

## **EXPERIMENTAL STUDIES OF SELF-SUSTAINING THERMAL AQUIFER REMEDIATION (STAR) FOR NON-AQUEOUS PHASE LIQUID (NAPL) SOURCES**

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### **Abstract**

Self-sustaining Thermal Aquifer Remediation (STAR) is a novel technology that employs smouldering combustion for the remediation of subsurface contamination by non-aqueous phase liquids (NAPLs). Smouldering is a form of combustion that is slower and less energetic than flaming combustion. Familiar examples of smouldering involve solid fuels that are destroyed by the reaction (e.g., a smouldering cigarette or peat smouldering after a wildfire). In STAR, the NAPL serves as the fuel within an inert, porous soil medium. Results from experiments across a range of scales are very promising. Detailed characterisation has focused on coal tar, a common denser-than-water NAPL (DNAPL) contaminant. Complete remediation is demonstrated across this range of scales. Visual observations are supported by chemical extraction results. Further experiments suggest that STAR can be self-sustaining, meaning that once ignited the process can supply its own energy to propagate. Costly energy input is reduced significantly. Comparison of large scale to small scale laboratory experiments, a volume increase by a factor of 100, suggests that STAR process efficiency increases with scale. This increase in efficiency results from reduced heat losses at larger scales while maximum the temperature achieved by STAR is unaffected. The research also demonstrates the controllability of STAR, where the termination of airflow to the reaction terminates the STAR process. The scale-up process provides important guidance to the development of full scale STAR for ex situ remediation of NAPL-contaminated soil.

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## Introduction

Nonaqueous phase liquids (NAPLs), such as chlorinated solvents, creosote, and coal tar, are a class of organic, hydrophobic compounds that are among the most frequently occurring, most hazardous, and most recalcitrant contaminants present in the subsurface throughout the industrialized world [1]. NAPLs typically occupy between 5% and 75% of the pore space in unconsolidated soils at sites where inappropriate disposal activities occurred. The remediation of land contaminated by NAPLs is a decades-old problem that no single solution has been able to address effectively [1-5]. Several different types of technologies have been developed to address this contamination. Some are successful in limited circumstances or at substantial cost [4,5]. In general, robust and cost effective solutions to highly recalcitrant compounds such as coal tar remain elusive.

The proposed NAPL remediation approach utilizes NAPL destruction by self-sustaining smouldering combustion. Combustion is the exothermic conversion of a carbon-based compound (i.e., fuel) to (primarily) carbon dioxide and water. Combustion of NAPL-contaminated soil is conventionally achieved by incineration, which utilizes 'flame combustion' (i.e., gasification of the fuel and burning in the gas phase). Incineration requires the continuous addition of energy and supplemental fuel, resulting in substantial treatment costs. In contrast, 'smouldering combustion' is the flameless burning of a condensed (i.e., solid or liquid) fuel that derives heat from surface oxidation reactions [6]. It generally burns through a wide range of temperatures, is oxygen deficient, spreads slowly and can infiltrate deep into a porous domain. It involves processes related to fluid flow, heat transfer and heterogeneous chemical reactions. Familiar examples of smouldering include a lit cigarette, smouldering polyurethane foam in furniture, and a peat fire; in all these cases the porous solid matrix is the fuel for the combustion reaction. STAR takes advantage of the ability of a liquid fuel to smoulder within an inert porous matrix (i.e., soil); the smouldering of liquids is relatively unstudied.

Many common NAPL pollutants, for example trichloroethylene (TCE), tetrachloroethylene (PCE), 1,1-dichloroethene (DCE) and coal tar, have theoretical heats of combustion comparable to that of wood and in excess of other wastes that are burnt successfully in other industries. When NAPL is embedded in soil, the soil acts as an insulator so as to conserve heat generated by the smouldering NAPL, which maximizes heat transfer to the unburnt NAPL. As a result, a single ignition can initiate a propagating, self-sustaining smouldering reaction through the contaminated soil pack without the addition of any outside fuel. Soil remediation is effected by the NAPL destruction that occurs in the process. The lack of ongoing chemical or energy addition and the absence of the need to treat recovered liquids suggest that STAR may be cost effective.

