4 . Why is this dubious?

Since 1995,^{19,20} the main criteria for acceptance of MHF have been that (a) MHF does not form an aerosol, and (b) that release beyond the refinery fence line is no more likely than with H_2SO_4 .²¹ The Safety Advisor's Report of 1995 [endnote 2] asserted that these criteria are met by MHF. That is, the Safety Advisor claims there is some aerosol formation by H_2SO_4 but not by MHF. In their October 2015 presentation, [endnote 20] Maher and Kaiser admitted this is "counterintuitive": H_2SO_4 has a vapor pressure of 0.001 mm Hg and boils at 337 °C, while HF

boils at 19.5 °C. Moreover, the "Goldfish" experiments of 1986 established that the release of HF from a pressurized vessel forms a dense aerosol/vapor cloud that can travel for miles.²² The Safety Advisor compared Quest Diagnostic's 1991 tests for aerosol formation when $H_2SO_4^{23}$ is the alkylation catalyst with subsequent studies with MHF.²⁴ Quest found [endnote 23] that 2.8% of the H₂SO₄ went a distance beyond 100 feet from the source nozzle; the rest rained out. The H₂SO₄ study was performed with a hydrocarbon mixture that emulated the constituents of an alkylation unit. The presence of hydrocarbons was a necessary condition for having any airborne acid at all. In contrast, the MHF release tests were conducted replacing the alkylation hydrocarbon reactants with *refrigerant*, "(G-124) with similar flashing properties".²⁵ None of the references documenting the Safety Advisor's assertions related to Quest's MHF study are accessible; they are personal communications and proprietary publications. The named refrigerant, G-124, is equally obscure. There is Honeywell's Genetron ® 124 which is CHClFCF₃,²⁶ which has the same chemical formula as the well-known refrigerant R-124.²⁷ I doubt that the mysterious G-124 is another species, because of the standardized numbering system for naming CFC refrigerants.²⁸ If the Safety Advisor claims that "G-124" is not CHClFCF₃, the identity of "G-124" ought to be subpoenaed.

Let me repeat this: Emulsion of the alkylation reactant hydrocarbons with H_2SO_4 was essential for a slight fraction of the H_2SO_4 becoming airborne when the pressurized mixture was released through nozzles, but in the MHF tests, a CFC refrigerant was substituted for the alkylation reactant hydrocarbons. All the scientific justifications for making this crucial substitution are in private and proprietary communications. No evidence of "similar flashing properties" [reference 1, p. 93] of "G-124" is presented. In fact, *the refrigerant substituted for the alkylation hydrocarbons differs in one utterly crucial respect: It is 4.74 times as dense as air*,²⁹ and 2 to 4 times as dense as the alkylation reactants! R-124 also has a higher ΔH_{vap} than most of the other species that would be in an alkylation vessel, which would make it a better coolant. The parameters are shown in Table 1.

Name	Boiling point, °C	Heat of vaporization	Gas density,
		at boiling point,	10^{-3} g/cm^3 ,
		$\Delta H_{\rm vap}$, kJ/mole	$\pm 0.1 \mathrm{x} 10^{-3} \mathrm{g/cm}^{3}$
$R-124 = CHClFCF_3$	-12	26.5	5.6 ³¹
butane	0	22	2.5
1-butene	-6.5	20.9	2.3^{32}
isobutane	~-10	21.3	2.5
propane	-42	15.7	2.0
propene	-47	18.7	1.18
1-pentene	+31	25.2 ³³	_
HF	+19.5	25.2	1.15
air	-190	-	1.18

Table 1: Gas phase properties³⁰ of alkylation reactants compared to R-124

An alkylation reaction mixture has roughly 50% by volume anhydrous acid – somewhat less when HF is used.^{34, 35} Presumably in these tests of MHF dispersion, equal volumes of MHF and refrigerant were mixed. (If more refrigerant were used, that would be cheating on steroids!) But since the refrigerant vapor is 4.74 times as dense as air, the resulting vapor phase mixture would be about 2.3 times as dense as air. Much to everyone's surprise, the ejected vapor mixture sank to the ground, and the water-soluble HF could be collected in pans of water distributed throughout the test chamber. The recovery of HF was better than 98%.

