## U.S. Department of Labor Occupational Safety and Health Ad. .....istration



### **Inspection Report**

Tue Jun 19, 2007 8:54am CSHO ID Supervisor ID Inspection Nr. Opt. Insp. Nr. Rpt ID Assignment Nr. 0524530 0 Exemption 7c 309287175 Exemption\_7c Marathon Petroleum Company, LLC Establishment Name (618) 544-2121 Site (618) 544-5092 Site 400 S. Marathon Ave. Site FAX Address Robinson, IL 62454 Phone P.O. Box 1200 (618) 544-2121 Mail Mail Mailing Address Robinson, IL 62454 Phone FAX Controlling Employer ID Exemption 4 Corp 7400 County 033 Ownership A. Private Sector City Previous Activity (State Only) R. Referral 900703927 Legal Entity Related Activity Satisfied Satisfied Type Number Number Type A. Accident 100841766 Exemption 4 Advance Notice? Employed in Establishment No Category H. Health No Interviewed? Covered By Inspection Exemption 4 Union? Yes Controlled By Employer Walkaround? Exemption 4 No Primary SIC 2911 Secondary SIC Inspected 324110 Secondary Primary NAICS NAICS Inspected NAICS A. Fatality/Catastrophe Reason No Inspection Inspection Type Scope of Inspection B. Partial Inspection Classification Strategic Initiatives National Emphasis Local Emphasis Anticipatory Warrant Served? Denial Date Date ReEntered Date ReDenied ReEntered No Anticipatory Subpoena Served? No 01/21/07 09:00 First Closing Conference 04/10/07 01:00 Entry Opening Conference 01/21/07 09:15 Second Closing Conference 05/25/07 02:30 Walkaround 04/10/07 08:00 05/25/07 03:00 Exit Days On Site Case Closed No Citations Issued Type ID Optional Information Exemption 5 CSHO Signature Date

## U.S. Department of Labor Cocupational Safety and Health Acamistration



### **Inspection Report**

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### U. S. Department of Labor Occupational Safety and Health Administration

Investigation Summary Pri May 25, 2007 3:38pm





Reporting ID	Investigation Summary Number	OSHA-36 Number	OSHA-36 Establishment Name
0524530	200841302	100841766	Marathon Petroleum Company, LLC
Event Date	01/20/07	Event Time	03:11 pm
Type of Event	hydrogen sulfide ex	posure	

Inspection Number/ Establishment Name	309287175 Marathon Petroleum Company, LLC
Injured/Deceased Name	Dan Gunraj
Sex:	M. Male
Age:	47
Injury:	A. Fatality
Nature:	02 Asphyxia
Part of Body:	28 Lung
Source of Injury:	35 Petroleum
Event Type:	08 Inhalation
Environmental Factor:	Exemption 5
Human Pactor:	Exemption 5
Task:	A Regularly Assigned
Substance Code:	1480 - HYDROGEN SULFIDE
Occupational Code	699 - MISCELLANEOUS PLANT AND SYSTEM OPERATORS

### Abstract:

On January 20, 2007, an operator working in the Hydrofluoric Acid (HF) Alkylation Unit was in charge of maintaining the neutralization pits. The operator was in charge of draining a Constant Boiling Mixture (CBM's) which contained HF acid and water out of the Polymer Surge Drum into a neutralization pit. The CBM's, low in pH were sent to the South neutralization pit to neutralize spent potassium hydroxide that was contained in the open-surfaced pit. Potassium hydroxide (KOH) is highly basic and CBM's are drained into the South pit to lower or neutralize the pH. The draining of CBM's is accomplished by pressurizing the Polymer Surge Drum with a constant supply of natural gas. The vessel is pressurized to 25-30 lbs of pressure and then a drain valve is manually opened and CBM's are forced out into the South neutralization pit. The operator visually watches the CBM's come out of a discharge pipe into the South neutralization pit. When the operator sees a color change, indicating that the CBM's have been evacuated from the vessel and polymer is now entering the South pit, the drain valve is then closed. The pH is checked manually with the use of litmus paper. When the solution in the South pit has reached a pH range of 7-9, the contents are then sent to the North pit for further treatment. Once the mixture is fully neutralized it is sent to waste water.

On the 19th, the operator had drained the CBM's out of the Polymer Surge Drum and performed an unusually "long draw". The draining of CBM's, which normally takes seconds, had taken 3 minutes. Depending on the position of the drain valve this could have introduced a large volume of polymer into the South pit. Polymer or acid soluble oils (ASO) have a low pH and contain sulfur compounds. Later that day a large volume of spent KOH was sent to the South pit. Approximately 940 gallons was sent to the pit. This would have been performed to further regulate pH.

On the 20th, the liquid level in the South pit was very close to the top of the edge. It was determined that prior to the accident, the drain valve on the South pit was turned in the open position a round-and-a-half. There is only one reason the drain on the South pit would have been opened; to lower the level in the pit because the contents were going to flow over the top of the pit. The drain on the South pit is normally never opened, due to the fact that the contents have to be sent to the North pit for further treatment.

Page 2

Fri May 25, 2007 3:38pm Investigation Nr. 200841302

The day of the accident, the operator opened the drain on the South pit and the head pressure from the South pit released vapors. The vapors traveled up to the operator and who lost consciousness. After the incident on the 20th, company testing indicated that when the pH in the South pit is lowered, the sulfur compounds in the mixture are released out of the solution into the air. No respiratory protection was worn by the operator. The operator was wearing an H2S dosimeter but it is undetermined at this time if the dosimeter was working properly. When other operators found the fallen operator, they stated that the H2S monitor was alarming. The highest reading from the operator's dosimeter was 95 ppm. The wind was blowing from the South but steam traps showed that the wind was also swirling near the pit.

Exemption 7c the operator died from acute hydrogen sulfide intoxication.

