#771363
IR#12-06-15-01

Phillips 66
San Francisco Refinery
1380 San Pablo Avenue
Rodeo, CA 94572

November 15, 2012

Mr. Michael Dossey
Accidental Release Prevention Engineer
Contra Costa County Hazardous Materials Programs
4585 Pacheco Boulevard, Suite 100
Martinez, CA 94553

Subject: Supplemental Information Report – Tk-294 Over-Pressure Incident

Dear Mr. Dossey:

Attached is a supplemental information report for the Tank 294 Over-Pressure Incident that occurred on June 15, 2012. This report addresses comments made in the County Hazardous Materials Programs' letter of August 16, 2012 and verbal comments received from County staff regarding the Incident Investigation Report.

We would be pleased to meet with County staff to discuss other information related to the incident, such as incident response, fence line monitoring, etc. at their convenience.

Sincerely,

James Ferris
Superintendent Health & Safety

cc : P. Stern

Enclosure

Rodeo Refinery
Tank 294 Over-Pressure Incident 061512-1
June 25, 2012

Supplemental Incident Information

This Supplemental Incident Information report addresses comments in the County Hazardous Materials Programs' letter of August 16, 2012 and verbal comments received from County staff regarding the Incident Investigation Report

1. Clarifications to the Summary of Event

The release from Tank 294 began at approximately 7:10 a.m. Tank 294 stores Sour Water and Light Hydrocarbons; sour water is untreated water containing dissolved Hydrogen Sulfide, Ammonia and Hydrocarbons. Light Hydrocarbons are comprised of gasoline (also called naphtha) range material that requires further processing to produce a finished product. Ammonia is highly soluble in water at the tank storage conditions and removal requires forceful processing in a stripping column using steam. Because of this property, ammonia would not be released to the atmosphere for this type of event.

2. Other Clarifications and Supplemental Information Regarding the Investigation Report

- **Tank 294 Follow-up Actions**

  The Incident Investigation Report recommended actions to inspect the tank at the point of failure and to test the operation of relief devices on the tank.

  The failed roof-to-shell seam on Tank 294 was inspected following removal of product and cleaning. The inspection revealed that the tank construction was consistent with the requirements of API-650 for a frangible roof design. There was no corrosion or other defects observed that contributed to the roof failure.

  Tank 294 has two relief devices: an 8" pressure-vacuum valve with a relief set point of 1.5" and a 20" emergency hatch with a relief set point of 2.5" water column.

  The pressure-vacuum valve was observed to have oil on top of the pallet, which is an indication that the valve lifted during this event. The oil comes from the channel surrounding the pallet that covers the vertical edge. The oil channel is designed to prevent vapor leakage; when the valve opens, it results in oil being pushed out of the channel onto the surrounding area. The edge of the device that seals the pallet showed accumulation of Krytox grease. (The grease is used to enhance the seal for odor mitigation.) Testing of the device as found resulted in a lifting pressure of 2.5". A second test conducted with the grease removed resulted in the device lifting at its setpoint of 1.5". It is believed that the grease used on the seal resulted in the higher lift pressure.

  The emergency hatch was tested in place on June 19 with a spring scale. The lifting force confirmed the operation at a lift pressure of 2.5". The hatch design incorporates a 20" pallet that is submerged in oil to prevent vapor leakage and odors. Inspection after removal of the device from the tank showed that the pallet had a bent lip. It is believed that the bent lip was caused by the pallet getting caught on the oil channel on one side,

which likely prevented the pallet from being completely pushed off the hatch and allowed it to return to its normal seated position after the overpressure event.

