Final Report

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

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EXECUTIVE SUMMARY

Contamination of soil and groundwater has increased by not only the extensive oil and gas developments in Canada over the past few decades but oil spills through leakages from underground storage tanks and pipelines. Cost reduction and efficiency enhancement have been always pursed in environmental remediation. It was reported that thermal treatments result in relatively higher remediation efficiency compared to other treatments such as bioremediation, chemical oxidation/reduction, and electrokinetic remediation. However, current thermal treatments and incineration requires high temperature heat (400~1,200 °C), consequently demanding high operating costs and producing greenhouse gases (GHG). To utilize the advantages of thermal treatment but reduce operating cost and energy consumption, the proprietary multi-functional stimulators for ex-situ remediation have been developed by the current research team using nanomaterials. Through a series of lab-scale testing, the developed stimulators have proven both technical and economic potential with outperformed technical results that can be summarized as 99% hydrocarbon removal and 82% DNAPL (diesel and tar) removal of soils contaminated with 100,000 mg/kg concentrations.

In this project, based on the outperformed technical results in petroleum hydrocarbon contaminated soil by ex-situ application of the stimulators, (1) multi-functional stimulators for in-situ application were developed, (2) the developed stimulators and their application method were evaluated in the aspects of heat generation as well as hydrocarbon remediation efficiency, and (3) the specially designed ex-situ prototype for application of the proprietary stimulators (T-Rex®) was validated in remediation of heavy hydrocarbons (crude oil) in soil.

To develop the multi-functional stimulators for in-situ application, various compositions of the candidate constituents were evaluated in the aspects of energy consumption and lag time for their activation, temperature generated by their activation, and controllability. One of the select constituents was emulsified with water-resistant material to delay its activation in the presence of soil moisture due to its high reactivity with water. The developed stimulators were successfully activated at low heat temperature (< 150 °C) and effectively generated additional heat through their exothermic chemical reactions in the lab-scale in-situ application, resulting in maximum soil temperatures in a range of 280 °C to 670 °C depending on soil conditions. In a separate test, it was confirmed that the developed stimulators were stable in the presence of soil moisture until they received proper heat temperature.

A series of lab-scale in-situ feasibility tests has proven that the generated heat and other mechanisms through the chemical reactions effectively degraded hydrocarbons in soil, resulting in remediation efficiency of 88 – 93 % in F2 and F3 hydrocarbons under 5 % hydrocarbon contamination and 10 – 12 % soil moisture conditions. However, it also has been confirmed that heat generation and remediation efficiency via exothermic chemical reactions of the stimulators are significantly influenced by soil characteristics that influence available oxygen content in soil pores. Although considerable removal of hydrocarbons (> 88 %) have been confirmed through the feasibility tests of the in-situ application, approximately 10,000 – 15,000 mg/kg of hydrocarbons still remained in the treated soil, which indicates that further reduction of hydrocarbon concentration is necessary to meet the Alberta Tier 1 Soil and Groundwater Remediation Guidelines which require concentrations less than 260 mg/kg for F2 and 2,500 mg/kg for F3 for the commercial land use. 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. This result indicates that the integrated in-situ remediation system comprising the stimulator assisted thermal treatment and the subsequent EK/EC treatment will greatly enhance the remediation efficiency with low energy consumption.

Based on the outperformed technical results of the stimulators assisted ex-situ prototype in remediating petroleum hydrocarbons (diesel and artificial creosote), lab-scale tests using the proprietary stimulators (T-REX®) and their ex-situ application prototype were performed to evaluate treatability for heavy hydrocarbons (crude oil) in soil. The effectiveness of the proprietary stimulators (T-Rex®) and the specially designed ex-situ prototype for their application was successfully validated to reduce heavy hydrocarbons in soil. The treatability test results have confirmed that the ex-situ remediation system was effective in extracting heavy hydrocarbons (F2 - F4+) present in soil and recovering light hydrocarbons (F2 – F3), which indicates that activation of the stimulators can crack the chemical bonds of the long-chained hydrocarbons. Both qualitative and quantitative results indicate that heat temperature over 400 °C is demanded to remediate relatively heavier hydrocarbons (> F3) and to enhance recovery of light hydrocarbons.

1. BACKGROUND

In Canada, numerous sites have been contaminated with petroleum hydrocarbons due to oil sludge and/or tailings ponds. According to Federal Contaminated Sites Inventory (FCSI), 3,164 sites were contaminated with petroleum Hydrocarbons (PHC) in 2013. Although the number of contaminated sites has been somewhat decreased from 3,866 in 2008, a number of sites has not been cleaned up yet. Especially, Alberta has vast oil sands that correspond to the third largest oil reserves in the world and underline 142,000 km^2 of land, which is a great advantage in oil and gas industry. On the other hand, the reserved oil itself and its development activities have become a long-term source of soil and groundwater contamination. Due to increasing public awareness and media attention, federal/provincial governments and oil industries are expected to clean up the contaminated sites for sustainable development as well as environment conservation.

Contamination of soil and groundwater has increased by not only the extensive oil and gas developments in Canada over the past few decades but oil spills through leakages from underground storage tanks and pipelines. The contamination typically causes adverse impacts on vegetation and human health by migrating off the contaminated site through groundwater flow, and also influences climate change through cycling of elements. Recently, approximately 795,000 liters of oil was spilled from the Keystone pipeline in South Dakoda in November 2017, resulting in extensive contaminated areas and potential groundwater pollution. Further, leakage of produced water generated from oil operations could be a source of soil and groundwater contamination (ex. Sulfolane Leaks in Edson, AB).

Cost reduction and efficiency enhancement have been always pursed in environmental remediation. Landfilling and incineration are still a major stream for contaminated soil treatments in Canada. However, landfilling is not a substantial treatment method due to potential contamination through leachate or volatile pollutants. A recent study revealed that thermal treatments result in relatively higher remediation efficiency compared to other treatments (McGuire et al. 2016), such as bioremediation, chemical oxidation/reduction, and electrokinetic remediation. However, current thermal treatments (400~500 °C) and incineration (800~1200 °C) requires high temperature heat, consequently demanding high operating costs and producing greenhouse gases (GHG) (Lee et al. 2000). Many studies have been conducted to improve remediation technologies but still not effective in treating huge contaminated areas due to high operating costs and low remediation efficiency. In addition, some of the remediation methods generate by-products and/or GHG during treatment processes, potentially causing secondary contamination. To minimize operating costs and potential secondary contamination, and enhance remediation efficiency, a cost-effective remediation system utilizing environment-friendly materials is demanded.

The proprietary multi-functional stimulators for ex-situ remediation have been developed by the current research team using nanomaterials. The lab-scale ex-situ remediation tests showed that the proprietary multi-functional stimulators produced extremely high heat (500~1,000 °C) intermittently with low energy supply, which is sufficient to decompose most of organic contaminants present in soil. A lab-scale ex-situ prototype has been also developed for application of the proprietary stimulators, and prototype testing results presented competitive remediation efficiency in petroleum hydrocarbons.

This project evaluated feasibility of the proprietary stimulators and their modified form not only in the in-situ application for remediating hydrocarbons in soil but also in the ex-situ prototype application for degrading persistent organic pollutants (POPs) and crude oil in soil through a series of lab-scale experiments. Three primary objectives are pursued including:

- Development of multi-functional stimulators for in-situ application.
- Performance evaluation of the developed stimulators and in-situ application method.
- Validation of the ex-situ prototype performance utilizing the proprietary stimulators for POPs and heavy hydrocarbon remediation.

2. METHODOLOGY

2.1. Development of Multi-functional Stimulators for In-situ Application

The fundamental mechanism of the proposed remediation approach is to generate high heat temperature and useful gaseous components through activation of exothermic chemicals and catalysts with low energy consumption. For cost- and energy-efficient activation of exothermic chemicals, selection of optimal chemicals and catalysts is one of the key research activities to achieve overall objectives of this project. A list of candidate exothermic chemicals and catalysts that are able to generate high heat temperature through their sequential chemical chain reactions at low heat temperature (< 150 °C), was prepared in consideration of their decomposition temperature, gas yield, cost, and toxicity. Various compositions of the candidate materials have been evaluated in the aspects of energy consumption and lag time for their activation, temperature generated by their activation, and controllability. One of the select chemicals immediately reacts with water. However, its activation produces hydrogen gas which is beneficial in degrading hydrocarbons and other contaminants through hydrocracking process. To control its reaction time and reactivity with water the chemical N was emulsified with proper material which is able to be decomposed at low temperature and delay activation of the chemical in the presence of water. Various coating material including paraffin wax, shellac, spray wax, gelatin, caramelized sugar, and flax seed oil were evaluated to determine the optimal emulsifying material for the highly reactive chemical component through a series of reactivity tests in soils with various water contents. The emulsified chemical N was thoroughly blended with other select chemical and catalyst components (chemicals A, C, N, T, catalysts Z1, Z2) to complete production of stimulators for in-situ application. Fig 1 shows an exemplar of the developed stimulators for in-situ application.

