Final Report

Remediation of Hydrocarbon Contaminated Soil and Groundwater using Heat-Activated Nano Stimulators

(GL # 19-RRRC-06)

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

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EXECUTIVE SUMMARY

In Canada, contaminated site stakeholders have favoured excavation and landfilling practices for source removal due to the speed and perceived cost-effectiveness of this method for 'remediating' hydrocarbon contaminated sites. However, landfill disposal is not a substantial treatment method due to potential environmental liabilities associated with the landfilled soil material for secondary contamination such as groundwater impacts by leachate and landfill gas migration towards off site. Internationally, conventional thermal desorption (i.e. low temperature incineration) and/or soil washing have been widely used for heavily contaminated soil and/or source material. However, with an ever increasing emphasis on sustainable remediation practices, contaminated site stakeholders are under increasing pressure to select more sustainable and innovative solutions minimizing environmental footprints caused by massive soil excavation, disposal at landfill and backfill with imported soils, and there is a demand for the evolution of a diverse number of in-situ and ex-situ remediation approaches. Furthermore, the developed and improved remediation technologies over the last few decades are still not cost-effective and potentially cause secondary contamination (e.g. GHG emissions, chemical residues, etc.).

In the first year (2018-2019) of the subject project, the research team successfully developed multi-functional stimulators using nanomaterials with technical and economic benefits, which utilize the advantages of thermal and chemical treatments for hydrocarbon impacted soil. A series of lab scale in-situ feasibility tests proved that the stimulators effectively generated heat and other remediation mechanisms through their activation thereby reducing concentrations of F2 and F3 hydrocarbons up to 93% in soils contaminated with 100,000 mg/kg diesel. Although the stimulator assisted in-situ remediation has shown significant removal of hydrocarbons, an additional remediation was required to meet the Alberta Tier 1 Soil and Groundwater Remediation Guidelines. It was confirmed that a lab-scale in-situ eletrokinetic/electrochemical (EK/EC) treatment as a subsequent remediation method further reduced residual hydrocarbons up to 50% in total hydrocarbons after 4 weeks of the onset of direct electric current application.

In the second year (2019-2020), further lab-scale tests were performed to improve the developed stimulator assisted in-situ application by identifying followings: (1) the impact of coating material dose in stimulator composition for various soil textures; (2) feasibility of a lab-scale integrated in-situ remediation system in hydrocarbon removal; (3) radius of influence (ROI) and depth of influence (DOI) for activated stimulators; (4) impact of multiple stimulator layers on hydrocarbon remediation; and (5) produced heat propagation in soils through modeling and simulation.

The lab-scale test results for the impact of coating material dose in the stimulator composition were inconsistent with our initial postulation that increase of field soil amount (i.e. increase of clay content) would reduce amount of coating material required for protecting spontaneous activation of stimulators and being activated by heat supply under the tested soil moisture conditions. In a specific range of coating material dose, its impact was negligible on the stimulator activation in the tested soils with over 25% of field soil, which implies that there may exist a critical soil composition to be considered for determination of the coating material dose. Soil that contains lower clay content than the critical composition may demand more coating material to protect stimulators from spontaneous activation without heat supply.

The lab-scale integrated in-situ remediation system was developed and its feasibility tests showed that the exothermic chain reactions of the stimulators were ideally propagated from the original heat source. In addition, the maximum temperature at all locations were not significantly different which indicates feasibility of Phase 1 treatment (stimulator-assisted thermal treatment) of the integrated in-situ remediation system for hydrocarbon removal. The subsequent Phase 2 treatment (EK/EC treatment) reduced up to 15% of hydrocarbons over the period of direct electric current application (4 weeks). However, further investigation is required as varying concentration reduction was observed over the length of the tested soil and majority of the concentration decline stopped or rebounded after 3 of the 4 weeks.

The radius of influence (ROI) tests concluded that stimulators immediately activate with onset of heat supply and that the ROI of activated stimulators can be expanded as wide as stimulator exists. However, analytical results presented only 33.3% of hydrocarbon removal, but this was likely due to reduced stimulator dose applied in the ROI tests. The depth of influence (DOI) test results showed that heat penetration did not effectively reach distances greater than 1 cm above and below the layer of stimulators. Due to the findings on DOI tests with a single layer of stimulators, multiple stimulator layers were evaluated to identify the synergistic impact in temperature increase and hydrocarbon remediation. However, no noticeable synergy impact was observed from the multiple stimulator layers. Finally, modeling and simulations were performed to identify influence of soil type on propagation of heat produced from the exothermic chemical reactions and compare the simulation results with experimental observations. The simulation results showed that impact of soil type and water content is limited for the heat propagation, presenting not significantly different temperature distribution in soils under different conditions.

1. BACKGROUND

Remediation of contaminated sites have had a major economic and environmental impact. The Federal Contaminated Sites Action Plan (FCSAP) reported that over 60% of Canada's remediation involves petroleum hydrocarbon (Government of Canada, 2020). Environmentally, contaminated sites have caused significant damage to water, soil, and air which can heavily impact human health and the environment. Additionally, the extensive developments in oil and gas industry over the past few decades have also caused major leakages and spills from the its underground storage tanks, pipelines, and during transportation. While major advancements to remediation of contaminated sites have been developed, cost reduction and enhancing the efficiency of processes are still being pursed.

While thermal treatments result in higher remediation effects, current thermal treatments often require high temperatures, which leads to high operating costs, and produces greenhouse gases (GHG) (Lee et al. 2000). Even though they can treat nearly all hydrocarbons, high temperature treatments, like incineration, vitrification and smoldering, often cause soil alternation (Vidonish et al. 2016). Negative soil alternations can include a decrease in fertility through the decomposition of minerals, salts, and other important nutrients within the soil and damage to parts of microbial ecosystem that is present.

In the first year (2018-2019) of the subject project, our research team has successfully developed the multi-functional chemical stimulators for the use of in-situ contaminated soil remediation by modifying the proprietary stimulators (T-REX®), in cooperation with our partner company (TRIUM Environmental Inc.). The developed stimulators were successfully activated at low heat temperature (< 150 °C) and effectively generated additional heat (280 - 670 °C) through their exothermic chemical reactions in the lab-scale in-situ application, reducing concentrations of F2 and F3 hydrocarbons up to 93% in soils contaminated with 100,000 mg/kg diesel. A lab-scale in-situ eletrokinetic/electrochemical (EK/EC) treatment was evaluated as a subsequent treatment method and the test results showed that EK/EC treatment is capable of further reducing concentration of residual hydrocarbons up to 50% in 4 weeks of direct electric current application.

In the second year (2019-2020), our research team further investigated in-situ application of the developed stimulators. To optimize dose of coating material for appropriate activation of stimulators under different soil types, impact of varying coating material doses was investigated for various soil textures. With the optimized coating material dose, radius of influence (ROI) and depth of influence (DOI) for the activated stimulators were examined. On top of that, synergistic effect of multiple stimulator layers was also evaluated in the lab-scale in-situ test. An integrated in-situ remediation system was developed through combining thermal/chemical treatment (Phase 1) with EK/EC treatment (Phase 2). By applying the integrated in-situ remediation system, rapid and highly effective thermal/chemical treatment is expected through the stimulators assisted in-situ remediation (short-term treatment) followed by gradual elimination of the residues from the precedent treatment via the EK/EC remediation method (mid-term treatment).

Long-term objective of the subject project is to commercialize the integrated in-situ remediation system and replace main streams of soils treatments with a goal of reducing remediation costs of contaminated sites without secondary contamination.

2. METHODOLOGY

2.1. Impact of Coating Material Dose in Stimulator Composition for Various Soil Textures

Through the prior lab scale feasibility tests, we have found that the chemical N in the developed stimulator plays an important role in triggering the exothermic chemical chain reactions which is the primary mechanism for degradation of hydrocarbons in this remediation technology, even without heat supply by releasing heat through spontaneously reacting with water present in soil. To control its reaction time and reactivity with water, the chemical N was emulsified with a coating material which can be decomposed at low temperature and delay activation of the chemicals in the presence of water. However, dose of the coating material needs to be determined for different environmental conditions such as soil moisture contents and soil textures (i.e. clay/silt contents). Based on previous tests, it was expected that overdosed coating material would impede exothermic chain reactions of the introduced stimulators in soils containing higher clay/silt contents under the same moisture condition. In addition, few prior tests showed spontaneous activation of stimulators, with no heat supply, in soils containing low clay/silt content (i.e. sandy soil). It is obvious that the stimulator reactions are influenced by different soil texture under the same moisture condition as soils containing higher clay/silt contents have higher water holding capacity. Hence, it is important to understand the correlation between coating material dose in the stimulator and soil texture of contaminated site for the best practice of the developing in-situ remediation technology.

To evaluate impact of various doses of the coating material on the stimulator activation, a series of small-scale chamber tests have been performed with four different soil textures under the same moisture condition. Testing setup was designed to mimic petroleum hydrocarbons present on groundwater as light non-aqueous phase liquid (LNAPL). A cylindrical Pyrex glass container (65 mm H X 125 mm D) was used as the testing chamber. As shown in Figure 1, testing setup basically consists of two soil layers and a layer of stimulators to represent contaminated soil area where the stimulators are introduced into. Diesel was spread out over the bottom soil layer to generate hydrocarbon contaminated soil. A cartridge heater was employed as a heating source for activation of stimulators and was controlled by a temperature controller (Omega CSC32). Changes in stimulator temperature were monitored through thermocouples at different distances from the heating source and the monitoring results were recorded using the Labview. Soil samples were collected before and after each treatment, extracted into organic solvent following the CCME Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil (Tier 1 Method) and analyzed by gas chromatography equipped with flame ionization detector (GC-FID) to quantify hydrocarbons in soil.

Four types of testing soils (Soils A, B, C, and D) were purposely prepared in the lab using commercially procurable sandy soil and field soil which was collected by the partner organization. The fractions of those two soils for each soil type are shown in Table 2 (section 3.1). 10% soil moisture content was applied for all the feasibility tests and the bottom soil layer alone received diesel hydrocarbons equivalent to 5 wt. %. Identical amounts of other chemical components were added for the stimulators except dose of the coating material. 150 °C of heat was supplied through the cartridge heater to initiate exothermic chemical reactions of the introduced stimulators. Experimental variables and test results are summarized in Table 2.

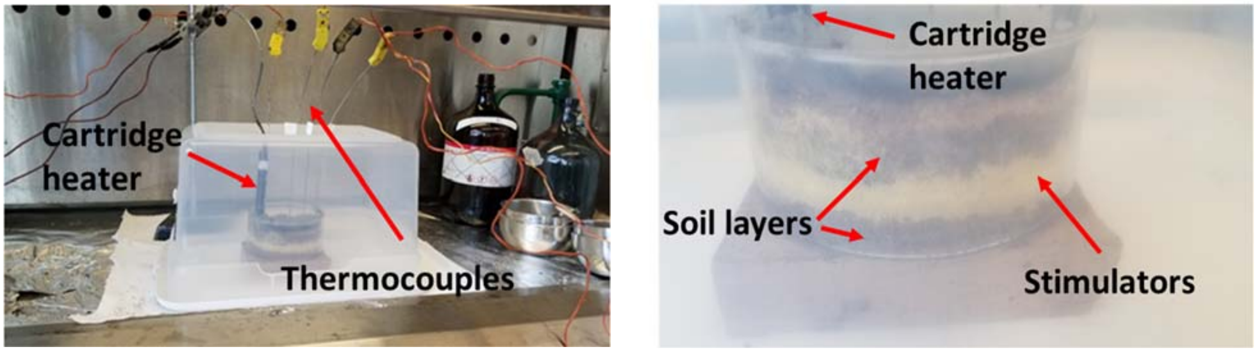

Fig 1. Experimental setup for a lab scale in-situ remediation utilizing stimulators.