I will not bother to further comment on the fact that an airborne reduction factor (ARF) of 65% was claimed for the MHF used in these tests.

How do the reasons for choosing HF over H_2SO_4 given by Torrance Refinery Manager Brian Ablett (at the January 13, 2016 CSB report-back) square with other known facts?

During the January 13, 2016 CSB report-back, Chairperson Sutherland asked Refinery Manager Ablett to explain the reasons for selecting HF over H_2SO_4 . Brian Ablett answered that the Torrance refinery processes unusually heavy crude, and there is a wider range of carbon chain lengths to be alkylated, and the carbon chain lengths are longer. This chemistry, Ablett said, favors HF over H_2SO_4 . However, according to a short paper³⁶ published online by DuPont, it is only the cost of catalyst that favors selection of HF. Less acid is required in an HF unit and the HF can be reclaimed and re-purified on site. Safety and environmental considerations unequivocally favor H_2SO_4 . The DuPont paper includes a pie chart asserting that 86% of new units licensed since 1990 have selected H_2SO_4 alkylation technology over HF. However, converting an existing HF alkylation unit to an H_2SO_4 unit entails installing chillers to keep the temperature around 4 °C in order to maintain good octane rating of the output. Exxon Mobil and its allies claimed that MHF makes HF as safe as H_2SO_4 ; that argument was needed in order to avoid the large conversion cost.

How well do existing models predict and quantify airborne release and dispersion?

HF is highly toxic; a few drops of anhydrous HF splashed on the skin can be fatal. Given the established alternative of H_2SO_4 , and of solid phase alkylation catalysts under development [see endnote 34], it is humane and wise to ban HF and MHF as an alkylation catalyst. However, if you are willing to accept the deaths of a few refinery workers, then you start arguing how far beyond the fence line HF might be allowed to travel, and whose predictions are more accurate. In the Goldfish HF release experiments [endnote 22], the aerosol plume at a distance 5 miles from the source still had near-fatal HF concentrations. The relevance of the Goldfish test [endnote 22] was questioned by oil industry experts. They objected that the test was performed on a smooth, dry lake bed in the Nevada desert, and the ground-hugging fog could roll on for miles; in an industrial setting, surface roughness and various obstacles would break up the cloud.

The petro-chemical industry developed gas dispersion computer modeling in the 1990s;³⁷ one of the experts in dense gas dispersion modeling is Geoffrey D. Kaiser,³⁸ who is also one of the principal authors of the Torrance Refinery Safety Advisor's reports. For a given distance from the source, these models (DEGADIS, SLAB, PEAC, ALOHA) all predicted HF levels that were smaller than the Goldfish measurements by a factor of 4 to 5. Modelers introduced an *ad hoc* "surface roughness" parameter that could tweak the computer predictions for HF into closer alignment with the Goldfish measurements.³⁹ The EPA catalogs some known alternative models that can be used for regulatory applications,⁴⁰ and links to a paper evaluating them.⁴¹ Dr. Sally Hayati and I applied two of the modeling tools offered by the EPA; one is in a tabulated format,⁴² and the other is an online tool⁴³ called RMP*CompTM. Some of the features and shortcomings of these older tools can be seen from the plots referenced in [endnote 37] and similar plots in Figures 5 and 6 below.

Both Figures 5 and 6 are log-log plots of the tabulated results for HF in Table 7⁴⁴ of "Risk Management Program Guidance for Offsite Consequence Analysis" referenced in [endnote 42]. In Figure 5, the "toxic endpoint level" has a constant value of 25 ppm, and the ordinate is the log of the distance at which the HF level dissipates to this "toxic endpoint level"; the abscissa is the log of the release rate (mass of HF released per minute).