# U. S. Department of Labor Occupational Safety and Health Administration

## Fatality/Catastrophe Report Tue Jan 23, 2007 3:54pm



Reporting ID	0524530	Previous Addivity (Type & Nully Bell)	R. Referr	ıl 9007	03927		Ever		1008417	66
Establishment Information	Establishment Name	Marathon Petroleum LLC		NAME OF THE PARTY		•	Num Emp	loyer ID		
	Site Address	400 S. Marathon Ave. Robinson IL 62454 Site (618) 544-2121	Robinson II. 62454 Site (618) 544-2121 Site (618) 544-5092 Phone FAX							033
	Mailing Äddress	P.O. Box 1200 Robinson, IL 62454							A CONTRACTOR OF THE CONTRACTOR	
	Event Address (ir different)	5								
Industry & Ownership	Type of Business		Primary SIC	2911	•	Prima NAIC		24110	No. of Exe Employees	emption 4
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Employee Representation	Group Name(s):	ENV. SAFETY + SECURI	ų нея.		Teleph	one	(elf	<u>8-544</u>	<u> ~ 2121</u>	X5434
Classification	A. Fatality		AMOUNT REALITY AND				•			70.0
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		hydrogen sulfide exposure (s						أسويسية پدرو الاستحداد الفاقة		
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	Deceased:	Dan Gunraj Exemption 7c	Exe	mptio	n 7c					
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4.	Inspection Planned?	Supervisor(s) Assigned	*		CSHQ(	s) Assi	gned	•	, , , , , , , , , , , , , , , , , , ,	
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JAN-23-2007	16:02	From: FAIRVIEW HTS	OSHA
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To:3095897326

P.3/3

Tue Jan 23, 2007 3:54pm Complaint Nr.

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Optional Information	Type ID.	Optional Information Value		
Comments				





## U.S. Department of Labor, OSHA FAIRVIEW HEIGHTS DISTRICT OFFICE

11 Executive Drive, Suite 11 Fairview Heights, IL 62208

Phone: (618) 632-8612 FAX: (618) 632-5712

DATE:	1-23-2007	·•
TO:	NATIL OFFICE, REGIONAL DEFICE	5) PEORIA AVEA CEGICE
FROM:	FAIRVIEW HOTS, IL OSHA	•
SUBJECT:	OSHA-36	
MESSAGE:	NOTE: Exemption 5	
Number of Pa	nges, including cover sheet: 3	

OSHA's Website: www.osha.gov



### U.S. Department of Labor Occupational Safety and Health Administration

## Inspection Narrative

Fri May 25, 2007 3:01pm						
				Inspec	tion Nr.	309287175
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John Swearingen		Engu	neering Mgr.		C M	
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### **OSHA INSPECTION NARRATIVE**

Company Name: Marathon Petroleum Company, LLC

Inspection Number: 309287175 Compliance Officer: Exemption 7c

This inspection of Marathon, located in Robinson, IL, was initiated on January 21, 2007. The inspection was initiated as the result of a fatality. This inspection was assigned to Exemption 7c by TL, Brian Bothast on January 30, 2007.

CSHO conducted the initial investigation on January 21, 2007.

Exemption 7c

Preliminary information given by the company to OSHA:

An operator working in the HF unit near the neutralization pits was found unresponsive after he failed to answer a call. Upon reaching the operator, two responders wearing continuous reading hydrogen sulfide monitors heard their monitor's alarm. The responders retreated, obtained SCBAs and removed the operator from the area. The operator died around 3:30 pm on Saturday, March 20, 2007.

On January 21, 2007, CSHO entered the site and met with Mike Parker, Chief Operator for Complex 6; Gayle Sandiford, EHS Manager; Kevin Bogard, Operations Manager; Von Meeks, Safety Supervisor; and John Swearingen, Manager.

Incident occurred in the HF Alkylation Department. The operator was found on the east side if the neutralization pits. Pits are used to neutralize acids and caustic materials. The area is taped off and company has taken pictures of area. The facility is operating at a reduced rate and fresh air is being used for teams entering the area. The liquid level is 4-5 feet below the top of the pit. The victims H2S monitor was going off when found. The monitor starts alarming at 10 ppm. The company has downloaded the data. There was a datalogger being used by the operator and the company is going to download that data. The pit should not have H2S in it and the company is trying to find out where it came from. The semplified has taken samples from the pits. The rescue team was dispatched when "man down" was called on the radio. They started CPR on victim, hooked up AED and was never given a sign to shock the victim. Administered CPR until hospital showed up. The Coroner is performing an autopsy tomorrow. The company is continuing its monitoring efforts outside of the taped off area. Plant 16 produces hydrogen sulfide but it is not in the Alkylation Unit.

The CSHO requested data: PSM program; downloaded information from personal monitor; process information; datalogger information to determine employees route taken; and accident report.

The shift worked was from 6 am to 6 pm. The operator had worked at facility for 16 months. New employees receive 5 weeks of general training followed by unit specific training.

The CSHO also requested copies of interviews conducted by the company.

The CSHO conducted interviews with individual that responded to the "man down" call.

Safety and Health

### Exemption 7c

- On January 25, 2007, CSHO and CSHO went back to the facility to obtain more information. The CSHO's met with Von Minks, Safety Director; Gail Sandiford, Safety; and John Swearingen, Manager.
- The CSHO asked them if they have an incident report created so the CSHO could review it. Gail stated that did not have anything written on paper, just a bunch of sticky notes.
- The company provided documentation on the victim's dosimeter for H2S and that it was calibrated. The highest reading on the operator was 95 ppm. The information was downloaded Sunday the 21<sup>st</sup>. The monitor was located on the hard hat and the highest reading was at 5:07pm. The dosimeter starts alarming at 10 ppm.
- The operator that found the victim had went to assist the victim and his dosimeter went off before he could reach the victim and training had told him that he should not go in any farther and the operator pulled out and called on the radio "man down". Two employees donned SCBA's and went in to retrieve the victim. The incident happened at 3:18 pm. At 3:49 pm *Exemption 7c* monitor read 75 ppm. After the event the levels measured at 100 ppm at 4:30 pm.
- The incident occurred in the Alkylation Department. There are neutralization pits, one is called the North pit and the other is called the South pit. These pits are open surface pits constructed out of concrete. There are Summa Canisters that hang above the pits that can grab a sample of air when needed. They usually only use these canisters when they get an odor complaint. They have taken samples Saturday night and have since sent them to the lab to be analyzed.
- A Corporate investigative team came onsite Saturday night. It is not standard procedure to use them. Doug Rogers was the lead for the team and he is from the Finley, OH plant.
- The victim was conducting rounds that would include checking temperature and pressure of equipment and pumps. The victim walked past the pits and walked around the furnace and double-backed towards the pits **Exemption 5** and the employee was found 15 minutes later.