2.2. Development and Feasibility Test of a Lab-Scale Integrated In-situ Remediation System

In the first year of the subject project, the lab-scale in-situ electrokinetic/electrochemical (EK/EC) treatment that was employed as the subsequent remediation method to further reduce the residual hydrocarbons after the stimulator assisted in-situ application, resulted in 47 – 50 % removal of total hydrocarbons (C10 – C34) 4 weeks after the onset of the direct electric current application. Based on this promising remediation capability of the EK/EC treatment, the integrated in-situ remediation system comprising the stimulator assisted thermal treatment and the subsequent EK/EC treatment was evaluated in the aspect of remediation efficiency by scaling up the contaminated soil volume.

A scaled-up test was performed utilizing the developed stimulators with a modified pressure cooker which has dimensions of 37.6 cm D x 30.3 H cm. This test was conducted to evaluate feasibility of the integrated in-situ remediation method in degrading hydrocarbons in soil. The integrated method comprises of the stimulator-assisted thermal treatment (Phase 1) and the subsequent electrokinetic/electrochemical (EK/EC) treatment (Phase 2). ROI (radius of influence) of the stimulator when completely activated was also evaluated during the Phase 1 treatment. As shown in Figure 2, testing setup, temperature monitoring, and soil sample extraction and analytical methods were the same as the small scale tests presented above. Three soil samples were collected at locations A, B, and C in Figure 2(c) before and after the Phase 1 treatment to quantify hydrocarbon removal through the thermal treatment alone.

Soil D composition that comprises of 75 % sandy soil and 25 % field soil was chosen for the test along with 10 % soil moisture condition. The chemical composition was also identical with the optimal conditions that showed the best performance in the aspects of stimulator activation and hydrocarbon removal rates in soil D. Diesel equivalent to 5 wt % was uniformly distributed over the surface of the bottom soil layer followed by evenly distributed stimulator. While 10 times greater amount of soil was applied in this test compared with a small scale test, reduced amount of stimulators equivalent to 6.75 times greater than chemicals used in the small scale test was introduced.

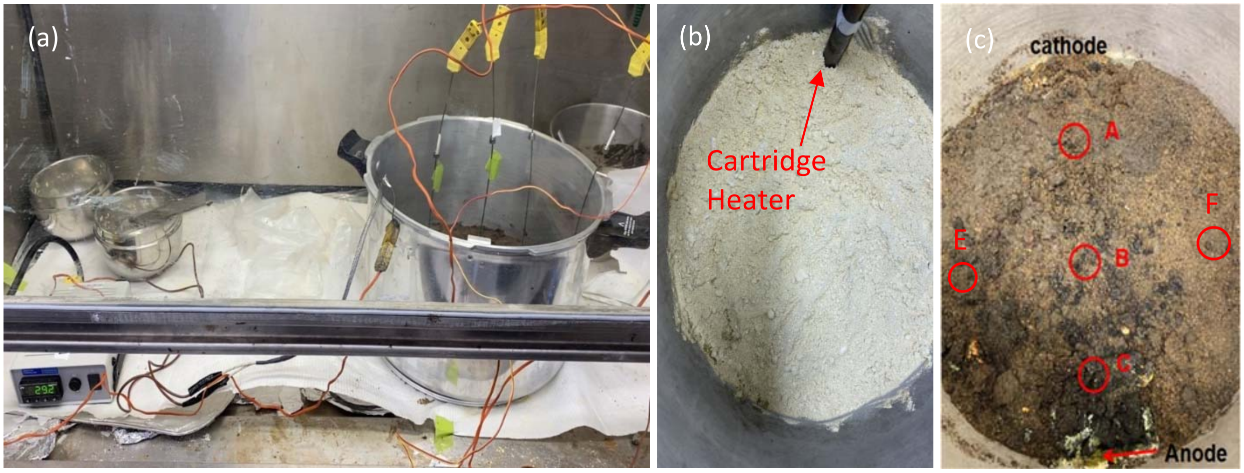

Fig 2. Experimental setup for a scaled-up in-situ remediation utilizing stimulators: (a) represents the overview of the scaled-up integrated in-situ test setup; (b) represents the chemical layer along with the cartridge heater before treatment; and (c) shows locations of the electrodes and soil sample collection.

Fig 3. Experimental setup for a scaled-up integrated in-situ remediation comprising of stimulators-assisted thermal

The lab-scale in-situ EK/EC treatment (Phase 2) was employed following the Phase 1 (stimulator-assisted thermal treatment) to evaluate technical feasibility in removal of the residues from the phase 1 treatment. For the feasibility test of the EK/EC treatment approach, the hydrocarbon residues in the tested soil were treated by the applied direct electric current (DC). To enhance electrolysis and electric current flow during the treatment, electrolyte solution comprising of sodium chloride and water equivalent to 40 wt % was added into the soil. The titanium electrodes were installed at each end of the test chamber with 29 cm distance as shown in Figure 3. The test chamber was covered with the modified lid to minimize volatilization of hydrocarbons and evaporation of water that were introduced into soil. Direct electric current (DC) was then applied with 1 V/cm of voltage gradient for 28 days.

Soil samples were collected from the locations A, B, and C in Figure 2(c) at 7, 14, 21, and 28 days after the onset of the electric current application to monitor changes in hydrocarbon concentrations. Additional soil samples were collected form the locations E and F in Figure 2(c) at 28 days in order to identify the EK/EC treatability of hydrocarbons in the soils located far from the electric current flow path which is a virtual realm where electroosmosis, electromigration, and electrochemical processes occur at. The soil sample extraction and analytical methods are the same as the small-scale test.

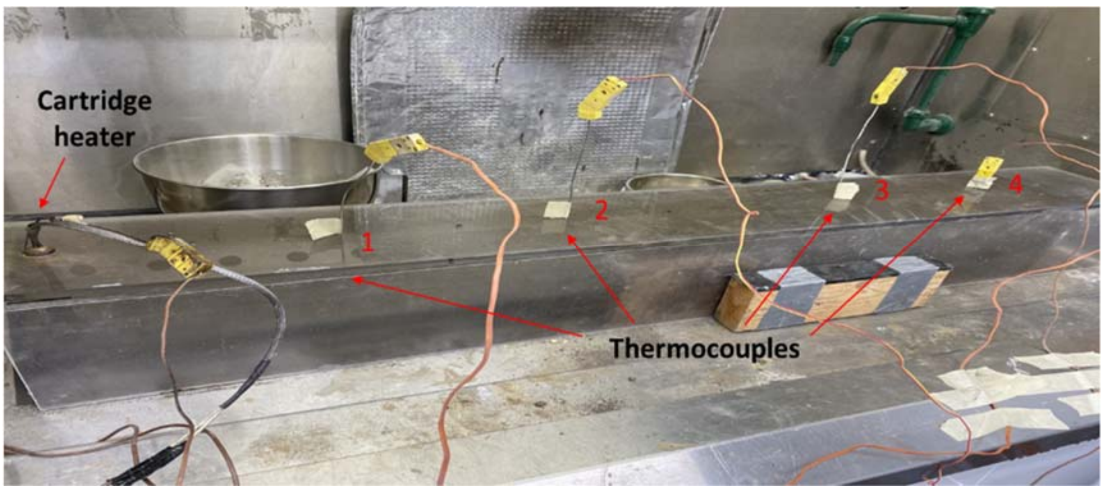

Fig 4. Experimental setup for a radius of influence (ROI) test of the activated stimulators with a 0.96 m long open top chamber.

2.3. Radius of Influence (ROI) and Depth of Influence (DOI) for the Activated Stimulators

A series of lab scale tests were performed to investigate the radius and depth of influence (ROI and DOI) for the activated stimulators in soils. For the ROI test, a 4.5 cm width X 4.5 cm height X 96 cm long open top chamber was employed with 0.5 cm height of lower soil layer, 2.5 cm height of upper soil layer, and a stimulator layer between those two soil layers. The soil used in this ROI test was a field soil which contained 10% moisture. The bulk density of the field soil filled in the chamber was approximately 1.09 g/cm3 which was quite consistent with the bulk density (1.05 g/cm3) employed in the small scale in-situ test in the first year of the subject project. 1 wt % of diesel was introduced in the soil for the lower soil layer and thoroughly mixed before it was filled in the testing chamber. A cartridge heater was placed at the one end of the long soil chamber and four thermocouples were located at 20, 40, 70, and 90 cm from the heater as shown in Figure 4. Temperature of the cartridge heater was controlled by a temperature controller (Omega CSC32). Height of the thermocouples were adjusted to monitor temperature at the stimulator layer in order to identify whether the stimulator at the locations where the thermocouples were located was successfully activated with generation of heat. The ratio of stimulator over the soil area was reduced to 75% of the stimulator ratio used in the small scale in-situ tests. The stimulator was activated by 150 °C heat from the cartridge heater and temperatures at the aforementioned locations were monitored through the thermocouples. In order to prevent potential generation of flame from the exothermic chemical reactions, nitrogen gas was flooded through the outer chamber which was made of acrylic as shown in Figure 4, while the testing was performed. After the testing, soil samples were collected from the lower soil layer at the same locations where the thermocouples were placed, extracted into organic solvent following the CCME Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil (Tier 1 Method) and analyzed by gas chromatography equipped with flame ionization detector (GC-FID) to quantify hydrocarbons in soil.

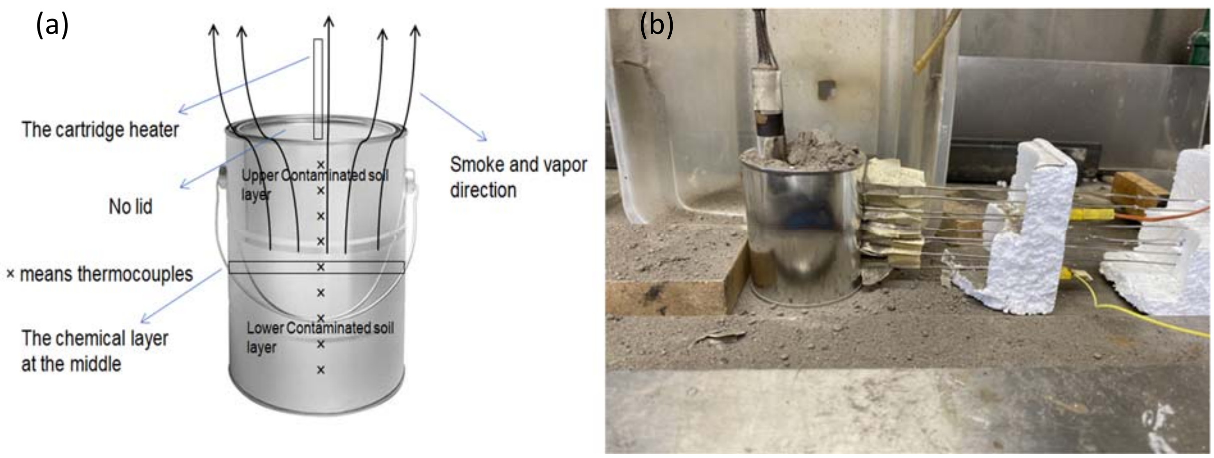

Fig 5. A schematic diagram (a) and an experimental setup (b) without a lid for the depth of influence (DOI) test.