Fig 1. Exemplar of the developed stimulators for in-situ application

2.2. Feasibility Tests of the Stimulators in In-situ Application

A series of lab scale feasibility tests have been performed utilizing the developed stimulators. Testing setup was designed to mimic two different contamination scenarios which are (a) well distributed petroleum hydrocarbons over soil depth and (b) 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 Fig 2, testing setup basically consists of two soil layers and a layer of stimulators to represent contaminated soil area where the stimulators are introduced into. While diesel was thoroughly mixed with sandy soil for scenario (a), diesel was spread out over the bottom soil layer for scenario (b). A cartridge heater was employed as a heating source for activation of stimulators and was controlled by a temperature controller (Omega CSC32). Changes in soil temperature were monitored through thermocouples at different distances from the heating source and the monitoring results were recorded using Labview. In addition to the contamination conditions, impact of water content, contaminant concentrations, and gas exchange in soil was investigated. 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.

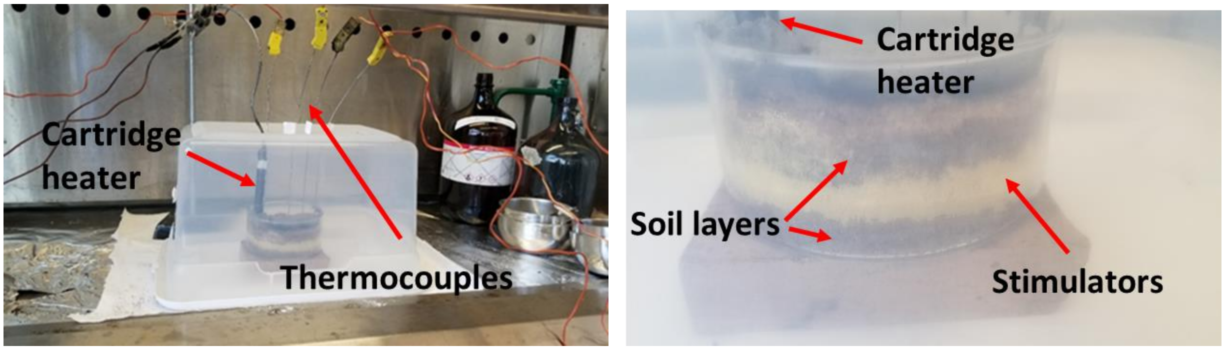

Fig 2. Lab scale feasibility testing setup for in-situ remediation utilizing the developed stimulators

2.3. Impact of Different Soil Type on In-Situ Application of the Stimulators

Field-collected soil was employed as the hydrocarbon impacted soil to identify the impact of different soil type on treatability of in-situ application of the stimulators. Test procedure is identical with the feasibility test method for scenario (b) in section 2.2, except using field soil containing much higher clay/silt contents instead of sandy soil. Amount equivalent to 10 % moisture content and 5 % diesel was applied into the field soil to generate the hydrocarbon impacted field soil. To estimate soil properties such as porosity, air- and water-filled porosity, volume and weight of the bottom soil layer was measured for both field and sandy soil. The treated soil samples were collected from the proximity of the chemical layer as well as overall location of the bottom soil layer. The sample extraction and analytical methods are described above.

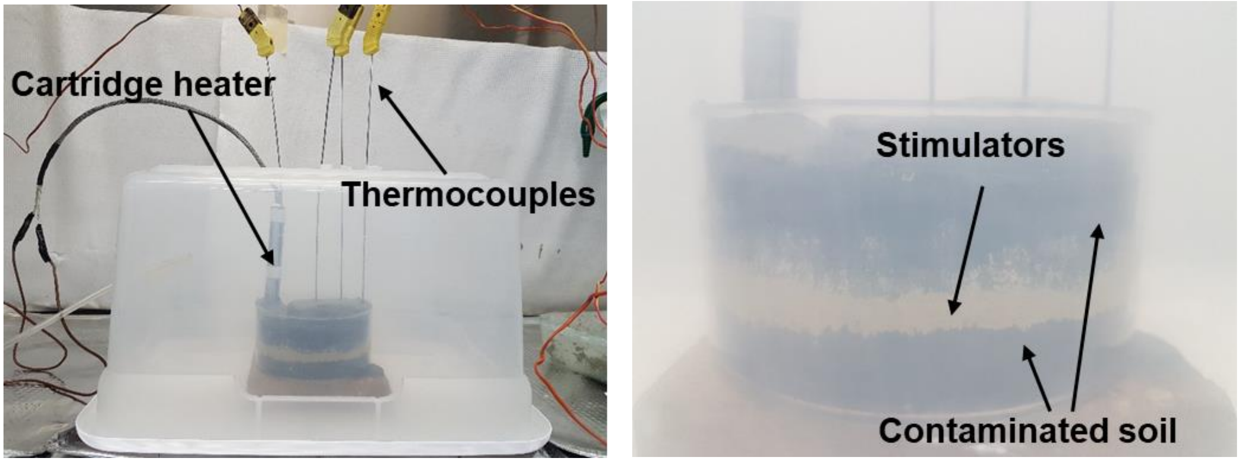

Fig 3. Lab scale testing setup with field soil for in-situ remediation utilizing the developed stimulators

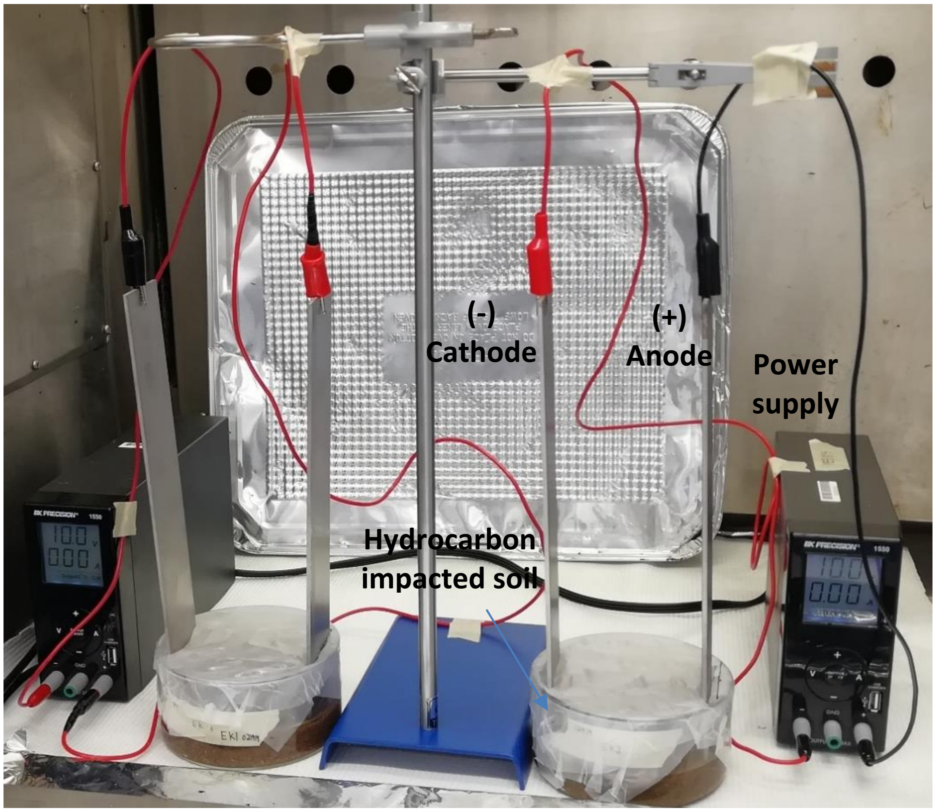

Fig 4. Experimental setup of the lab-scale in-situ electrokinetic/electrochemical (EK/EC) treatment for hydrocarbon impacted soil.

2.4. Feasibility Test of the In-situ Electrokinetic/Electrochemical Treatment

The lab-scale in-situ electrokinetic/electrochemical (EK/EC) treatment was employed as the subsequent remediation method and evaluated for technical feasibility in removal of the residues from the aforementioned stimulator assisted in-situ remediation. For the feasibility test of the EK/EC treatment approach, the hydrocarbon impacted soil was treated by the direct electric current (DC) application. The hydrocarbon impacted soil was prepared by injecting 5 g of diesel and 100 g of water into 500 g of sandy soil to generate approximately 1 % diesel and 20 % moisture content in soil. To enhance electrolysis during the treatment, 25 g of sodium chloride was dissolved into the water before it was added into soil. The contaminated soil was filled in the test chamber (10 cm wide x 5 cm high X 10 cm long) and the 0.3 cm thick x 5 cm wide X 30 cm long titanium electrodes were installed at each end of the test chamber with 10 cm distance as shown in Fig 4. The chamber was covered with a plastic paraffin film to minimize volatilization of hydrocarbons and evaporation of water that were added into soil. Direct electric current (DC) was then applied with 1 V/cm of voltage gradient for 28 days. Duplicate tests were performed in parallel under identical conditions. Soil samples were collected at 0, 1, 2, 3, 7, 14, 21, and 28 days after the onset of the electric current application to monitor changes in hydrocarbon concentrations. The sample extraction and analytical methods are described above.