Self-sustaining thermal aquifer remediation (STAR) is a novel, patent-pending (UK Application 0525193.9 and International Application PCT/GB2006/004591) remediation technology that is being developed to use smouldering combustion to remediate NAPL-contaminated soils and sediments. In this paper, a select number of initial experiments are reported to demonstrate the potential of STAR. This paper focuses on the effect of scale as STAR proceeds from beaker to column to drum experiments as steps towards full field scale application.

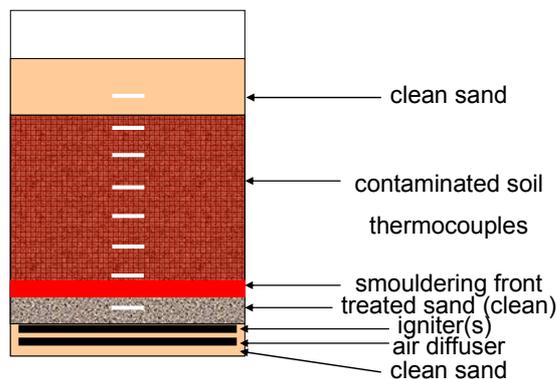
## Experimental

Coal tar, the focus of the experiments presented in this paper, is a common pollutant in the industrialized world and is typically found as a tarry waste at locations of former manufactured gas plants. Coal tar is a DNAPL that exhibits significant exothermic potential, relatively high viscosity and low-to-moderate volatility. Coal tar is a complex mixture of hydrocarbons that is formed as a by-product of coal refining processes. As each process is different, the composition of coal tar can vary widely. Common constituents include benzene, toluene, phenols and polycyclic aromatic hydrocarbons (PAHs), all of which are toxic and many of which may be carcinogenic.

For the beaker, column, and drum experiments presented, an artificial waste was employed to ensure homogeneity and reproducibility. Industrial coal tar (Coppers UK Ltd, UK) was thoroughly mixed with coarse sand (Leighton Buzzard 8/16, WBB Minerals Ltd, UK) in batches. For the beaker and column experiments, a single batch was prepared with target concentrations of 0.07 kg coal tar / kg sand for an

approximate saturation of 25% (resulting in a coal tar mass of 0.12 kg/m<sup>3</sup> of sample). For each drum experiment, three separate batches were combined, with a resulting saturation of approximately 19% (0.09 kg/m<sup>3</sup>).

Small and intermediate laboratory scale experiments were conducted in quartz glass beakers (Figure 1). The diameter of the beaker was 11cm and the height of the contaminated soil pack was 5cm, for a total volume of contaminated soil of 475cm<sup>3</sup>. The diameter of the column was 14 cm and the height of the contaminated sand pack was 10 cm, for a total volume of contaminated soil of 1040cm<sup>3</sup>. An air injection device was placed in the bottom of the apparatus and covered in a thin layer of clean sand. An ignition device was placed on top of the clean sand. The contaminated sand mixture was placed on top of the ignition device. The contaminated soil was covered with a final layer of clean sand. Thermocouples were placed at 1cm intervals along the centreline throughout the soil in the apparatus. This experimental setup is similar to those used to study smouldering in other disciplines [6].



**Figure 1.** Schematic diagram of experimental setup including soil packing and approximate equipment placement; thermocouple number and placement varied with experimental scale

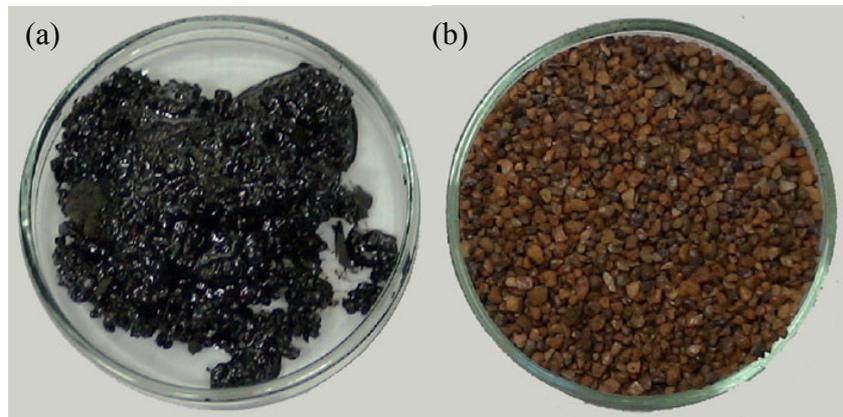
The 'drum' experiment was conducted in a 330L steel chemical drum (Greif UK Ltd, UK) with an outer diameter of 63.5cm, a height of 53cm and a total volume of contaminated soil of 163,000cm<sup>3</sup>. The drum was filled with 12.5kg of clean sand, followed by an air delivery device, then 12.5 kg sand, then the ignition device, followed by the coal tar/coarse sand mixture placed in 1kg increments. A removable ring was placed within the drum during the filling process to fill the outer 2cm with clean sand. Once emplaced, the soil was disturbed using tools to break up any large agglomerates that may have formed. Inconel sheath thermocouples (TC Direct, UK) were placed in the drum between batches initially in 1cm increments but increasing to 5cm increments as distance from the igniters increased. Once all of the contaminated sand was placed in the drum, 75kg of clean sand was placed to absorb any coal tar that might expand with heating as well as aid in filtration of any gas emissions.

