Recovery System Performance of an Oil Refinery

Corpus Christi, Nueces County, Texas

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Contents

1. Introduction
2. Objectives
3. Study Area
4. Geology of the Area
5. Onsite Monitoring, Observation, and Recovery Wells
6. Creating LNAPL and Groundwater Surface Contour
7. Recovery Performance Summary of the Site
8. Conclusion
9. Future Work

Reference
1. Introduction

The Hydrocarbon plume is a legacy issue known to exist since 1960. Any leakage on the tanks and underground pipelines or dispensing operations could cause plume migration onto the groundwater. It is important for petroleum companies to prevent the possible migration of hydrocarbon plume under their refinery site toward offsite. Preventing aquifers to be polluted by the plume is also another significant point to be taken into account. To control this process, the refinery sites have to be investigated very carefully. Observation and monitoring processes are very crucial at this point to figure out if any unexpected situation is happening. Any prospective oil spill will harm the environment, all the living animals on it, and the human health that may be exposed to hazardous waste indirectly through various ways.

2. Objectives

The objective of this term project is classified in three categories:

- Define the importance of the geology for refineries.
- Emphasize the groundwater surface elevation and LNAPL Thickness by creation the contour lines.
- Analyze the existing performance of recovery system, which includes both LNAPL (Light Non-Aqueous Phase Liquids) and Groundwater, in an oil refinery.

3. Study Area

The area is known as Corpus Christi Ship Channel Harbor, which is in Nueces County. Actually, in that area there are 6 different oil companies that are currently working actively for oil production. They have separate observation and remediation systems in operation as an obligation to TCEQ (Texas Commission of Environmental Quality). However, the main focus area of mine is one of the refineries that I gathered data from. This data consist of stratigraphy of the soil, LNAPL properties such as density and viscosity, recovery rates for 11 well in selected area. We won’t use explicitly all those data in this project, but some conclusion parts are directly related to them. From the data, the exact locations of wells for all facilities were determined as the beginning part of this study. The data consist of the easting and northing point, which is also known as UTM system (Universal Transverse Mercator), for each well in the area. We knew from
the data that the locations are in CGS_North_American_1927 – geographic coordinate system. To understand which projected coordinate system will be used for locating the wells in ArcGis took time in the beginning. Finally, NAD_1927_StatePlane_Texas_South_FIPS_4205 is verified as our projected coordinate system.

For the figures along the report, the World Topographic Map was used as our basemap.

Figure 1. Wells and CPT (Cone Penetrating Testing) Zone

Figure 1 illustrates all the monitoring, observation, and recovery wells along with the CPT zones for 6 facilities in total. The green ones represent the CPT zone, which I will detail later, and the red ones represent all types of wells without grouping them specifically. The number of CPTs is 140, while the number of wells is 272. A few of the wells will be plugged and abandoned due to the fact that no longer remediation or monitoring process will be needed in that specific area.
4. Geology of Area

Geology and soil science have an important role for investigation and resolving the subsurface contamination problems. For instance, in the Walter Creek watershed in the Central Iowa, geologists and soil scientists along with environmental engineers gave effort to solve the groundwater contamination problem (Simpkins and Burkart, 1996).

It is good to emphasize the importance of the geologic formations in the area because soil properties are directly related to these formations. Texture, permeability, porosity, and specific yield are some important soil properties. They must be considered thoroughly because they provide the information about the subsurface water flow capabilities, our ability to reach groundwater and oil by wells, and groundwater contamination as well.

Figure 2 illustrates the geologic formation of the Nueces county and specifically the area where the wells are located. The figure was provided from the USGS-Texas Water Science Center and Texas Water Development Board’s study which aimed to make a digital copy of Geologic Atlas of Texas. The Bureau of Economic Geology at the University of Texas at Austin make some progress to have and advanced map for this work as well.

The deposits on the figure are known as quaternary (alluvium) deposits. This deposit can be found near the rivers and streams. Unconsolidated gravel, silt, sand and clay are inundated regularly in these deposits. The base of this formation is mostly dominated with coarse grain-sized gravel and finer silt is found upper part of this formation. Poorly sorted gravel particles result in variable porosity (low to high) in this formation. Low permeability can be seen in some parts of the formation because of the silty and clayey cement.

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Figure 2. Geologic Map of Nueces County

$Qb$ on the figure represents the Beaumont Formation, known as a class of alluvium deposits as well, which is beach deposits and barrier islands. This formation comprise of mostly gravel, sand, silt and clay. The finer grain-sized clay and silt cause low permeability in the formation as well as high water holding capacity, poor drainage, high compressibility. This formation is emphasized particularly because most wells are located above this formation.

The thick and long continuous line represents the normal fault in the area.