### Normal Operations:

In Complex 2, Unit 7, in the Alkylation Department the main function of this unit is to take hydrofluoric acid out of the polymer stream. Hydrofluoric acid (HF) is used as a catalyst for the HF Alkylation Unit. HF is a clear, colorless, corrosive liquid with a sharp, penetrating odor. It is hygroscopic and when mixed with the water, it forms a white vapor cloud which resembles steam. HF has a very low pH. HF is normally contained in what is called Constant Boiling Mixtures (CBM's). CBM's are combination of HF acid (37%) and water (63%). In the Acid Regenerator labeled 7C-14, polymer which is acid soluable oils (ASO) and CBM's are held and transferred to the Polymer Surge Drum labeled 7C-15. There the mixtures are left to settle out for 5 to 6 hours. The polymer will settle out on top and the CBM's will settle to the bottom. The operator will then transfer the CBM's and polymer down stream to the Polymer Storage/Neutralization Drum labeled 7C-39 or the CBM's will be drained out of the Polymer Surge Drum to the South Neutralization pit. The South Neutralization Pit is where spent potassium hydroxide(KOH), from the Propane KOH Treater labeled 7C-10, which is highly basic, is sent when the discharge valve begins to plug because the KOH is spent. When a changeout of KOH is conducted on 7C-10, KOH Treater, the spent KOH is piped to the South

Neutralization Pit. This change-out occurs every 3 to 5 months. When the spent KOH is sent to the South Pit, the KOH has to be neutralized before it can be sent to waste treatment. The South pit now having a high pH needs to have an acid added to it to lower the pH to neutral. This is accomplished with the addition of CBM's. CBM's have a very low pH from the HF acid. CBM's can be drained from the bottom of the Polymer Surge Drum. When spent KOH is sent to the South Pit, CBM's would be drained from the Polymer Surge Drum to the South Pit every 5 to 6 hours. The pH is checked periodically to see how many more additions of CBM's will be necessary to achieve a 7-9 pH. Manual tests are conducted on the pits by the operators with the use of Litmus paper. Once the correct pH is obtained the liquid in the South pit is transferred into the North Pit for further treatment if necessary. Once the pH is maintained the operator will call waste treatment and request permission to send the mixture to the acid sewer. When transferring any materials out of vessel 7C-15, Polymer Surge Drum, the vessel has to be put under pressure with the addition of purchase gas (natural gas). 25 to 30 lbs. of constant pressure is applied to the vessel. All of the valves on 7C-15 are manually operated valves. When transferring CBM/s to the South Pit the operator pressurizes 7C-15, open the drain valve and watches the discharge pipe to see the material coming out in the South Pit. When the operator sees a color change that indicates that all of the CBM's have evacuated the vessel and the addition of polymer would be entering the pit. The operator would shut the drain valve and check the pH of the pit. The operator would radio to the Control Room Boardman and tell him how many seconds of CBM's were drawn from 7C-15 to the pit. The normal draw time for CBM's is approximately 45 seconds. Once the CBM's have been drawn to the pit the valves would be lined up so the polymer would be sent downstream to the Polymer Storage Drum, 7C-39. Once the polymer was sent to 7C-39 the valves would be closed and the purchased gas would be turned off and residual gas sent to the flare. 7C-15 would then be ready to receive material from 7C-14

Timeline of operations and activities leading up to and including the incident:

Jan 15, 2007 @ 12:55 am – Educted CBM's from Polymer Surge Drum; 32 seconds.

@ 1:15 pm – Educted CBM's from Polymer Surge Drum; 30 seconds.

January 16, 2007 – KOH changeout of 7C-10.

and the process would start all over.

@ 1:15 pm - Drew CBM's from Polymer Surge Drum for 40 seconds.

January 17, 2007 @ 7:30 am – Drew CBM's from Polymer Surge Drum for 45 seconds.
@ 6:50 pm, Drew CBM's from Polymer Surge Drum, duration unknown.

January 18, 2007 @ 2:30 am – CBM's from Polymer Surge Drum, unknown duration.

@ 9:45 am - CBM's from Polymer Surge Drum for 47 seconds.

@ 4:55 pm – CBM's from Polymer Surge Drum, unknown duration.

January 19, 2007 @ 1:00 am – CBM's from Polymer Surge Drum, unknown duration. @ 8:35 am – CBM's from Polymer Surge Drum, drew for 3 minutes. Fixed and

- personal alarms activated.

  @ 8:39 am alarm activated on RIE building and H2S monitors on employees near RIE building are activated.
- @ 8:40 am alarm is cleared.
- @ 2:10 pm CBM's drawn from Polymer Surge Drum, 33 seconds, pH in South pit was 9.0.
- @ 3:00 pm to 4:15 pm spent KOH from 7C-41 to South Pit 940 gallons,

remaining spent KOH to wastewater at 4:15 pm.

- @ 9:55 pm CBM's drawn from Polymer Surge Drum, 40 seconds.
- January 20, 2007 @ 4:30 am CBM's drawn from Polymer Surge Drum, 40 seconds.
  - @ 3:06 pm Dan records 7C-43 Polymer Neutralization Drum alkalinity, last entry into datalogger.
  - @ 3:06 to 3:11 pm incident occurs.
  - @ 3:11 pm alarm activated, hydrocarbon alarm activated North of Alky pit, cleared after 15 seconds.
  - @ 3:13 pm alarm activated, H2S alarm activated inside of analyzer building at the Platformer. Alarm cleared after 3 minutes 34 seconds. CBM draw expected around 3:00 pm, no evidence of CBM drawn.
  - @ 3:15 pm alarm activated, H2S alarm ground mounted at Unit 67 Tail Gas Unit
  - @ 3:15 to 3:30 pm Alky operator discover down at the pits, H2S alarm went off on operator who found victim. Victim's face shield down and rubber gloves on; victim's H2S monitor going off at 95 ppm.