In each experiment, air delivery was initiated and the ignition device was activated for a limited duration and then turned off. Temperature profiles at all thermocouples were recorded continuously to monitor the progress of the reaction front. The beaker and column experiments were run to completion (i.e., until STAR self-terminated due to no NAPL remaining). The drum experiment was terminated prior to completion, with the air injection terminated after approximately 360 minutes of operation.

## Results and Discussion

### *Extent of Remediation*

In the beaker experiment, the igniter (i.e., energy input) was active for 70 minutes, and the strong STAR reaction was observed to continue for an additional 30 minutes until it self-terminated due to an absence of fuel (i.e., NAPL). Figure 2 shows a representative sample of the contaminated sand before and after the experiment. The contaminated sand was completely remediated to the extent detectable by sight/touch/smell. Gas chromatographic analysis of heated dichloromethane extraction of all organic compounds from the soil confirmed that all coal tar compounds were reduced to below detection limits. This result was confirmed by more than 10 repeats of the beaker experiment.



**Figure 2.** Coal tar in coarse sand (a) before treatment by STAR and (b) after treatment by STAR

In the column experiment, the igniter was active for 95 minutes and the STAR reaction was observed to continue for an additional 55 minutes (and was demonstrated to be self-sustaining, as more fully described in the next section). The reaction self-terminated when all the NAPL was destroyed. Excavation of the column revealed completely remediated sand to the same extent as the beaker experiments. Dichloromethane extractions analysed by gas chromatography confirmed these results. Complete remediation was confirmed also by more than 10 repeats of the column experiment.

In the drum experiment, the igniter was active for 360 minutes and the STAR reaction was observed to continue for an additional 180 minutes. The reaction was demonstrated to be self-sustaining. The reaction terminated immediately when airflow was terminated, demonstrating the controllability of the STAR process. Visual inspection during the excavation process offered insight into the stages of the smouldering reaction at various locations throughout the field experiments. Excavation was carried out carefully to correlate the layers of material to the observed temperature profiles. Chemical analysis is pending.

The top layer of initially clean sand showed signs of coal tar expansion (Figure 3(a)). The sand below this 5cm layer appeared clean visually (Figure 3(b)). The reddish colour of the STAR-treated sand may be a result of oxidation of the iron that occurs naturally in this particular sand, a common observation in soils after wildfires [7]. Excavation to the igniters showed two clear paths surrounded by black charred coal tar and coarse sand, suggesting channelling may have been significant in this experiment (Figure 3(c)), an observation that verified the conclusions suggested by the thermocouple data (see next section).



**Figure 3.** Excavation of the prototype field experiments revealed a variety of materials that corresponded well to observed temperature profiles. (a) Incomplete smouldering was observed at the top of the clean sand cap, (b) cleaned sand was observed through the majority of the sand pack and (c) a cone of charred coal tar in sand with two channels of clean sand was observed in the 20cm space above the igniters.

