M501: MEASUREMENT OF HAZARDOUS SUBSTANCES INCLUDING RISK ASSESSMENT

CASE STUDY 5 – HIGH ENERGY PETROLEUM

High Energy Petroleum's main business activity is the storage and distribution of petrol (gasoline); however it does operate a small refinery. This exercise involves a maintenance task which occurs periodically – the cleaning of leaded product storage tanks.

SITUATION TO BE STUDIED

Tetraethyl lead (TEL) is an alkyl (or organic) lead compound [$(C_2H_5)_4$ Pb] and is used to raise the octane number of gasoline to prevent "knocking" in internal combustion engines. The concentration of lead alkyl in gasoline varies but is typically around 0.2 – 0.4 g/L. TEL is blended into gasoline at the refinery through automatic injection systems and hence TEL handling in a refinery does not usually pose an exposure risk except in the case of leaks or spillages.

Gasoline (petrol) is stored at refineries and distribution terminals in various size tanks typically 10-15 metres high and 20-30 metres in diameter (photograph 1). Periodically these tanks have to be emptied and cleaned of sludge, which accumulates on the bottom of the tank, and rusty scale which forms on the inside lining of the tank. The cleaning of tanks used for leaded product is potentially hazardous owing to the presence of flammable and toxic vapours, including lead and hydrocarbons.

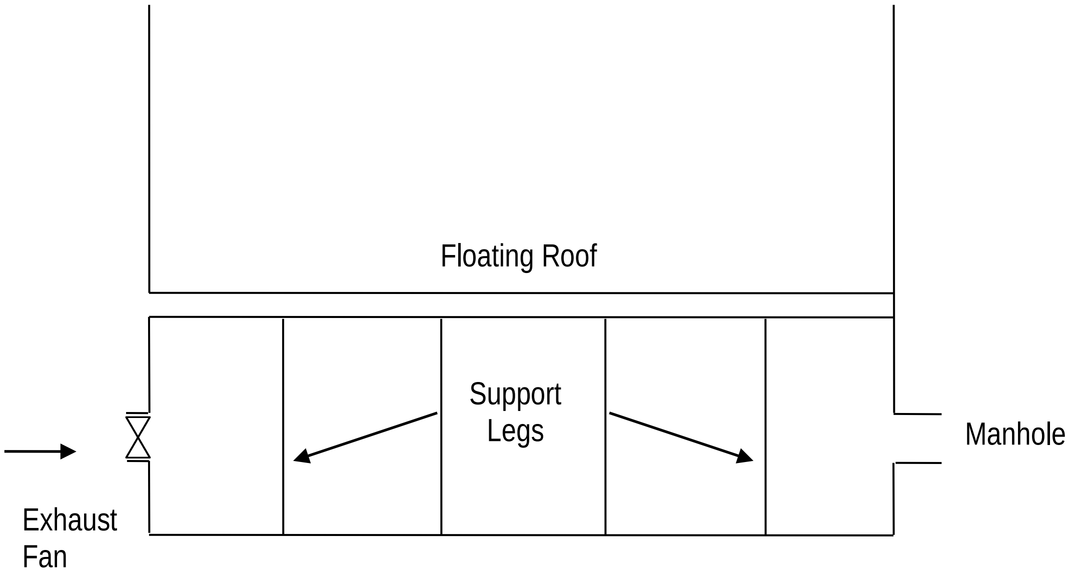
Once the tank has been cleaned it is inspected both visually and with x-ray equipment and any repairs carried out. This can involve the grinding and welding of steel plate. If the tank is to be take out of leaded service it must also be grit blasted and epoxy lined. This prevents the "leaching" out of organic lead which has been absorbed into the floor and wall of the tank.

Tanks which have contained leaded product at some time in the past and have since been used for other non-leaded products, and which have not been epoxy lined, may give off toxic vapours even after several years in non-lead use.

In the situation under study, a floating roof storage tank 10.6 metres high and 19.5 metres in diameter and was used for a number of years for leaded gasoline. It was to be emptied, cleaned, de-scaled by grit blasting, inspected, repaired (if necessary) and coated internally with a “two-pack” polyurethane paint.

Note: A “floating roof” floats on top of the product to prevent loss of vapours during filling. As the product is removed from the tank the roof falls until it rests on “legs” 1.7 metres from the tank floor.

This tank has two 90 cm diameter manholes (photograph 2) located diagonally opposite each other and positioned about 0.5 metres above ground level.



(Source: D Rhodes – *reproduced with permission*)

During the course of the maintenance exercise the following work procedures were followed.

1. The tank is emptied of product down to a level where the viscosity of the sludge prevents further removal through pipework (usually about 30 cm from floor).

2. All product lines to and from the tank are isolated.

3. Both manhole covers are unbolted and removed.

4. Tank left to ventilate naturally for a couple of days.

5. A 610 mm diameter axial flow extraction fan is mounted in one of the manholes and let run for 24 hours (at the static pressure of 37 Pa the fan's capacity is 10,000 m^3/hr).

6. With the fan still running, a terminal operator ensures the atmosphere is less than 5% of the Lower Explosive Limit (LEL) before taking a sludge sample. The terminal operator enters the tank with a well-maintained full-face air supplied breathing apparatus (BA). Air lines are solvent resistant. Protective clothing includes rubber boots, PVC gloves and impervious full suit. Urinary leads before and after check OK.