Exemption 7c and Exemption 7d

### Events leading up to and including the fatality:

On January 20, 2007, an operator working in the Hydoflouric Acid (HF) Alkylation Unit was in charge of maintaining the neutralization pits. The operator was in charge of draining a Constant Boiling Mixture (CBM's) which contained HF acid and water out of the Polymer Surge Drum into a neutralization pit. The CBM's, low in pH were sent to the South neutralization pit to neutralize spent potassium hydroxide that was contained in the open-surfaced pit. Potassium

hydroxide (KOH) is highly basic and CBM"s are drained into the South pit to lower or neutralize the pH. The draining of CBM's is accomplished by pressurizing the Polymer Surge Drum with a constant supply of natural gas. The vessel is pressurized to 25-30 lbs of pressure and then a drain valve is manually opened and CBM's are forced out into the South neutralization pit. The operator visually watches the CBM's come out of a discharge pipe into the South neutralization pit. When the operator sees a color change, indicating that the CBM's have been evacuated from the vessel and polymer is now entering the South pit, the drain valve is then closed. The pH is checked manually with the use of litmus paper. When the solution in the South pit has reached a pH range of 7-9, the contents are then sent to the North pit for further treatment. Once the mixture is fully neutralized it is sent to waste water. The day before the incident the operator had drained the CBM's out of the Polymer Surge Drum and performed an unusual "long Draw". The draining of CBM's, which normally takes seconds, had taken 3 minutes. Depending on the position of the drain valve this could have introduced a large volume of polymer into the South pit. Polymer or acid soluble oils (ASO) has a low pH and contains sulfur compounds. Later that day a large volume of spent KOH was sent to the South pit. Approximately 940 gallons was sent to the pit. This would have been performed to further regulate pH.

Exemption 7d

Marathon's HAZOP did not address any Human Factors for the Polymer Surge Drum, 7C-15 or for the Neutralization Pits. Such issues found were that the surge drum is pressurized with natural gas to transport the materials out of the vessel. The drain valve can be opened to transfer materials to the South pit and the operator could leave the area and forget to shut the drain valve off allowing all of the contents of 7C-15 to evacuate to the South pit creating an overfill situation and an unlimited supply of natural gas would be released to atmosphere creating a

catastrophic event. Everything in the area is manually operated, there are no level indicators or automatic shutoffs on the neutralization pits, all valves on 7C-15 are manual valves. Management stated that everything in that part of the unit is manual due to the corrosive nature of the environment and that instrumentation could not be maintained in that environment. Another reason that was given was because transferring of CBM's is not conducted on a regular basis and is operator controlled when conducting the transfer. Note: CBM's are transferred to the pit every 6 hours for 4-7 days following a KOH transfer which occurs every 3-5 months.

- On April 13, 2007, Exemption 7d the cause of death was from acute hydrogen sulfide intoxication.
- Marathon stated that H2S was not known to be present in the Alkylation Unit. Doug Rogers stated that the KOH stream has some sulfur in it.
- [Marathon's MSDS for polymer/acid soluble oil (ASO) states that it can contain significant concentrations of HF with smaller amounts of acidic impurities such as organic fluorides, polymetric nitrogen, and sulfur containing compounds.]
- Brad Scott, Technical Service Manager stated that there used to be a MTBE Unit that would take some of the mercaptum sulfides, which are heavy sulfides, out of the KOH stream. In the mid 90's, Illinois outlawed MTBE and the unit was removed allowing the sulfides to stay in the KOH stream. This hazard was never identified after the removal of the MTBE unit.
- Doug Rogers stated that post incident they have determined that when they bring the pH of the South pit down to 7, around the 10pH range, hydrogen sulfide would offgas. The CSHO requested why this was and was given the following answer:

"As the pH of a complex basic solution (solution with more than one basic reactant: KOH, KS, KF, Polymer, etc...) is lowered, each basic component in the complex solution will have its own reaction kinetics. As acid is added to a solution each reactant in the solution will begin to react with the acid according to it own equilibrium reaction kinetics. In general, the most reactive component will react first, followed by the second most reactive component, and the solution will continue to react with the acid addition (lowering of the solution pH) until the entire solution reaches equilibrium. Also, as the solution pH continues to be reduced the amount of the most reactive compounds will decrease and shift or slow down that particular reactant's reaction rate. It may be possible that the most reactive sulfidic components in the complex solution reacts more quickly at a pH of 10 and liberates more H2S at a pH of 10 than it would at a lower pH. As the solution pH decreases the remaining amount of sulfidic reactant is reduced and the rate of H2S evolution could also decrease".

Marathon management stated that newer facilities have covers on their neutralization pits.

This facility used to have covers on the pits and was a recommendation from the PHA team in 1994. The covers were installed and the corrosive HF acid ate them

away. Management stated the covers were used to control the odor problems. The installation of the Acid Relief Neutralizer (ARN) System stopped the draining of CBM's to the pit. The ARN system would transfers the CBM's to an acid header which would take the gases to the flare. Since the installation of the ARN system the covers were not needed due to the odor issue was considered resolved. The covers were also a safety issue due to operators having to stand on the covers and open a hatch to check pH. The vapors would collect in the pit and would come out in a cloud at the operator and the corrosiveness of the chemical played a role in the instability of the structure when standing on the covers. The covers were removed and guardrails were installed.

The CSHO asked management since the CBM's were being taken care of in a closed system called the ARN, why wasn't a closed system installed to take care of the spent KOH stream preventing any hazardous chemical from being dispensed into the South pit. Management stated that they agreed with the question and reason but were not sure who made the decision. Brad Scott stated that chemical engineers had done the chemistry and were probably the ones who made the decision.

### Exemption 7d

Marathon's A-5 Operator Duties states: The Area #5 Operator is to operate the outside equipment on the HF Alkylation Unit. The operator's routine duties include:

#5. Monitor the pH of condensate, cooling water, neutralizing pits, and KOH water to the Relief Gas Scrubber;

#32. Monitor the level in the South pit and send in samples to the lab when it needs vacuumed.

None of the procedures identify how to conduct monitoring or how the neutralization pits would be maintained during emergencies, upset conditions, and normal operations.

### Post Incident:

Since the incident no CBM's are being drawn to the pit. The drain valve on 7C-15 has been locked out and the discharge line from 7C-10 KOH Treater has been removed from the south pit. The South pit has been vacuumed out. The spent KOH from 7C-41 has been tested and determined to contain sulfides and is not being sent to the North pit. The KOH is being sent to a vac-truck and taken off site. The spent KOH from 7C-10 is going to be sent to a frac tank.