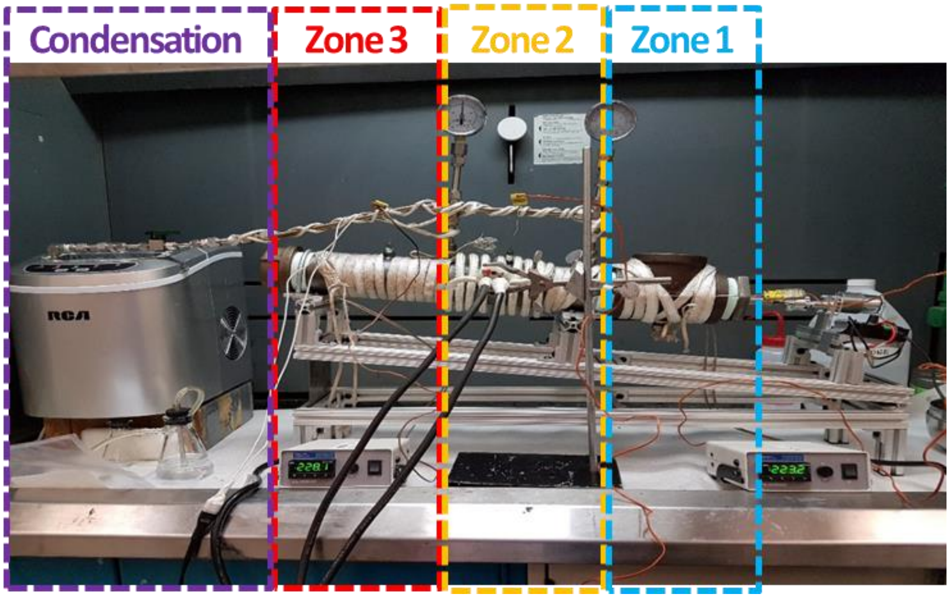

Fig 5. Lab scale ex-situ prototype setup with a condensation unit.

2.5. Stimulator Assisted Ex-situ Prototype Test for Crude Oil Impacted Soil

Based on the outperformed technical results of the stimulators assisted ex-situ prototype in remediating petroleum hydrocarbons (diesel and artificial creosote) and persistent organic pollutants (POPs) including volatile organic compounds (VOCs) and pesticides, lab-scale tests using the proprietary stimulators (T-REX®) and their ex-situ application prototype were performed to evaluate treatability in the heavy hydrocarbons impacted soil. The lab scale ex-situ prototype consisted of three heating zones for the following purposes: (a) zone 1 for de-moisturization; (b) zone 2 for remediation; and (c) zone 3 for prevention of vapor re-condensation and final extraction. Each zone was heated up with different temperatures depending on remediation demands. While zone 1 and 3 were heated by rope heaters for relatively low temperature, zone 2 was heated by an induction coil which was connected to an induction heater. The soil mixture containing contaminated soil and the developed chemical stimulators was injected into the main pipe through the inlet which was the opening of the T-joint as shown in Fig 5. The auger that was placed inside the main pipe and a motor system drove the injected soil forward, allowing the soil pass through each zone. The treated soil was then collected at the end of the main pipe. Vapor generated during the treatment process was collected through outlet tubing under vacuum application and then was re-condensed while it was passed through condenser tubing. The whole prototype system was inclined to prevent stagnancy of any liquid which was formed by re-condensation of vapor.

The heavy hydrocarbons impacted soil was prepared by adding 50 g of crude oil into 450 g of sandy soil which is equivalent to 10% concentration, followed by thorough hand mixing. Then the soil mixture was mingled with stimulators before introduced into the remediation system. The crude oil was provided by TRIUM Environmental Inc., a partner company, and it was extracted from Saskatchewan. The auger motor speed was set at 0.29 rpm to allow soil inside the pipe to have 25 minutes of soil retention time (SRT). The contaminated soil was then injected into the prototype unit preheated with different temperatures for each zone, which were 230 °C, 400 °C, 300 °C (zone 1/2/3) for medium heat temperature conditions and 220 °C, 250 °C, 200 °C (zone 1/2/3) for low heat temperature conditions. The inlet was immediately plugged to make the system completely closed. Negative pressure (-86 kPa) was applied to the system immediately after the plugging in order for suction of the generated vapor and following condensate recovery in the condensation unit. The recovered condensate was collected into an Erlenmeyer flask with an inlet which was connected to the vacuum tubing. Weight of the collected liquid was measured to determine the ratio of the recovered liquid to the added amount. During the treatment, temperatures for each zone and pressure of the system were monitored in real-time. Heating and vacuum application were stopped 60 minutes after the onset of soil injection. The treated soil was extracted at the opening of zone 3 by pushing the auger shaft in the pipe toward the direction of zone 3. The collected soil samples were extracted into the solvent mixture (acetone:hexane = 1:1) following the CCME Reference Method for the Canada Wide Standard for Petroleum Hydrocarbons in Soil (Tier 1 Method). The recovered condensates were diluted into the solvent mixture with appropriate dilution factors. The soil extracts and the diluted condensates were analyzed on a GC-FID. Table 1 shows the experimental conditions that were employed for the lab-scale ex-situ prototype tests with crude oil impacted soil.

Table 1. Test parameters for the lab scale ex-situ prototype tests with crude oil impacted soil.

	Medium Heat + T-Rex	**Low Heat + T-Rex**
Temp. (°C, Zone 1/2/3)	**230/400/300**	**220/250/200**
Soil Retention Time (min)	25	25
Test duration (min)	60	60
Soil (g)	450	450
Crude oil (g)	50 (10%)	50 (10%)
T-Rex (g)	7.5 (1.5%)	7.5 (1.5%)
T-Rex additives (g)	1.25 (0.25%)	1.25 (0.25%)

3. RESULTS

3.1. Feasibility of the Stimulators in In-situ Application

Changes in soil temperature were monitored through thermocouples at locations of 1, 2, and 3 inches distant from the heating source. The introduced stimulators were immediately activated with onset of the heat supply (150 °C) and soil temperatures significantly increased in a short time period as shown in Fig 6. The increased temperatures were in a range of 280 °C to 670 °C and it is believed that the variation in the generated heat temperature is associated with distribution and amount of the stimulators introduced into the testing soil. The fact that testing with greater amount of stimulators showed relatively higher soil temperature generated by their activation supports our postulation. However, the soil temperature increase can be influenced by other physicochemical soil properties such as soil moisture content, gas exchange rate, and amount of hydrocarbons present in soil that can be used as fuel. High moisture content can hinder prompt increase of soil temperature by consuming the generated heat for vaporization. In soils with low gas exchange rates, i.e. low available air (or oxygen) in soil, the generated temperature increase can be limited as an amount of air (or oxygen) becomes a limiting factor in exothermic chemical chain reactions. Experiments that were set up with bentonite cover on the top soil layers for minimization of gas exchange between atmosphere and the testing soil, exhibited relatively lower temperature increase compared to testing setup without the bentonite cover.

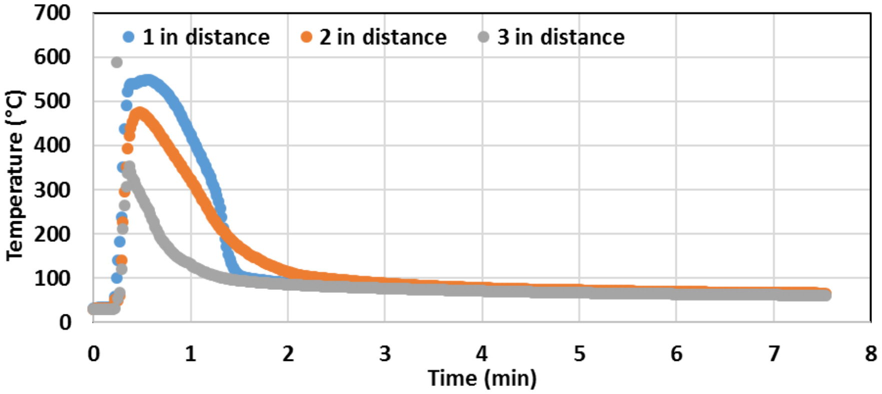

Fig 6. Example of temperature profile during a feasibility test utilizing the developed stimulators.