5. Onsite Monitoring, Observation, and Recovery Wells

First of all, I have to clear that onsite will refer here to the area where I will mainly focus on. Unlike the injection and production wells in the refinery area; monitoring, observation and recovery wells are used for controlling and remediating the groundwater by any contamination regarding to the oil extraction and dispensing processes in the refinery. So, there are 88 recovery, 85 observation, and 24 monitoring wells in the selected area along with 6 CPT zone wells. These well’s locations are shown in the figure below.
The purpose of using these wells is:

- **CPT (Cone Penetrating Testing):** It is considered one of the effective methods to provide soil properties and delineating the soil stratigraphy.

- **Observation Wells:** They are used only for gauging. The thickness of hydrocarbon is determined by using observation wells near to the recovery wells.

- **Monitoring Wells:** They are used both sampling and gauging. Interim Corrective Actions (ICA) is very important in case of oil release to minimize the contaminant migration in lateral extent and reducing the concentration of Phase-Separated Hydrocarbon (PSH). This topic will not be detailed in this report. However, to determine if the ICA is proficient for its purpose or remediation is going on well, monitoring process is the way to measure its efficiency. For understanding its effectiveness, the following parameters are monitored:
  - Hydrocarbon volume that has been recovered
  - Phase-Separated Hydrocarbon Thickness
- Benzene Concentration in Dissolved Phase

Recovery Wells: The main reason for using recovery wells is extracting the groundwater and LNAPL (Light Non-Aqueous Phase Liquid)

The parameters which are measured in a groundwater sample of an oil refinery area are shown in the Figure 4 below. Metals, Volatile Organics, and SemiVolatile Organics are listed in the figure with their critical Protective Concentration Limits (PCLs). Units of PCLs are mg/L.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Well ID: Critical PCLs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metals (SW846 6010 &amp; 6020A)</td>
<td></td>
</tr>
<tr>
<td>Arsenic</td>
<td>1</td>
</tr>
<tr>
<td>Barium</td>
<td>200</td>
</tr>
<tr>
<td>Chromium (Total)</td>
<td>10</td>
</tr>
<tr>
<td>Lead</td>
<td>1.5</td>
</tr>
<tr>
<td>Nickel</td>
<td>150</td>
</tr>
<tr>
<td>Volatile Organics (SW846 8260B)</td>
<td></td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>0.5</td>
</tr>
<tr>
<td>1,4-Dioxane</td>
<td>19</td>
</tr>
<tr>
<td>2-Butanone (MEK)</td>
<td>4400</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.5</td>
</tr>
<tr>
<td>Carbondisulfide</td>
<td>750</td>
</tr>
<tr>
<td>Chloroform</td>
<td>4.3</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>70</td>
</tr>
<tr>
<td>Methyl tert-butyl ether (MTBE)</td>
<td>73</td>
</tr>
<tr>
<td>Toluene</td>
<td>100</td>
</tr>
<tr>
<td>m &amp; p-xylene</td>
<td>1000</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>1000</td>
</tr>
<tr>
<td>SemiVolatile Organics (SW846 8270C)</td>
<td></td>
</tr>
<tr>
<td>1-Methylnaphthalene</td>
<td>510</td>
</tr>
<tr>
<td>2,4-Dimethylphenol</td>
<td>1150</td>
</tr>
<tr>
<td>2-Methylphenol (o-Cresol)</td>
<td>570</td>
</tr>
<tr>
<td>4-Methylphenol / 3-Methylphenol</td>
<td>57</td>
</tr>
<tr>
<td>Benzenethiol (Thiophenol)</td>
<td>0.073</td>
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<tr>
<td>Bis(2-ethylhexyl) phthalate</td>
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</tr>
<tr>
<td>Diethylphthalate</td>
<td>5800</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>57</td>
</tr>
<tr>
<td>Phenol</td>
<td>2190</td>
</tr>
</tbody>
</table>

Figure 4. Concentration of Concern Parameters in Groundwater Sample
Although the PCL for benzene concentration is 0.5 mg/L in the table, we know from the TCEQ’s reports that 0.005 mg/L is considered the current PCLs to meet the requirement of Residential Area Groundwater Class. All the oil facilities in the area are held accountable to provide the benzene concentration under the PCLs by TCEQ².

### 6. Creating LNAPL and Groundwater Surface Contour

Before creating the LNAPL contour lines by using Apparent LNAPL Thickness (ANT), which is provided from observation wells adjacent to the recovery wells, a point needs to be cleared. ANT has a huge impact on estimating LNAPL recovery from groundwater.

Figure 5 gives a demonstration of confined and unconfined groundwater / LNAPL and ANT effect on such mediums.

![Figure 5. The effect of ANT on confined/unconfined medium³](image)

Using ANT for estimating the LNAPL thickness in the formation is adequate and feasible for unconfined groundwater and LNAPL medium because ANT enables us to have the correct measurement for thickness. On the other hand, confining layer in the confined layer misguides

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² TCEQ UPDATE BULLETIN, Remediation Division, Petroleum Storage Tank Fact Sheet, March 2009

³ Source of Figures are H2A Environmental Ltd.
us if we use ANT for predicting the LNAPL thickness because it doesn’t show the correct LNAPL thickness in the formation. Therefore, ANT could cause an exaggeration problem for confined and perched groundwater. It causes a logarithmic exaggeration on recovery estimates, which will results in a remediation failure and costs a lot of money. That’s why, to determine if groundwater is confined or unconfined, we have to use diagnostic gauge plots that show the trend of changes of LNAPL Thickness versus Air LNAPL Interface Elevation (AOI), LNAPL Water Interface Elevation (OWI), and Corrected Groundwater Surface Elevation (CGWS).  