Figure 5: Log-log plot; the *y*-axis is the log_e of the "toxic endpoint radius", or distance from the HF source at which the HF concentration has dissipated to a "toxic endpoint level" of 25 ppm; the *x*-axis is the log_e of the source release rate, in lbs/min. The parameters are as described in [endnote 46]. In context of the discussion here, note that $log_e(500) = 6.2146$; $log_e(5000) = 8.5172$. The plot of $log_e(endpoint radius) vs. log_e(release rate)$ has nearly the same slope for all the toxic endpoint levels that I checked. Here the fitted slope s = 0.4840 which is very close to 0.5. Thus, for any toxic level, the endpoint distance is proportional to the square root of the release rate.

From Figure 5 we see that the endpoint distance d obtained from the models provided by the EPA⁴⁵ satisfies

$$\log_{e}(d) = s\log_{e}(M) + const,$$
 Equation (12a)

where *M* is the release rate and *s* is the slope. Ignore the additive constant, for now. Therefore, $d \propto M^s$. Equation (12b)

The fitted slope, $s = 0.4840 \simeq 0.5$. Thus, for any the toxic endpoint level, the endpoint distance is proportional to the square root of the release rate.

$$d \propto M^{\frac{1}{2}}$$
;
 $M \propto d^2$. Equation (12c)

In Figure 6, a similar reverse engineering analysis is applied to the toxic endpoint level *vs*. distance for three different release rates of HF. Again the linearity of the log-log plot implies a simple exponential relationship. If the toxic endpoint level is *V*, the slope of the fitted lines gives

$$d \propto V^{-0.5}$$
; Equation (12d)
 $V \propto d^{-2}$. Equation (12e)



EPA models for log (endpoint dist) vs. log (endpoint level) for 3 release rates

Figure 6: Log-log plot of $\log_{e}(\text{toxic endpoint distance}) vs. \log_{e}(\text{toxic endpoint level or "value"})$ for three different release rates of HF. Numerical parameters are as per [endnotes 42 and 44]. The endpoint levels are in units of mg/liter; 1 ppm = 0.82 mg/m³ = 0.082 micrograms/liter; 25 ppm = .0205 mg/liter. The fitted slope of the three lines, *s*, is close to *s*= -0.55. In the subsequent discussion, I approximate this as *s*= -0.5.⁴⁶

Equations (12a) to (12e) say that the dense gas is dispersed close to the ground and the concentration falls off from the source level as the square of the distance. This is an intuitive result, but all the physics is buried in the constant of proportionality. You can tweak the parameters of the model to best match the real tests. To some extent, this is the computational equivalent of reading tea leaves.

Reverse-Engineering MHF, Antonie K. Churg, Ph.D <u>achurg@socal.rr.com</u> (310) 539-6506

Nonetheless, the proportionality relationships from these numerical models are consistent with what we have inferred about the Sulfolane additive to HF. Crucial information about MHF at the Torrance Exxon Mobil refinery was withheld. Sally Hayati found clues in the Ultramar-Valero application to license an MHF alkylation unit in nearby Wilmington. On pdf page 31 of the "Worst Case Analysis" [linked in endnote 4], it is stated:

"The second specific conclusion that can be drawn from the study is that the modifications to the Alkylation Unit (ALKY) produce a significant reduction in the potential worst-case impact following a release of hydrofluoric acid bearing fluids. The implementation of the ReVAP process, with its use of the acid additive which reduces the volatility of the acid phase, results in an 7.9% reduction in the maximum hazard distance."