Soil samples collected before and after each treatment were extracted into the solvent mixture following the CCME Reference Method described above and the extracts were analyzed by a GC-FID to quantify reduction of hydrocarbons in soil. Chemical analysis results clearly showed that the proposed stimulator assisted in-situ remediation approach is promising in degrading petroleum hydrocarbons in soil. Fig 7 shows hydrocarbon (F2 and F3) concentrations before and after treatment using the developed stimulators when petroleum hydrocarbons were present on the bottom soil layer. Overall, hydrocarbon concentrations were significantly decreased through the stimulator assisted thermal treatment. As shown in Fig 8, hydrocarbon removal rates increased up to 90 % in the most recent tests under 10 % water content and 5 % hydrocarbon contamination in the bottom soil layer. Relatively higher removal of hydrocarbons was observed in soil samples collected from the proximity of a stimulator layer (Fig 8). This result is consistent with relatively lower removal rates (39 – 62 %) in well distributed hydrocarbons over soil depth. The same trend was observed in testing with low hydrocarbon contamination (1 %), indicating that contaminants located out of remediation influencing range has low probability to be treated regardless of contamination extent. Although 90 % of hydrocarbons (155,000 mg/kg) was eliminated from the tested soil through the proposed in-situ method using stimulators, approximately 15,000 mg/kg of hydrocarbons remained, which indicates that further investigation is necessary to reduce this residual amount of hydrocarbons in soil to meet the Alberta Tier 1 Soil and Groundwater Remediation Guidelines that require concentrations less than 260 mg/kg for F2 and 2,500 mg/kg for F3 for the commercial land use.

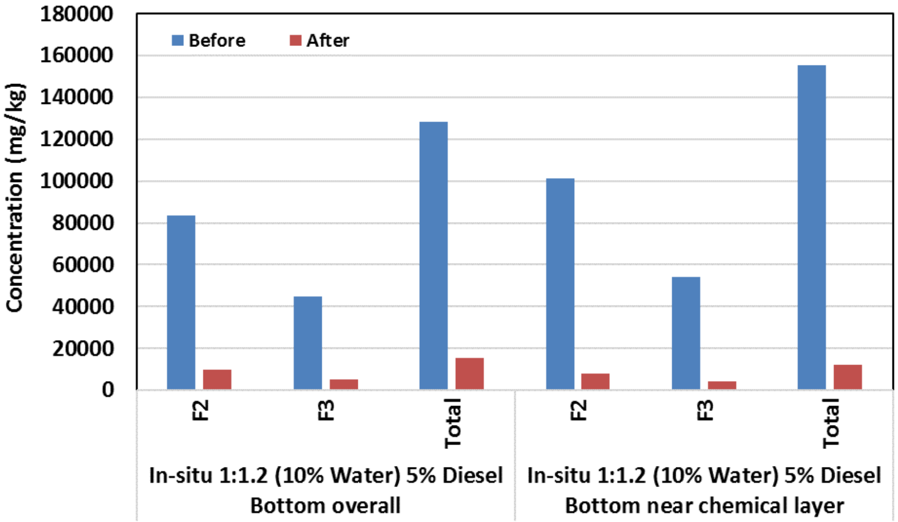

Fig 7. Hydrocarbon (F2 and F3) concentrations before and after treatment using the developed stimulators.

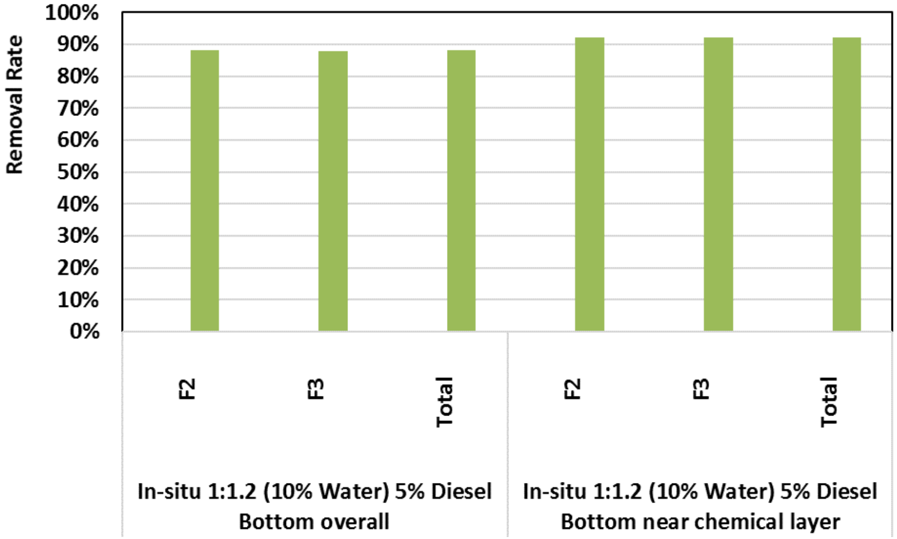

Fig 8. Removal rates of hydrocarbons (F2 and F3) before and after treatment using the developed stimulators.

The developed stimulators and in-situ application approach were also tested under 12 % soil moisture content to evaluate their treatability and stability in higher water saturated soil conditions. In general, the primary target contaminant, light non-aqueous phase liquid (LNAPL), is located on the surface of groundwater. Therefore, the stimulators are required to be stable under high soil moisture content and to be capable of remediating contaminants under those conditions. The test setup was the same as prior lab-scale feasibility tests. Differences from the prior tests were that higher moisture content (12 %) was applied and that amount of the stimulators components was increased accordingly along with greater amount of coating material.

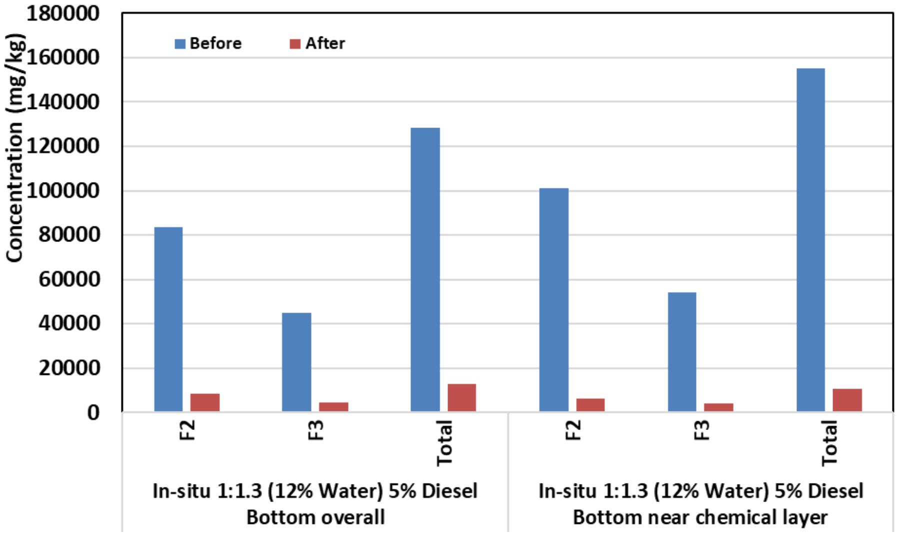

Fig 9. Hydrocarbon (F2 and F3) concentrations before and after treatment using the developed stimulators under 12 % soil moisture content.

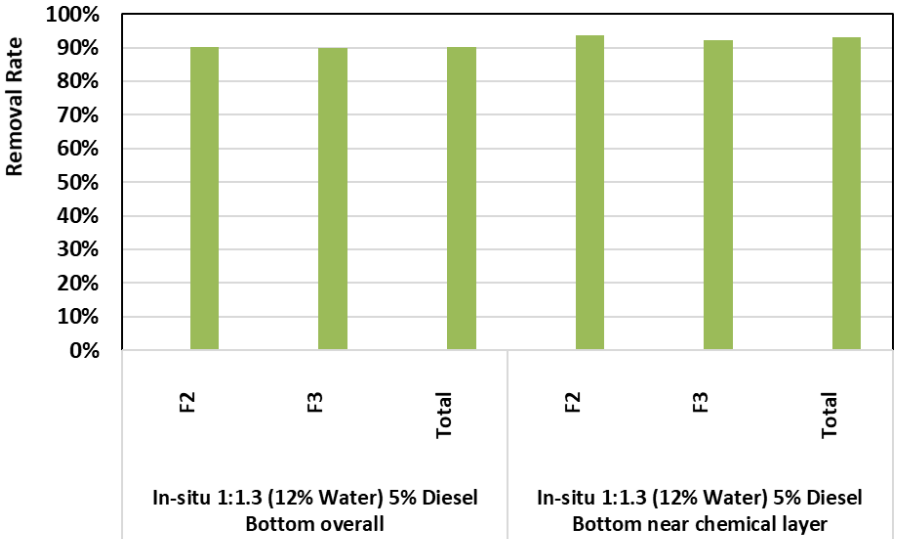

Fig 10. Removal rates of hydrocarbons (F2 and F3) before and after treatment using the developed stimulators under 12 % soil moisture content.