The two Tank 294 relief devices have a combined capacity for light hydrocarbon vaporization of approximately 0.36 MMSCF/HR. Engineering estimates for the event conditions yield a vapor flow rate in Tank 294 greater than the total relief design capacity (See Attachment 1, which provides calculations for the range of expected operating conditions). The presence of butane in the hydrocarbon stream was a significant contributor to the vaporization that occurred in the system. This rate of light hydrocarbon vaporization resulted in the capacity of the relief devices being overwhelmed; consequently the tank split at the roof-to-shell weld. Based on the rapid vapor surge that occurred and vapor rate calculations, we conclude that the operation of the 8" relief device or the 20" emergency hatch were not factors contributing to the tank roof rupture. The events leading to the high vaporization rate are further described below.

- **Clarification of Operational Events at MP-30**

  At MP-30, vessel F-202 accumulates light gasoline range material from the overhead of the dehexanizer (See Figure 1). This light gasoline range material is the feed stream for Hydrotreating Unit 229 and contains butane at levels of 15 – 25 volume percent. The F-202 accumulator provides separation of the light gasoline from condensed water. An oil-water interface level indicator controller (LIC-239), measures the water level in F-202 and opens the control valve as necessary to maintain the appropriate water level. This control is necessary to prevent water from being carried over into the Unit 229 feed. The water from F-202 flows to Sour Water Accumulator D-206, which is then pumped to Tanks 269 or 294.

  The level indicator is a relatively simple measuring device common in industry. Its design uses a float inside a vertical column (pipe) that is connected to vessel F-202. This float sits on the oil-water interface and transmits its relative position in the column via an electric signal. It is believed that the float "hung-up" in the column, causing a false level indication – that would result in control valve LIC-239 remaining open, causing a loss of the oil-water interface that allowed light hydrocarbons to flow to D-206. Consequently, liquid (comprised of a higher volume of light hydrocarbon) was pumped at a rate higher than normal to Tank 269 beginning at approximately 5 a.m. The operator noticed this higher rate approximately 1 hour later. Once the operator became aware of the malfunction, appropriate steps were taken to troubleshoot and correct the operation.

  Based on learnings from this incident, Preventative Maintenance (PM) for this type of instrument has been developed that consists of two parts: (1) operational personnel can observe the level at the field sight-glass for comparison to the level that is transmitted to the control room and take an extra step of "blowing-down" the liquid in the level column to remove any debris that may have accumulated, ensuring that an accurate level indication is recovered after this action, and (2) maintenance personnel can check the electrical signal from the device to ensure it matches the observed level.

These two PM programs have been implemented (operator check once/shift and instrument signal check once/week) to prevent the recurrence of this type of malfunction.

The Refinery Work Order System was queried for information regarding repairs to LIC-239 over the past five years. For the period December 30, 2010 to January 24, 2011, maintenance work was required and performed on LIC-239. In addition, in August 2011 and May 2012, a job order was initiated for LIC-239 to calibrate the instrument. Therefore, this limited maintenance with respect to LIC-239 does not indicate that a recurring problem with LIC-239 was one of the root causes of this incident.

- **Clarification of Overpressure Cause**

The key event leading to the Tank 294 overpressure is the flow reversal from the Tank 269 transfer line, causing a high rate of light hydrocarbons to discharge to the tank. Rapid vaporization of the butane resulted in a pressure surge that overwhelmed the capacity of the relief devices. Engineering calculations lead us to conclude that the rate of hydrocarbon flow from MP-30, by itself, would not generate a hydrocarbon vaporization rate high enough to cause a tank rupture. However, the combined flow from these two streams did create such a condition. Refer to Figures 2A – 2D.

Figure 2A. On June 14, before the event, sour water from Units MP-30, U-240 and U-250 were all lined up to Tank 294. Tank 294 was providing feed to the U-236 sour water stripper.

Figure 2B. At approximately 6:00 p.m. on June 14, for inventory control, a transfer of water was initiated from Tank 294 to Tank 269. Tank 294 is located at an elevation of 244 ft and Tank 269 is at an elevation of 127 ft. This transfer is conducted by gravity flow by partly opening a valve on the transfer pipeline at Tank 269. This line-up also redirected the flow from Units MP-30, U-240 and U-250 to Tank 269. Tank 294 continued to provide feed to the U-236 sour water stripper.