To further investigate impact of the activated stimulator in upper and lower soil layers in the aspects of temperature change and treatability of hydrocarbons, the depth of influence (DOI) tests were performed under different conditions including soil types and confinement of testing soils. Preliminary test which was conducted with the small scale glass chamber showed that the influence of the activated stimulator reached less than 3 cm from the surface of the stimulator layer, which led us to set up the DOI test with relatively narrower temperature monitoring locations in the upper and lower soil layers. A cylindrical metal can (9.5 cm height X 8.5 cm inner diameter) was modified to perform this DOI test by producing nine holes for thermocouples (x marks in Figure 5) on the side wall and punching a hole for the cartridge heater on the lid. 4.4 cm height of upper and lower soil layers were filled in the testing chamber and approximately 0.7 cm height of the stimulator layer was located between those two soil layers as shown in Figure 5. Soils were thoroughly mixed with diesel equivalent to 1 wt % prior to being filled in the testing chamber. A cartridge heater was located at the furthest end of the chamber from the holes for thermocouples in order to minimize direct impact of the heater on temperature change while they monitored over the course of the testing. Nine thermocouples were inserted horizontally through the holes on the side wall to monitor temperature changes at different locations which were 0.5, 1, 2, and 3 cm distant from the surface of the stimulator layer and in the middle of the stimulator layer as shown in Figure 5. The ratio of stimulator over the soil area was reduced to 75% of the stimulator ratio used in the small scale in-situ tests, which was the same as the ROI testing soil received. Three DOI tests were performed under different conditions and the experimental variables are shown in

Table 1. The stimulators were activated at 150 °C and soil samples were collected within 1 cm distance from the chemical layer surface after termination of the tests. Soil sample extraction and analytical method were the same as the ROI test above.

Table 1. Experimental variables for the depth of influence (DOI) tests.

Test	Soil Type	Bulk Density	Moisture Content	Confinement
A	100% Field soil	1.2 g/cm^3	10%	No (without lid)
B	75% Field soil + 25% Sandy soil	1.2 g/cm^3	10%	No (without lid)
C	75% Field soil + 25% Sandy soil	1.2 g/cm^3	10%	Yes (with lid)

(a) (b)

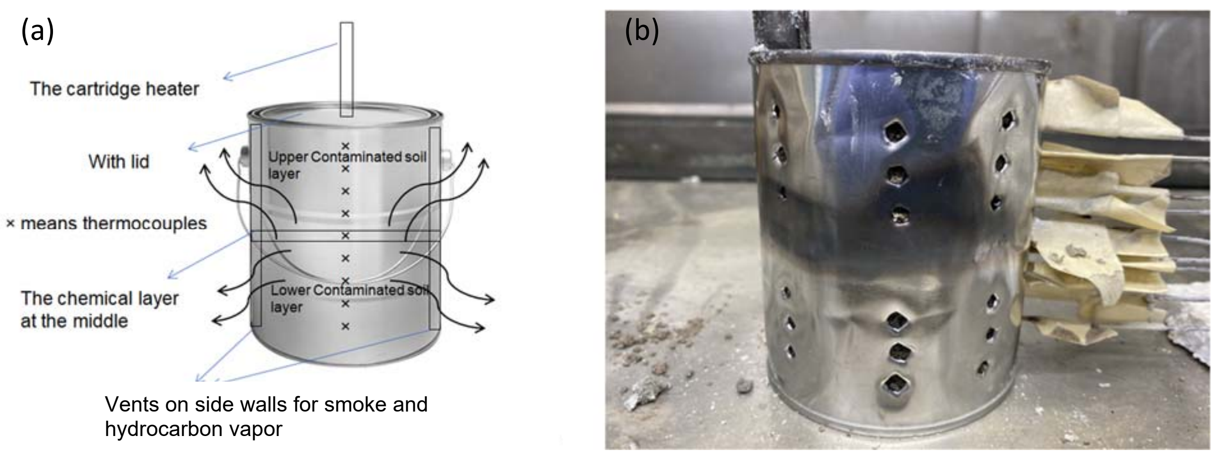

Fig 6. A schematic diagram (a) and an experimental setup (b) with a lid for the depth of influence (DOI) test.

The DOI test A was performed with 100% field soil containing 10% moisture in the cylindrical testing chamber without lid. Figure 5 shows a schematic diagram and an experimental setup. In the DOI test B, a soil mixture comprising of 75% field soil and 25% sandy soil was employed to identify the impact of soil type on transfer of heat produced from the stimulator activation. The testing chamber was open without a lid to allow the identical conditions except soil type. In the DOI test C, a soil mixture comprising of 75% field soil and 25% sandy soil which was identical with the DOI test B, was applied in the testing chamber with a lid in order to identify impact of the confinement condition in temperature change as well as hydrocarbon remediation. To allow smokes and vapors produced during activation of the stimulator, vents were produced on the side walls as shown in Figure 6. In this test, the test chamber was sealed with a lid to mimic confined condition in the real field. The other experimental conditions were identical with test B.

2.4. Impact of Multiple Stimulator Layers on Hydrocarbon Remediation

Based on the findings from the DOI tests, application of multiple stimulator layers was evaluated to identify their synergistic impact in temperature increase and hydrocarbon remediation. In this test, 3 cm height of upper and lower soil layers were placed above and below the 2 cm height of contaminated soil layer and 0.7 cm height of the stimulator layers were located between the upper/lower soil layers and the contaminated soil layer as shown in Figure 7. And only five thermocouples were employed to monitor temperature changes in the area between those two stimulator layers. The other experimental parameters and procedures were the same as the DOI test C above.

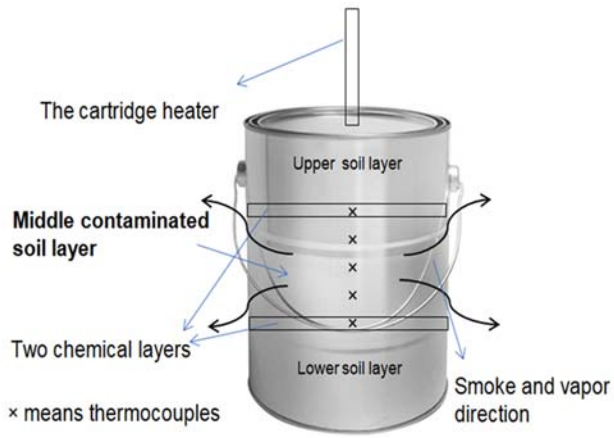

Fig 7. A schematic diagram of experimental setup with double layers of stimulator.

2.5. Modeling and Simulation of the Produced Heat Propagation in Soils

This simulation focuses on the heat distribution of produced heat propagation in different types of soil. Soils consulted was coarse, medium, and fine soil types, each having different percentage of varying clay, slit, sand and quartz contents, from which their data is presented in Tarnawasky et al. (2000). In implementing the simulation, thermal conductivity was correlated with temperature and water content.

From Tarnawasky et al. (2000),

$$\lambda = \lambda_d + (\lambda_{sat} - \lambda_d)Ke \tag{1}$$

where

$$Ke = \frac{a + bT + cS_r + dS_r^2}{1 + eT + fS_r + gS_r^2} \tag{2}$$

where thermal conductivity is λ, and subscript d indicating dry saturation, sat is full saturation. For Eq. (2), T is temperature, S_r is degree of saturation and a to g are formulated constants from same literature.

The relationship between water content and degree of saturation is the following (Barounis and Philpot 2017),

$$wc = e * \frac{S_r}{G} \tag{3}$$

where *wc* is the water content in percentage, e is void ratio, and *G* is the specific gravity. For common soils, specific gravity is normally averaging around 2.65 for soils and will be kept as a constant for this case.

Additionally, heat capacity and density were related through its water content. The dry bulk density is used to find the overall density through water content by,

$$\rho = \rho_{db} * (1 - wc) \tag{4}$$

where ρ is the density of the overall soil, and ρ_{db} is dry bulk density of the soil. Volumetric heat capacity was then found through literature (Abu-Hamdeh 2003) and presented below as,

$$C_v = \ -0.224 - 0.00561N + 0.753\rho_{db} + 5.81wc \tag{5}$$

C_v is the volumetric heat capacity, and N is the sum of sand and clay contents in percentages. Volumetric heat capacity is then converted to Specific heat capacity (C_p) by,

$$C_p = \frac{C_v}{\rho} \tag{6}$$

The initial conditions are presented in Figure 8. The simulation measures the temperature of soil after the reaction and assumes that the initial temperature of the chemical layer after the reaction is at 800 °C and that the surroundings is kept constantly at 25 °C. Water content and soil types are varied to identify their effect on changes in temperature.

Temperature was then determined by solving the partial differential equation for transient conduction model as shown in Eq. (4) for heat transfer in MATLAB R2019.

$$\rho C_p \frac{\partial \mathrm{T}}{\partial \mathrm{t}} - \nabla \cdot (k\nabla T) = f \tag{7}$$

where ρ is the density, C_p is the specific heat, k is the thermal conductivity, and f is the heat generated inside the body. In this simulation it was assumed that *f* is zero as soil does not generate heat by themselves and heat is transferred from the activated stimulator.

To model the actual experiment, temperatures at 0.5cm, 1cm, 2cm and 3 cm from the chemical layer were calculated. The simulated results are described in section 3.5.

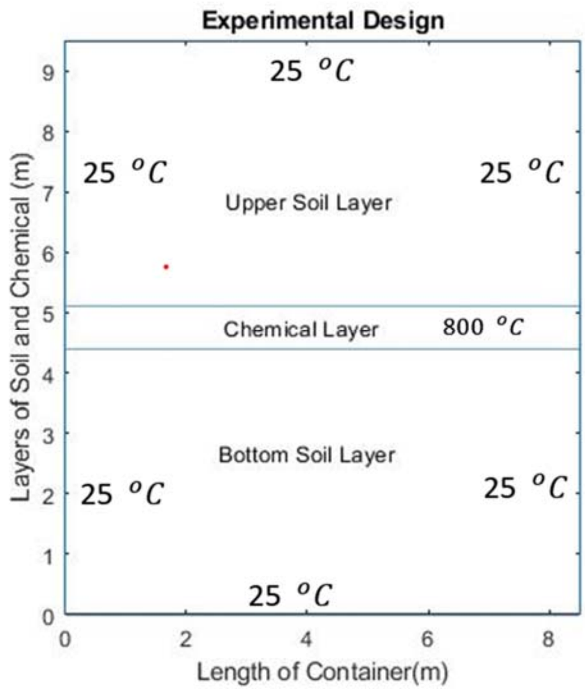

Fig 8. A schematic diagram of experimental setup for simulation.

3. RESULTS

3.1. Impact of Coating Material Dose in Stimulator Composition for Various Soil Textures

The previous lab scale tests clearly showed that overdosed coating material would impede exothermic chain reactions of the introduced stimulators in soils containing higher clay/silt contents under the same moisture condition. In addition, few prior tests showed spontaneous activation of stimulators, with no heat supply, in soils containing low clay/silt content (i.e. sandy soil), indicating that the stimulator reactions are influenced by different soil texture under the same moisture condition as soils containing higher clay/silt contents have higher water holding capacity. Hence, impact of the coating material dose in the stimulator composition was investigated under different soil textures to understand their correlation, thereby developing the best practice strategy for the different soil textures.

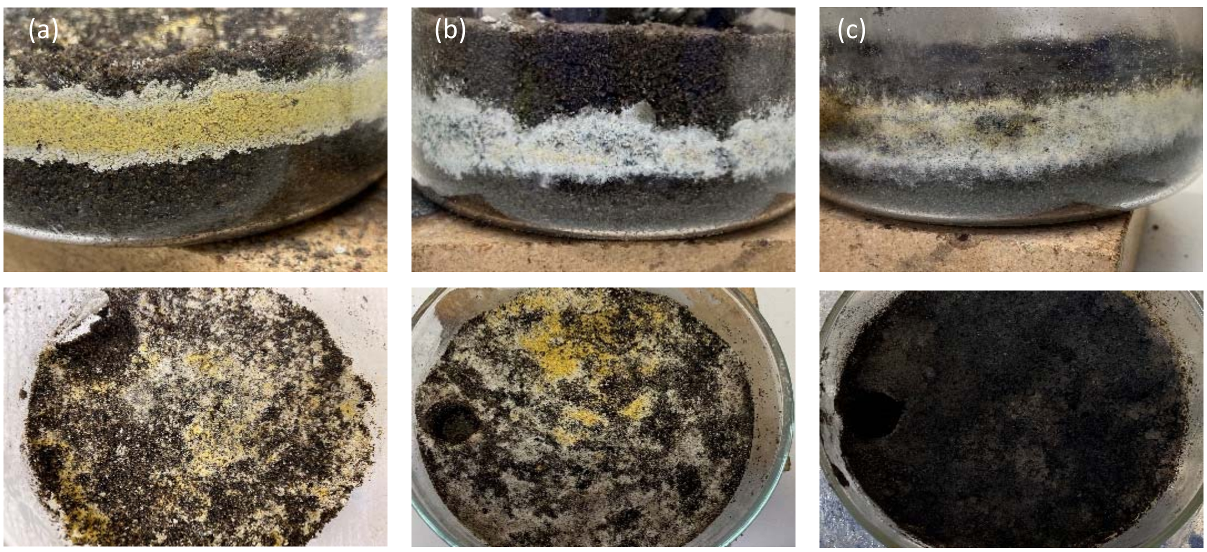

Fig 9. Comparison of testing soils (soil C) that received various doses of coating material: 18 g (a), 12 g (b), and 9 g (c) after heat supply.