The stimulators with increased amount of a coating material were stable under the increased moisture content conditions until they received the heat supply. In the prior unsuccessful tests, without an increase of the coating material amount, the stimulators were activated when they contacted moisture present in soil layers, which indicates that ratio of coating material to the stimulators components as well as soil moisture content can be important factors for stability of the stimulators under highly water saturated soil conditions. Chemical analysis results demonstrated that the new combination of the stimulators and coating material was effective in eliminating petroleum hydrocarbons in soils. Fig 9 shows hydrocarbon (F2 and F3) concentrations before and after treatment using the developed stimulators under 12 % soil moisture content when petroleum hydrocarbons were present on the bottom soil layer. Overall, hydrocarbon concentrations were significantly declined and relatively greater reduction was observed in the soil samples collected from the proximity of a stimulator layer compared to the soils randomly collected from the bottom soil layer. This trend is consistent with the prior test results. As shown in Fig 10, removal rates of hydrocarbons were 90 % in the soil sample collected randomly and 93 % in the soil samples from the proximity of a stimulator layer.

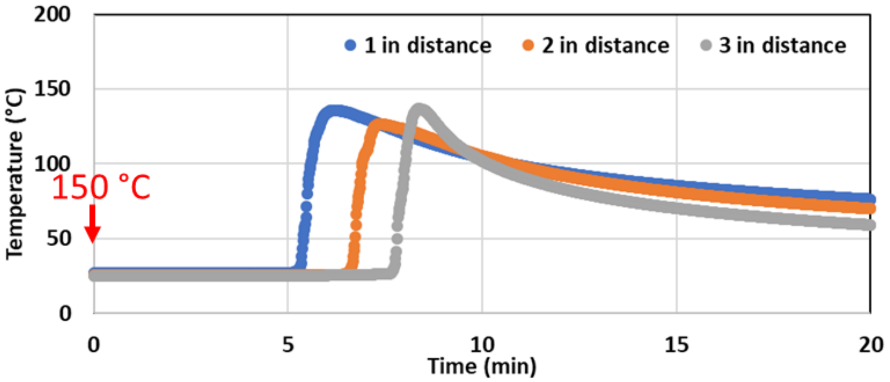

Fig 11. Temperature profile during an in-situ remediation of the hydrocarbon impacted field soil utilizing the developed stimulators.

3.2. Impact of Different Soil Type on In-Situ Application of the Stimulators

A lab-scale feasibility test of the stimulators assisted in-situ application was performed using field-collected soil containing much higher silt/clay contents than sandy soil in order to identify the impact of different soil type on treatability of the remediation approach in degrading hydrocarbons present in soil. Temperature monitoring results show that the temperature increase by activation of the stimulators was relatively lower compared to the prior tests using sandy soil. The increased temperatures were in a range of 127 °C to 137 °C (Fig 11). It is also observed that the temperature increase associated with the exothermic chemical reactions was relatively delayed compared to the testing with sandy soil. In sandy soil, the increased temperature at the further locations reached the maximum temperature within 0.1 min (0.03 – 0.1 min) after the maximum temperature appeared at the location 1-inch distant from the heat source (Fig 6). However, in the field soil, the maximum temperature at locations with 2- and 3-inch distance from the heater appeared approximately 1 min (0.97 – 1.23 min) after reaching the maximum temperatures at the closer locations (Fig 11). This discrepancy indicates that higher clay and silt contents in soil impede propagation of heat that is generated through the exothermic chemical reactions over the stimulator layer, and that the exothermic chemical reactions are associated with available oxygen content in soil. The estimation of soil porosity based on the volume and weight of the bottom soil layers, showed that total porosities were 0.49 and 0.59 for sandy soil and field soil respectively. Although it appears that field soil contains relatively higher total and air-filled porosity than sandy soil based on the estimation, the available oxygen content in soil pores can be relatively smaller compared to sandy soil due to abundance of very small pores (micropores) in the field soil containing higher silt/clay content. The physical properties of the testing soils are shown in Table 2.

Table 2. Physical properties of testing soils.

Soil	**area (cm^2)**	**height (cm)**	**volume (cm^3)**	**Wet soil (g)**	**Wet bulk density (g/cm^3)**	**Dried soil (g)**	**Dry bulk density (g/cm^3)**	**Porosity (Φ)**	**Water-filled porosity (Θ, cm^3/cm^3)**	**Air-filled porosity (Φ_a)**
Sandy Soil	122.7	1.2	147.3	218.7	1.485	196.9	1.337	0.488	0.149	0.339
Field soil	122.7	1.7	208.6	218.7	1.049	196.9	0.944	0.590	0.105	0.485

With the less increased temperature, hydrocarbon removal rates in field soil were significantly lower than treated sandy soil. Fig 12 and 13 show hydrocarbon (F2 and F3) concentrations and their removal rates before and after treatment in field soil using the developed stimulators under 10 % soil moisture content when petroleum hydrocarbons were present on the bottom soil layer. Removal rates of hydrocarbons were 72 % in the soil sample collected randomly and 49 % in the soils from the proximity of a stimulator layer. This result is inconsistent with the prior results in sandy soil that showed higher hydrocarbon removal rates at the location close to the stimulator layer. This is presumably because of relatively higher heterogeneity and lower hydraulic conductivity (K) in the field soil that hinders vertical movement of the introduced hydrocarbons over the surface of bottom soil layer, consequently influencing distribution of hydrocarbons in soil. The hydrocarbon residues present in the upper body of the bottom soil layer could show considerably lower concentrations when they are blended with uncontaminated soil in the lower body of the soil layer.

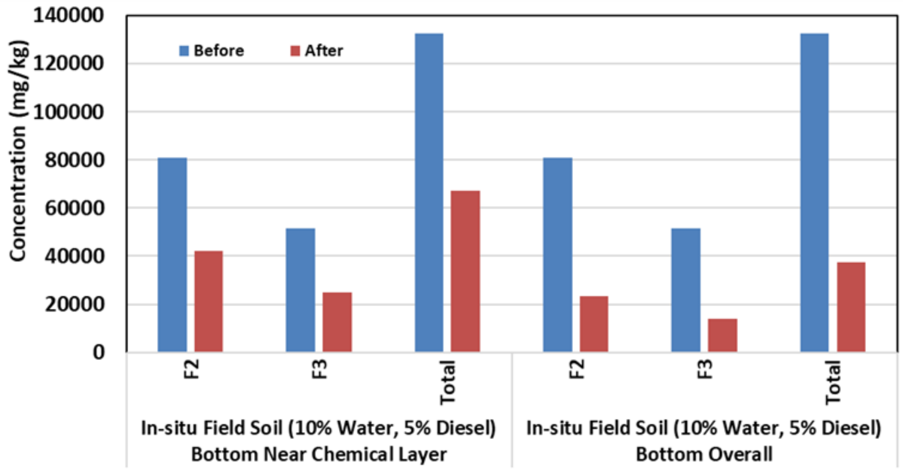

Fig 12. Hydrocarbon (F2 and F3) concentrations before and after treatment using the developed stimulators in field soil containing 10 % moisture content.

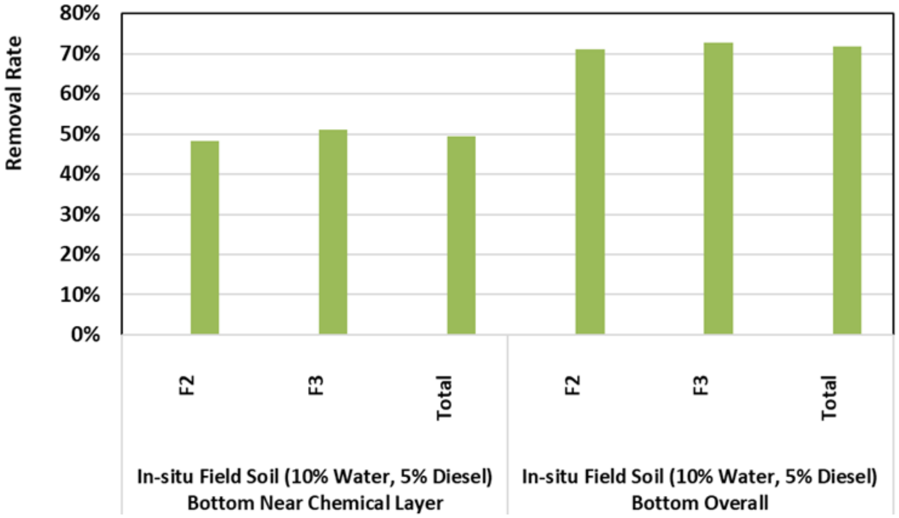

Fig 13. Removal rates of hydrocarbons (F2 and F3) before and after treatment using the developed stimulators in field soil containing 10 % moisture content.

