

REMEDICATION OF FLARE PIT SOILS USING SUPERCRITICAL FLUID EXTRACTION

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Many sites are contaminated with petroleum hydrocarbons (PHCs). In some cases, these PHCs may be biorecalcitrant and therefore the soils contaminated with these PHCs are not amenable to remediation by biological treatment methods. Examples of sites containing biorecalcitrant PHCs are old flare pit sites. Flare pits are earthen pits that were once used for the storage and disposal of natural gas and crude oil wastes. Alberta's oil patch contains thousands of flare pits that need remediation and reclamation. At some sites, the soils in and around these flare pits are highly contaminated with biorecalcitrant PHCs that current remediation technologies such as bioremediation and, more rarely, composting, may be limited. Remediation of sites containing high concentrations of biorecalcitrant petroleum hydrocarbons (PHCs) is usually performed by means of excavation and landfilling. New, more effective treatment technologies are therefore being investigated to treat these types of soils.

Supercritical fluid extraction (SFE) is a potential treatment technology for the remediation of flare pit soils. This research focuses primarily on the use of a laboratory scale SFE system to investigate the extraction of PHCs from contaminated flare pit soils at various temperatures and pressures ranging from 40°C to 80°C and 9 MPa to 19 MPa, respectively. Preliminary experiments using flare pit soils obtained from sites across Canada are currently underway. The effects of pressure, temperature and extraction time on the extraction efficiency of the process will be investigated. It is anticipated that the highest supercritical fluid (SCF) density will yield the best extraction efficiency. Since the flare pit soils under investigation are aged and weathered soils, the effect of longer extraction times on the extraction efficiency will also be studied. The obtained results will allow the identification of optimum conditions for the SFE extraction. These results will provide the necessary information for potentially developing SFE as a fast and effective technology for remediation and decommissioning of flare pits in Alberta and elsewhere in Canada.

INTRODUCTION

Several thousand flare pits exist in Alberta [1]. These flare pits are the earthen pits that were used to store and burn off waste/fluids produced during crude oil and petroleum processing. As of December 1996, the provincial government of Alberta has banned the use of these flare pits, and have requested that the oil and gas industry remediate former flare pit sites. Of the flare pits in Alberta, it is believed that most are decades old with certain ones being 20-30 years old, since drained and buried [1]. The soil present in these weathered flare pits have a high degree of partitioning of PHCs to the soil organic carbon, which reduces the solubility and hence the degradability of these hydrocarbons. The binding of PHCs to the soil is largely influenced by the nature of the soil (textural class and organic matter content, for example). Flare pit soils have irregular consistencies in terms of texture and porosity, and some are impacted with inorganic co-contaminants such as heavy metals and brines. Flare pit soil may contain high molecular weight hydrocarbons and recalcitrant compounds that are not

easily biodegradable. The above-mentioned characteristics of flare pit soils make them particularly difficult to remediate [2].

Very few studies dealing with the remediation of flare pit soils have been published. Technologies currently being used to deal with contaminated flare pit soils include excavation followed by landfilling, thermal treatment, bioremediation and composting. Both excavation followed by landfilling and thermal treatment can be implemented relatively quickly, but they can be costly. In the case of thermal treatment, the process may adversely affect the quality of the soil. For example, Catalan *et al.*[3] found that, after thermal treatment, the treated soil contained high levels of salts and had a very low pH, indicating production of acidic compounds during the treatment process. In addition, thermal treatment may lead to the formation of toxic air contaminants that require treatment before release to the atmosphere [3]. With respect to bioremediation and composting, although these processes have the advantages of being non-invasive and relatively cost efficient, both technologies may be slow and time-consuming. Chaw and Stoklas [4] found that after nine months of composting, the levels of petroleum hydrocarbons in the flare pit soil were still higher than regulatory limits. The composted soil was also more sodic and saline, thereby rendering it unsuitable for reclamation or revegetation [4].

Also, flare pit soils are believed to contain predominantly heavy PHCs (i.e. n-alkanes ranging from C₁₆ to greater than C₅₀). These heavier PHCs have low water solubilities and are often bound strongly to the soil matrix [5], thus reducing their bioavailability and consequently their biodegradation. In addition, the physical and chemical properties of the flare pit soils, the composition of the contaminated crude oil and the composition of the soil micro flora also influence the bioremediation process [6]. The ability of microbes to degrade hydrocarbons is restricted to certain species, or strains within species [6]. Moreover, the bioremediation process is difficult to monitor and control, reliable cost and performance data have been difficult to obtain, and the bioremediation process can take anywhere from several months to many years [7]. Thus, there is a need to develop fast, cost effective, alternative techniques for remediation of contaminated soils.