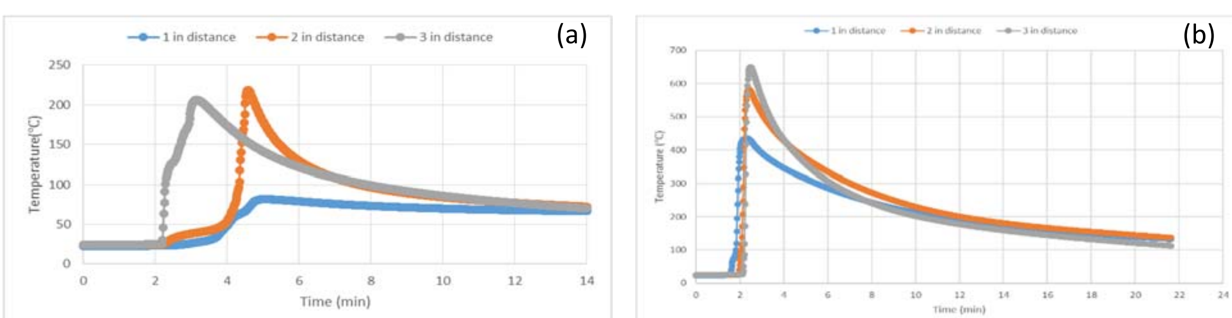

Fig 10. Comparison of temperature increase by activation of stimulators that received 12 g (a) and 9 g (b) of coating material in soil C.

Figure 9 shows observations of testing soils (soil C) that received various doses of coating material after treatment with heating temperature at 150 °C. When the stimulator was composed of 18 g of coating material, the chemical layer was partially activated remaining mostly yellow color after treatment although its boundaries which directly contacted with moist soil turned to white (Figure 2(a)). This result clearly shows that water in soil promotes the stimulator activation. Limited amount of or no smoke was generated over the treatment and temperature change was not noticeable. It appears that the overdosed coating material impeded activation of the chemical N which acts as a trigger for the whole exothermic chemical chain reactions. When reduced the amount of coating material to 12 g, most of the chemical layer turned to white with only little amount of inactivated yellow stimulator at the end of treatment (Figure 9(b)), resulting in temperature increase up to 215 °C (Figure 10(a)). When applied with 9 g of coating material, the chemical layer was completely activated with no inactivated part (Figure 9(c)), consequently resulting in rapid temperature increase up to 651 °C (Figure 10(b)). Application of 9 g of coating material generated relatively higher additional heat temperature compared to temperature produced by stimulator containing 12 g coating material, indicating that 9 g of coating material is more appropriate to achieve better remediation performance in soil C.

Table 2. Experimental variables and test results for impact of coating material dose on stimulator activation in different soil texture.

Coating Material Dose	Soil A S: 0% F: 100%	Soil B S: 25% F: 75%	Soil C S: 50% F: 50%	Soil D S: 75% F: 25%	Soil E S: 100% F: 0%
6g	Full activation (Max T: 668 °C)				
9g	**Full activation (Max T: 741 °C)**	**(I) Full activation (Max T: 554 °C)**	**(II) Full activation (Max T: 651 °C)**	**(III) Full activation (Max T: 546 °C)**	
12g		Most turned to white (Max T: 212 °C)	~75% turned to white (Max T: 215 °C)	No activation	
16g			No activation	No activation	Spontaneous activation without heat
18g	Most turned to white (Max T: 137 °C)		No activation		Full activation (Max T: 280-670 °C) *tested in Year 1

* S: Sandy soil, F: Field soil

Table 2 shows all test results along with coating material doses applied in the four different soil types. The test results obviously indicate that application of 9 g coating material is beneficial for the tested soil conditions in the aspects of stimulator activation as well as operating cost. For all four soil textures, stimulators that received 9 g of coating material produced relatively higher temperature when activated, compared to applications of other doses. Temperature profiles of the tested soils that received stimulators containing 9 g coating material are shown in Figure 11. In all four soil textures, temperatures rapidly increased by the released heat from the exothermic chemical reactions, followed by gradual decline. All the maximum temperatures reached over 500 °C which is high enough to decompose most recalcitrant soil contaminants, indicating stimulators with 9 g coating material is capable of producing high heat temperature for the remediation process regardless of soil texture tested in these experiments. However, the relationship between the produced maximum temperatures and the tested soil textures cannot be determined from these experiments since any obvious trend was not observed from the test results.

It was initially postulated that the least amount of coating material for protecting spontaneous activation of stimulators and being able to be activated by heat supply would be reduced with the increased amount of field soil. However, when applied 12 g of coating material, stimulator was not activated in soil D with less field soil but partially activated in soil B and C, which was inconsistent with the initial postulation. No significant influence of coating material dose in a specific range, from 9 to 12 g, was observed on the stimulator activation in tested soils containing field soil over 25% fraction, indicating that there may exist a critical soil composition to be considered for determination of the coating material dose, especially between soil D and E. Much more coating material is needed to protect stimulators from spontaneous activation without heat supply when the fraction of sandy soil exceeds the critical composition.

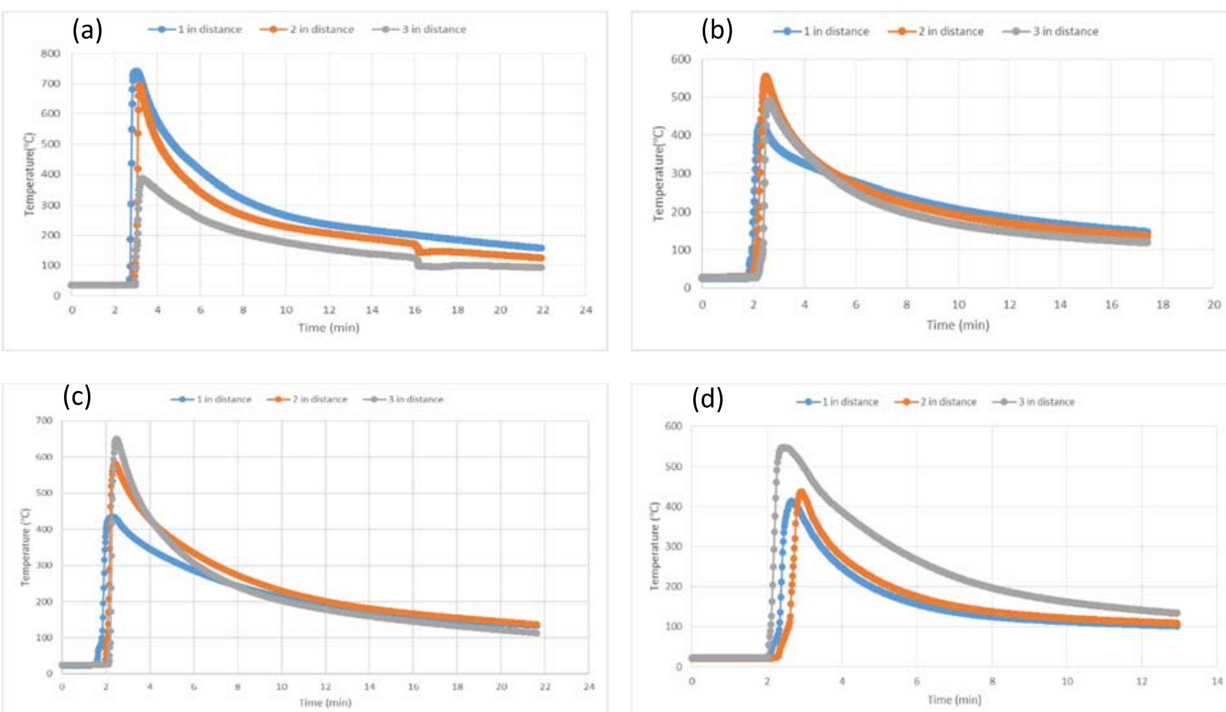

Fig 11. Comparison of temperature increase by activation of stimulators that received 9 g of coating material in soil A (a), soil B (b), soil C (c), and soil D (d).

As expected, hydrocarbon removal through the stimulator activation was also influenced by the soil texture. The relatively higher hydrocarbon removal rates were achieved in soil D with less fraction of field soil at both the bottom surface of the stimulator and the overall bottom soil area (Figure 12). Also, the analytical results show that the hydrocarbon removal rates decreased with increased fraction of field soil. The results of soil A were not included for the comparison due to the lack of corresponding bottom samples. These results imply that the hydrocarbon removal may be much sensitive to soil texture rather than the temperature variation from the stimulator activation when the produced temperature is in a range which is capable of decomposing target contaminants. Abu-Hamdeh and Reeder (2000) found that high ratio of field soil can reduce the soil thermal conductivity. When provided the same amount of heat, temperature in soils with higher clay content can be relatively lower than that in soils with lower clay content within a certain time period.

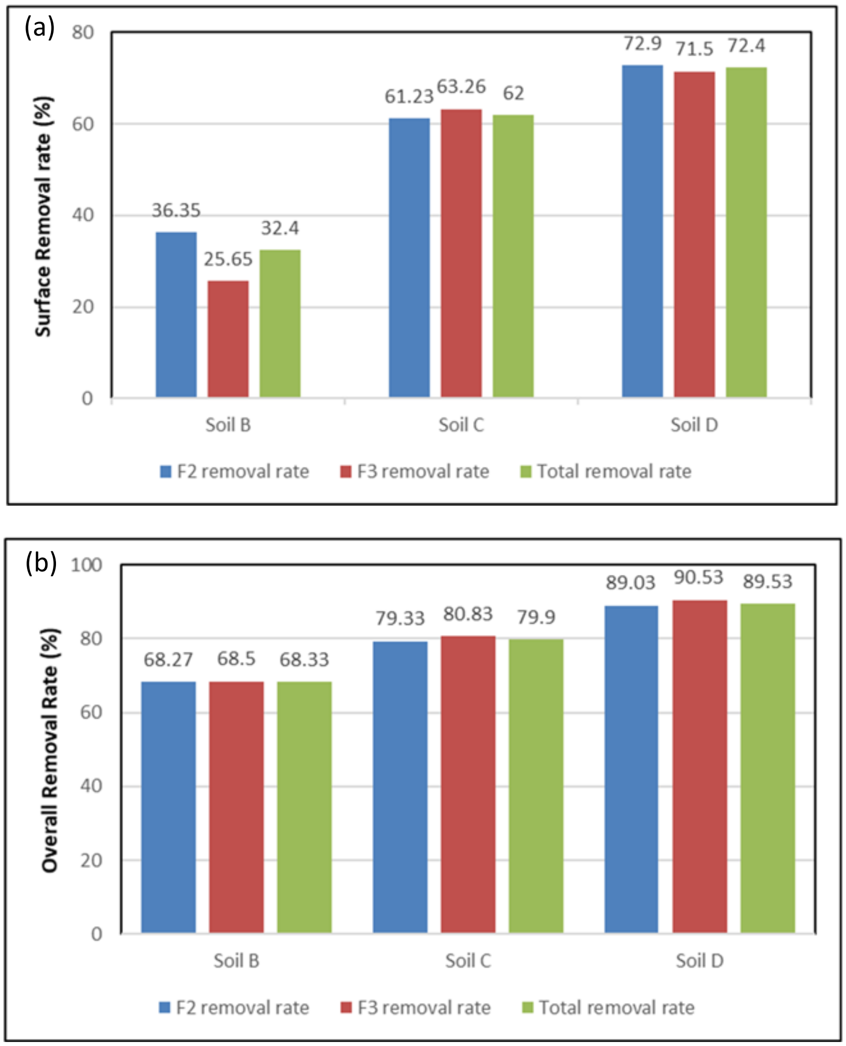

Fig 12. Removal rates of hydrocarbons (F2 and F3) at the bottom surface of the chemical layer (a) and the overall bottom soil before and after treatment using the developed stimulators containing 9 g coating material in soil B, C, and D.

