Kuwait Environmental Remediation Program (KERP)

Predictive Kinetic Model for Bioremediation of Crude Oil Contaminated Soil in Arid Environment.

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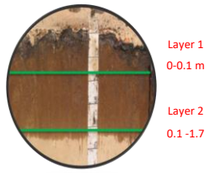
Background :

Kuwait's oil wells were damaged and set on fire during the Iraqi invation in 1990-91 resulting:
Millions of barrels of Crude Oil Spilled over the Land and Seashore
World Worst Environmental Disaster on 114 Sq. Km of Kuwait landscape
Over 50 million tons (e.g. 26 million m^3) of contaminated soil with crude oil constituents (e.g. TPH, SVOC, VOC)

1990 -1991 2016-2017

Objectives

To evaluate different bioremediation techniques
To verify first order kinetic decay model is valid
To predict the decay and time to achieve cleanup criteria under loadings for two various bioremedation systems



Challenges of bioremediation in Kuwait's Soil :

*Rainfall = 100 mm/yr
*Evaporation 35.5 mm/day in July & August
*Infiltration rate 15-100 cm/hr
*T: Summer over 45-55oC
T:Winter 12.7oC ; dip to 5 oC
*very low organic matter
*very low nutrients

*Sandy Medium to coarse texture
*No water retention

*PH:Average 7.0-7.5
Slightly alkaline

*Elevated salinity in some areas.
In shallow groundwater depth.

*Contaminant: Various compounds vary in toxicity, solubility, hydrophobicity, weathered., aging. etc

Bioremediation System

Passive — Natural attenuation

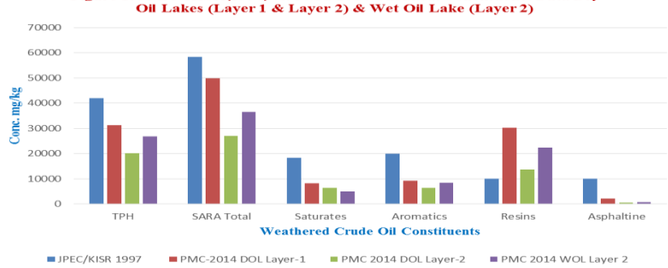
Definition

Without human intervention other than monitoring of contaminant levels against time. It relies on evaporation, photo-oxidation and biodegradation of the contaminants.

Past & Recent Studies (1997 & 2014)

Characterisation of highly weathered crude oil material was tested in general areas of South Burgan in KOC from wet oil lake and dry oil lake materials layer 1 & layer 2 for TPH HEM),VOC, SVOC & SARA (Saturates, Aromatics, Resins and Asphaltenes (SARA).
Statistical Analysis performed on all samples from 1997 & 2014 and trend is shown in Figure 1

Figure 1: JPEC/KISR(1997) vs. PMC 2014 Chemical Constituents Data Dry Oil Lakes (Layer 1 & Layer 2) & Wet Oil Lake (Layer 2)



1997 : 66% Saturated/Aromatics, 34% Resins/ Asphaltenes → 2014 : 53% - 63% Saturates/Aromatics, 47%- 37% Resins/ Asphaltenes

Little degradation has been observed of crude oil constituents (e.g. aromatic, aliphatic and asphaltenes) with the exception of resins has increased slightly in recent testing areas

