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In situ remediation of diesel spill inside a power and desalination plant at Muscat, Oman

D. Nahmad, Eco-Logic Environmental Engineering-USA, RAY International Group; R. Rasheed and B. Muzzaffar, RAY International Group-Oman

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Abstract

After a large spill of diesel ~80 m3 of diesel inside a power and desalination plant in Oman near Muscat; adjacent to the diesel fuel storage tanks and affecting an estimated volume of more than 2,000 m3 of soil in a complex underground plume, a novel and in situ protocol (Free-RAD Technology) for a complete remediation was applied to bring the Total Petroleum Hydrocarbon (TPH) levels below the acceptable threshold (< 1% W/W). The process was able to treat the affected soil layers without affecting the existing equipment and pipe layout in the plant including all underground piping and electrical installation. The process is based on the release of selectively active free-radicals via a chemical reaction that facilitate the rapid oxidation of the hydrocarbons into CO_2 and H_2O. The project was successfully completed within 4 months and without affecting any of the routine operations inside the plant.

An environmental Survey was conducted to do a geo-chemical evaluation of the site for areas and volumes impacted with any concentration above 1.0% TPH - including the vadose zone, the tidal water table and the permanent water table. After volumetric / concentrations modeling, and based on the specific capillarity of the soil, a model to effectively dose chemicals at different levels and locations was established; injection ports were installed. Extraction points were drilled for the recovery of free diesel in the inter-phase (wet/dry) zone. Chemical dosage was determined by injection well, injection and monitoring was conducted in parallel.

After four months from the spill, sampling in the heavily impacted area as well as the perimeter of the spill showed complete treatment at all levels from the ground. This allowed the plant to operate without any changes in the routine dynamics. No major digging and plant disruption or equipment removal was needed. The site was cleared by the Ministry of Environment and Climate Affairs of Oman, shortly after close out report was submitted and the site inspection was conducted.

This process can be applied in sites where excavation is extremely disruptive or expensive. Computer

modeling allows for an accurate representation of all the impacted areas as well as the dynamics of the plume in volumes and times. The method allows for direct in-situ treatment with minimum changes of the site topography and has little or no impact to surfaces and structures located below ground within the impacted area.

Introduction

The Middle East is one of the driest places on the planet. Average rainfall ranges between 20-40cm per year compared to 72cm globally and droughts are frequent in the region[i]. Recently, global share of Reverse Osmosis (RO) has increased owing to the development of better membranes and reductions in energy consumption[ii]. Due to the high energy consumption of the RO systems usually they are coupled in installations together with Power Generation Plants.

This particular Power and Desalination Plant utilizes RO technology to deliver 120,000 cubic meters per day of potable water. Gas and steam turbines based on a combined cycle deliver 678 MW of electrical power to the Sultanate’s electrical grid. The site is located in the South Batinah region, approximately 80km northwest of Muscat and lays 300m south of the shoreline. The plant also stores large volumes of diesel fuel, as an alternate fuel, in case of any natural gas supply disruption. This fuel is stored in large tanks inside the plant.

On October 2013, an operator observed a leak from a flange located on fuel-oil recirculation valve. The root cause analysis found that the leak caused by a failed gasket that was used to secure one blind flange. The gasket material was not suitable for use with fuel oil, and upon failure resulted in the loss of more than 80,000 liters ($80m^3$) of diesel fuel. (Fig.1) Geological and chemical assessments were conducted to establish a volumetric and space distribution model that accurately described the geo-chemical plume in a three dimensional space. Based on the assessment and equipment layout of the impacted area it was determined that an in situ chemical oxidation (ISCO) of the site was the most appropriate due to the fact that excavation and soil removal was practically impossible on all affected areas.

Fig. 1

Lab tests revealed that the geochemistry of the site would fall within the limits of the ISCO technology known as Free-RAD; porosity, stoichometrics and rate of reactions were determined as to provide the data for injection rates, location of the wells and a mechanism to monitor/control the process. During the course of 4 months the site was fully remediated to <1.00% in Total Petroleum Hydrocarbons (TPH).