In soil B with relatively higher field soil fraction, the hydrocarbon removal rates at the overall bottom soil area were much higher than ones at the bottom surface of the stimulator, with much higher hydrocarbon concentration at the surface after treatment (Figure 13). One probable reason is that the vaporized hydrocarbons from the deeper soil area were accumulated near the bottom surface of the chemical layer as finer particle size soils have less intrinsic permeability by forming narrow pore throat where vaporized hydrocarbons can pass through.

According to Ma et al. (2014), when the spilled diesel oil infiltrates through the porous media the heavy components are trapped onto fine media by capillary pressure and adsorption forces, holding them closer to the surface of the finer particle size materials. On the other hand, the light components infiltrate deeper. In case of the larger particle size materials, however, all the hydrocarbons infiltrate deeper. Light hydrocarbons can be volatilized much easily through porous media with larger pore sizes compared to media with relatively smaller pore sizes. Experiments by Ma et al. (2014) imply that the volatilization rates of diesel can be enhanced with decreased soil particle size when diesel is spilled on the compacted soil surface, which is inconsistent with our results. This inconsistency is presumably attributed to the relatively higher thermal conductivity of sandy soil compared to clayey or silty soil as mentioned above. The temperature variations were monitored at the middle of the chemical layer. Therefore, actual temperatures at the bottom soil layer might show different trend from the temperature profiles in Figure 11 due to the different intrinsic permeability and thermal conductivity that are resulted from different soil texture.

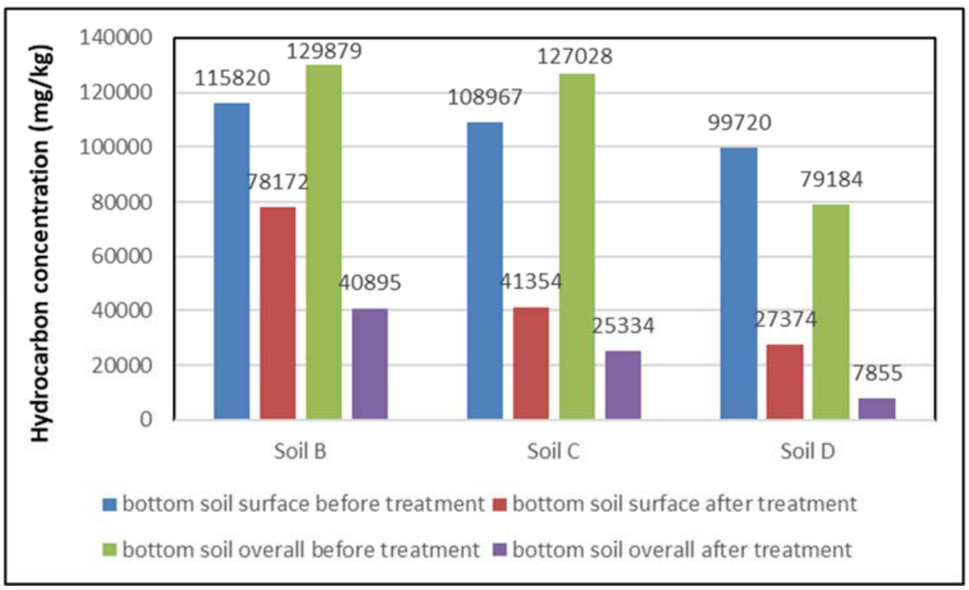

Fig 13. Total hydrocarbon concentrations before and after treatment using the developed stimulators containing 9 g coating material in soil B, C, and D.

3.2. Development and Feasibility Test of a Lab-Scale Integrated In-situ Remediation System

The lab scale integrated in-situ remediation system comprising the stimulator assisted thermal treatment (Phase 1) and the subsequent electrokinetic/electrochemical (EK/EC) treatment (Phase 2) was evaluated in the aspect of remediation efficiency in this task. It was observed that temperatures rapidly increased with the onset of the heat supply (150 °C) and reached the maximum temperatures within a minute. As shown in Figure 14, the maximum temperature was observed at the location where was the closest from the heat source then the order followed the distance from the heater. This result indicates that the exothermic chain reactions of the stimulators were ideally propagated from the proximity to far location from the heat source. In addition, the maximum temperatures at different locations were not significantly different, showing a range of 616 – 664 °C. From these results, it is confirmed that the ROI of the activated stimulators is greater than 14.8 in. Further experiment is required to determine the exact ROI of the stimulator.

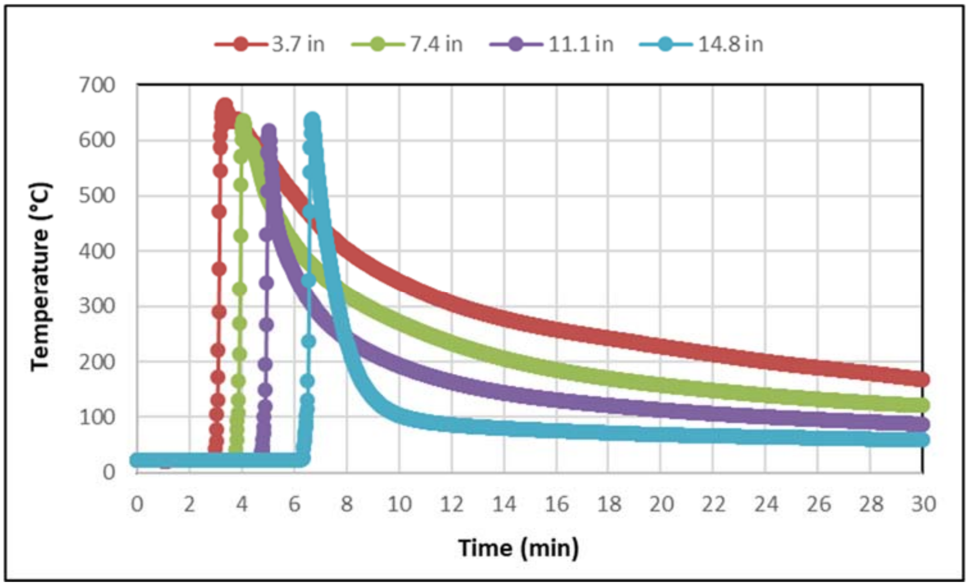

Fig 14. Temperature profiles at different locations in the integrated in-situ remediation during the Phase 1 treatment (stimulator-assisted thermal treatment).

Analytical results showed that the total hydrocarbon removal rates ranged from 57 % to 71 % after the phase 1 treatment (stimulator-assisted thermal treatment). These results were slightly lower than the corresponding small-scale test result (72 %) from the same soil texture (soil D), which is shown in Figure 12(a). After applying EK/EC treatment for a week, the total hydrocarbon removal rates increased to 73 ~ 77 %, reducing approximately 6 ~ 16 % of hydrocarbons. As shown in Figure 15, total hydrocarbon concentration continuously declined at location A over the treatment period. However, the concentration decline stopped at 3rd week after EK/EC treatment and it was rebounded at locations B and C. The concentration rebound may be associated with diffusion of hydrocarbons from soils that have not been properly remediated through the EK/EC treatment. Concentrations at locations E and F were much higher than the monitored locations A, B, and C at 28 days, indicating that these areas have not been treated by the phase 2 treatment. The uninfluenced realm is presumably attributed to the particular behavior of the applied electric current that tends to show the straight path between electrodes. It is probable that higher concentration of hydrocarbons at the uninfluenced areas diffuses toward the treated areas with lower concentration in order to reach equilibrium due to the concentration gradient between those areas. EK/EC treatment was stopped at 28 days. Although considerable amount of hydrocarbons were remediated through the integrated in-situ remediation method resulting in total hydrocarbon removal rates of 72 - 86 %, the concentrations of residues were still higher than the regulation. However, it is expected that continual application of electric current under proper electrolyte condition will further reduce the residual hydrocarbons over time, resulting in concentrations lower than the regulation. To prove this postulation additional test with longer EK/EC treatment is demanded.

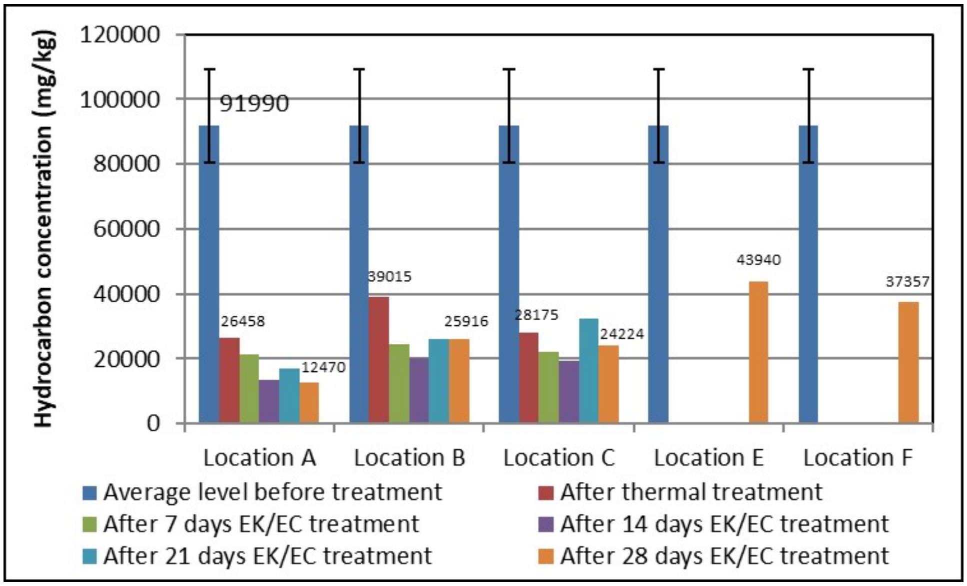

Fig 15. Hydrocarbon (F2 and F3) concentrations before & after stimulator-assisted thermal treatment (Phase 1) and 7, 14, 21, 28 days after the onset of EK/EC treatment (Phase 2).

3.3. Radius of Influence (ROI) and Depth of Influence (DOI) for the Activated Stimulators

A series of lab scale tests were performed to investigate the radius and depth of influence (ROI and DOI) for the activated stimulators in soils. The ROI test was conducted with a long open top chamber (4.5 cm width X 4.5 cm height X 96 cm) and a field soil which contained 10% moisture as described in section 2.3. As shown in Table 1 (section 2.3), three DOI tests were performed under different conditions and the experimental variables. The DOI test A was performed with 100% field soil containing 10% moisture in the cylindrical testing chamber without lid, while the DOI test B was conducted with a soil mixture comprising of 75% field soil and 25% sandy soil without a lid. In the DOI test C, a soil mixture comprising of 75% field soil and 25% sandy soil which was identical with the DOI test B, was applied in the testing chamber with a lid in order to identify impact of the confinement condition in temperature change as well as hydrocarbon remediation.