Lack of enough data over 16 years of span to carry out and verify first order

Active — Biostimulation / Bioaugmention

	Biostimulation	Bioaugmention
Definition	catalyzes natural attenuation processes by adding nutrients ,oxygen, water and to utilize indigenous microbial populations.	introduces of improved microorganism strains to degrade a particular contaminant.
Case study	Field Case study from oil lake in Kuwait (JPEC, 1997-1999)	Laboratory Case study from oil lake in Kuwait (Ecophile, 2014)
Bioremediation system	Soil pile, Landfarm and windrows	Bioaugmentation
Quantity	3,000 m3 of contaminated soil	500 g of contaminated soil
Initial TPH	3-5%	4-5%
Microorganism	Indigenous	Cultivated
Nutrients	N and P as (5% to m3)	N and P
Water Content	1 to 20 L/m3 per day depending on season	10 to 15 %
Temperature		35C
Ventilation system	force air, Tilling and overturning;respectively	Tilling and overturning to distribute oxygen and water
Period	over 12 months	2 months
TPH	TPH degraded to an average of 90% in Landfarming TPH degraded to an average of 83% in Windrows	TPH levels dropped from 4.9% to 3.1% 37%
Crude oil as TPH %	4.0%	4.9%
Kinetic Equation	Y=3.44 e-0.004x	Y=4.87 e-0.008x
R_2	0.944	0.989
k Decay Constant (1/day)	0.008	0.004
Half-Life time ($t_{1/2}$)(days)	**165 days**	**86 days**
Field & Laboratory Bioremediation System		

Figure 3: Biostimulate Field Test -TPH Degredation vs. Time (Days)

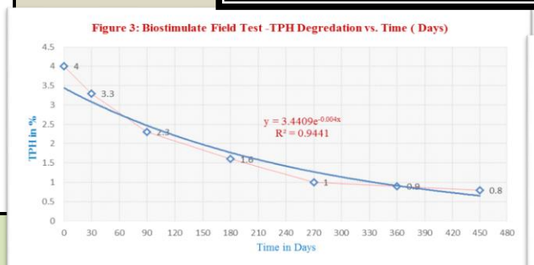
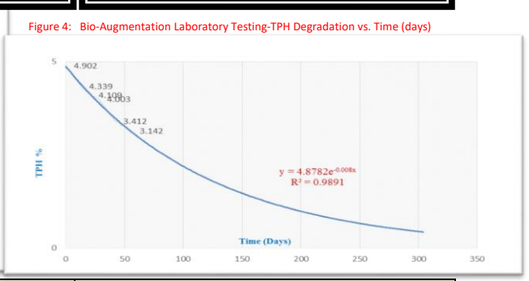


Figure 4: Bio-Augmentation Laboratory Testing-TPH Degradation vs. Time (days)



Initial Concentration (C_0) %	Bio-stimulated Predicted Time (days) Ct= 2%	Ct= 1%	Ct= 0.5%	Kinetic Equation Y	Bio-augmented Predicted Time (days) Ct= 2%	Ct= 1%	Ct= 0.5%	Kinetic Equation Y
10%	402	576	749	-0.004x+2.97	201	288	375	- 0.008x+2.3
8%	347	520	694	-0.004x+2.08	173	260	347	-0.008x+2.09
6%	274	448	621	-0.004x+1.79	137	224	311	-0.008x+1.79
4%	173	347	520	-0.004x+1.39	87	173	260	-0.008x+1.39
3%	101	275	448	-0.004x+1.04	51	137	224	-0.008x+1.05

Planned Field Scaled Up Remediation

Kinetic models & predictions to be reviewed and refined for full scale-up bioremediation systems.
Degradation of asphaltenes and resins will be defined and estimated by incorporating detailed testing for SARA and TPH fractions during long term performance.
Half-lives and constant decay rates of highly weathered crude will be refined on full scale strategies & variable initial loadings.
Challenge and explore the performance of either bioremediation systems under higher petroleum hydrocarbons levels to establish its toxicity or progress of treatments.

Summaries & Conclusions

First-order kinetic decay is an appropriate model for highly weathered crude oil degradation for Kuwait's contaminated soil.
Experimental data of TPH degradation is in good correlation with the first-order kinetic model, R2>95
Half-lives derived indicate bio-augmentation system (86 days) is twice faster than bio-stimulation system (165 days).
Bioaugmentation system may offer better & sustainable alternative to long term remediation in terms of time schedule/throughput.
Highly weathered crude oil constituents ($t_{1/2}$ > 86 days) are persistent in environment.