Figure 2C. At approximately 5 a.m. on June 15, level indicator controller LIC-239 at MP-30 malfunctioned, resulting in light hydrocarbons being pumped to Tank 269. At 6:35 a.m., Tank 269 experienced an initial high pressure alarm. The transfer pipeline between Tank 294 and 269 becomes filled with light hydrocarbons that are vaporizing.

Figure 2D. At approximately 7:10 a.m., the vaporizing hydrocarbon in the transfer pipeline caused the flow to reverse to Tank 294. The surge flow of light hydrocarbons in the transfer pipeline combined with the light hydrocarbons from MP-30 result in a high rate of vaporization in Tank 294, overwhelming the capacity of the Tank 294 relief devices.

Previous engineering hazard analysis did not foresee and/or contemplate this unlikely scenario of a flow reversal with a high rate of light hydrocarbon vaporization. As described above and indicated by the calculations on Attachment 1, even a maximum rate of light hydrocarbons being pumped directly to Tank 294 from MP-30 would not

have provided the force necessary to create an overpressure strong enough to split the tank roof-to-shell seam. It was the unlikely scenario of the flow reversal with the high rate of light hydrocarbon vaporization that created excessive pressure in the tank, which in turn overwhelmed Tank 294's two emergency pressure relief devices. When that occurred, the frangible tank roof-to-shell weld seam split, as it was designed to do in the event of such an overpressure situation.

Attachment 1
Tank 294 Over-pressure Calculations

Assumptions

MP-30, F-202 Butane composition from sample:	15%
MP-30, F-202 Butane composition design data:	25%
MP-30, D-206 flow to Tank 294, minimum:	30 bbl/hr
MP-30, D-206 flow to Tank 294, maximum:	150 bbl/hr
Tank 269 flow to Tank 294, minimum:	400 bbl/hr
Tank 269 flow to Tank 294, maximum:	480 bbl/hr

Calculations

Vaporization rate in Tank 294 from simulation model:

From MP-30, minimum case:	0.03 MMSCFH
From MP-30, maximum case:	0.13 MMSCFH
From Tank 269 transfer line, minimum case:	0.32 MMSCFH
From Tank 269 transfer line, maximum case:	0.47 MMSCFH
Combined flow, minimum case:	0.35 MMSCFH
Combined flow, maximum case:	0.60 MMSCFH

Relief Device Capacity

Light hydrocarbon relief capacity using Vendor Relief Valve Pressure Graphs:

Tank 294 8" Relief Valve:	0.07 MMSCFH
Tank 294 20" Emergency Hatch:	0.29 MMSCFH
Tank 294 Total Relief Capacity:	0.36 MMSCFH

Conclusions

1. Light Hydrocarbon flow from F-202 could lift the Tank 294 8" relief device, and potentially lift the 20" emergency hatch, but would not cause an overpressure in Tank 294 to split the frangible weld seam.
2. Reverse flow from Tank 269 transfer line could deliver a high enough rate of light hydrocarbons to exceed the capacity of both relief devices on Tank 294 and create an overpressure condition that would cause the frangible roof-to-shell weld seam to fail.