In the ROI test, the introduced stimulators were immediately activated with the onset of heat supply, increasing temperatures significantly at the stimulator layer as shown in Figure 16. The maximum temperatures increased by activation of the stimulators reached around 600 °C at all the monitored locations except the location of 40 cm distance (point 2) from the heater. The maximum temperature at the point 2 was approximately 255 °C which was much lower than the other maximum temperatures. This inconsistent temperature increase might be associated with unevenly distributed stimulators at the point 2 location. The temperature profiles show apparently that the stimulators were sequentially activated from the heater toward the other end of the testing chamber. It is evident that the ROI of the activated stimulator can be expanded as wide as the stimulator exists. However, analytical results indicate that only 33.3% of hydrocarbons on average was effectively remediated through the generated heat. This low removal rates may be attributed to the reduced stimulator dose (75%) compared to the amount applied in the small scale in-situ tests.

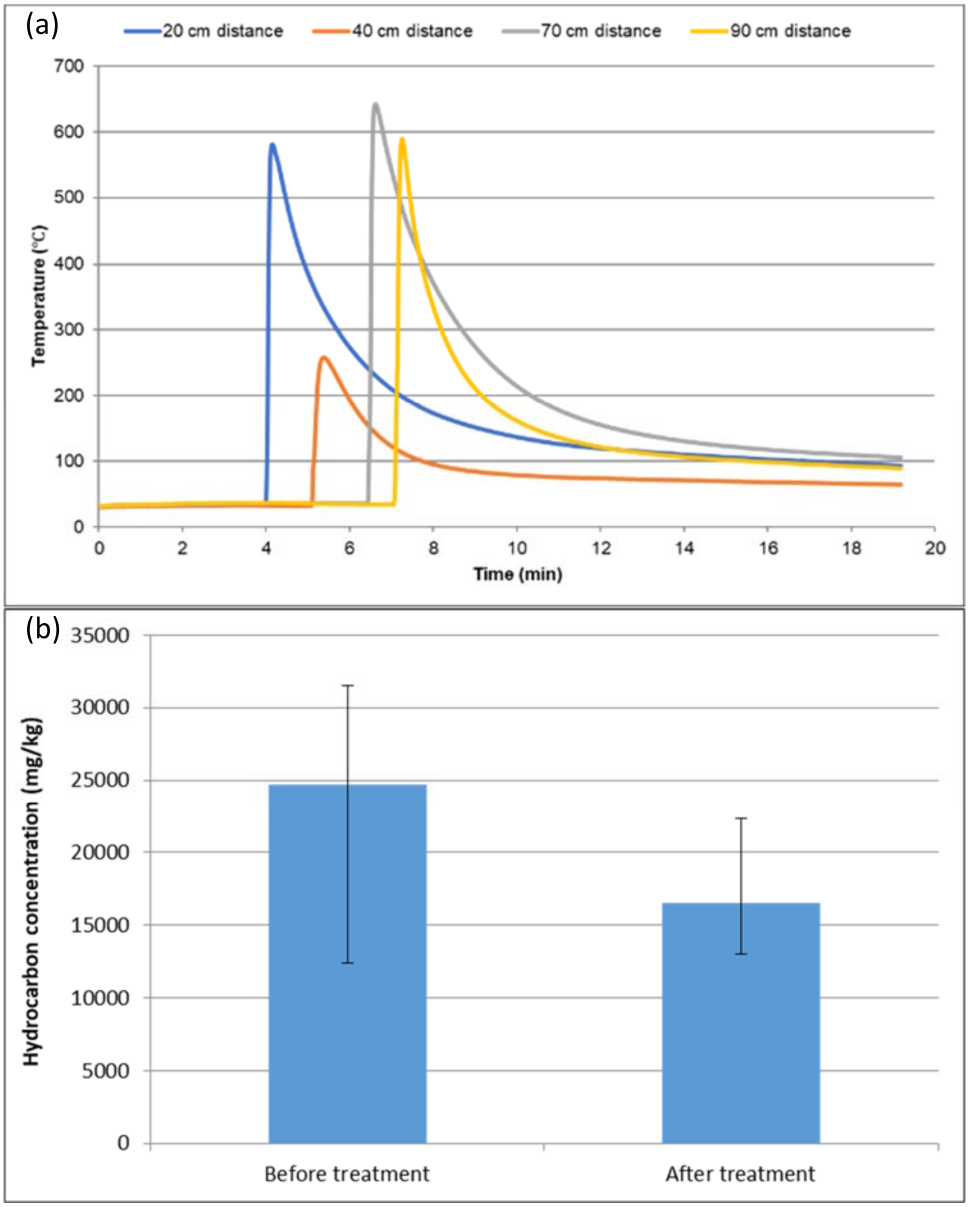

Fig 16. Temperature profiles at 20, 40, 70, and 90 cm distance from the heat source (a) and hydrocarbon concentrations before and after activation of the stimulators (b).

The DOI test A was performed with 100% field soil containing 10% moisture in the cylindrical testing chamber without lid. Figure 5 shows a schematic diagram and an experimental setup. While activation of the stimulator significantly increased temperature up to 824 °C at the stimulator layer, the generated high temperature heat did not extend beyond 1 cm distance from surface the stimulator layer as shown in Figure 17 (a), indicating that the DOI of the activated stimulator was approximately 1 cm above and below the layer. At locations of 0.5 cm distance from the chemical layer surface, the maximum temperatures were 292 and 255 °C, presenting slightly higher temperature at the lower soil layer. However, it is not obvious that the impact of the generated heat reached out more effectively in the lower layer as the maximum temperature at locations of 1 cm distance was slightly higher in the upper soil layer than the lower one. It might be associated with the heterogeneity of soils which may provide locally variable bulk density and preferential pathway that influence heat transfer rates through the soil pores. Overall, analytical results show that hydrocarbons in soil were not effectively degraded through the activation of stimulators (Figure 17(b)). Increase of the hydrocarbon concentrations might be attributed to operational error in sample extraction or analytical variations in the GC-FID system. Among the sampling locations, soil sample from the point 4 (0.5 cm distant above the stimulator layer) showed relatively lower concentration.

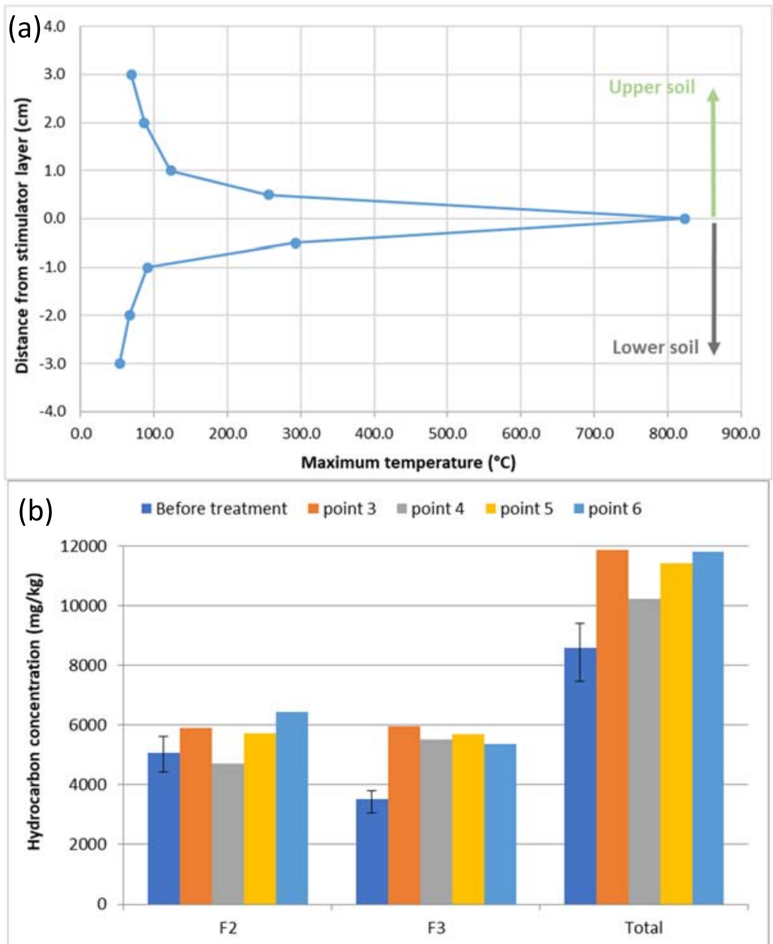

Fig 17. Maximum temperatures at different vertical distances from surface of the stimulator layer (a) and hydrocarbon concentrations before and after activation of the stimulator (b) in 100% field soil under unconfined condition.

In the DOI test B, a soil mixture comprising of 75% field soil and 25% sandy soil was employed to identify the impact of soil type on transfer of heat produced from the stimulator activation. The testing chamber was open without a lid to allow the identical conditions except soil type. The temperature profile of maximum temperatures at the different vertical locations was quite identical with the one from the testing with 100% field soil above, except the maximum temperature at 0.5 cm below lower surface of the stimulator layer which showed only 117 °C (Figure 18(a)). This relatively lower maximum temperature in the lower soil layer might be associated with inconsistent compaction or soil heterogeneity as mentioned above. The temperature profile indicates that 25% change in fraction of soil type may be insufficient to affect heat transfer rates in soil. Analytical results indicate that F2 hydrocarbons can be effectively remediated at the region within 1 cm distance above the activated stimulator, presenting 50-63% removal rates (point 3 and 4 in Figure 18(b)). However, changes in F3 hydrocarbon concentrations were insignificant, indicating that the activation of the stimulator did not effectively remediate the F3 hydrocarbons even at the close region. Relatively lower hydrocarbon concentration at the point 4 (0.5 cm distant above the stimulator layer) is consistent with the testing with 100% field soil. The total hydrocarbon removal rate at the point 4 was 42%.

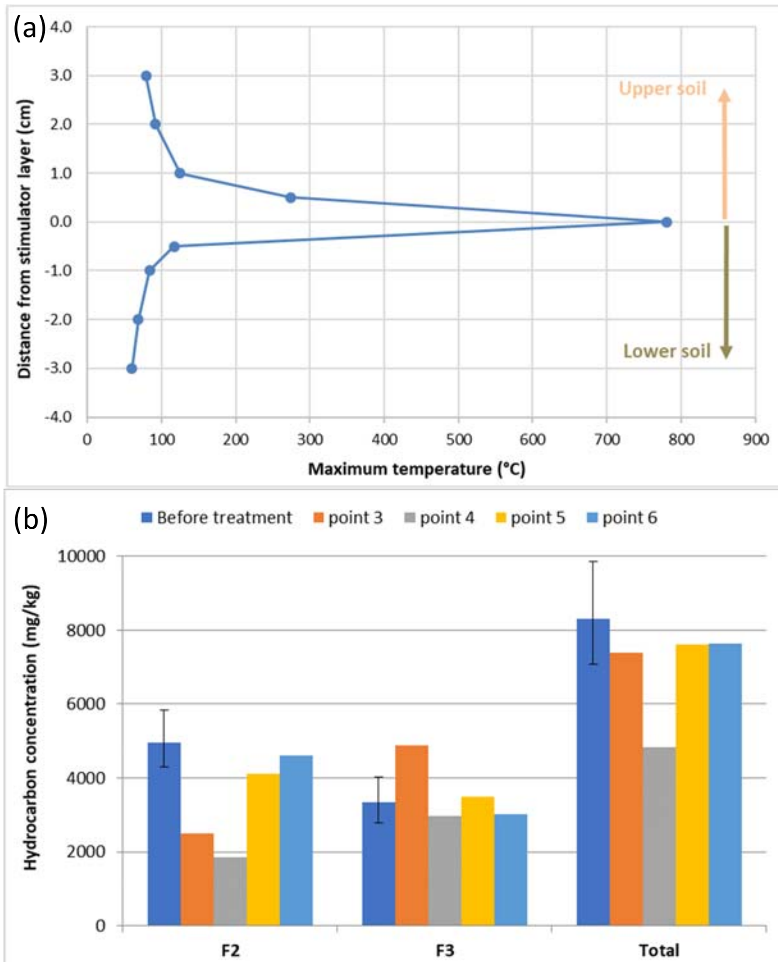

Fig 18. Maximum temperatures at different vertical distances from surface of the stimulator layer (a) and hydrocarbon concentrations before and after activation of the stimulator (b) in soil mixture of 75% field soil and 25% sandy soil under unconfined condition.