Statement of Theory and Definitions

In situ Chemical Oxidation is a technique being used to remediate contaminated soil and ground water[iii]. The process is based in the use of chemical reactions that can release short lived highly active free radicals (ions) that in turn oxidize contaminants into non hazardous or less hazardous compounds. In the case of hydrocarbons, like diesel, a total oxidation will render only two by-products carbon dioxide (CO_2) and water (H_2O). Some of the reactions require a catalyst to maintain and enhance the process of radical production. Compounds like ozone (O_3), sodium permanganate (NaMnO4), potassium permanganate (KMnO4), sodium persulfate (Na2S2O8) and hydrogen peroxide (H2O2) have been used to create the required radicals to promote and consume the oxidation process. Metallic salts are also employed as catalysts to speed up and maintain the rate of reaction. The most important free radicals required to complete the reactions are Hydroxyl radicals (-OH), Super oxide radicals (O2-), Hydronium radicals (H3O+) and Sulfate free radicals (SO4-). The best example is the Fenton's reaction as indicated in the figure below[iv] where is combined with the Haver-Weiss reaction (Fig 2):

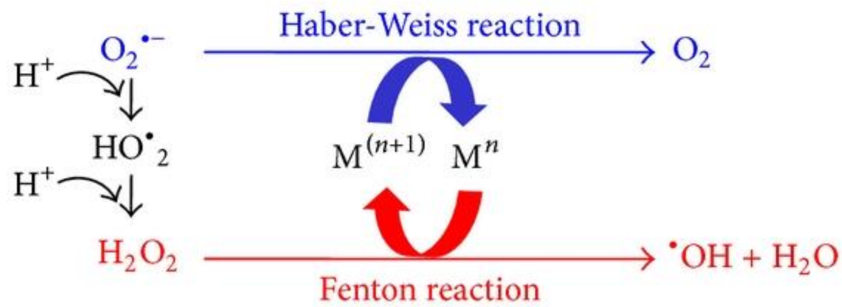

Fig. 2

Transition metals including copper, nickel, cobalt and vanadium can be used but iron in the form of a salt is the most commonly used.

In our case, a modified Fenton's reaction was combined with the application of a diluted "piranha solution" (Sulfuric acid H2SO4 + Hydrogen peroxide H2O2) to produce the required free radicals to complete the oxidation processes without any additional hazards.

The use of both reactions can carry significant risks during the implementation phase due to the potential development of toxic gases and the uncontrolled reaction producing high volumes of steam and releasing high amounts of energy that can be the cause of explosions or bodily harm. Additional considerations will have to be analyzed prior to prescription of this technique in the field:

- Geological and chemical analysis and plume development. 3D modeling and site assessment. Soil type and soil porosity / capillarity. Water table level.
- Liquid/soil ratios, contaminant type, and reaction times. Profiling these variables requires carefully designed column studies (using multivariable, multilevel factorial design experiments)[v].
- Site constraints, especially geohydraulic considerations, will impact how the technology is applied. *In-situ* applications (treating the soil in place using sprayers, sprinklers or nozzle injectors) have the advantages of less exposure of workers, less impact of site constraints, and typically less cost[3].

The technology was implemented using a lattice of injection ports located strategically as the plume geometry was defined. Injection took place at different levels at each injection point and intersection of the injected materials between adjacent injection wells was critical in order to avoid "hot spots" (untreated soil volumes). Chemical addition was done from top to bottom and the use of monitoring wells was necessary to keep the reaction rates under control.

The use of a GC-MS, retort analysis and gravimetric techniques for laboratory quality control helped in the field application after the initial dosing to enhance treatment in heavily contaminated areas and to stop treatment in areas where the quality of concentration was already met. Excavated soil that was extracted to do the extraction wells during the emergency was treated on surface using the same chemistry applied in batches inside a concrete mixer. The treated batches were piled up until lab confirmation of treatment was given and at the end of the project the material was used to fill back the extraction wells.