Supercritical fluid extraction (SFE) is currently being investigated as a solvent extraction process for the remediation of contaminated soils and may potentially be applicable to the remediation of flare pit soils. Various studies have investigated the use of SFE process for removing toxic organic compounds from contaminated soils. SFE has been used to recover and measure the extraction efficiencies of petroleum hydrocarbons (PHCs), polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs and dioxins), phenols, chlorinated phenols, metals, and many pesticides and herbicides from contaminated soil, sediment and other environmental matrices [8, 9, 10, 11, 12, 13, 14]. Most of the studies on the extraction of PHCs using supercritical carbon dioxide (SC CO₂) have been conducted using spiked soils. Few research studies have been published related to the extraction of PHCs from real contaminated soils [14, 15, 16].

The objectives of this research are therefore to investigate, on laboratory scale, the ability of SFE to remove heavy PHCs from flare pit soils. Through conducting a number of extractions at different conditions of temperature (40°C to 80°C), pressure (8.9 MPa to 19 MPa) and mixing speed (100rpm to 500rpm), this research will help identify the optimum conditions for remediating flare pit soils. Preliminary experiments using flare pit soils obtained from sites in province of Alberta, Canada are currently underway. The effects of pressure and temperature, soil type and extraction time on the extraction efficiency of the process are being investigated.

MATERIALS AND METHODS

Chemicals

Chemicals used in this research include diesel oil, SAE 10-30W motor oil, n-decane, hexadecane, tetratriacontane and pentacontane. These chemicals are used to prepare calibration standards for gas chromatograph (GC) analysis using a GC equipped with a flame ionization detector (GC/FID). In all sample preparation, toluene is used as the solvent.

Soils

The flare pit soils being investigated in this research were collected from two sites located in the province of Alberta (Canada). The collected soils were transported to the Department of Civil and Environmental Engineering at the University of Alberta where they were homogenized and sieved (2mm sieve). The prepared soils were then stored at 4°C prior to use. Sub-samples from each soil were analyzed and their properties are summarized in Table 1. According to the data shown in Table 1, the electrical conductivity (EC) for Soil 2 exceeds the Canadian Soil Quality Guidelines [17]. For both Soil 1 and Soil 2, the PHC content exceeds the required soil quality criteria as per the Canada Wide Standards of Petroleum Hydrocarbons in soil in an industrial area [18].

Table 1. Characterization of Flare pit soils (FP soil) being investigated

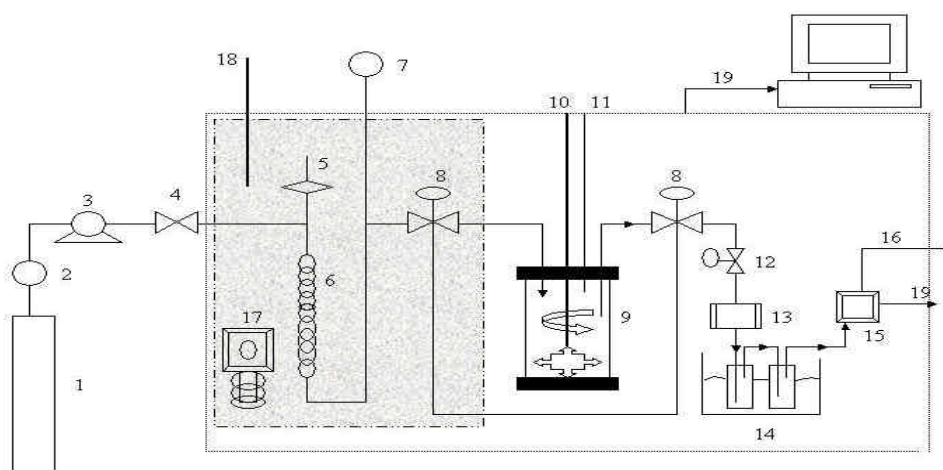
PARAMETER	SOIL 1	SOIL 2
<i>Particle Size Distribution</i>		
Sand (>50µm) (% w)	95.57	41.94
Silt (2-50µm) (% w)	0.17	43.94
Clay (<50µm) (% w)	4.27	14.12
<i>Soil Type</i>	sand	loam
<i>Electrical Conductivity (EC) (dS/m)</i>	3.249	5.67
<i>Sodium Adsorption Ratio (SAR)</i>	3.31	10.47
<i>Petroleum Hydrocarbon Content (PHC)*</i>		
F2 (C ₁₀ -C ₁₆) mg/kg	3300	19000
F3 (C ₁₆ -C ₃₄) mg/kg	17000	64000
F4 (C ₃₄ -C ₅₀) mg/kg	12000	34000

* as defined in [18]