In the DOI test C, a soil mixture comprising of 75% field soil and 25% sandy soil which was identical with the DOI test B, was applied in the testing chamber with a lid in order to identify impact of the confinement condition in temperature change as well as hydrocarbon remediation. As shown in Figure 19(a), the maximum temperature of the activated stimulator (609 °C) was relatively lower than temperatures from the prior two DOI tests (824 and 780 °C). This might be because of oxygen availability from the atmosphere as the prior two DOI tests setup allowed much greater surface area of the upper soil layer to be exposed to the atmosphere while soils in the test C were exposed to atmosphere through the venting holes only. The importance of available oxygen content from the atmosphere in activation of stimulators as well as temperature increase was well proved through a series of the small scale in-situ tests.

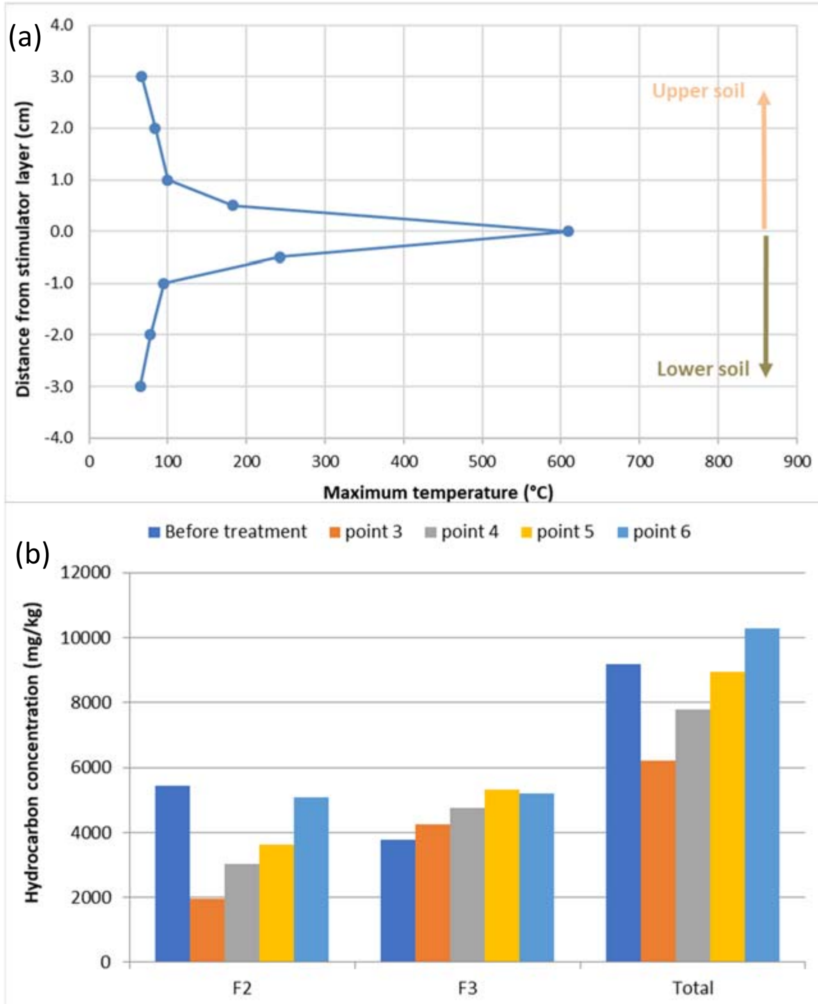

Fig 19. Maximum temperatures at different vertical distances from surface of the stimulator layer (a) and hydrocarbon concentrations before and after activation of the stimulator (b) in soil mixture of 75% field soil and 25% sandy soil under confined condition.

The temperature profile of maximum temperatures at the different vertical locations indicates that confinement of the soil layer may not significantly influence in transfer of heat produced from the activated stimulators in soils. Analytical results present effective reduction of F2 hydrocarbons at close distance (within 1 cm) from the activated stimulators under confined condition, resulting in 33-64% removal rates at points 3, 4 (1 and 0.5 cm distant above the stimulator layer), and 5 (0.5 cm distant below the stimulator layer), however F3 hydrocarbons were not remediated through the stimulator activation as shown in Figure 19(b). This trend is consistent with the prior DOI test B. The maximum temperatures observed were 243, 183, and 100 °C for points 5, 4, and 3 respectively, but the hydrocarbon removal rates were reverse order, i.e., total hydrocarbon concentrations were 8,955, 7,786, and 6,198 mg/kg for points 5, 4, and 3 respectively, which is inconsistent with our hypothesis that higher hydrocarbon reduction was expected at locations with higher temperatures. This result indicates that the hydrocarbon removal may be attributed to other factors out of high temperature. To prove influence of other factors, further investigation needs to be performed.

Through the series of DOI tests above it can be concluded that the DOI of the activated stimulators is approximately 1 cm above and below the surface of the activated stimulator layer and that hydrocarbons above the stimulator can be more effectively remediated compared to those below the stimulator.

3.4. Impact of Multiple Stimulator Layers on Hydrocarbon Remediation

Based on the findings from the DOI tests, application of multiple stimulator layers was evaluated to identify their synergistic impact in temperature increase and hydrocarbon remediation. The experimental parameters and procedures were the same as the DOI test C, except application of two stimulator layers as described in section 2.4.

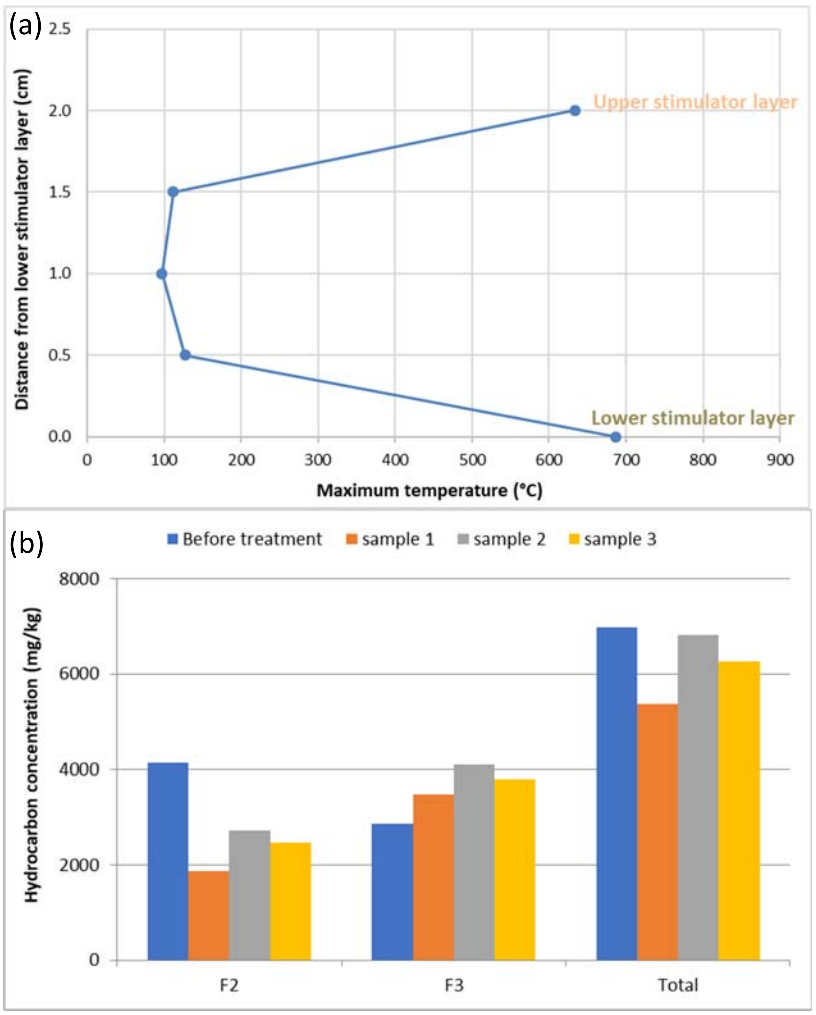

Fig 20. Maximum temperatures at different vertical distances from surface of the lower stimulator layer (a) and hydrocarbon concentrations before and after activation of the stimulator (b) in soil mixture of 75% field soil and 25% sandy soil under confined condition.

The temperature profile of the maximum temperatures at different vertical locations between the applied two stimulator layers, shows relatively lower maximum temperatures (112 and 127 °C) at 5 cm distant locations from the stimulator layer surface than the maximum temperatures from the DOI test B setup with one stimulator layer, indicating adverse influence rather than synergistic impact by applying a multitude of stimulator layers (Figure 20(a)). Analytical results of hydrocarbons in soils also support this conclusion, presenting no or insignificant improvement in reduction of hydrocarbons in soils at the region between those multiple stimulator layers. This result is inconsistent with our hypothesis that a multitude of stimulator layers would increase temperature and further reduce hydrocarbons in soils between them.

3.5. Modeling and Simulation of the Produced Heat Propagation in Soils

Soil modeling and simulations were developed to identify influence of soil type in propagation of heat generated from the activated stimulators. All parameters required for simulation were defined and their representative values for three different soil types are shown in Table 3. The representative values were first presented by Tarnawasky et al. (2000).

Table 3. Characteristics of soils for simulation

Soil type	Mass fraction of Clay, m_{clay}	Mass faction of Slit, m_{slit}	Mass fraction of Sand, m_{sand}	Dry Bulk Density, ρ_{db} (kg/m^3)
Coarse	0.093	0.113	0.718	1140
Medium	0.439	0.682	0.162	1270
Fine	0.468	0.205	0.120	1420

The characteristics of thermal conductivity and specific heat capacity are shown in Figure 21.

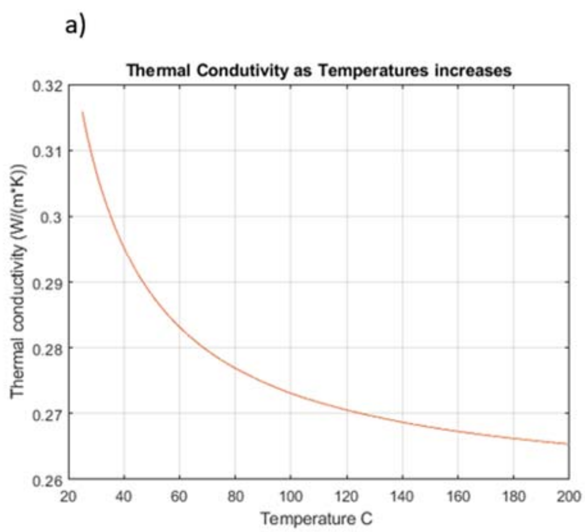

Fig 21. Calculated data values for Coarse Soil. a) Thermal Conductivity changes at 10% water content, b) Specific heat capacity changes with varying water contents

Figure 22 shows the simulation result of fine, medium, and coarse soils, with their respective temperature change and max temperature. As the soil goes from coarse to fine, the maximum temperatures increase, as does the time it takes for it to increase.