We can translate this statement into the airborne reduction factor (ARF) that Ultramar-Valero assumed for the MHF they were planning to use. The ARF is the percentage reduction in HF released when the modifier suppresses volatility. For example, an ARF of 50% means the amount of HF released is cut by half. Formally we would write:

$$ARF \equiv (1 - M_2/M_1) \times 100$$

where M_2 corresponds to the suppressed HF release, and M_1 to the unbridled release. Now, Equation (12c) describes a relationship between the relative distances and the relative releases:

$$(d_2/d_1)^2 = M_2/M_1.$$
 Equation (14)

If the toxic endpoint distance decreases by 7.9%, then we must have $d_2/d_1 = 0.921$. Then, with $(0.921)^2 = 0.8482,$

$$M_2/M_1 = 0.8482,$$

ARF = 15%. Equation (15)

The consistency with our other inferences about the ARF of MHF suggests that Equations (12c) and (12d) are reasonably valid for comparing ratios. In Figure 6, the line for 5,000 lbs/min (i.e. a total release of 50,000 lbs) is not quite parallel to the other two. Evidently the calculation of absolute distance magnitude is problematical, particularly for very large releases. However, terrible accidents can and do happen. Given the massive quantity of HF at these refineries, escape of 50,000 lbs of HF should not be ruled out by an independent analyst. Equation (12b) says that the toxic endpoint distance of a 50,000 lb release should be larger, by a factor of $10^{1/2}$ =3.16, than the toxic endpoint distance of a 5,000 lb release. The oil companies assume a maximum release of 5,000 lbs, and, depending on their claims about the ARF, they calculate a 20 ppm toxic endpoint distance of 3.2 to 4.6 miles. But if a 50,000 release occurs, then the same assumptions about the ARF give a toxic endpoint distance of 10.1 to 14.55 miles. Figure 7 displays some of these impact zones on a map of the region. The figure includes the impact zone for the 50 ppm toxic endpoint level. More than one hour of exposure to 50 ppm HF can have long term health effects or even death. This paper has presented evidence that MHF as it is being used is essentially no different from HF, and all the claims about the safety of MHF are fraudulent.

Reverse-Engineering MHF, Antonie K. Churg, Ph.D achurg@socal.rr.com (310) 539-6506 Page 11 of 15

Equation (13)

Torrance Exxon Mobil

Wilmington Valero







Figure 7: Two sets of circles centered on the ExxonMobil and Valero refineries show the impact zones of various leaks. Most of the Congressional Districts in Los Angeles County are in the 20 ppm impact zone of either the Torrance or the Wilmington refinery.

On the left, the inner gray circle (radius 3.2 miles) centered on the ExxonMobil/Torrance refinery represents ExxonMobil's worst-case scenario (20 ppm exposure, 5,000 lbs released).

On the right, the corresponding inner gray circle (radius 4.5 miles) represents Valero's "worst case scenario" [endnote 4].

The red circles (radius 7.6 miles) represent the 50 ppm HF toxic endpoint distance as calculated by Drs. Sally Hayati and Antonie Churg for 50,000 *lbs MHF released over 10-minutes – the entire contents of the HF acid settler vessel*, not some external pipe. An ARF of 26% is assumed, giving credit for 20% ARF due to Sulfolane additive, plus 6% ARF for barrier mitigation.

The black circles (radius 13.7 miles) represent the 20 ppm level as calculated for the same event.

Biographical background of the author:

Antonie Churg holds a Ph.D. in Physical Chemistry, U. of Chicago; dissertation: microwave spectroscopy of gas phase OH free radical. Subsequent postdoctoral and research work was in academic experimental biophysics of enzyme reactions and computer modeling of their reaction mechanisms. She has engaged in numerous science-in-the-public-interest efforts. These include work (as an undergraduate) on the Mt. Sinai, NY, asbestos project under Irving Selikoff, M.D., and later as co-organizer of the 1987 California Legislative hearings on Livermore and Los Alamos nuclear weapons labs.

Endnotes:

¹² The quantity $-(X_1 \log_e X_1 + X_2 \log_e X_2)$ is often called the *binary entropy function*.

- ¹⁴ The enthalpy of solution of HF can be compared with other species here: <u>http://sites.chem.colostate.edu/diverdi/all_courses/CRC%20reference%20data/enthalpies%20of%20solution%20o</u> <u>f%20electrolytes.pdf</u>.
- ¹⁵ <u>http://www.sciencedirect.com/science/article/pii/S002196147180112X</u> gives the enthalpy of solution of HF in water published in the Ph.D. thesis of Walter Wm. Rodenburg in 1968.
- ¹⁶ Water compromises the octane rating of the product: <u>http://www.slideshare.net/treasurebintyahyaahmad/441-</u> <u>introduction-9</u>, slide 13.