Experimental setup

Figure 1 provides a schematic of the lab-scale SFE apparatus. Two ISCO 500D syringe pumps, operating in continuous mode, are used to pressurize the CO₂. A 300 mL stainless steel extraction vessel (Autoclave Engineers, Division of Snap-Tite Inc., Pittsburgh) contains the contaminated soil. The extraction vessel is equipped with a MagneDrive™ mixing system and an insulated heating water jacket. The vessel is heated to the desired temperature by recirculating hot water (maintained at required temperature using a circulating water bath) through the insulated heating jacket. A thermistor probe and a pressure transducer (Omega) monitor the temperature and pressure of the system. Downstream of the extraction vessel, the SC CO₂ containing dissolved contaminants passes through UV-Vis detector (Gilson) that records absorbance at two different wavelengths. Following UV-Vis detector, the SC CO₂ is

depressurized through a heated metering valve. The contaminants are collected in two traps: the first trap containing glass beads and the second trap containing 10mL of toluene. The depressurized CO₂ then passes through a totalizer/mass flowmeter and is finally vented to the fumehood. Data from the pressure transducer, flowmeter, thermistor probe, UV-Vis detector, and the pumps (both flow and pressure) are recorded by a computer using LabView™ software (National Instruments).



LEGEND

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|-----------------------------|-------------------------------------|--------------------------------------|
| 1. CO ₂ cylinder | 8. Three way Ball valve | 14. Traps (in ice water bath) |
| 2. Filter | 9. Extraction vessel | 15. Mass-flowmeter/totalizer |
| 3. ISCO syringe pump | 10. Impellor (magnetic drive mixer) | 16. CO ₂ vent to fumehood |
| 4. Check valve | 11. Thermocouple | 17. Heated circulating water bath |
| 5. Pressure relief valve | 12. Heated metering valve | 18. Thermometer |
| 6. Preheating coil | 13. UV-Vis detector | 19. Data acquisition |
| 7. Pressure transducer | | |

Figure 1: Lab-scale Supercritical fluid extraction (SFE) apparatus

SFE Extractions

Experiments consist of placing the contaminated soil in the extraction vessel. The vessel is then pressurized and heated to desired pressure and temperature. The extractions include a 60-minute static extraction period followed by a 30-60 minutes dynamic extraction period. One static period and one dynamic period constitute one cycle. Most of the SFE runs will be performed in double cycle mode.

Prior to and following SFE extractions, the soil will be analyzed for F2, F3 and F4 PHC fractions. This analysis will be conducted in the Environmental Engineering laboratories, University of Alberta, using Soxhlet extraction followed by GC/FID analysis based on the Reference Method for the Canada Wide Standard for Petroleum Hydrocarbons in Soil - Tier 1 Method [5]. Extraction efficiencies will be considered reasonable if PHC levels are below regulatory limits as outlined in the Canadian Council of Ministers of the Environment (CCME) guidelines. Occasionally, soil obtained after SFE will be sent to the laboratory in the

Department of Earth and Atmospheric Sciences to determine certain soil properties. This analysis will identify if the SFE process alters the soil properties in any way.

Preliminary results

Preliminary experiments have been conducted to identify the amount of soil that can be placed in the extraction vessel. The amount of soil should be such that the soil can be adequately mixed and that extractions can be carried out successfully in a reasonable time. Experiments have been conducted with different amounts of contaminated soil (20g, 50g, and 100g of Soil 1) and at conditions of pressure and temperature of 12.41 MPa and 13.79 MPa, and 60°C, respectively. Based on visual observations of the extracts, results suggest that extractions can be carried out using 50g of soil. More experiments and quantitative analysis of the soil after extraction must be completed before definite conclusions can be made.

A few double cycle SFE extractions have been performed at pressure conditions of 12.41 MPa, 13.79 MPa and 15.17 MPa, and temperature conditions of 40°C and 60°C. The mixing speed was constant at 300rpm. Average percentage recoveries of the contaminants (g of PHCs) extracted during two 60minute dynamic extractions resulted in 85-96% extraction. Soil remaining in the vessel after extraction has yet to be analyzed for confirmation of these preliminary results.

FUTURE WORK AND ANTICIPATED RESULTS

Several extractions will be performed under different conditions of temperature and pressure, ranging from 40°C to 80°C for temperature, and from 8.9 MPa to 19 MPa for pressure. Each extraction condition will be repeated to ensure reproducibility. The temperature and pressure will be modified in order to determine the optimal extraction conditions, yielding the highest extraction efficiency.

In terms of the optimal temperature and pressure conditions, research suggests that the optimum conditions of temperature and pressure are those that lead to the highest density of the supercritical fluid. The high density will lead to a high solubility of the analyte in the SCF and hence a better extraction efficiency. The literature also states that the extraction efficiency increases with an increase in temperature due to an increase in the kinetics of desorption of the contaminant from the soil.