![Theoretical Basis for Diagnostic Gauge Plot Trends](image)

Figure 6. Theoretical Basis for Diagnostic Gauge Plot Trends

The LNAPL Thickness is in the x-axis; and AOI, OWI, and CGWS are in the y-axis creates the Diagnostic Plot Trends. Simply, by following the trends in Figure 6 will let us consider whether the formation is unconfined, confined, or perched.

After explaining the importance of Apparent LNAPL Thickness, we can now form the contours of LNAPL and groundwater surface by using ArcGIS. Groundwater Surface Contour and LNAPL Contour maps are very useful maps if we are working on unconfined groundwater. It is a contour map of potentiometric surface, and equal elevation lines are used to create the contour lines in the map. To build these maps, the corrected groundwater surface elevations and the

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4 LNAPL Thickness Revitalized, Applied NAPL Science Review Volume 1, Issue 1 - January 2011
5 Diagnostic Gauge Plots, Applied NAPL Science Review Volume 1, Issue 2 - February 2011
apparent LNAPL thickness will be used. These data gathered from the observation wells around the recovery wells. To construct the contour maps is important because they provide us the direction of groundwater and LNAPL plume flow. Another reason that why these maps are crucial because it gives us the distribution of LNAPL in the site as well.

Figure 7. LNAPL Thickness Contour Map

In Figure 7, the LNAPL contour has been depicted. Apparent thicknesses that are assigned for each well were measured in April 12, 2011. For creating this map, each well that is described as a point feature in ArcGIS was converted to a raster feature. Among the interpolation methods, the Inverse Distance Weighted method, which fitted best to the data, was used. The last step was creating the contour map by using contour tool in 3D Analyst. The dark color on the left picture illustrates where the apparent LNAPL thickness (ANT) is at its highest point. While the color goes lighter, ANT decreases as well.

Figure 8 shows the groundwater surface contour. For creating this contour map, the corrected groundwater surface elevations, which were measured in April 12, 2011, were used. Krigging interpolation method was the most suitable one for the elevation data. And, finally contour maps were constructed by building contour lines. In the left picture, the dark blue illustrates us the highest groundwater elevation in the field. Through the stream, decreasing trend in the groundwater elevation is observed.
To sum up the last two figures, we end up with that the flow direction for both groundwater and LNAPL is expected to go toward the Corpus Christi Inner Harbor.

7. Recovery Performance Summary of the Site

The data for recovery rates is very limited to analyze. We have two kinds of data for onsite well recovery rates to be used in this project. The first one is the recovery rates for the first half of 2011, from January to June, includes all recovery wells rate in the site and the values are in total with a unit of gallon. Figure 9 shows us the total groundwater recovery rates for previously mentioned time period. The scale of the points shows how the recovery is higher or lower in those specific wells.
Figure 9. Total Groundwater Recovery Rates in gallon (January 2011 – June 2011)

Figure 10 is also a demonstration of total hydrocarbon recovered from each wells. The area which is marked with a red circle has the most recovery rates along the recovery wells. The future work will be related to this area.

Figure 10. Total Hydrocarbon Recovery Rates in gallon (January 2011 - June 2011)

Figure 11 is basically shows how the Interim Corrective Action (ICA) works. Since 1998, the recovery system for groundwater and hydrocarbon has been in operation. And the last data we have for the recovery rates relates to 2011. 2011 is the peak year since 1998 for both recoveries. The values next to the each graph are in barrels.
8. Conclusion

The fluid level data and hydrocarbon recovery estimates demonstrate the PSH plume beneath the refinery continues to be recovered. The LNAPL removed from groundwater at facility is piped to the recovered oil tanks and recycled without exposure to potential receptors.

9. Future Work

This term paper will be a part of my thesis research, which is referred as the future work. First thing that will be done for the future work is to make a 3D visualization for borehole logs for the wells that data are available. This work couldn’t have been done in this project because lacking of enough data for this particular work. We have some information about the borehole log, however since it is not clear which part is referred in that logs, it is preferred not to be used in here. Second thing could be to create time series catalog for all available data that will be gathered in the future. And, the last future work will be the
simulation results that will be done for the selected area shown in Figure 10 by using LDRM (LNAPL Distribution and Recovery Model)

Reference


2 TCEQ UPDATE BULLETIN, Remediation Division, Petroleum Storage Tank Fact Sheet, March 2009

3 Source of Figures are H2A Environmental Ltd.

4 LNAPL Thickness Revitalized, Applied NAPL Science Review Volume 1, Issue 1 - January 2011

5 Diagnostic Gauge Plots, Applied NAPL Science Review Volume 1, Issue 2 - February 2011