¹ Dr. Sally Hayati not only found most of the crucial papers cited in this report, but more importantly, focused the investigation on the low additive concentration in MHF, the changes in additive concentration over time, and the magnitude of the HF inventory of an alkylation unit. She also identified the H_2SO_4 issue as suspect and found important clues to the airborne reduction factor of MHF in the Valero/Ultramar environmental permit document linked in endnote 4. These clues are alluded to in endnote 9 and discussed at the end of the paper.

² Torrance Refinery Safety Advisor 's Evaluation of Modified HF Alkylation Catalyst, Final Report, May 1995 by principal authors Steven T. Maher and Dr. Geoffrey D. Kaiser; the report is available as http://psbweb.co.kern.ca.us/UtilityPages/Planning/EIRS/clean_fuels/Appendices/Appendix%20H_Torrance%20R eport%2017May95FinalR1_PUB.pdf.

³ <u>https://en.wikipedia.org/wiki/Sulfolane</u>. Note that this entry indicates that while Sulfolane is stable as a solvent, it eventually degrades into acidic byproducts. The breakdown of Sulfolane might well be accelerated in the harsh environment of the alkylation unit, and the breakdown products would very probably interfere with the desired alkylation reactions.

⁴ "Worst-Case Consequence Analysis For Ultramar's Wilmington Refinery Alkylation Improvement Project", Quest Consultants, Inc., September 2004. <u>http://www.aqmd.gov/docs/default-source/ceqa/documents/permit-projects/2004/ultramar-valero/appc252.pdf?sfvrsn=2</u>.

⁵ <u>http://www.eng-tips.com/viewthread.cfm?qid=191312</u>.

⁶ Our source for Phillips' US patent is: <u>https://www.google.com/patents/US5654251</u>; a pdf copy can be downloaded.

⁷ Our source for Phillips' European patent is: <u>http://www.google.com/patents/EP0796657B1?cl=en</u>.

⁸ The Merck Index, Ninth Edition, 1976, Merck & Co., Inc., Rahway N.Y.

⁹ See the "Worst-Case Consequence Analysis..." linked in endnote 4 above. The 15% airborne reduction factor was deduced by the author and is described later in the paper.

¹⁰ $p_{\rm HF} = 1080$ mm Hg, the vapor pressure of pure HF at 30°C. Rigorously, Equation (2) should be written as $p_{\rm Raoult} = (1-f_{\rm S})p_{\rm HF} + f_{\rm S}p_{\rm S}$, where $p_{\rm S}$ is the vapor pressure of Sulfolane at 30 °C. The normal boiling point of HF is 19.5 °C. The boiling point of Sulfolane is 285 °C; at 30 °C, the vapor pressure of Sulfolane is effectively zero.

¹¹ Both first and second degree polynomials were checked; the first degree polynomial fit had -0.0579; the second degree fit had -0.0603. The second degree term was zero. These polynomial coefficients were derived for the using mole percent, not mole fraction.

¹³ The published results for the solvation enthalpy of HF in water at infinite dilution are for T = 25 °C, i.e. 298 °K; this should be valid for 30 °C.

¹⁷ An aerosol is defined as a sub-micron cloud of liquid particles that travel greater distance than ordinary droplets; see, e.g. https://en.wikipedia.org/wiki/Aerosol. The term, "flash atomization" or "flash evaporation" refers to the formation of an aerosol when the pressure over a liquid at temperatures above the normal boiling point is released into the atmosphere.