Description and Application of Equipment and Processes

Right after the incident, contingency measures were applied to stop the leak and to remove the maximum volume of diesel form the ground as soon as possible. For this purpose, nine boreholes were immediately dogged after the incident; these boreholes were approximately 1.5 m in width by 1.5 m in length and 3.2 m in depth (Fig.3). They reached approximately 0.2 m below the level of the permanent water table. The boreholes were used to pump daily accumulated diesel fuel floating on top of the water table and allow verifying the site stratigaphy and laboratory determination of soil porosity / permeability. The diesel / water mix recovered from the boreholes was pumped into a gravity separator and then the water recovered was sent to the waste water treatment plant. The recovered fuel was sampled and stored for further disposal; during the project, 21.8 m3 of free fuel was recovered using this method. (Fig. 4)

Fig. 3

Fig. 4

The leaked fuel oil flooded the immediate leak area and completely saturating the soil layers, this area was designated as the Highly Impacted Area (HIA), and the diesel fuel came to a rest on the water table – at a depth of approximately 3 meters. A second impacted zone known as the Perimetral Affected Lower Area (PALA) was established. The PALA was the region that had been affected within 40,000 ppm to 10,000 ppm on the TPH. There was no visual determinable damage; however, upon sampling it was found that the diesel had migrated to this region at deeper depths.

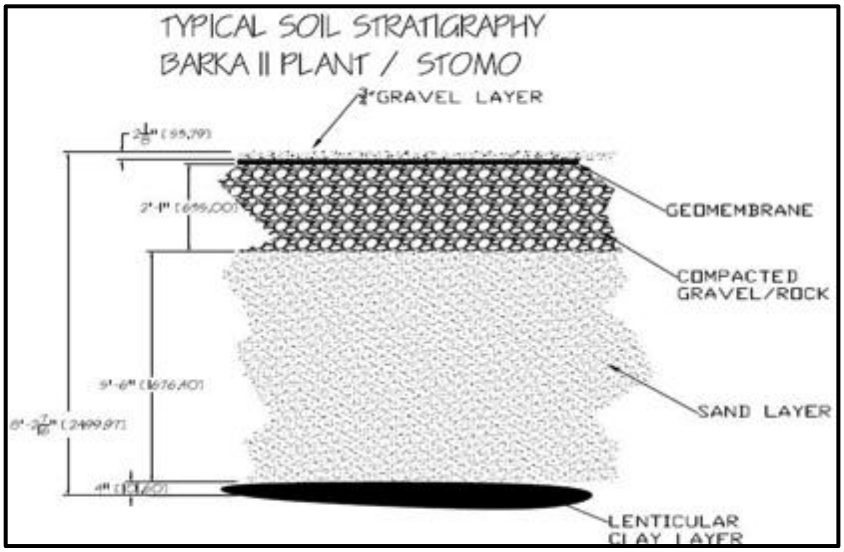

Fig. 5

The stratigaphy of the site shown above (Fig. 5) included a layer of imported gravel (~3/4”) at the very top, below this layer; there is a geo-membrane for soil stabilization and support which is completely permeable. The next layer is a man made layer of compacted gravel, sand and rocks followed by a layer of sand and at 2.3m depth a very compacted clay layer starts at the same level that the capillary layer sits. It seems under initial inspection that between the clay layer and the salty water below, they form a physical barrier for the diesel to move forward down. Using a field retort kit and a core sampler samples were taken and determined the TPH concentration and the HIA (with a saturation level between 7.8% to 12.4% TPH) and the PALA with a concentration above 1.0% to 7.8%) the areas were plotted and using a simple krigging technique the volumes were determined for the soil to be treated. (Fig. 6)