The victim's H2S monitor has been sent to a third party for testing and as of April 11, 2007, results have not been received from the third party.

Recommended citations:

29 CFR 1910.119(m)(2): Marathon did not perform an incident investigation of an

overfill or the South Neutralization pit that occurred in

November 2006.

29 CFR 1910.119(e)(3)(i): Marathon did not address the hazards of the process in the

HAZOP for the Neutralization pits.

29 CFR 1910.119(e)(3)(vi): Marathon did not address human factors in the HAZOP for

the Alkylation Department.

29 CFR 1910.119(f)(1): Marathon did not implement operating procedures for the

safe operation of the Neutralization pits or drawing CBM's

out of 7C-15 to the Neutralization Pits.

29 CFR 1910.119(f)(1)(E): Marathon did not address emergency shutdown and

emergency operations for Educting CBM's out of 7C-15.

29 CFR 1910.1000(b)(2): Exposure to hydrogen sulfide above the peak concentration

of 50 ppm.

### **Closing Conference**

On May 25, 2007, the CSHO held the closing conference per the FIRM with Gail Sandiford, Doug Rogers, Von Meeks, John Swearingen, and Wayne McGlone. The CSHO went over the recommended citations. The CSHO went over the OSHA 3000 with them. Doug Rogers asked about the status of VPP and how OSHA views them since they had a fatality. The CSHO told them that he was not part of the VPP process and that it would have to be brought up to the Area Director. The CSHO thanked them for their time and ended the conversation.

### **Coverage Information**

The company receives and ships materials outside the state of IL.

**CSHO PPE**: None needed.

Penalty Reduction Factors

Size =

Exemption 5

Good Faith = "

Exemption 5

History =

Exemption 5

## U. S. Department of Lab... Occupational Safety and Health Administration



### Worksheet

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Dan Gunraj

Fri May 25, 2007 2:59pm

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### OSHA - 1B

Company Name: Marathon Petroleum Company, LLC

Inspection Number: 309287175

Date/Time: April 10, 2007

Standard Allegedly Violated: 29 CFR 1910.119(e)(3)(i): The process hazard analysis did not address the hazards of the process:

### **Instance Description:**

Hazards-Operation/Condition-Accident/Equipment - At Marathon Petroleum Company, the process hazard analysis did not address all of the hazards of the covered process:

a. The hazards of natural gas due to draining 7C-15 Polymer Surge Drum too long;

b. The hazards related to the mixture and release of hazardous chemicals in the neutralization pits.

The 1994 HAZOP, Node 115, stated that no level due to draining 7C-15 too long had a consequence of adding a small amount of acid vapor into the pit. The 2003 HAZOP revalidation, Node 25-29, stated that this particular node had "no credible cause". The term "no credible cause" was defined by management and means "No potential process hazards were determined by the HAZOP team for the particular deviation". The HAZOP team did not address that when the contents of 7C-15 were evacuated into the neutralization pit, there was a likelihood for the natural gas pressurizing the vessel to enter into the neutralization pit and find an ignition source creating catastrophic consequences. Marathon's 1994 HAZOP stated that draining 7C-15 too long had a risk matrix of 4 on the likelihood scale, which would mean it was likely to occur annually. Node 31-18, from 2003 HAZOP states problems with fuel gas and states that it is "Not Applicable" The unlimited supply of fuel gas can be evacuated from the Polymer Surge Drum, 7C-15 into the South Neutralization Pit.

### Exemption 7c and Exemption 7d

The 1994 HAZOP, Node 327, stated that wrong concentration of the neutralization pit, such as, low pH water and possible loss of containment of acid, had a medium risk on the risk matrix. Protection was accomplished with the wearing of personal protective equipment and checking the pH of the pits once per shift.

The 2003 HAZOP Revalidation, Node 31-14, Problems with composition of the pits stated "No credible cause".

After the incident on January 20, 2007, the company acknowledged that when the neutralization pits are lowered, the sulfur compounds contained in the solution off-gas and are released when the

pH is lowered to 10.

Brad Scott, Technical Service Coordinator, stated that Marathon used to have an MTBE Unit which would take out some of the heavy sulfurs, mercaptum sulfides out of the polymer stream. In the mid 90's, Illinois outlawed the MTBE's therefore allowing the heavy sulfurs to remain in the stream.

Marathon's MSDS on Acid Soluble Oils, states that sulfur compounds are contained in the mixture. The acid soluble oils or polymer would be released into the pit when CBM's were drained from vessel 7C-15.

The potential for hydrogen sulfide in the neutralization pit was high based on the sulfur molecules being introduced into the pit with the addition of polymer. A long draw from the Polymer Surge Drum could introduce large amounts of sulfur containing polymer into the South pit.

Equipment: Not identifying hazards of the process in the process hazard analysis.

Location - Complex 2, Alkylation Unit

Injury/Illness: Death, severe acid burns, and H2S intoxication.

Measurements: Interviews with management

Exposed Employee Name: Dan Gunraj, Alkylation Unit Operator.

Photo: N

**Probability:** Exemption 5

Employer Knowledge of the Condition: Brad Scott, Technical Service Coordinator had knowledge that a prior operation, which removed sulfur compounds, was removed from the process and the sulfur compounds were still in the KOH stream. Gail Sandiford, EHS Manager, had knowledge that hydrogen sulfide was present in operations adjacent to the Alkylation Unit and required all employees to wear H2S dosimeters in the plant.

<u>Comments:</u> Doug Rogers, Corporate Investigator, stated that when the highly basic solution of potassium hydroxide is lowered with the addition of hydrogen fluoride, hydrogen sulfide is released at about a pH range of 10. Mr. Rogers stated that this was identified post incident.

# U. S. Department of Lal . Occupational Safety and Health Administration



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### OSHA - 1B

Company Name: Marathon Petroleum Company, LLC

Inspection Number: 309287175

Date/Time: January 20, 2007

Standard Allegedly Violated: 29 CFR 1910.1000(b)(2): Employee(s) were exposed to an airborne concentration of Hydrogen Sulfide listed in Table Z-2 in excess of the peak concentration of 50 ppm:

### **Instance Description:**

*Hazards-Operation/Condition-Accident/Equipment* – On or about January 20, 2007, an operator at the Neutralization Pits was exposed to hydrogen sulfide above the peak concentration of 50 ppm.