Figure 1
MP-30 Sour Water Collection System
Simplified Process Flow Diagram

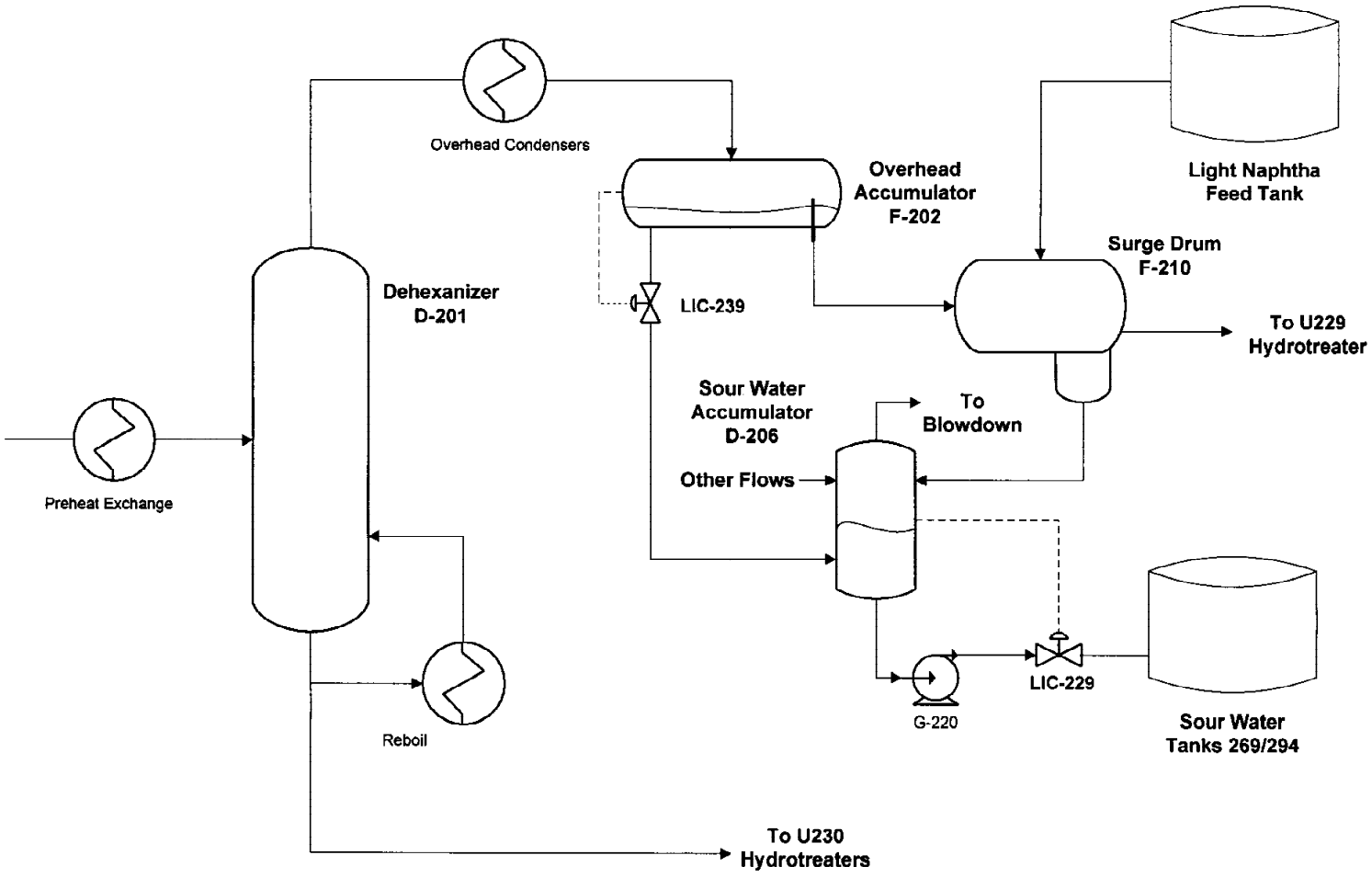