3.3. Feasibility Test of the Electrokinetic/Electrochemical Treatment

A series of the lab-scale feasibility tests has proven that the developed stimulators and their application approach were effective in reducing hydrocarbons present in soils. The outperformed technical results can be summarized as 88 – 93 % hydrocarbon removal in the soil with 10 – 12 % moisture content. However, further reduction of hydrocarbon concentration is necessary to meet the Alberta Tier 1 Soil and Groundwater Remediation Guidelines that require concentrations less than 260 mg/kg for F2 and 2,500 mg/kg for F3 for the commercial land use. Hence, the lab-scale in-situ electrokinetic/electrochemical (EK/EC) treatment was employed as the subsequent remediation method and evaluated for technical feasibility in removal of the residues.

The collected soil samples were extracted following the CCME Reference Method for the Canada Wide Standard for Petroleum Hydrocarbons in Soil (Tier 1 Method). The extracts were analyzed on a gas chromatograph equipped with the flame ionization detector (GC-FID). The analyzed hydrocarbon concentrations and their removal rates are exhibited in Fig 14 and 15 respectively. Hydrocarbon concentrations at Day 0, i.e. pre-treated soils, were relatively lower than concentrations at Day 1. This was presumably due to not enough time for equilibrium of the added hydrocarbons in the 20 % moisturized soil. Hence, the hydrocarbon removal rates were determined based on the concentrations at Day 1. The analytical results show 57 – 61 % removal of F2 (C10 – C16), 28 – 40 % removal of F3 (C16 – C34), and 47 – 50 % of total hydrocarbons (C10 – C34) at Day 28 since the onset of the direct electric current application. It appears that there was a variance in the trend of declining hydrocarbon concentrations at Day 3 and 14, presenting no reduction or slight increase in concentrations. This might be because only single soil sample was collected from each test chamber at each sampling event. Although the soil samples were collected by the random sampling method that randomly collects soil more than 10 increments, there might be regional heterogeneity in distribution of hydrocarbons, resulting in less representativeness of the collected soils. Despite the variance at some data points, the experimental results indicate that the EK/EC treatment approach was effective in remediating low concentration hydrocarbons in soil. In addition, the other studies have demonstrated that this electric current application is effective in eliminating other soil contaminants including, but not limited to, heavy metals, polycyclic aromatic hydrocarbons (PAHs), and crude oil (Lu et al. 2014; Jeon et al. 2015; Falciglia et al. 2015; Ammami et al. 2015).

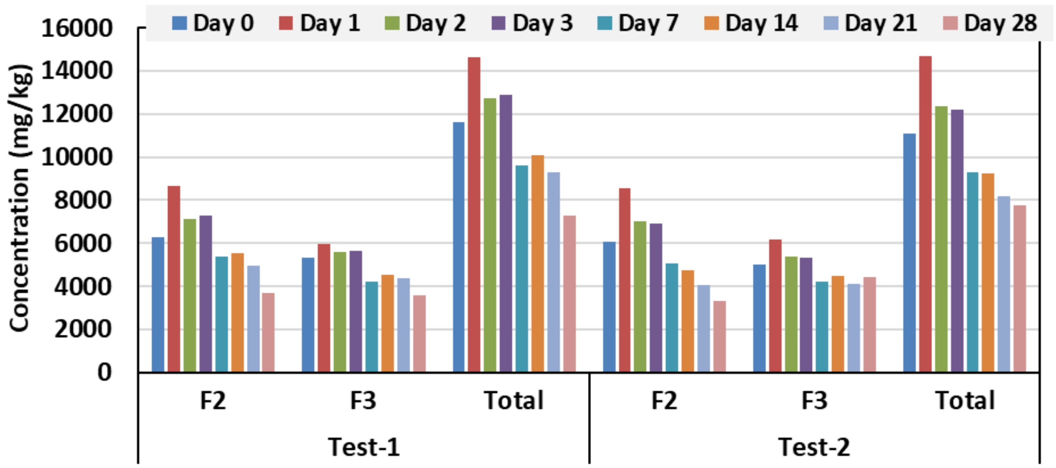

Fig 14. Hydrocarbon (F2 and F3) concentrations over the course of the treatment using the direct electric current application (DC) with 1 V/cm of voltage gradient.

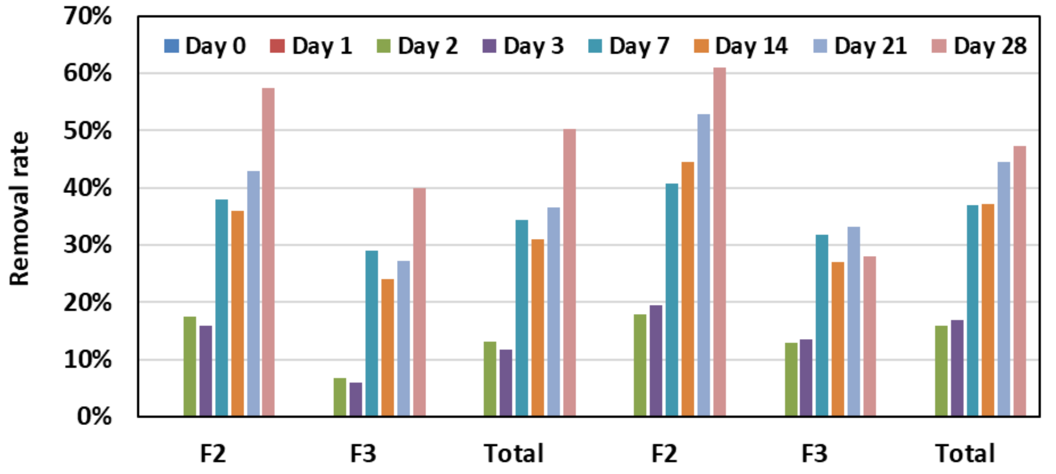

Fig 15. Hydrocarbon (F2 and F3) removal rates over the course of the treatment using the direct electric current (DC) application with 1 V/cm of voltage gradient.

3.4. Stimulator Assisted Ex-situ Prototype Test for Crude Oil Impacted Soil

Based on the outperformed technical results of the stimulators assisted ex-situ prototype in remediating petroleum hydrocarbons (diesel and artificial creosote) and persistent organic pollutants (POPs) including volatile organic compounds (VOCs) and pesticides, lab-scale tests using the proprietary stimulators (T-REX®) and their ex-situ application prototype were performed to evaluate treatability in the heavy hydrocarbons impacted soil. During the treatment, changes in temperature, pressure, vaporization, and re-condensation were monitored based on visual observations. The experimental setup and observations during each treatment were presented in Fig 16 and 17 for medium and low heat conditions respectively. While the applied negative pressure stayed at slightly reduced and stable pressure (-80 ~ -82 kPa) over the period of treatment under medium heat condition, the treatment under low heat conditions showed relatively stronger negative pressure (-85 ~ -86 kPa) for the most test period, except slightly lower pressure (-80 kPa) monitored at 30 min after the soil injection. The relatively lower negative pressure was presumably related to the vaporization of hydrocarbons through thermal treatment as well as gas production from chemical reaction. This postulation can be supported by the observation that relatively greater amount of white vapor was generated from the treatment under medium heat condition compared to the low heat condition. The generated vapor was partially re-condensed through the condensation unit. Weight of the recovered condensate was measured at the end of the experiment to determine the ratio of the recovered condensate to the introduced crude oil. The amount of recovered condensate was relatively higher in the treatment under medium heat condition (11.78 g) that is equivalent to 23.56% of the added crude oil, compared to low heat condition (2.97 g) that is equivalent to 5.94% of the added crude oil. The less amount of recovered condensate is associated with the lower reduction of hydrocarbon concentrations in the treatment under low heat condition that will be shown below.

Fig 18 shows the GC-FID chromatograms for pre- and post-treated soil samples under medium and low heat conditions. The chromatograms clearly show that hydrocarbons were significantly reduced by the employed treatment methods, with relatively higher reduction under medium heat condition. They qualitatively indicate that most F2 and F3 hydrocarbons were remediated in the medium heat applied treatment whereas most F2 and part of F3 were degraded in the treatment under low heat condition. Quantitative results support the aforesaid positive impact of the medium heat condition in hydrocarbon reduction, showing higher removal rates (97 % for F2, 100 % for F3) than the low heat applied treatment (97 % for F2, 53 % for F3) as shown in Fig 21 and 22. The both qualitative and quantitative results indicate that low heat condition was not appropriate to remediate hydrocarbons beyond F3 but effective in F2 degradation. The results also indicate that heat temperature over 400 °C is necessary to treat relatively heavier hydrocarbons (> F3).

