Self-Sustaining Treatment for Active Remediation (STAR): Overview of Scientific Principles and Initial Field Applications for the Treatment of Coal Tar in Soils

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Summary

This presentation will provide an overview of the scientific principles behind Self-Sustaining Treatment for Active Remediation (STAR), and summarize the five years of proof-of-concept research that has been successfully conducted to date. In addition, this presentation will provide the design and results of the first *in situ* STAR pilot study. The *in situ* pilot study involved the application of the technology at a former cresol manufacturing facility in New Jersey and was designed to test STAR at a large scale and under saturated conditions (i.e., below ground surface and below the water table).

Introduction

Coal tar contamination at manufactured gas plant (MGP) sites and hydrocarbon-impacted soils associated with the oil and gas industry are complex problems that only a handful remedies are capable of addressing in a cost effective and timely manner. STAR – based upon *in situ* smouldering combustion – is an innovative approach that has significant potential for the remediation of sites impacted by such non aqueous phase liquids (NAPLs).

Combustion is the exothermic oxidation of a fuel. In the case of a carbon-based compound, the products are primarily carbon dioxide, water, and energy. The combustibility of NAPLs is a characteristic that has been successfully exploited through the *ex situ* incineration of NAPLs and contaminated soil (Howell *et al.,* 1996). Incineration is achieved primarily via flaming combustion which involves the gasification of a fuel and its exothermic oxidation in the gas phase. Incineration of NAPLs by flaming combustion is energy inefficient (i.e., high heat losses); as a result, incineration requires the continuous addition of fuel and, often, supplemental energy.

Smouldering combustion, in contrast, is the exothermic oxidation of a condensed phase (i.e., solid or liquid) occurring on the fuel surface (Ohlemiller, 1996). Smouldering is limited by the rate of oxygen transport to the fuel's surface, resulting in a slower and lower temperature reaction than flaming (Rein, 2009). Importantly, smouldering can be self-sustaining (i.e., no energy input required after ignition) when the fuel is embedded in or itself a porous medium. Self-sustaining smouldering occurs because the solid acts as an energy sink and then feeds that energy back into the unburnt fuel, creating a very energy efficient reaction (Howell *et al.,* 1996).

NAPL smouldering is different from existing thermal remediation techniques. *In situ* thermal remediation requires the continuous input of energy in order to primarily volatilize and, in some cases, thermally degrade (pyrolize) and mobilize (via viscosity reductions) the organic phase. All of these processes are endothermic and remediation continues as long as externally supplied energy input is sustained throughout the NAPL-occupied porous medium. In contrast, NAPL smouldering has the potential to create a combustion front that (i) initiates at a single location with the NAPL-occupied porous medium, (ii) initiates with a one-time, short-duration energy input, (iii) propagates through the NAPL-occupied medium in a self-sustained manner, and (iv) destroys the NAPL wherever the front passes. NAPL smouldering is different from *in situ* combustion for enhanced oil recovery in that the latter is designed to generate heat and pressure that will mobilize the entrapped oil toward recovery wells. NAPL smouldering, in contrast, may benefit from avoiding the recovery (and thus treatment) of NAPL and/or water.

This work presents an overview of the scientific principles behind STAR, and summarizes the five years of proof-of-concept research that has been successfully conducted to date. Furthermore, the design and results of the first STAR pilot study, focusing on an *in situ* application of the technology at a former cresol manufacturing facility in New Jersey, will be presented.

Proof-of-Concept (POC) Experiments

Proof-of-concept (POC) laboratory experiments have been conducted at the University of Edinburgh and the University of Western Ontario over the course of the past five years to demonstrate the viability of STAR as a NAPL remediation technology. Summaries of these earlier studies are presented in Pironi *et al.* (2008) and Switzer *et al.* (2009). In addition, a pair of field experiments of STAR applied in an *ex situ* manner for the treatment of soil contaminated with both coal tar and mixed oily waste were completed in Summer 2008.