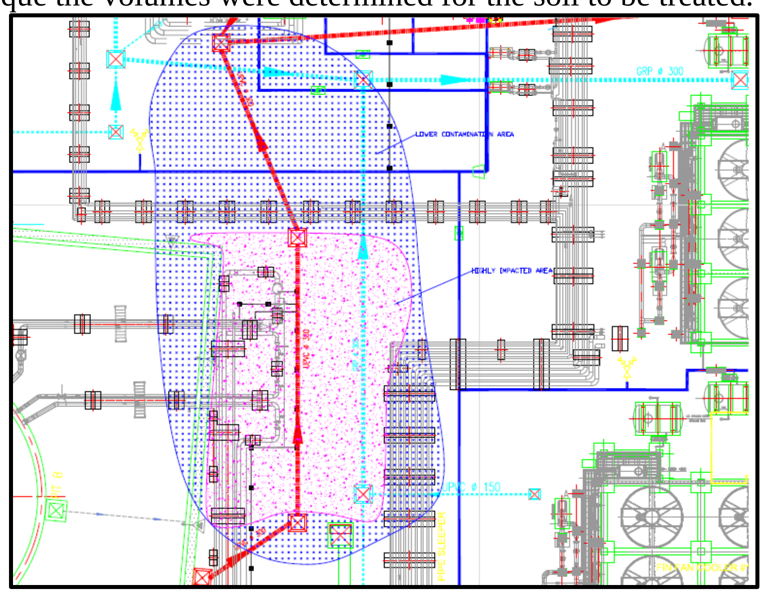

Fig. 6

The HIA was rounded up at 883.65 m3 and the PALA encompassed a total volume of 1,184 m3. However, it must be noted that these values were ascertained during the initial site assessment, and over the course of the project, the PALA would have increased steadily via capillary action.

As a result, a solution had to be devised, in order to treat all contaminated material from the HIA and PALA (soil and gravel) to below 1.00% TPH, in accordance with Ministry of Environment and Climate Affairs (MECA) guidelines, and to remove all free diesel which had permeated to the water table. The most critical factor in this scenario was the evident migration of the diesel towards the sea, as it is only approximately 300 meters from the leak location.

The material extracted from the digging of the nine boreholes was at saturation levels; this material was treated using the Free-Rad technology under batch conditions using a cement mixer. (Fig.7) The treatment area was lined with a high density polyethylene liner and the material was moved into two piles: treated and untreated materials more than 60 m3 of soils were treated using this technique during the first three weeks of the project.

Fig. 7

Based on the physical distribution of the fuel in the soil and the permeability of the layers the diffusion radius was calculated and the injection levels were determined in order to cover completely the whole volume of contaminated material.

14 injection wells were installed each with three levels of injection; a final superficial level was also used for the top layers. Three monitoring wells were also drilled for water removal and sampling of contamination on tidal waters. The chemistry was applied from top to bottom and this included a first wash with a modified piranha solution followed by the addition of a proprietary catalytic compound and allowing for soaking at least 24 hrs. A dosage of stabilized hydrogen peroxide was injected to start the desired reactions. Rate of reaction, temperature and gas generation were monitored at all times to prevent high energy uncontrollable reactions. (Fig.8)

The dynamics of the technology are complex and involve a set of chemical compounds, which are used to trigger a series of highly reactive free-radical intermediates. A series of transition, propagation and chain terminating reactions deliver a strong free radical species that completely oxidize the hydrocarbon compounds into carbon dioxide (CO2) and waster (H2O). It begins with a catalytic decomposition that creates hydroxyl radicals, which are very strong oxidizing agents. A chain-propagating sequence usually takes place, which can also generate superoxide ions, hydro peroxide ions, and organic radicals. These radicals all combine in the oxidation process of the organic molecules.

Fig.8

Samples were continuously taken as the chemical addition continued to monitor the progress and the presence of "hot spots" additional dosages were determined once the TPH concentration was determined.

Presentation of Data and Results

Throughout the continuous quality determination / assurance in the field we were able to establish dosage rate and further chemical addition required to pass the needed threshold for MECA approval. Once determined in the field that the soil was treated below 1.00% TPH we requested the plant operator to send representatives to collect final samples and to maintain the chain of custody of these samples to be taken to Sultan Qaboos University (SQU) for final analysis and reporting to MECA.

HIA results after two chemical dosages (Top Layers):
The following 24 results were obtained after the combined first and second stage spraying of the HIA. Based on the 1st results, the 'hotspots' were identified and a stronger dose of oxidant was applied to reduce TPH further in the 2nd stage. The 12 results for each spray correspond to 12 evenly spread out locations across the entire HIA. (Fig. 9)

Table 1

Location	2nd Spray TPH%	1st Spray TPH%
1	0.64	0.92
2	0.71	1.00
3	0.69	0.62
4	0.50	1.89
5	0.61	1.63
6	0.22	0.26
7	0.74	1.12
8	0.65	0.56
9	0.00	0.00
10	0.51	0.36
11	0.32	1.10
12	0.78	0.92