7. Laboratory analyses shows sludge to comprise:

Table 1 – Analyses of Leaded Sludge

CONSTITUENT	AMOUNT
Iron oxide (rusty scale)	60%
Water	29%
Gasoline	10%
Total lead (as Pb)	1000 ppm
Organic lead (as Pb)	25 ppm

* Gasoline however can contain up to 5% benzene which has an exposure standard of 0.5 ppm (1.6 mg/m^3). Benzene is slightly more volatile than gasoline (petrol).

8. A work permit is raised to allow four contractors to begin removing sludge under the charge of the contractor supervisor. The sludge is shovelled into open pales and handed through the manhole and emptied into an open skip for transportation off site. PPE requirements on permit for those inside the tank include Tyvek impervious coveralls, air-supplied BA, PVC boots and gloves.

Air supply is from a diesel powered air compressor located outside the tank adjacent to the skip (the respirator air lines supplied by the contractor were subsequently found to be of poor quality PVC and which were showing signs of wear). Rests and meal breaks were taken in a construction shed adjacent to the tank. The temperature during the day rose to 33°C with little air movement.

9. All four presented themselves for pre-work urinary leads with results normal. At the end of the day samples 1 and 2 were taken; samples 3 and 4 had to be taken the following afternoon as the contractors had failed to present themselves to the medical centre. The first two gave readings of 87 µg/litre and 110 µg/litre. The two samples taken from the workers the next afternoon were well within the normal range.

Table 2 – Urinary Leads of Workers Removing Sludge

	BEFORE	AFTER
Worker 1	38 µg/litre	87 µg/litre
Worker 2	56 µg/litre	110 µg/litre
Worker 3	50 µg/litre	46 µg/litre
Worker 4	40 µg/litre	49 µg/litre

10. Upon the removal of the sludge the tank floor was water washed and dried. There were some isolated small puddles of gasoline remaining on the floor. Tests for oxygen content, lead in air and explosivity were conducted by a plant operator wearing air-supplied BA. Inspection revealed the need for a number of floor plates to be welded.

Table 3 – Atmospheric Levels of Pb, O_2 and Explosimeter Reading Inside Cleaned Tank

Oxygen	20.7% (+/- 0.2%)
Organic lead	<0.04 mg/m^3 (lower detectable limit)
Explosimeter reading	<5% of LEL (the lower detectable limit of the instrument)

Note 1. The lower explosive limit (LEL) for gasoline is about 1.4% (14,000 ppm). 5% of the LEL is used by the oil industry as a limit above which no hot work such as welding is permitted.

2. There is no suitable personal sampling system for alkyl lead. The method involves absorbing the lead into cyanide solution followed by chemical reaction and colorimetric determination.

11. Based on the above results the extraction fan was turned off and the decision was made that air-supplied respiratory protection was no longer required.

Organic respirators were made available but there was no record of who used them. As a precautionary measure a static lead-in-air monitor was set up just inside the tank approximately 10 metres from where the welding was to take place. Readings were taken every 1.5 hours during the welding (takes about one hour to obtain a sufficient sample).

Table 4 – Results of Static Samples for Lead-in-air

Reading 1	0.04 mg/m^3
Reading 2	0.08 mg/m^3
Reading 3	0.12 mg/m^3
Reading 4	0.11 mg/m^3
Reading 5	0.11 mg/m^3

12. An oxygen monitor with alarm set at 20% was located adjacent to the welding activity.

13. Three metal trades' personnel, including one welder, spent seven hours inside the tank. The welder had a visor to prevent flash burns, cotton overalls and other welding protective clothing. All three provided urine samples prior to commencing work and again at the end of the day. Normal rest breaks and lunch were taken.

Table 5 – Urinary Leads For Welders

SAMPLE	PRE SHIFT	POST SHIFT
Welder	56 μg/litre	167 μg/litre
Fitter 1	67 μg/litre	190 μg/litre
Fitter 2	65 μg/litre	148 μg/litre

14. Once the tank is cleaned it is ready to be grit blasted using a garnet/slag material. Workers agree to be monitored for personal exposure to dust and lead. The rust and scale to be removed has a lead content of 0.5%. Dust samplers were worn for five hours to sample inhalable dust according to statutory requirements. The dust fraction collected on the filter was 0.2 mg and the flowrate was 2.0 L/min.

QUESTIONS

1. Why is skin contact a source of exposure to TEL?

2. In Table 2 why did samples 1 and 2 show elevated exposures but not samples 3 and 4?

3. List all the hazards you believe a competent occupational hygienist should investigate in the described tank cleaning operation.

4. If they were using breathing apparatus why were there elevated urinary leads (Table 2)? Explore all possible causes.

5. Does the explosimeter reading indicate a safe atmosphere to work in? If not, why not?

COMPONENT	EXPOSURE STANDARD
Gasoline	900 mg/m^3
Total lead (as Pb)	0.15 mg/m^3
Alkyl lead (as TEL)	0.10 mg/m^3

Note: Molecular weight for gasoline = 80

6. What else, if anything, would you monitor for specifically? What monitoring procedure and equipment would you use?

7. What do the static lead-in-air results tell you about the atmosphere inside the tank and the nature of the welders' working environment?

8. Give an explanation why the urinary leads in Table 5 are elevated when the results in Table 4 indicate acceptable airborne lead levels?

9. What was the lead exposure for the sample described in Work Procedure No. 14?

10. If a method was available, would personal sampling for alkyl lead have provided more useful information? Why?

(Source: University of Wollongong)

Photograph 1 – Typical Fuel Storage Tanks

Source: University of Wollongong)

Photograph 2 – Typical Entry Manhole

Note: This case study is based on a range of archive materials adapted to create a case study for student use. It does not represent any particular company or situation past or present. Any resemblance to current people, organisations or companies is coincidental.