¹⁸ https://www.princeton.edu/cbe/people/faculty/sundaresan/group/publications/pdf/62.pdf ; this model was a collaboration between Mobil and Chemical Engineering Department, Princeton University. The Princeton model for aerosol suppression depends on the "additive" jointly vaporizing with the HF. We know the additive is Sulfolane. The vapor pressure of Sulfolane is $\sim .01$ mm Hg, while HF has a vapor pressure >760 mm. See, for example, http://sulfolane.com/pdf/study vapor pressure.pdf or

http://www.ddbst.com/en/EED/PCP/VAP_C542.php. It is hard to understand how one Sulfolane molecule could magically drag 10,000 HF molecules to the ground. The aerosol suppression might be even less than the vapor

- pressure suppression. ¹⁹ Stipulation and Order, September 30, 1994, ordered by the Superior Court of the State of California for the County of Los Angeles, People of the State of California vs. Mobil Oil Corporation, Case No. C 719 953.
- ²⁰ The acceptance criteria in the 1995 Stipulation and Order are cited by Maher and Kaiser in their 1995 report [endnote 2], as well as in their presentation to the Torrance City Council, October 13, 2015: $\frac{\text{http://torrance.granicus.com/MetaViewer.php?view_id=8\&clip_id=12719\&meta_id=236674}{\text{H}_2\text{SO}_4 \text{ is the alkylation catalyst used by two thirds of US refineries.}}$
- ²² The seminal paper is the "Goldfish" study of 1986: Blewitt, D.N., J.F. Yohn, R.P. Koopman, and T.C. Brown, 1987, "Conduct of Anhydrous Hydrofluoric Acid Spill Experiments," International Conference on Vapor Cloud Modeling, Boston, MA; Center for Chemical Process Safety of the American Institute of Chemical Engineers, New York. This journal can be found in some libraries; http://www.worldcat.org/title/international-conferenceon-vapor-cloud-modeling-november-2-4-1987-boston-marriott-cambridge-cambridgemassachusetts/oclc/16867354 and at Amazon, UK: http://www.amazon.co.uk/International-Conference-Modeling-Cambridge-Massachusetts/dp/0816904243. The lead scientist, Ronald Koopman is now an independent consultant: http://www.laohamutuk.org/Oil/LNG/Refs/042KoopmanLNG05.pdf ; email address: rpkoopman@comcast.net; tel (925) 443-5324.
- ²³ <u>http://www.questconsult.com/pdf/paper44h.pdf</u>, David W. Johnson, "Sulfuric Acid Release Report".
- ²⁴ Jersey, G.R., K.W. Schatz, M.K. Chalam, R. Muralkdhar and K.C. Hoover (1993), "Large-Scale Release Testing of a Modified HF Catalyst," Presented at the 1993 AIChE Summer National Meeting, August 1993: American Institute of Chemical Engineers, New York.
- ²⁵ The Safety Advisor 's 1995 report, reference 1 above, discusses the HF "release phenomenology" on pp. 91-94.
- ²⁶ http://www.honeywell-refrigerants.com/americas/product/genetron-124/; Material Safety Data Sheet: http://msdsresource.honeywell.com/ehswww/hon/result/result_single.jsp?P_LANGU=E&P_SYS=1&C001=MSDS&C997= C100%3BESDS US%2BC102%3BUS%2B1000&C100=*&C101=*&C102=*&C005=000000009886&C008=& C006=HON&C013:
- ²⁷ MSDS for R-124: <u>http://www.hudsontech.com/wp-content/themes/hudson/pdfs/msds/R-124/ARKEMA_R-</u> 124.pdf; R-124 thermodynamic data:

https://www.chemours.com/Refrigerants/en_US/assets/downloads/h62445 hcfc124 push.pdf