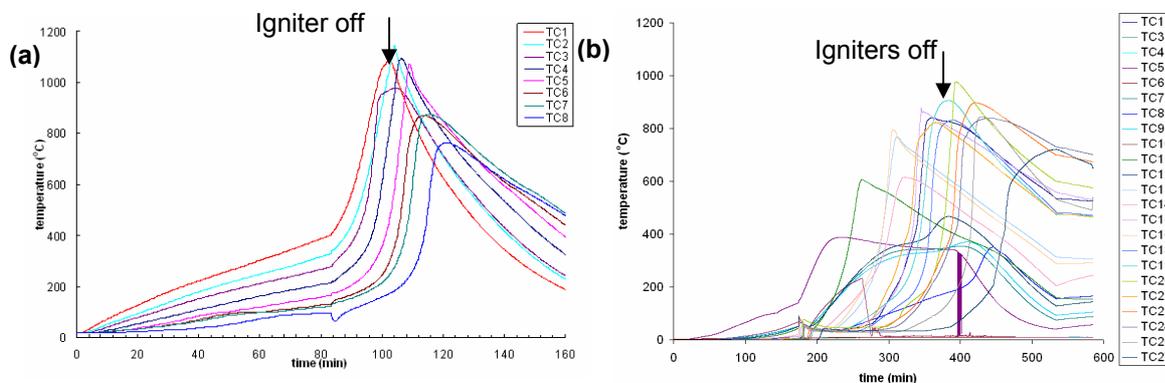
These observations suggest that manipulation of the STAR process by the airflow supplied to the smouldering reaction (e.g., decreasing airflow when the front appears to be accelerating and termination of airflow to stop the reaction) has the potential to be used as an operational control during field scale remediation.

### *Self-sustainability*

Typical STAR experiments have temperature profiles similar to the smouldering data shown in Figure 4. Temperatures at each location appear to follow a similar trend. Initially, temperatures increase slowly with time as the soil and coal tar heat endothermically. A sharp transition is observed where temperatures increase at a much faster rate as the STAR process initiates (i.e., NAPL ignition). The peak temperature is reached after ignition. The temperature declines from this maximum as the NAPL fuel is consumed at that location. Similar behaviour is observed at subsequent thermocouple locations as the smouldering front propagates through the contaminated sand pack.

The STAR process seems to become *self-sustaining* when the igniter is switched off and the observed temperatures continue to reach similar maximum values. Declining maximum temperatures may suggest that the reaction may reach extinction at some distance from the igniter. While complete remediation may be observed in the small scale experiment, the smouldering reaction may extinguish and complete remediation may not be achieved in an infinitely tall column of the same diameter. In the intermediate scale laboratory experiment, the smouldering reaction is self-sustaining (Figure 4(a)). The top thermocouple was placed in the clean sand region; a decline in observed temperature is expected at this point.

In the drum experiment, the igniters were turned off and peak temperatures were observed to rise as time and distance from the igniters increased, suggesting a stronger self-sustaining reaction (Figure 4(b)). The low initial and subsequent rise in peak temperatures compared to laboratory experiments suggests that initial smouldering may have been very close to extinction (insufficient airflow) but as distance from the igniters increases, the reaction may have grown stronger because of better mixing with air in the sand pore space.



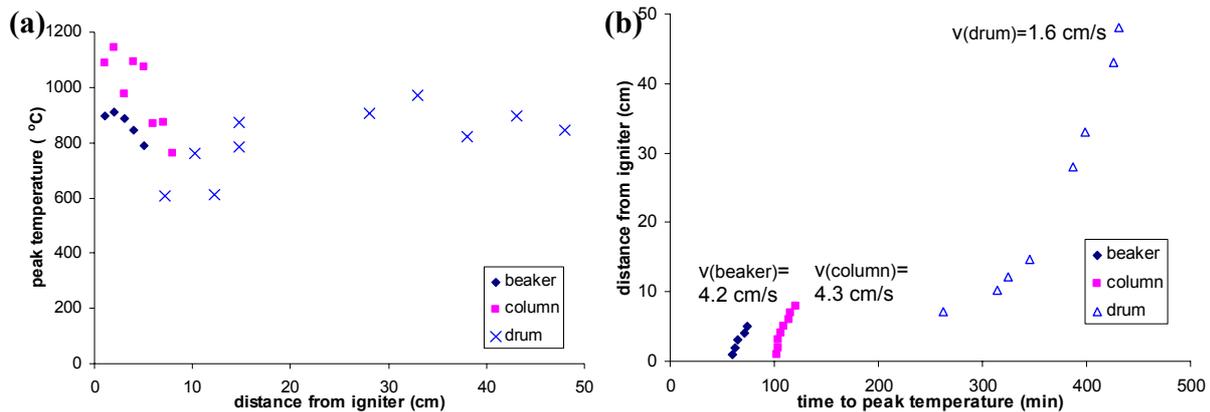
**Figure 4(a)** Smouldering profile of coal tar in coarse sand as observed in the column experiment and **(b)** Smouldering profile of coal tar in coarse sand as observed in the drum experiment