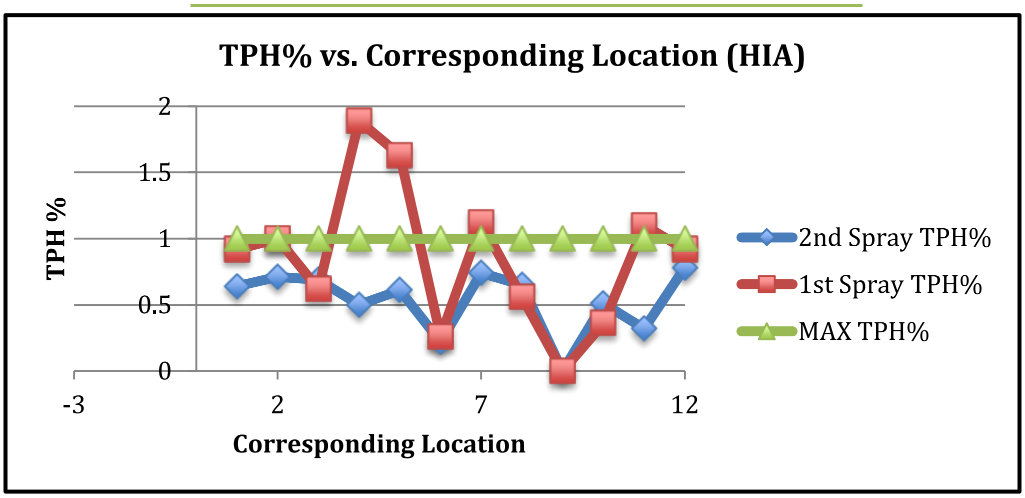

Fig.9

HIA & PALA results after chemical dosages (Lower Layers):
The following 19 results were obtained from the 7 sampling points. As explained previously, 3 samples were taken from each location, however only 1 sample was managed from Location 5 due to obstructions. (Table 2)

Table 2

Location 1	
Depth (m)	TP H%
1.60	0.77
2.20	4.30
2.70	2.53

Location 2	
Depth (m)	TP H%
1.60	0.33
2.20	3.63
2.70	1.27

Location 3	
Depth (m)	TP H%
1.60	0.00
2.20	0.75
2.70	0.00

Location 4	
Depth (m)	TP H%
1.60	1.70
2.20	0.67
2.70	0.00

Location 5	
Depth (m)	TP H%
1.60	0.00
2.20	-
2.70	-

Location 6	
Depth (m)	TP H%
1.60	0.00
2.20	5.39
2.70	0.67

Location 7	
Depth (m)	TP H%
1.60	0.00
2.20	1.99
2.70	2.14

Please refer to the following diagram for sample locations (Fig. 10):