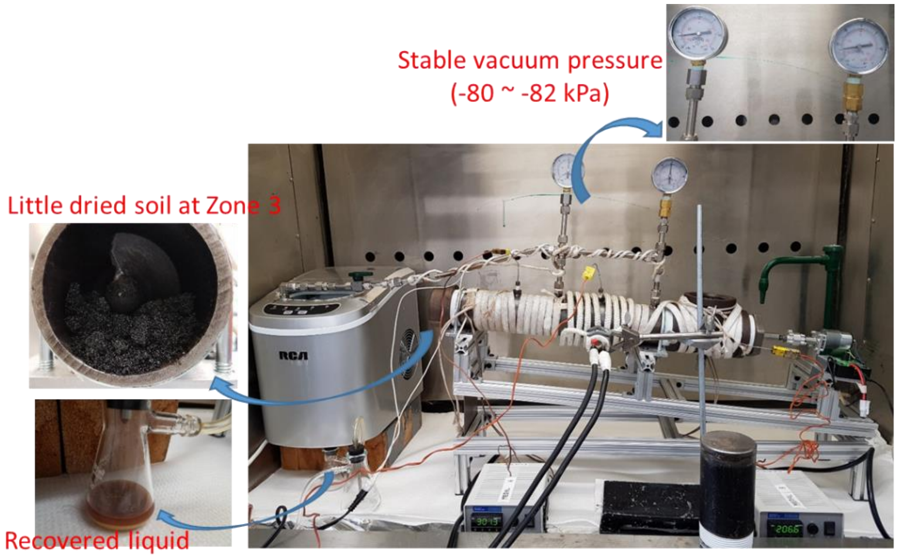

Fig 16. Lab-scale ex-situ prototype setup and observations during the treatment of medium heat combined with stimulators.

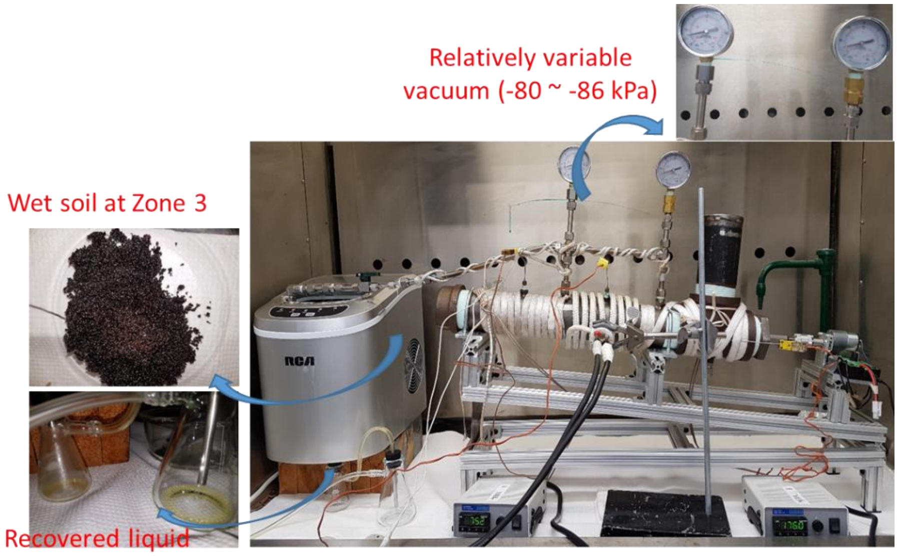

Fig 17. Lab-scale ex-situ prototype setup and observations during the treatment of low heat combined with stimulators.

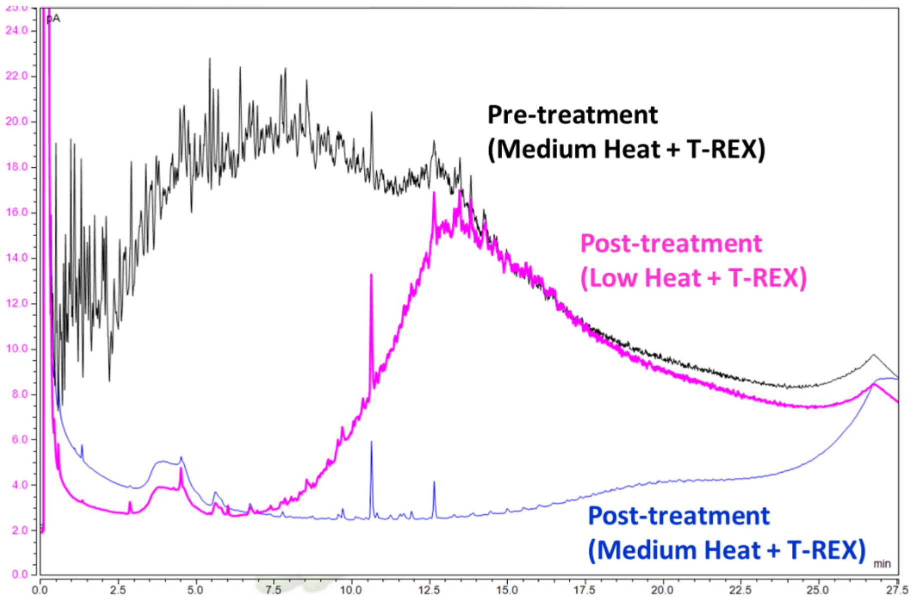

Fig 18. GC-FID chromatograms for pre- and post-treated soil samples under medium and low heat conditions.

GC-FID chromatograms of the recovered condensates under medium and low heat applied treatments are shown in Fig 19 and 20 along with the chromatograms for the pre- and post-treated soil samples. Analytical results indicate that much considerable amount of lighter hydrocarbons were generated through the thermal treatment regardless of the heat conditions, compared to hydrocarbons in the pre-treated soils. Quantitative composition of the hydrocarbons is shown in Fig 23. Both F2 and F3 concentrations were significantly increased in the recovered condensates compared to concentrations in the pre-treated soils. Considering their dilution factor (1:50), much higher amount of lighter hydrocarbons were produced through cracking process of heavy hydrocarbons than which appears in the chromatograms, indicating presence of heavier hydrocarbons (F4 and F4G) that cannot be analyzed by the current GC-FID. The both qualitative and quantitative analytical results of the recovered condensates as well as the post-treated soil samples prove that the stimulators-assisted ex-situ remediation system is effective not only in remediating heavy hydrocarbons impacted soil but in recovering recyclable hydrocarbons.

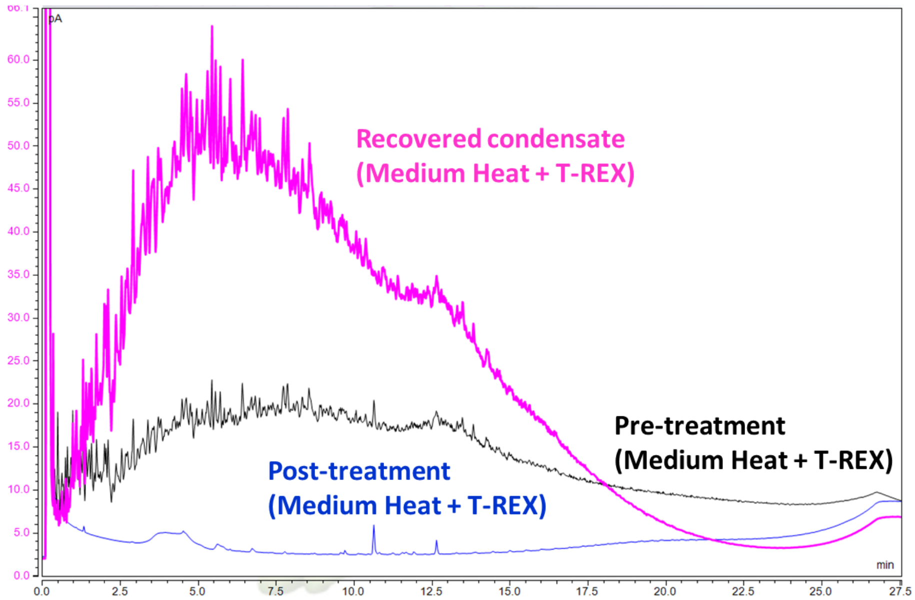

Fig 19. GC-FID chromatograms for pre- and post-treated soil samples and recovered condensate under medium heat condition.

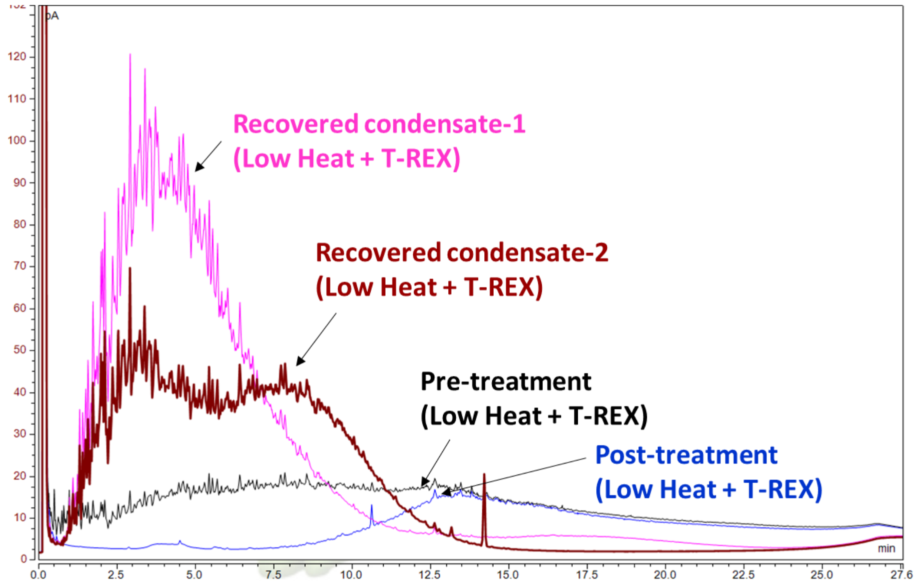

Fig 20. GC-FID chromatograms for pre- and post-treated soil samples and recovered condensate under low heat condition.