### *Observations and Repeatability of Experiments*

The beaker and column experiments were demonstrated to be highly repeatable, with consistent results across more than 10 trials each within measurement uncertainty. The drum experiment was repeated once. Similar trends were observed and no conclusions were contradicted between the two experiments. Initially, the smouldering reaction appeared to be sustained only slightly above extinction and then transitioned to self-sustaining smouldering as distance from the igniters increased.

The comparison of peak temperatures between the drum, column, and beaker experiments suggests that trends varied with scale (Figure 5). In the drum experiments, peak temperatures seemed to rise as distance from the igniters increased; however, the maximum temperature of all experiments was

observed in the column experiment (Figure 5(a)). Comparison of the times to reach the peak temperatures suggested that these trends were related to scale as well. If the airflow rate in each experiment is normalised by the area of the cylinder, the resulting oxidant darcy flux allows for some comparison. The average air velocity in the drum in the field experiments was significantly lower than those in the laboratory experiments, so the speed of the smouldering fronts are not expected to be similar. In the smaller scale experiments, the time to reach the peak temperature seems to be a linear function whereas in the drum experiment, the peak temperatures appeared to be reached faster as distance from the igniter increased (Figure 5(b)).



**Figure 5(a)** Peak temperature versus distance did not seem to vary according to scale **(b)** Propagation velocity of the smouldering front (distance from the igniter versus time to peak temperature) seemed to be affected by scale; the smouldering front appeared to accelerate with distance in the drum experiment.

These observations indicate that the smouldering front accelerated as distance from the igniters increased in the drum experiments and the smouldering reaction was self-sustaining. Because of the increase in scale, heat losses from the boundaries were not as significant as the laboratory experiments. Overall, the drum experiments demonstrate that the STAR process is more robust (i.e., less sensitive to precise timing, more sustainable, more energy efficient) at larger scales. The implications for a commercial field application are promising: as scale increases, the speed and thus efficiency of the STAR process may increase as well. The increase in scale may allow for successful operation at leaner airflow conditions and perhaps leaner contaminant saturations, both significant benefits for full scale remediation operations.

## Conclusions

Self-sustaining Thermal Aquifer Remediation (STAR) is a promising novel technology under development for the remediation of NAPL-contaminated soil. STAR has the potential to be implemented in both in situ and ex situ modes. Experiments focused on ex situ applications of STAR at three scales have demonstrated that smouldering combustion of liquid coal tar in an inert soil matrix is a real phenomenon and that it achieves remediation through NAPL destruction. Importantly, like a lit cigarette in an ashtray, the process is self-sustaining after a one-time ignition, suggesting a potential for substantial cost savings over energy intensive remedial techniques. Peak temperatures up to 1000 degrees C were observed at substantial distances from the ignition source well after it was extinguished. In addition, the experiments demonstrate that STAR can be terminated by the operator, providing confidence that the process can be controlled. Moreover, when allowed to run to completion, the process is observed to be self-terminating when no NAPL remained. Substantial heterogeneity is observed to induce channelling of the reaction in the drum experiments, and it is expected that better homogenization of the material and the process apparatus will reduce these effects. In all experiments, substantial volumes of soil contaminated with coal tar up to 25% of the pore space were qualitatively observed, and quantitatively verified, to be entirely

remediated. Furthermore, it was demonstrated that the STAR process increases in efficiency at larger scales due to a reduction of heat losses to the outside environment.

It is acknowledged that a number of issues remain before STAR is commercialized. Rigorous air monitoring for gaseous emissions is necessary, although significant cooling and filtering of emissions by the clean soil cap has already been observed. Characterisation and monitoring of emissions are underway. Further experiments are investigating the range and interrelationship of operating parameters including NAPL saturations, NAPL types, soil types, oxidant types, and the influence of heterogeneity. Current research includes prototype field scale demonstrations of STAR for ex situ treatment of coal tar-contaminated soil.

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