### Exemption 7d

the operator died from acute

hydrogen sulfide intoxication.

Operators in the facility are required to wear hydrogen sulfide direct reading monitors. The deceased operator wore theirs on their hardhat. When the operator was removed from the scene the hard hat was left at the scene. The highest reading recorded was a peak of 95 ppm. When other operators found the fallen operator, they witnessed that the monitor was alarming. No respiratory protection was worn by the deceased when working at the neutralization pit.

Doug Rogers stated that post incident they have determined that when they bring the pH of the South pit down to 7, around the 10pH range, hydrogen sulfide would off gas. The CSHO requested why this was and was given the following answer:

"As the pH of a complex basic solution (solution with more than one basic reactant: KOH, KS, KF, Polymer, etc...) is lowered, each basic component in the complex solution will have its own reaction kinetics. As acid is added to a solution each reactant in the solution will begin to react with the acid according to it own equilibrium reaction kinetics. In general, the most reactive component will react first, followed by the second most reactive component, and the solution will continue to react with the acid addition (lowering of the solution pH) until the entire solution reaches equilibrium. Also, as the solution pH continues to be reduced the amount of the most reactive compounds will decrease and shift or slow down that particular reactant's reaction rate. It may be possible that the most reactive sulfidic components in the complex solution reacts more quickly at a pH of 10 and liberates more H2S at a pH of 10 than it would at a lower pH. As the solution pH decreases the remaining amount of sulfidic reactant is reduced and the rate of H2S evolution could also decrease".

The operator that found the victim had went to assist the victim and his dosimeter went off before he could reach the victim and training had told him that he should not go in any farther and the operator pulled out and called on the radio "man down". Two employees donned SCBA's and went in to retrieve the victim. The incident happened at 3:18 pm. At 3:49 pm Exemption 7c Exemption 7c monitor read 75 ppm. After the event the levels measured at 100 ppm at 4:30 pm.

### Exemption 5

*Equipment:* Hydrogen sulfide exposure over the peak concentration of 50 ppm at the Neutralization Pit.

Location - Complex 2, Alkylation Unit at the Neutralization Pit.

Injury/Illness: Death, intoxication.

Measurements: Interviews with management and employees. Note: Evidence of IDLH concentration is 100 ppm from the NIOSH Pocket Guide. Based on the IDLH and Coroner's Report, evidence supports the operator was exposed to H2S at a level that exceeded the PEL.

Exposed Employee Name: Dan Gunraj, Alkylation Unit Operator.

Photo: N

Probability: Exemption 5

Employer Knowledge of the Condition: Kevin Flexter, Complex Chief Operator had knowledge that operators were in charge of transferring CBM's into the pit. The Chief Operator told the other operators not to transfer CBM's to the pit during daylight hours because there were too many contractors around and they had been getting alarms in the past. The day of the incident the operator was given permission to perform draining of CBM's to the pit.

Comments: Gail Sandiford, EHS Manager stated that H2S was never a concern in the pit area.

Other Information: After the incident the operator's direct reading monitor was sent to a third party for non-destructive testing. Two identical monitors were sent to be evaluated and tested to find out the limitations, interferences, and monitoring properties before the operator's monitor was to be tested.

At the current time testing has only been conducted on the two monitors. One of the monitors was found to take 3 -5 minutes to accurately detect a known concentration of hydrogen sulfide. The other test showed that one of the monitors did not read a concentration of 125 ppm of H2S when put in a high humidity/steam environment and them immediately into a freezing environment (trying to mimic the weather condition on January 20, 2007).

At the current time the operator's monitor in question had not been tested.

Note: Marathon indicated they do not have documented readings from the H2S direct reading monitor before the fatality and two hours following the fatality due to the time readout of the monitor. The monitor will only record that last 10 alarms and then it will overwrite the oldest reading.

## U. S. Department of Lab

### Occupational Safety and Health Administration



### Worksheet

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29 CFR 1910.119(e)(3)(vi): The process hazard analysis did not address human factors:

At Marathon Petroleum Company, the process hazard analysis did not address human factors on the covered process:

- The hazards of a natural gas release due to draining 7C-15 Polymer Surge Drum too long or leaving a. drain valve open;
- b. The hazards of overfilling the neutralization pits.

### \*\*\*THIS ITEM REQUIRES DOCUMENTATION OF ABATEMENT\*\*\*

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### OSHA - 1B

Company Name: Marathon Petroleum Company, LLC

**Inspection Number:** 309287175

Date/Time: January 21, 2007

Standard Allegedly Violated: 29 CFR 1910.119(e)(3)(vi): The process hazard analysis did not address human factors of the process:

### **Instance Description:**

Hazards-Operation/Condition-Accident/Equipment – At Marathon Petroleum Company, the process hazard analysis did not address human factors on the covered process:

a. The hazards of a natural gas release due to draining 7C-15 Polymer Surge Drum too long or leaving drain valve open:

b. The hazards of overfilling the neutralization pits.

The 1994 HAZOP, Node 115, stated that no level due to draining 7C-15 too long had a consequence of adding a small amount of acid vapor into the pit. The 2003 HAZOP revalidation, Node 25-29, stated that this particular node had "no credible cause". The term "no credible cause" was defined by management and means "No potential process hazards were determined by the HAZOP team for the particular deviation". The HAZOP team did not address that when the contents of 7C-15 were evacuated into the neutralization pit, there was a likelihood for the natural gas pressurizing the vessel to enter into the neutralization pit and find an ignition source creating catastrophic consequences. Marathon's 1994 HAZOP stated that draining 7C-15 too long had a risk matrix of 4 on the likelihood scale, which would mean it was likely to occur annually. Node 31-18, from 2003 HAZOP states problems with fuel gas and states that it is "Not Applicable" The fuel gas can be evacuated from the Polymer Surge Drum, 7C-15 into the South Neutralization Pit.