- ²⁸ The refrigerant "R-number": For saturated hydrocarbons, subtracting 90 from the concatenated numbers of carbon, hydrogen and fluorine atoms, respectively gives the assigned R#. So Concatenation of 2C, 1H, 4F gives an R number of 214 – 90 = 124; https://en.wikipedia.org/wiki/Refrigerant.
- ²⁹ <u>http://www.hudsontech.com/wp-content/themes/hudson/pdfs/msds/R-124/ARKEMA_R-124.pdf</u>, Material Safety Data Sheet (MSDS) for R-124 refrigerant.
- ³⁰ Data are from Wikipedia or http://webbook.nist.gov/ except as where noted explicitly for the density of R-124 and 1-butene.
- ³¹ Density of R-124 is from the MSDS in reference 26 above.
- ³² Density of 1-butene is from <u>http://chemicalland21.com/</u>industrialchem/organic/1-BUTENE.htm .
- $^{33}\Delta H_{vap}$ of 1-pentene from http://webbook.nist.gov/cgi/cbook.cgi?ID=C109671&Units=SI&Mask=7&Type=HVAP-<u>FORM2&Plot=on#HVAP-FORM2</u> happens to be the same as ΔH_{vap} of HF, also from the NIST.gov data: http://webbook.nist.gov/cgi/cbook.cgi?ID=C7664393&Mask=4#Thermo-Phase
- ³⁴ The ratio of volume of conventional alkylation catalyst (HF or H_2SO_4) is given in an accessible source: the Petroleum Technology Development Journal, January 2013, Vol. 3, No. 1,

<u>http://ptdjournal.com/2013/Akpabio Neeka Review Petroleum Refinery Acid.pdf</u>. This article is noteworthy also because it gives an overview of the state of solid phase alkylation catalyst development.

- ³⁵ I had the impression from other sources that the HF volume percent is closer to 20%, but I am being conservative in this discussion. A 4:1 mixture of refrigerant and HF would make the fraud even more glaring.
- ³⁶ <u>http://www.dupont.com/content/dam/assets/products-and-services/consulting-services-process-technologies/articles/documents/H2SO4_vs_HF.pdf</u>. See their Table 2 on pdf p. 7 for a comparison of HF and H₂SO₄ with respect to unit investment, utility costs, catalyst and chemicals, safety/environmental considerations, product quality, and feed type/isobutane availability.
- ³⁷ <u>http://www.aristatek.com/About/history.aspx</u>; <u>www.aristatek.com/Newsletter/NOV08/TechSpeak.pdf</u>. This resource compares several gas dispersion modeling computer programs with field experiments.
- ³⁸ <u>http://www.epa.gov/sites/production/files/2013-11/documents/technical_background_document_for_offsite_consequence_analysis_for_anhydrous_aqueous_amm_onia_chlorine_and_sulfur_dioxide.pdf</u>.
 ³⁹ "Concentration" means the centerline concentration in the plume. For a given computer program (DEGADIS,
- ³⁹ "Concentration" means the centerline concentration in the plume. For a given computer program (DEGADIS, SLAB, PEAC, ALOHA), the results are low by the same factor for all distances. See the reference cited in endnote 37.
- ⁴⁰ <u>http://www3.epa.gov/scram001/dispersion_alt.htm</u> EPA Technology Transfer Network Support Center for Regulatory Atmospheric Modeling, Alternative models: Executables, source code and documentation.
- ⁴¹ "Evaluation of Dense Gas Simulation Models", May 1991, by James G. Zapert, Richard L. Londergan, and Harold Thistle, TRC Environmental Consultants, Inc., and EPA Technical Representative Jawad S. Touma. http://www3.epa.gov/ttn/scram/userg/other/DenseGasEvaluations.pdf.
- ⁴² "Risk Management Program Guidance for Offsite Consequence Analysis", US EPA, April 1999, and reissued in March 2009: <u>http://www2.epa.gov/sites/production/files/2013-11/documents/oca-chps.pdf</u>.
- ⁴³ The EPA's online gas-dispersion modeling tool allows both online and offline calculations. The online version runs in Firefox and Safari: <u>http://www.epa.gov/rmp/rmpcomp</u>; <u>https://cdxnodengn.epa.gov/cdx-rmp-maintain/action/rmp-comp</u>.
- ⁴⁴ Reference Table 7, Dense Gas Distances to Toxic Endpoint, 10-minute Release, Urban Conditions, F Stability, Wind Speed 1.5 Meters per Second, p. 64 of the pdf file in [endnote 42].
- ⁴⁵ Reference 36 seems to me to imply that the EPA is using the DEGADIS and SLAB software.
- ⁴⁶ In Figure 6, the slopes of the fitted lines are -0.5571, -0.5521, -0.6071 for the release rates 250 lbs/min, 500 lbs/min and 5,000 lbs/min, respectively. Note again, as mentioned in [endnote 44], that the total release occurs over a duration of 10 minutes.