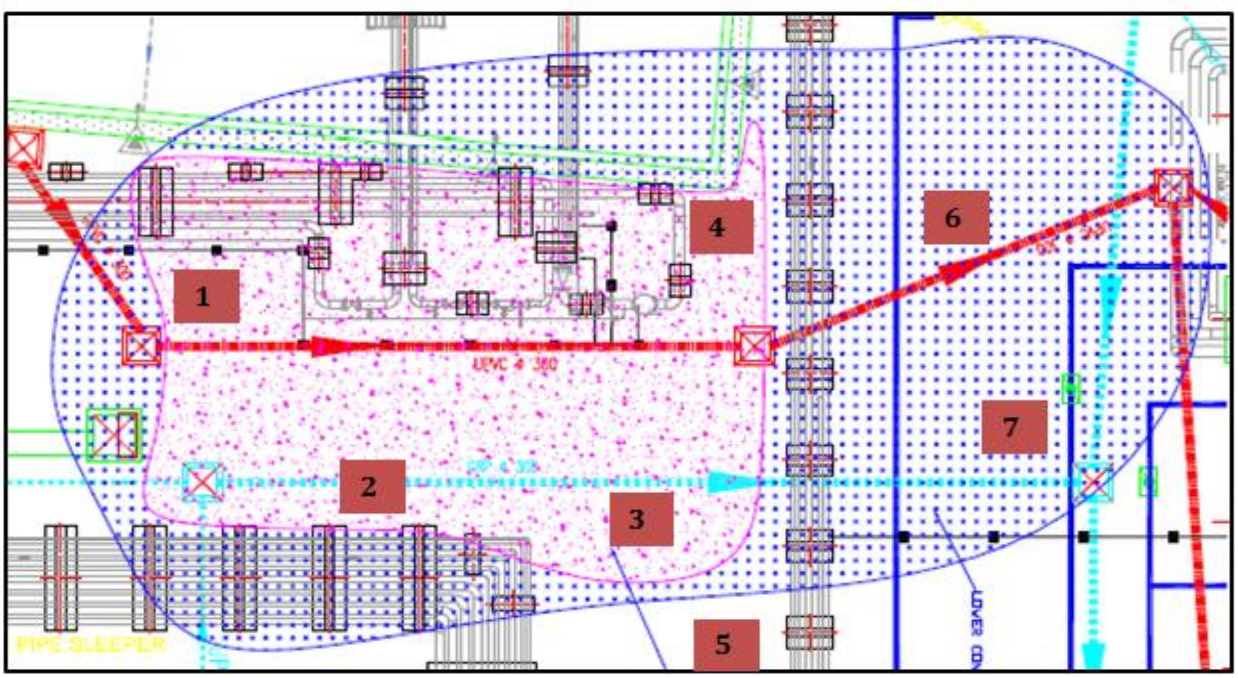

Fig.10

Results on excavated soil treated ex situ

Sultan Qaboos University (SQU) provided the following results, for the 6 grab samples that were collected from the pile of treated soil. (Table 3)

Table 3

SAMPLE	TPH%
1	0.35
2	0.48
3	0.44
4	0.43
5	0.57
6	0.53

The following scatter graph illustrates the tabulated results. (Fig. 11)

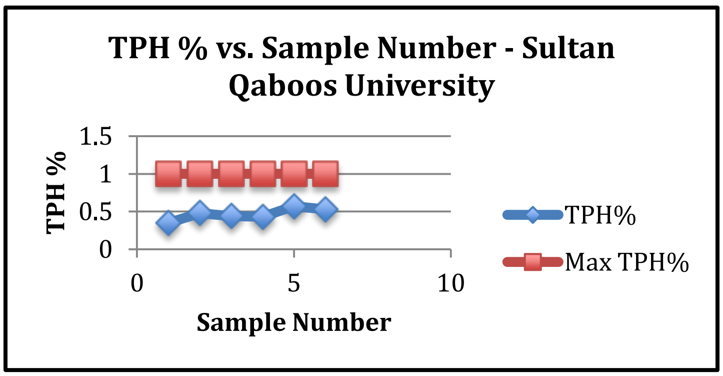

Fig.11

After all analytical results were accepted by MECA and they visited the site for inspection; approval was granted to restore the site to its original state by placing back the excavated material in the boreholes and level the site. After site restoration, final site inspection and closeout report presented to MECA, the site was completely cleared. The whole process including permitting, technology implementation and final clearing took 25 weeks.

This project was later nominated for the Oman Green Awards 2014.

Conclusions

Fig.12

This is the first time this technology was applied in the Sultanate of Oman with excellent results. Before and after treatment is as shown in Fig. 12. A full restoration was achieved without affecting the daily operations of the plant or removing existing equipment and lines. Soil excavation was kept at minimum (~60m3) just enough to operate the boreholes on site. The timeframe for the whole project is extremely short considering all liaisons with the Environmental Authorities (Permits, site inspections and reports approvals) are included in the project as well as third party lab validation reports.

Acknowledgments

We would like to extend our sincere thanks to the Owners, Operators, Engineers and Supervisors of the plant for their support, without which this project would not have been successful. Special mention of gratitude to Environment Inspection and Control team at Ministry of Environment and Climate Affairs, Oman for their support and faith in carrying out this novel technique of in-situ remediation at a critical location. We are certainly thankful to the personnel of the Central Laboratory, College of Agricultural & Marine Sciences - Sultan Qaboos University. Last but not the least; we are ever so appreciative to the field crew, for being exceptionally motivated and hardworking throughout the term of the project.

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