These experimental studies successfully demonstrated a number of key properties of the STAR process: (1) STAR requires only a short duration energy input (i.e., ignition) at a single location to initiate the reaction; (2) STAR is then self-sustaining, such that the reaction propagates itself through the NAPL without additional energy input, (3) STAR is self-terminating, such that the reaction naturally ceases when no NAPL remains, and (4) STAR avoids injecting costly fluids or conveying NAPL or contaminated groundwater to the surface for treatment. Further benefits of the technology that were identified during these studies include (5) STAR can be applied *in situ* or *ex situ*, (6) STAR is easily applied to the most recalcitrant compounds such as coal tars, heavy oils, and petroleum hydrocarbons (as they are the most exothermic), (7) very rapid clean-up is possible (~ 1 m per day), and (8) essentially non-detect total petroleum hydrocarbons (TPH) is observed in post-treatment soils.

As an example of the treatment efficiency of STAR, Figure 1 presents photographs of a coal tar contaminated sand before and after treatment for a STAR treatability study conducted at the ‘bin’ scale (treatment volume = 2.5 cubic meters). Pre-treatment concentrations of coal tar were on the order of 31,000 milligrams per kilogram (mg/kg) total petroleum hydrocarbons (TPH) (+/- 14,000 mg/kg), and post-STAR treatment concentration were approximately 10 mg/kg TPH (+/- 4 mg/kg). The visual appearance of STAR-treated soils and the level of contaminant destruction resulting from STAR as observed in this experiment is typical of most of the studies conducted at the Universities of Edinburgh and Western Ontario.

a)

b)

Figure 1: 'Before' (a) and 'after' (b) photographs of coal-tar impacted soil treated with STAR

In Situ Pilot *Test*

A pilot test to evaluate the efficacy of STAR to treat coal tar-impacted soils was conducted at a former cresol manufacturing plant in Newark, New Jersey. The test was conducted in a 9-foot fill unit overlying a peaty clay aquitard in a 20 foot by 60 foot pilot test area (PTA) located within the former lagoon area of the site. The PTA contains more than four feet of highly saturated and mobile coal tar located at the bottom of the fill unit, and was sectioned off from the rest of the site by sheet piling. The PTA was instrumented with thermocouples to track the combustion front and the surface was sealed with concrete to allow for vapour collection and treatment.

The objectives of the test were to 1) demonstrate STAR in the field under saturated conditions; 2) maintain self-sustaining smouldering combustion; 3) propagate the combustion front away from the ignition point; and 4) identify operation issues.

Ignition was achieved after approximately 25 hours of preheating (Figure 2). The observed temperature at the ignition well peaked at approximately 1340 degrees Celsius, then dropped off rapidly to near ambient temperatures (18 degrees Celsius) as the combustion front moved away from the ignition point.

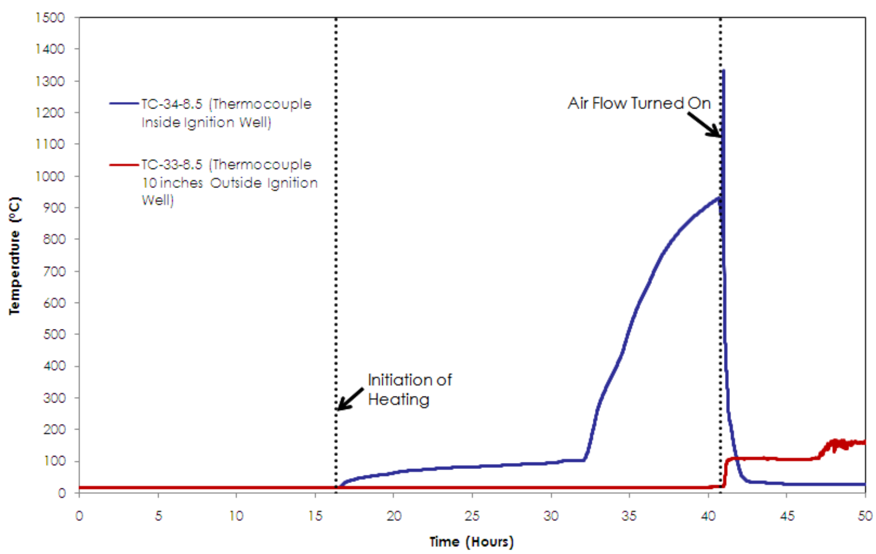

Figure 2: Thermocouple profiles demonstrating STAR ignition during the *in situ* pilot study

Figure 3 presents gas emissions data and an estimate of the mass of coal tar destroyed during the pilot test. The early time emissions data (i.e., prior to t = 88 hours) show the ratio of carbon monoxide to carbon dioxide concentrations decreasing as a function of time, demonstrating that the smouldering reaction is become more efficient as the reaction proceeds. Self-sustaining smouldering combustion was achieved below ground surface and below the water table (i.e., fully saturated conditions) and maintained for approximately 9 days. In total, a mass of between 200 and 350 kilograms of coal tar was destroyed during the test. In addition, the test was shown to be less sensitive to insufficient air flow than previously observed in laboratory testing.