Exemption 7c and Exemption 7d

The 1994 HAZOP, Node 326, stated high level of the neutralization pit, such as, failure to drain pit to waste water which would overflow to grade and liquid back-up in acid sewers in the unit. The risk matrix had designated this to have a medium risk. Protection was to be accomplished with the wearing of personal protective equipment and following operating procedures. This medium risk required a PHA Further Study, Item #75 stated failure to drain pit to waste water. The recommendation for this item was "Study team made no recommendation". A PHA Action

Completion Form from March 25, 1997, stated "The routine draining to the pit has been eliminated with the installation of the new Acid Relief Neutralizer ARN System, no further action required. This item is complete".

The 2003 HAZOP Revalidation, Node 31-32, higher level of the pits stated "No credible cause". The 2004 Compliance Audit acknowledged that CBM's were still being drained into the pit to neutralize the KOH stream. There were no operating procedures implemented for the safe operation of the neutralization pits.

Exemption 7c and Exemption 7d

Equipment: Not identifying human factors of the process in the process hazard analysis.

Location - Complex 2, Alkylation Unit

Injury/Illness: Death, severe acid burns, and H2S intoxication.

Measurements: Interviews with management

Exposed Employee Name: Dan Gunraj, Alkylation Unit Operator.

Photo: N

Probability:

Exemption 5

Employer Knowledge of the Condition: Kevin Flexter, Chief Complex Operator, had knowledge that operators pressurized the Polymer Surge Drum with natural gas and that there was a potential for the contents of the vessel to be evacuated into the pit. Doug Rogers, Corporate Investigator, Dan Phillippe, PSM Coordinator, and Gail Sandiford, EHS Manger, all agreed that the human factors were not identified in that process for the natural gas in 7C-15 Polymer Surge Drum.

### Comments:

## U. S. Department of Lal. ... Occupational Safety and Health Administration



### Worksheet

Fri May 25, 2007 2:59pm

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29 CFR 1910.119(f)(1): The employer did not develop and implement written operating procedures that provided clear instructions for safety conducting activities in each covered process consistent with the process safety information and which addressed the elements listed in 29 CFR 1910.119(f)(1)(i) through (f)(1)(v):

At Marathon Petroleum Company, operating procedures were not developed for the following activities:

- a. The transferring of the Constant Boiling Mixtures (CBM's) from the Polymer Surge Drum, 7C-15 to the Neutralization Pits, 7D-2;
- b. The neutralization of potassium hydroxide with the addition of hydrofluoric acid and water;
- c. The transferring of chemicals from the South pit to the North pit; and
- d. Upset conditions of the Neutralization Pits.

### \*\*\*THIS ITEM REQUIRES DOCUMENTATION OF ABATEMENT\*\*\*

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### OSHA - 1B

Company Name: Marathon Petroleum Company, LLC

Inspection Number: 309287175

Date/Time: January 21, 2007

Standard Allegedly Violated: 29 CFR 1910.119(f)(1): The employer did not develop and implement written operating procedures that provide clear instructions for safely conducting activities involved in each covered process:

### **Instance Description:**

*Hazards-Operation/Condition-Accident/Equipment* – At Marathon Petroleum Company, operating procedures were not developed for the following activities:

- a. The transferring of the Constant Boiling Mixtures (CBM's) from the Polymer Surge Drum, 7C-15 to the Neutralization Pits, 7D-2;
- b. The neutralization of potassium hydroxide with the addition of hydrofluoric acid and water;
- c. The transferring of chemicals from the South pit to the North pit; and
- d. Upset conditions of the Neutralization Pits.

The operating procedures for Educting CBM's from the Polymer Surge Drum to the Neutralizer, 7C-39, did not address the draining of CBM's to the pit for the neutralization of potassium hydroxide that was contained in the South Pit after a KOH change-out. There are no draining procedures contained in the normal operating procedures.

Marathon did not have written operating procedures that covered the neutralization of KOH in the South pit with the addition of CBM's. There was nothing written or documented for the safe operation, steps for each operating phase, normal operation, emergency operations, upset conditions, and any special or unique hazards.

Chief Complex Operators stated that there is nothing written on the safe operation, maintaining, and upset conditions for the neutralization pits.

Gail Sandiford, EHS Manager, stated that there are no procedures for transferring CBM's to the pit from 7C-15 and that the Neutralization Pits have no operating procedures prior to the incident.

Exemption 7c and Exemption 7d

Ed Turner, Chief Complex Operator, stated that pressurizing 7C-15 to send CBM's to the South Pit is not needed to push the contents out of the vessel. Ed stated that the drain valve can be opened and the contents of the vessels would be evacuated by gravity.

Kevin Flexter, Chief Complex Operator and other operators stated that 7C-15 is pressurized with natural gas no matter if the CBM's are going down stream or if the CBM's are going to the South Pit. There are no written procedures for this operation.

Marathon's A-5 Operator Duties states: The Area #5 Operator is to operate the outside equipment on the HF Alkylation Unit. The operator's routine duties include:

#5. Monitor the pH of condensate, cooling water, neutralizing pits, and KOH water to the Relief Gas Scrubber;

#32. Monitor the level in the South pit and send in samples to the lab when it needs vacuumed.

There are no other procedures for the safe operation of the pit and what to do in upset conditions such as pit overflow.

Doug Rogers, Corporate Investigator, stated that there is an exothermic reaction that occurs in the pit.

*Equipment:* No operating procedures for transferring CBM's from 7C-15 to the South Pit and no procedures for the neutralization of KOH in the South Pit.

Location - Complex 2, Alkylation Unit

Injury/Illness: Death, severe acid burns, and H2S intoxication.

Measurements: Interviews with management

Exposed Employee Name: Dan Gunraj, Alkylation Unit Operator.

Photo: N

### **Probability:**

Exemption 5

Employer Knowledge of the Condition: Brad Scott, Technical Service Coordinator, Gail Sandiford, EHS Manager, Von Meeks, Safety Director, Doug Rogers, John Swearingen, Manager, Kevin Flexter, Chief Operator, and Ed Turner, Chief Operator, had knowledge that KOH is changed out and sent to the South Pit and the addition of CBM's is used to lower the pH of the solution.

### **Comments:**

## U. S. Department of Lal Occupational Safety and Health Administration

### Worksheet

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### OSHA - 1B

**Company Name:** Marathon Petroleum Company, LLC

Inspection Number: 309287175

Date/Time: April 10, 2007

<u>Standard Allegedly Violated:</u> 29 CFR 1910.119(f)(1)(E): The employer did not develop and implement written operating procedures that provide clear instructions for safely conducting activities involved in emergency operations:

### **Instance Description:**

*Hazards-Operation/Condition-Accident/Equipment* – At Marathon Petroleum Company, written operating procedures for Educting CBM's out of the Polymer Surge Drum did not address emergency operations.