FIGURE 2A. Tank 294 Over-Pressure - Thursday June 14, 2012

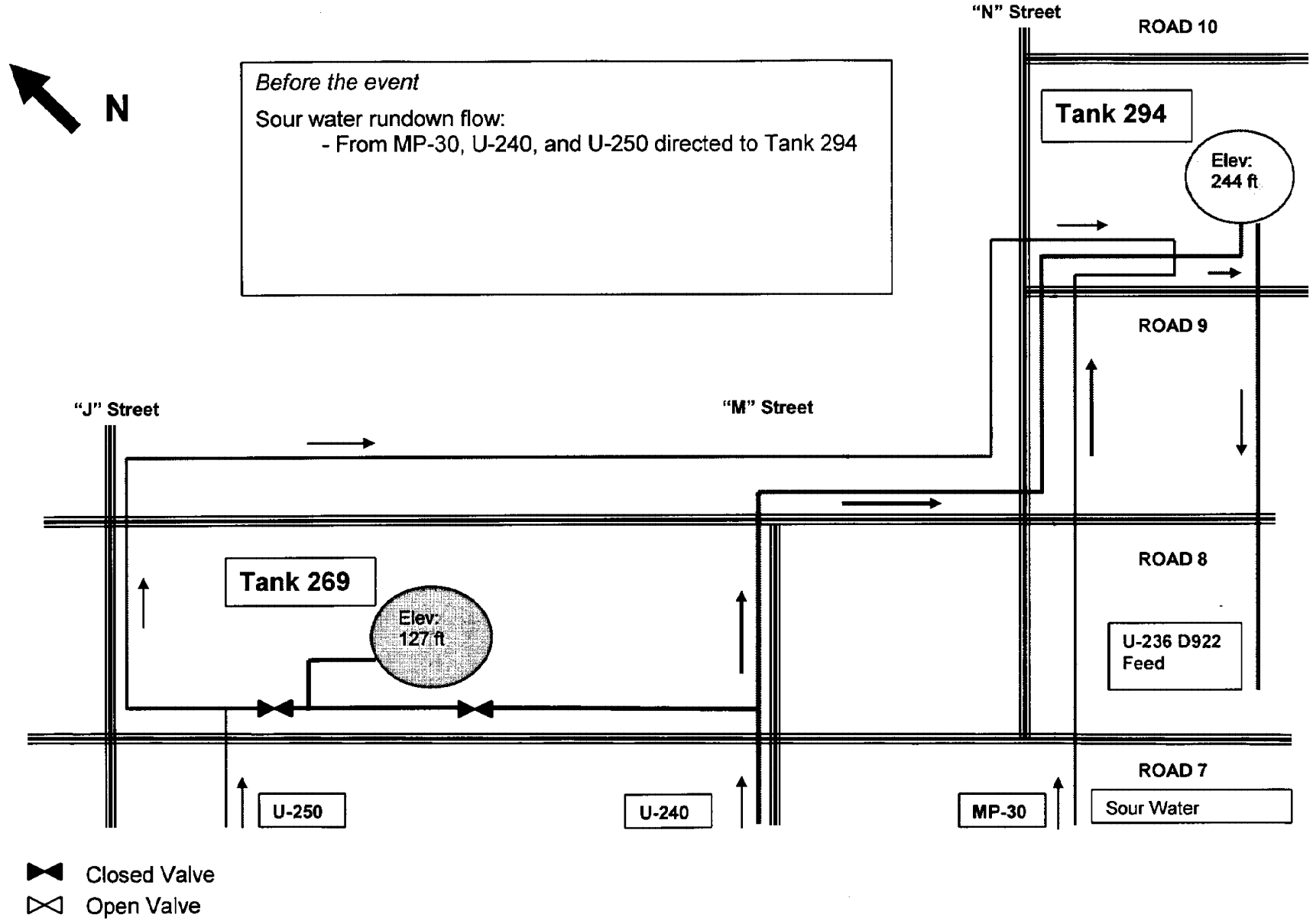

FIGURE 2B. Tank 294 