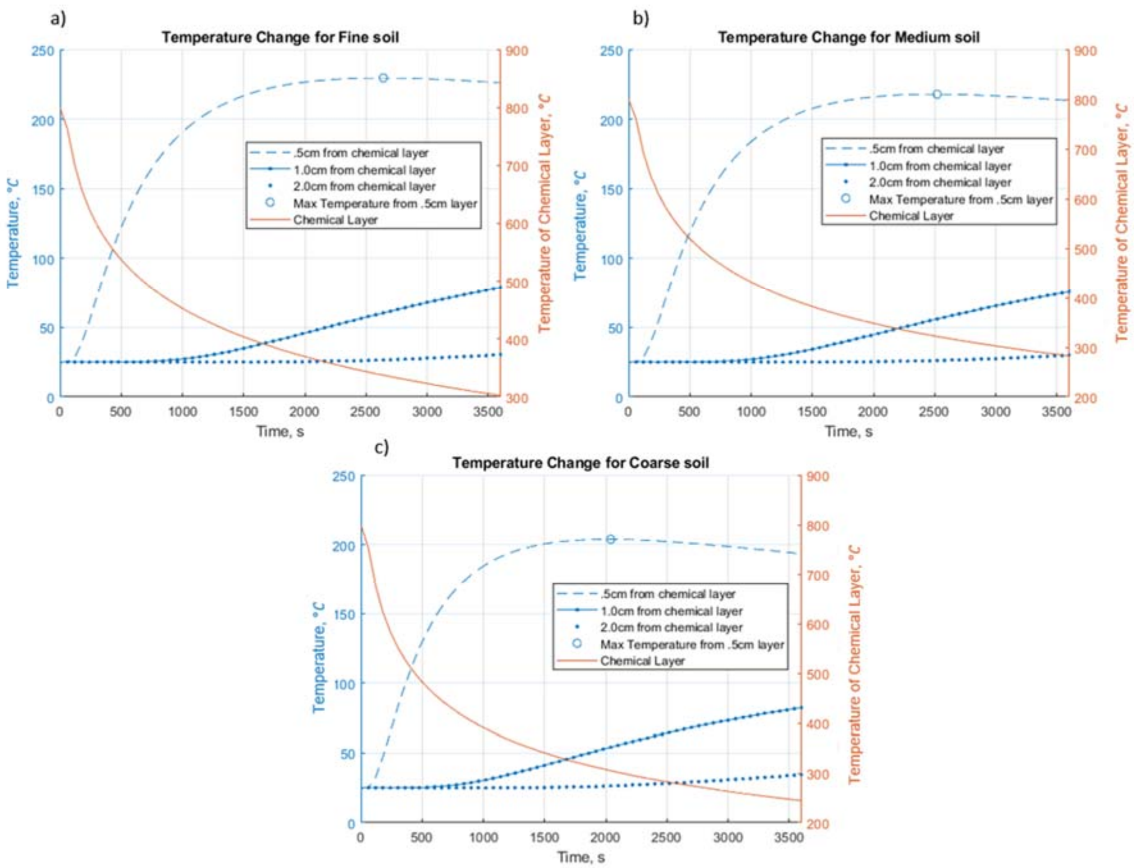

Fig 22. Temperature distribution of heat propagation at 10% water content (a) fine soil (b) medium soil (c) coarse soil

Fine soil showed the greatest change in temperature at 0.50 cm above the chemical layer. The remainder of the layers showed similar results with negligible differences. A series of simulations also correlates closely with the experimental data gathered in section 3.3. Figure 22 shows a similar result with respect to maximum average temperature at each vertical layer of the soil over a longer period of 20,000 seconds.

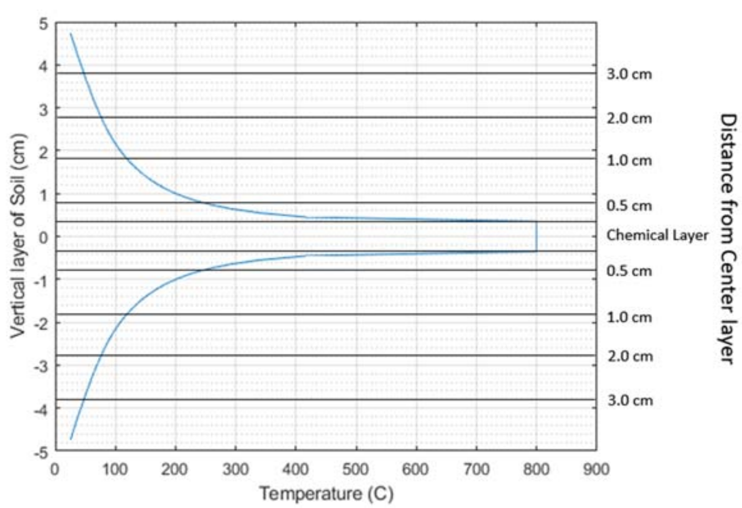

Fig 23. Maximum temperature at vertical layers from simulation

The simulation results showed an acceptable agreement with the actual experiment results. The result suggests that regardless of the soil type, vertical heat transfer rate through soil medium sharply drops along with the displacement. In this regard, applying an appropriate heat conductor to increase the heat transfer rate can be considered.

For impact of varying water content, coarse soil alone was used for simulations. Water content was varied with 5%, 10%, 20% and 30% and temperatures of the soil at 0.5 cm from the chemical layer were simulated.

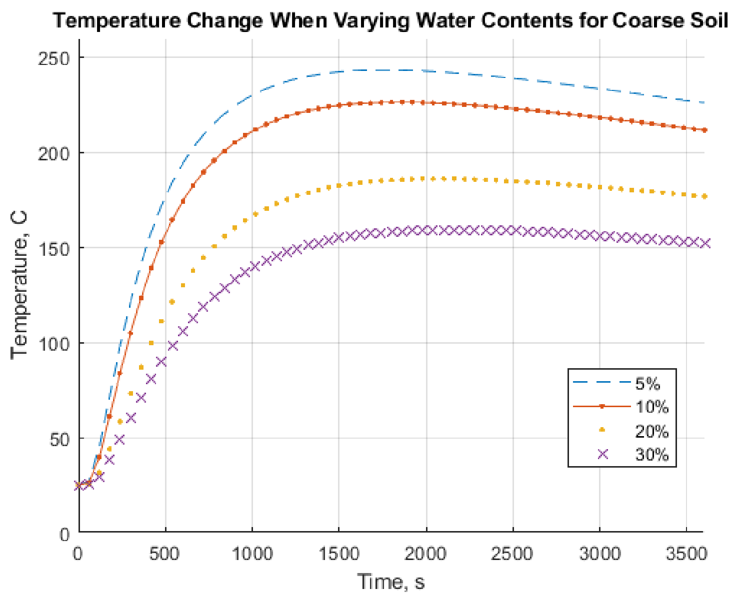

Fig 24. Relation of water content with respect to temperature change

As the water content increases, the maximum temperature of the soil decreases, and the time taken to reach the maximum increases. Therefore, it can be concluded that the water content does have a high influence on the heat transfer of this experiment as the required amount of water-resistance material depends on the water content within subjected soil.

4. CONCLUSIONS

Through this project, the stimulator developed in the first year (2018-2019) of the subject project was further investigated for in-situ application to remediate hydrocarbon impacted soils. To optimize composition of stimulator for their best performance under different soil types, impact of varying coating material doses was investigated for different soil textures. Based on the determined composition of stimulator, radius of influence (ROI) and depth of influence (DOI) for the activated stimulators were evaluated in order for designing optimal application of the stimulators. Moreover, an integrated lab-scale in-situ remediation system was developed through combining stimulator assisted thermal treatment (Phase 1) with EK/EC treatment (Phase 2) and its feasibility test was performed.

Finding optimal dose of coating material is paramount for appropriate activation of stimulators thereby generating high temperature heat and inducing other chemical reactions for hydrocarbon remediation. In a specific range of the tested coating material doses, their influence was limited in the aspects of protecting stimulators from spontaneous activation under moisturized soil conditions as well as being activated appropriately with low temperature heat supply. Specifically, impact of coating material dose was negligible in activating stimulators in the tested soils containing over 25% of field soil, indicating that there may exist a critical soil composition to be considered for determination of the coating material dose. The test results imply that soils with greater fraction of sandy soil than the critical composition may require greater dose of coating material to avoid any possibility of spontaneous stimulator activation.

Experiments in both the integrated in-situ remediation test chamber and a one-dimensional long open chamber confirmed that the radius of influence (ROI) of activated stimulators can be expanded as wide as stimulator exists. On the other hand, the depth of influence (DOI) test results presented that heat penetration did not effectively reach distances greater than 1 cm vertically from the location where heat was generated through exothermic chemical reactions. A separate test with multiple stimulator layers also confirmed that vertical heat propagation through soil was very limited with no synergistic effect from a multitude of stimulator layers in the aspects of temperature increase and hydrocarbon removal. Simulation results by the developed model was consistent with the experimental results, presenting limited vertical heat propagation in soil. Simulation results also showed that influence of soil type and water content is not significant in heat propagation.

Feasibility of the Phase 1 treatment (stimulator-assisted thermal treatment) in the integrated in-situ remediation system was well proven by ideally propagated exothermic chemical chain reactions and quite uniformly distributed high temperature heat from the chemical reactions in the tested chamber. Analytical results presented that the Phase 1 treatment reduced hydrocarbons up to 71% with decreased amount of stimulators compared to the small scale in-situ tests. The subsequent Phase 2 treatment also showed considerable reduction of hydrocarbons (approx. 15%) for 4 weeks, however concentration decline varied at different locations in the tested soil and the concentration reduction stopped or rebounded at later time of the testing period. Although varying hydrocarbon reduction was observed in the test, it is expected that continual application of electric current under proper electrolyte condition will further reduce the residual hydrocarbons over time. To prove this postulation additional test with longer EK/EC treatment is demanded. Successfully developed integrated in-situ remediation system will provide rapid and highly effective thermal/chemical treatment through the stimulators assisted in-situ remediation (short-term treatment) followed by gradual elimination of the residues from the precedent treatment via the EK/EC remediation method (mid-term treatment).

RECOMMENDATIONS

The lab-scale feasibility tests have proven that the developed stimulators significantly reduced hydrocarbons present in soil. However, effectively transporting the stimulators into the target soil region can be challenging. One of the stimulator constituents is highly reactive in the presence of water. Although this constituent is emulsified or encapsulated with water-resistant material, the blended stimulators must be kept from water or highly moisturized circumstance until they get activated via the heat supply. This characteristic requires that the delivery method should be able to rapidly transport the stimulators into the destination. Hence, the delivery methods need to be investigated in the scaled-up test to validate stability of the stimulators during transportation and to evaluate effectiveness in distribution of the stimulators.

The findings of this work have pointed out that available oxygen content in soil pores is crucial in the aspects of generating additional heat through the exothermic chemical reactions and degrading hydrocarbons in soil. Available oxygen content can be influenced by soil texture (i.e., fractions of clay, silt, and sand), soil moisture content, soil organic matter (SOM), soil biota, and soil fauna. In addition, most soils, especially in deep area, are under anaerobic or very low oxygen conditions. Therefore, further investigation is demanded to understand the minimum oxygen content in soil for generating the ideal heat temperature that is able to decompose target contaminants. Once the required oxygen content for the best performance of the introduced stimulators, oxygen can be provided into the reaction area by injecting atmospheric air through injection well or other delivery methods.

Potential generation of toxic by-products from the exothermic chemical reactions was thoroughly investigated through literature surveys during the process of constituent selection in order to prevent secondary contamination in soil by application of the stimulators. However, toxicity analysis has not been performed with the actual soil samples treated with the stimulators. Although theoretical chemical reactions have been investigated, this analysis is necessary to verify that activation of the stimulators and additives, such as catalysts, does not leave any toxic by-products which generate secondary contamination in soil.

The specially designed ex-situ prototype for application of the proprietary stimulators (T-Rex®) was prepared to verify its effectiveness in reducing heavy hydrocarbons such as crude oil and bitumen in soil. The original intent was to build a pilot scale test setup and perform tests at a Trium's partner site in China. However, due to current COVID-19 pandemic situation, the treatability test has to be implemented in the future. It is expected that the ex-situ remediation system would be effective in extracting heavy hydrocarbons (F2 - F4+) present in soil and recovering light hydrocarbons (F2 - F3) upon activation of the applied stimulators that would crack the chemical bonds of the long-chained hydrocarbons. Both qualitative and quantitative results need to be evaluated to confirm the influence of heat source temperature and relevant performances in the remediation.

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