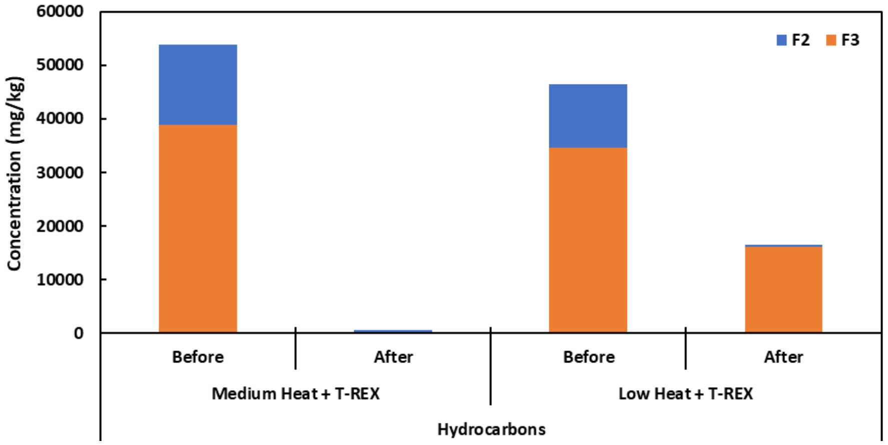

Fig 21. Hydrocarbon (F2 and F3) concentrations in soils before and after the stimulators-assisted thermal treatment under medium and low heat conditions.

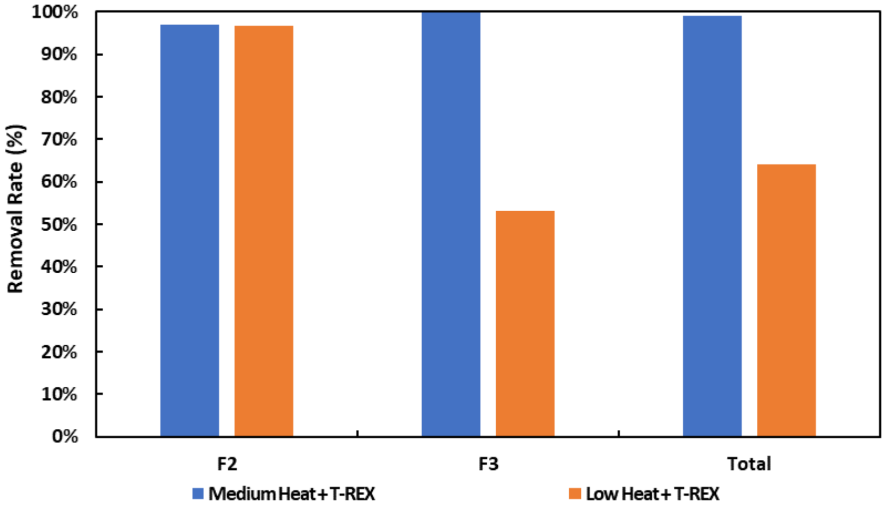

Fig 22. Removal rates of hydrocarbons (F2 and F3) in soils before and after the stimulators-assisted thermal treatment under medium and low heat conditions.

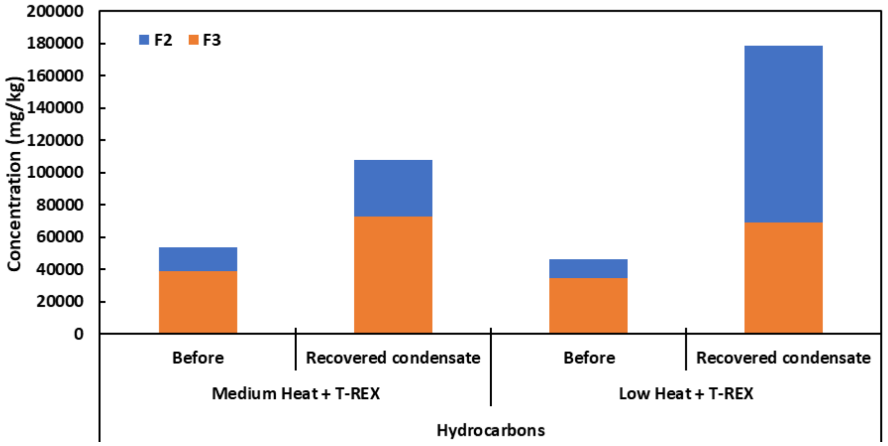

Fig 23. Hydrocarbon (F2 and F3) concentrations in soils before the stimulators-assisted thermal treatment and recovered condensates under medium and low heat conditions.

4. CONCLUSIONS

Through this project, multi-functional stimulators for in-situ application were developed, the developed stimulators and their application method were evaluated in the aspects of heat generation as well as hydrocarbon remediation efficiency, and the specially designed ex-situ prototype for application of the proprietary stimulators (T-Rex®) was validated in remediation of heavy hydrocarbons (crude oil) in soil.

The developed stimulators were successfully activated at low heat temperature (< 150 °C) and effectively generated additional heat through their exothermic chemical reactions in the lab-scale in-situ application, resulting in maximum soil temperatures in a range of 280 °C to 670 °C depending on soil conditions. In a separate test, it was confirmed that the developed stimulators were stable in the presence of soil moisture until they received proper heat temperature. The generated heat and other mechanisms, such as hydrocracking and oxidation, through the chemical reactions were able to effectively degrade hydrocarbons in soil. The remediation efficiency was 88 – 93 % in F2 and F3 hydrocarbons under 5 % hydrocarbon contamination and 10 – 12 % soil moisture conditions. However, heat generation and remediation efficiency through exothermic chemical reactions of the stimulators can be influenced by soil properties, such as moisture content and pore sizes, that influence available oxygen content in soil pores. The test results have shown that oxygen content can be one of limiting factors in the exothermic chemical reactions.

The lab-scale in-situ electrokinetic/electrochemical (EK/EC) treatment that was employed as the subsequent remediation method to further reduce the residual hydrocarbon after the stimulator assisted in-situ application, showed 47 – 50 % removal of total hydrocarbons (C10 – C34) 28 days after the onset of the direct electric current application. This result indicates that the integrated in-situ remediation system comprising the stimulator assisted thermal treatment and the subsequent EK/EC treatment will greatly enhance the remediation efficiency with low energy consumption. The contaminated soils can be primarily treated by the stimulators assisted in-situ remediation method in a short-term period (~ 30 minutes) then residues in the treated soils can be further remediated by the subsequent in-situ EK/EC remediation approach in a long-term period (~ 4 weeks). Higher removal rate is expected with application of the EK/EC treatment for a longer period since the prior studies show the greater reduction of hydrocarbons with a longer application time.

The effectiveness of the proprietary stimulators (T-Rex®) and the specially designed ex-situ prototype for their application was successfully verified to reduce heavy hydrocarbons such as crude oil in soil. The treatability test results have confirmed that the ex-situ remediation system was effective in extracting heavy hydrocarbons (F2 - F4+) present in soil and recovering light hydrocarbons (F2 - F3), which indicates that activation of the stimulators can crack the chemical bonds of the long-chained hydrocarbons. Both qualitative and quantitative results indicate that heat temperature over 400 °C is demanded to remediate relatively heavier hydrocarbons (> F3) and to enhance recovery of light hydrocarbons.

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.

In addition to the oxygen content in soil, influencing distance of remediating process induced by the exothermic chemical reactions of the stimulators, needs to be further investigated as higher reduction at the proximity of the stimulator layers has been observed in a series of lab-scale tests. With understanding of the influencing distance, multiple layers of chemical stimulators can be employed to enhance remediation efficiency and minimize contaminant residues after the stimulator assisted in-situ application.

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 lab-scale ex-situ prototype tests have demonstrated that the proprietary stimulators (T-Rex®) and the specially designed prototype for their application were effective in degrading heavy hydrocarbons and recovering light hydrocarbons. The recovered and re-condensed light hydrocarbons can be used as fuel to supply heat for the remediation system. Moreover, in pilot scale ex-situ prototype, zero emission can be achieved by recycling the generated gaseous components into a heat generator (e.g. boiler) which consequently produces additional heat for thermal treatment.

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