Over-Pressure - Thursday June 14, 2012

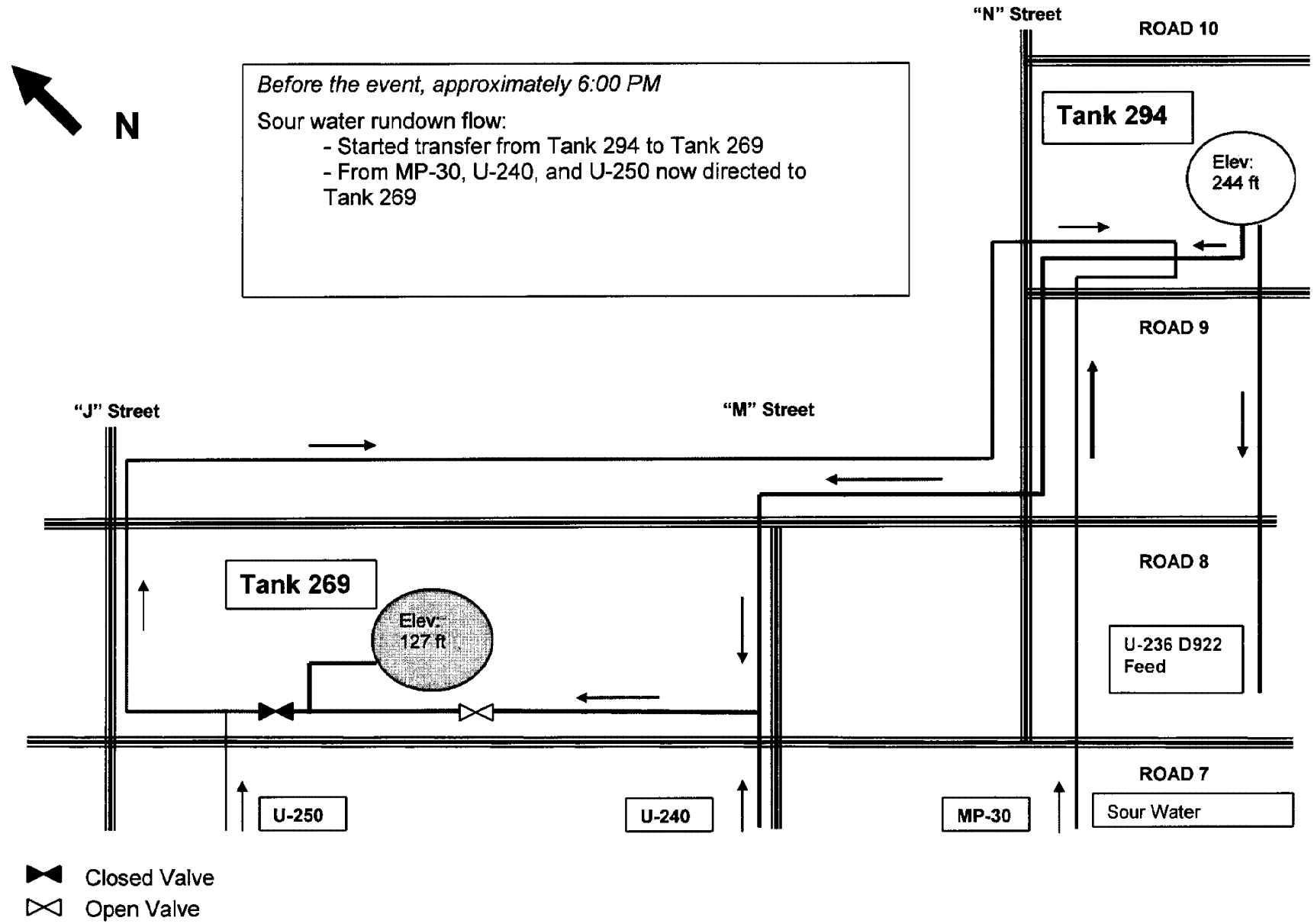

FIGURE 2C. Tank 294 Over-Pressure - Friday June 15, 2012

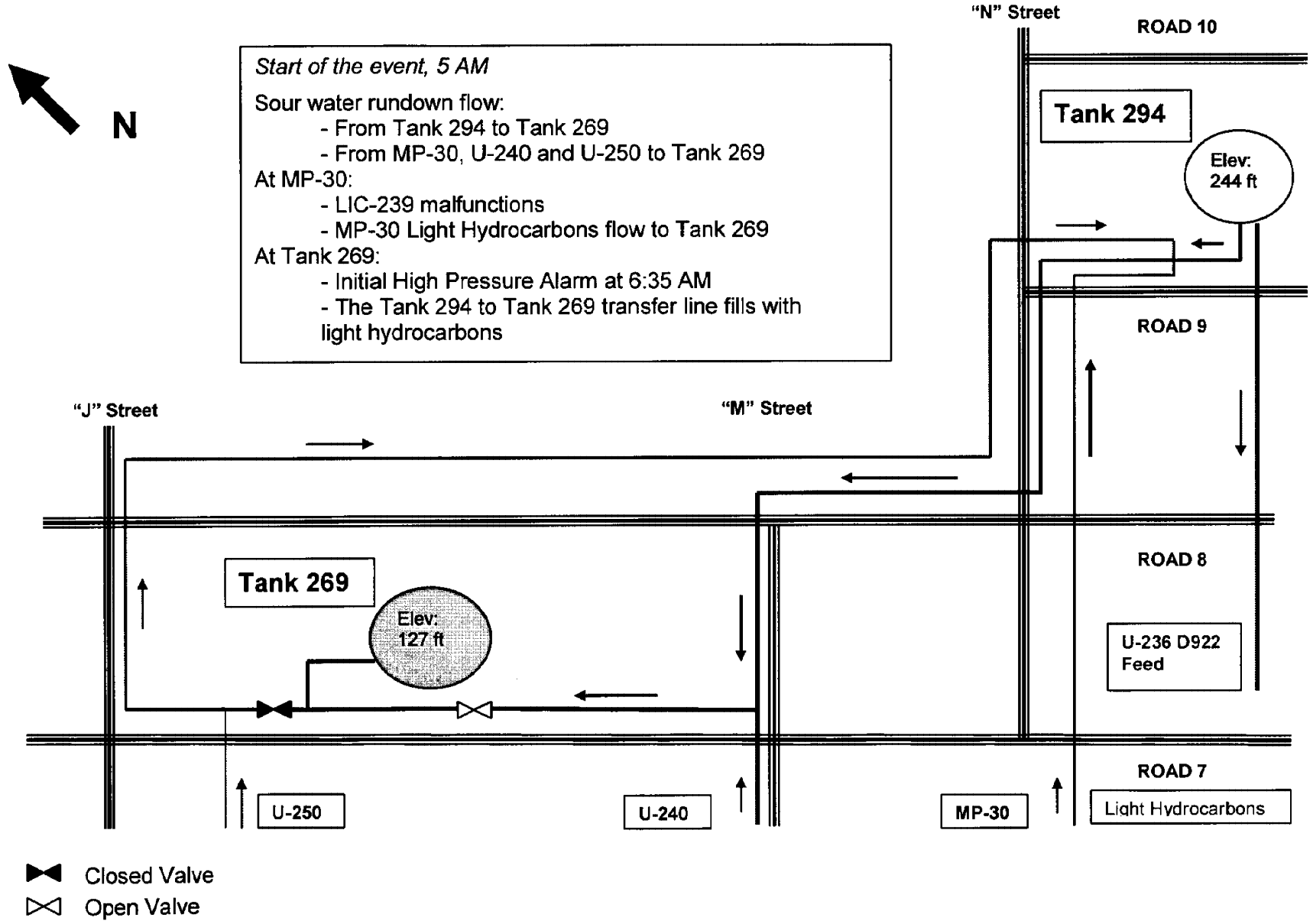

FIGURE 2D. Tank 294 Over-Pressure - Friday June 15, 2012