CSB request Pamphlet 74 update presentation Bd mtg 4 13 17

Dear Members of the Board:

We still badly need the Board to scrutinize what the Chlorine Institute [CI] and its allies are doing to try to minimize the perception of the disaster risks of chlorine gas releases.

Cl's latest March 2017 Revision 1 of Edition 6 of Pamphlet 74, Guidance on Estimating the Area Affected by a Chlorine Release, despite widespread skepticism from many quarters, merely doubles down on its earlier stunning estimates of huge reductions in downwind distances in chlorine gas release travel. Revision 1 is based still allegedly only on results from the field tests from Jack Rabbit I, as well as new models and calculation methodologies that differ from previous versions of Pamphlet 74. Neither Edition 6 from 2015 nor Revision 1 from 2017 fully explains the inputs, assumptions and impacts of the new methodology.

You have already received a letter asking CSB assistance from the Washington Fire Chiefs association. Since CI clearly went gas model-shopping for years before releasing Edition 6 of Pamphlet 74 in June 2015, concerned groups and agencies badly need a challenging inquiry by the Board and an independent third-party expert review both of the methodology used and comparison with some major alternative gas models and assumptions.

Revision 1 to Edition 6 raises even more questions about exactly which modeling factors, assumptions and biased shenanigans account for the dramatic assertions of downwind gas cloud travel risk reductions [compared with previous editions of Pamphlet 74]:

1. The Gas Modeling Improvements Gang had long voiced explicitly their aims to re-calculate every element along the whole chain of atmospheric modeling and transport methodologies used in dense gas release work, from source terms to health effects, to challenge frontally the "over-estimations" of downwind gas cloud risk they saw in previous gas modeling. And they set about funding and coordinating a series of model developments and field testing work seemingly designed candidly to accomplish a reduction in perceptions of chlorine gas release risks.

Revision 6 now explains, for example, that the "health effects" factor will not be presented graphically in the "footprints", as helpfully in previous editions, mainly by the "instantaneous" concentrations [e.g., 20 ppm] of chlorine gas at any given point downwind, but by two ERPG levels that involve concentration over time, e.g., 3 ppm or 20 ppm exposure over one hour. This is of course a reduction in safety-conservatism in guidance for emergency responders, and suitable more for healthy male "war-fighters" than for vulnerable parts of the population such as elderly, children, asthmatics, etc.

2. Revision 1 admits [p. 18] there are of course lots of assumptions in the use of a complex methodology such as HPAC, but these are not listed fully nor are the impacts of various major

assumptions assessed or explained, such as the direction of the release jet of chlorine, the aerosol formation v. evaporation, terrain, meteorology. For example, the release is said to be onto concrete, but with no indication of whether the jet is directed into a hole in the ground as in the Jack Rabbit I tests – which clearly is designed to inhibit the downwind travel of the release cloud.

3. Revision 1 makes no effort, in short, to explain why the new estimates are so dramatically lower than previous estimates. Revision 1 only suggests [p. 56] that there may be some important new risk minimization impacts from inclusion of new source inputs and reactivity with soil modeling in the new HPAC modeling.

It would be interesting to see how the chlorine industry's own liability lawyers and their stock prices react to the proclamations of the Good News on chlorine downwind risks. Since the publication of Pamphlet 74 on the CI website is not exactly trumpeting it to the world, it would be helpful if the CSB and the NTSB would make pointed inquiries to CI asking much more transparency of how this alleged miraculous safety improvement was accomplished.

Regards,

Fred Millar