The operating procedures for Educting CBM's from the Polymer Surge Drum to the Neutralizer, 7C-39, did not address the emergency operations such as the potential for valve failure or the release of natural gas to the atmosphere. The only written procedures that Marathon created for 7C-15, Polymer Surge Drum was for normal operations and how to transfer material to the neutralizer, 7C-39.

Gail Sandiford, EHS Manager, stated that there are no procedures for transferring CBM's to the pit from 7C-15 and that the Neutralization Pits have no operating procedures prior to the incident.

Ed Turner, Chief Complex Operator, stated that pressurizing 7C-15 to send CBM's to the South Pit is not needed to push the contents out of the vessel. Ed stated that the drain valve can be opened and the contents of the vessels would be evacuated by gravity.

On May 9, 2007, Kevin Flexter, Chief Complex Operator and other operators stated that 7C-15 is pressurized with natural gas no matter if the CBM's are going down stream or if the CBM's are going to the South Pit. There are no written procedures for this operation.

On May 10, 2007, Brad Scott, Technical Assistant Coordinator, stated if an operator pressurized 7C-15 with gas and dumped the contents into the pits and left the drain valve open, gas would come through and you would have to go back to the drain valve to shut it off.

On May 10, 2007, Greg Dugger, Process Specialist, stated that gas could definitely come through the pit if drain valve was left open.

Equipment: No emergency operating procedures for 7C-15.

Location - Complex 2, Alkylation Unit

Injury/Illness: Death, severe acid burns, and H2S intoxication.

Measurements: Interviews with management

Exposed Employee Name: Dan Gunraj, Alkylation Unit Operator.

Photo: N

Probability:

Exemption 5

Employer Knowledge of the Condition: Brad Scott, Technical Service Coordinator, Gail Sandiford, EHS Manager, Von Meeks, Safety Director, Doug Rogers, John Swearingen, Manager, Kevin Flexter, Chief Opertor, and Ed Turner, Chief Operator, had knowledge that material is transferred out of 7C-15, Polymer Surge Drum every 5 to 6 hours.

<u>Comments:</u> On May 15, 2007, the CSHO asked Gail Sandiford, EHS Manager, if there were any emergency, upset, start-up and shut-down procedures for educting CBM's from 7C-15. Gail stated that she had asked the Operation Department and they do not have those procedures. All other work is learned through training.

# U. S. Department of La 1 Occupational Safety and Health Administration

### Worksheet

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### OSHA - 1B

Company Name: Marathon Petroleum Company, LLC

**Inspection Number: 309287175** 

Date/Time: November 2006

Standard Allegedly Violated: 29 CFR 1910.119(m)(2): An incident investigation was not initiated as promptly as possible, and not later than 48 hours following the incident:

### **Instance Description:**

*Hazards-Operation/Condition-Accident/Equipment* — The employer never conducted an incident investigation for occurrences relating to an Alkylation Operator overfilling the neutralization pit.

Operators are in charge of removing Constant Boiling Mixtures (CBM's) out of the Polymer Surge Drum. CBM's contain hydrofluoric acid and water. CBM's are drawn from the Polymer Surge Drum into the South Neutralization Pit. The hydrofluoric acid is used to neutralize potassium hydroxide that is in the South pit.

On January 31, 2007, during a meeting with Dan Phillippe, PSM Coordinator; Gail Sandiford, EHS Manager; Wayne McGlone, Engineering Manager; and Von Meeks, Safety Supervisor,

### Exemption 6

Long draws out of the drum would have the potential to add large amounts of polymer or Acid Soluble Oils (ASO) into the neutralization pit. For reasons unknown the pit was overfilled in November of 2006, actual date unknown. An interview with the Complex Chief Operator stated that Dan Gunraj, Operator overfilled the pit and it took him three days to clean up the mess.

On January 19, 2007, Operator, Dan Gunraj, conducted what was called a "long draw" of 3 minutes on the Polymer Surge Drum. Incident INC-12539 was created and titled H2S Alarms Sound and Bad Odors Noticed: Incident date and time was January 19, 2007 at 9:25 am. States: Alky Operator was drawing CBM to South pit to try to neutralize it at the time. This was what Kevin Flexter, Complex Chief Operator had entered into the description of the incident report.

On March 26, 2007, the CSHO requested the incident report from Von Minks, Safety Supervisor; and Gail Sandiford, Safety Manager. Gail stated that she could not find any supporting documentation or data on the incident, it was never officially reported but would like an incident report filed. The Chief Complex Operator, Kevin Flexter had knowledge of the incident but nothing was done to document the incident.

On May 9, 2007, an interview with Chief Operator, Kevin Flexter stated that Chief Operator, Ed Turner was the supervisor onsite when Dan Gunraj overfilled the South pit in November 2006.

*Equipment:* No incident investigation from November 2006 over filling of the Neutralization Pit.

Location - Complex 2, Alkylation Unit at the Neutralization Pit.

Injury/Illness: Death, severe acid burns, and H2S intoxication.

Measurements: Interviews with management

Exposed Employee Name: Dan Gunraj, Alkylation Unit Operator.

Photo: N

Probability:

Exemption 7c

<u>Employer Knowledge of the Condition:</u> Kevin Flexter, Complex Chief Operator had knowledge that an operator had overfilled the Neutralization Pit in November 2006 and an incident report was not created.

<u>Comments:</u> Gail Sandiford, EHS Manager, stated that she could not find any supporting documentation or data on the incident, it was never officially reported but would like an incident report filed.

On May 9, 2007, Kevin Flexter stated that the pit was overfilled on November 2006 and that Ed Turner was the Chief Operator that helped the deceased operator clean it up with steam lances and water. Kevin stated that overfilling of the pit has happened before and that *Exemption 7c* has also seen it over flow before.

On May 10, 2007, Gail Sandiford, EHS Manger, stated that she heard of overfilling of the pit could happen after the incident occurred. She stated that the deceased operator overfilled the pit last summer Exemption 5