The properties that affect the SFE process include the type of soil matrix, its physical and chemical properties (e.g. porosity, pore size, particle size, water content), the type of contaminant and the extent of the contaminant's adsorption [19]. It is believed that of the soil types, clay has the strongest affinity for the organic contaminants followed by loam and silt [14]. The extraction from a porous matrix depends on the solid-fluid interface, the rate of diffusion/desorption of the analyte from the pores, and consequently on the diffusion of the analyte from the external surface of the particle to the bulk fluid [19, 20]. It is believed that soil with a smaller particle size will have larger surface area, and thus will have a stronger affinity for the contaminants. This affinity will result in a reduction of the amount of contaminant available to dissolve in the SCF and thus, a reduction in extraction efficiency of the contaminant. Cocero *et al.* [21] concluded in their study that a better extraction is obtained from the soil with bigger particle size because for the aged soil, pollutants are more strongly adsorbed on to the soil and the effect of particle size is not as important as bond forces. Since the flare pit soils being investigated are aged and weathered soils, it is anticipated that the extraction efficiency of PHCs from the sandy soil (Soil 1) will be higher than that obtained from the loam soil (Soil 2). Mass transfer limitations will also affect the extraction efficiencies [19, 20].

Based on the review of the relevant literature, it is expected that SFE will prove to be an effective method to remediate flare pit soils. It is anticipated that the results of this research will provide valuable insight into the applicability of SFE as a remediation technology for real contaminated soils. If SFE is able to effectively, quickly remove the contaminants from the flare pit soil, it is feasible that this technology could be developed into an effective and acceptable remediation technology for contaminated soils.

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REFERENCES

- [1] COOK.V.S, CHU, A., GOODMAN R. H. Water Air Soil Pollut., Vol. 133, **2002**, p. 297.
- [2] APRIL, T., FOGHT, J., CURRAH R., Canadian Journal of Microbiology, Vol. 46, **2000**, p. 38.
- [3] CATALAN, J.J.L., JAMALUDDIN M.K.A., MOORE, R.G., URSENBACH, MEHTA, S.A., Journal of Canadian Petroleum Technology, Vol. 37, **1998**, p.35.
- [4] CHAW, D., STOKLAS U., Compost Sci. Util., Vol. 9, **2001**, p.322.
- [5] CCME, Reference Method for Canada-Wide Standard for Petroleum Hydrocarbons in Soil-Tier 1 Method, **2001**, http://www.ccme.ca/pdfs/final_phc_method_rvsd_e.pdf.
- [6] BAHERI, H., MEYSAMI P., J. Hazard. Mater., Vol. B89, **2002**, p.279.
- [7] RISER-ROBERTS, E., Remediation of petroleum contaminated soils, FL, **1998**, 542 p.
- [8] LOW, K-C.G., DUFFY J.G., TrAC, Vol. 14, **1995**, p.218
- [9] LAITINEN, A., MICHAUX, A., AALTONEN, O., Environ. Tech., Vol. 15, **1994**, p.715.
- [10] HAWTHORNE, S.B., LAGENFELD J.J., MILLER D.J., BURFORD. M.D., Anal Chem., Vol. 64, **1992**, p.1614.
- [11] LAINTZ, K.E., WAI, C.M., YONKER, C.R., SMITH, R.D., Anal. Chem., Vol., 64, **1992**, p.2875.
- [12] LEE, C.M., GONGAWARE, D., Environmental Technology, Vol. 18, **1997**, p.1157.
- [13] LEE, C.M., GONGAWARE, D., Environmental Technology, Vol. 19, **1997**, p.65.
- [14] ECKERT-TILOTTA, S. E., HAWTHORNE, S.B., MILLER, D.J., Fuel, Vol. 72, **1993**, p.1015.
- [15] HAWARI, J., HALASZA, A., BEIRUTY, A., SAS, I., TRA, H.V., Int. J. Environ. Anal. Chem., Vol. 66, **1997**, p.299.
- [16] HAWARI, J., BEAULIEU, C., OUELLETTE, D., PONTBRIAND, Y., HALASZ, A.M., VANTRA, H., Int. J. Environ. Anal. Chem., Vol. 60, **1995**, p.123.
- [17] CCME, Canadian Soil Quality Guidelines for the protection of Environmental and Human Health, **2001**, p.1.
- [18] CCME, Canada-Wide standards for Petroleum Hydrocarbons (CWS PHC) in Soil, **2001**, http://www.ccme.ca/assets/pdf/phcs_in_soil_standard_e.pdf
- [19] TOMASKO, D., Separation Science and Technology, Vol. 30, **1995**, p.1901.
- [20] HAWTHORNE, B. S., BOWADT S., J. of Chrom. A, Vol. 703, **1995**, p.549.
- [21] COCERO, J.M., ALONSO, E., LUCAS S., Ind. Eng. Chem. Res., Vol. 39, **2000**, p.4597.