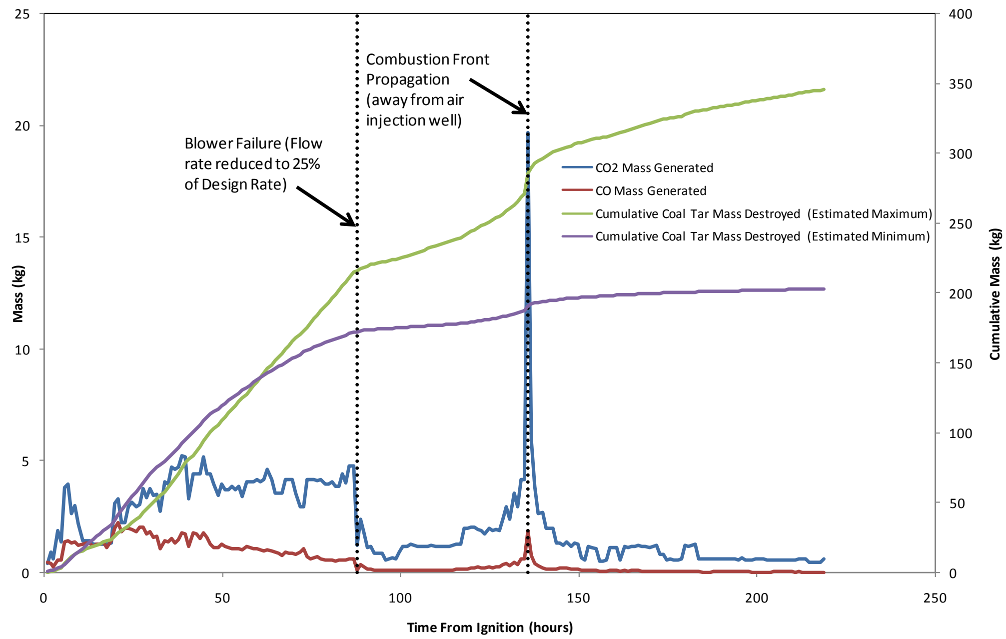

Figure 3: Air emissions data and estimate of coal tar mass destroyed during the pilot test

Conclusions

STAR has been demonstrated to be highly effective for the treatment of soils contaminated with recalcitrant compounds such as coal tar and petroleum hydrocarbons. Field pilot studies have identified important design considerations for both the *in situ* and *ex situ* applications of the technology. STAR is also cost effective, by taking advantage of the low energy requirements of the smouldering combustion process and by avoiding the need to inject viscous amendments (e.g., electron donor, chemical oxidants) or recover water or NAPL for subsequent above ground treatment. We are actively developing collaborations with industry for additional in situ and ex situ pilot trials.

Acknowledgements

We would like to acknowledge the support of John Vidumsky at DuPont Corporate Remediation Group regarding STAR technology development. Smouldering combustion of liquids as a remediation concept is pending patent approval (UK Application 0525193.9, PCT Application PCT/GB2006/004591, and National Phase applications filed (e.g., USA 12/086323 and Europe 06820460.1; priority date 10 December 2005)).

References

Howell, J.R.; Hall, M.J.; Ellzey, J.L., 1996, Combustion of hydrocarbon fuels within porous inert media: Prog. Energy Combust. Sci., 22, 121–145.

Ohlemiller, T.J., 1996, Modeling of smouldering combustion propagation: Prog. Energy Combust. Sci., 11, 277–310.

Pironi et al,, 2009, Small-Scale Forward Smouldering Experiments for Remediation of Coal Tar in Inert Media: Proceedings of the Combustion Institute 32 (2), pp. 1957-1964, doi:10.1016/j.proci.2008.06.184.

Rein, G., 2009, Smouldering Combustion Phenomena in Science and Technology: International Review of Chemical Engineering 1(1), pp. 3-18.

Switzer et al., 2009, Smouldering combustion: A novel remediation process for non-aqueous phase liquids in porous media: Environmental Science and Technology, 43, pp. 5871–5877.