

FULLY-CONTINUOUS SUPERCRITICAL FLUID EXTRACTION OF NAPHTHALENE FROM SOIL SLURRIES

M. Fortin, W. Stiver*

School of Engineering, University of Guelph, Guelph, Ontario, N1G 2W1
Canada

Email: wstiver@uoguelph.ca Fax: 1-519-836-0227

The research objective was to build a fully-continuous lab-scale supercritical fluid extraction process to remove naphthalene from soil slurries. Both the carbon dioxide and the soil slurry were pumped into an extraction vessel simultaneously and continuously for the duration of an experimental run. Delhi Loamy Sand spiked with approximately 10 000 ppm (wt) of naphthalene and water comprised the soil slurry. Carbon dioxide with no added modifiers was used as the supercritical fluid. The operating temperatures of the carbon dioxide remained constant at 43°C while the slurry temperature varied from 40 to 80°C. The pressure ranged from 5.61 MPa to 7.86 MPa. For most of the experiments a 0.3% soil content was used, but later experiments were as high as 7%. The mass transfer coefficients were as high as $4.6 \cdot 10^{-4} \text{ s}^{-1}$. These preliminary tests revealed that a fully-continuous SFE operation is possible and that with some optimization, a full-scale system would be feasible thus increasing the application of SFE not only in the extraction of contaminants from soil but also into other applications of SFE as well.

Keyword(s): supercritical extraction, fully-continuous, soil slurry

INTRODUCTION

Brownfield sites, contaminated soils and sediment are a significant global environmental challenge. Supercritical fluid extraction (SFE) offers the potential to treat sites with heavy oils, polynuclear aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and/or metal contamination. Once in the soil, these contaminants seep into the groundwater or are transported into the air. They can be absorbed by plants and vegetables that are then consumed. All of these transportation modes eventually result in human uptake of these dangerous contaminants. Stricter environmental laws are now forcing the cleanup of polluted sites.

Many research groups have and continue to study SFE for the purpose of soil remediation. Presently, SFE is costly and its operation is complex. Montero *et al.* computed the cost of SFE for naphthalene contaminated soil at \$120-\$150US/tonne [1]. The cost of landfilling, however, is about \$50US/tonne as long as the soil can be sent to a municipal landfill and the transportation costs are low [2].

The typical laboratory SFE soil set-up involves a batch system. Soil is loaded into the extraction vessel and then the supercritical carbon dioxide (SC-CO₂) flows through the system either continuously or in a batch-wise fashion. This makes it difficult and inconvenient to handle large volumes of soil. Laitinen *et al.* suggested that the reason why SFE equipment is in batch mode is because it is difficult to feed the solid material from ambient pressure to the high pressures required for the treatment [3]. It was proposed that making a soil slurry mixture and then continuously pumping it through a soil-fluid contactor would reduce the costs. Furthermore, Laitinen suggested that “a great leap forward in soil cleaning would be if an effective apparatus for continuous high pressure extraction of polluted soil could be developed” [3].

Until recently, water content was always seen as a big problem. Some researchers found that adding 10% water into the contaminated soil improved the extraction process but they also discovered any more than that hindered the process [3]. Reindl and Hofler also found that water in amounts from 1 to 10% (by weight) enhanced extractions [4].

Laplante demonstrated that extracting naphthalene from soil slurry using SFE (at water contents of 50%, 100% and 200%) performed just as effectively as from dry soil [5]. This fact led the way for the current research involving a continuous system with soil slurry.

The main objective of the research was to design, build and test a fully continuous laboratory scale supercritical fluid extraction process for removing naphthalene from soil slurry. This would make SFE for the purpose of soil cleaning less expensive and lead to potential implementation in the field.

MATERIALS

An Isco 500D Series syringe pump delivered the CO₂ in a continuous fashion and a 700 mL vessel was used. To avoid eroding the slurry pump and set-up, the sand component of the Delhi Loamy Sand was sifted out so that only the silt and clay component were used in the soil slurry mixture. The soil to water ratio in most experiments was approximately 0.0027 g_{ds}/g_{sl} or 0.3% but later experiments were as high as 7%. The naphthalene concentration in the soil was 10 mg_n/g_{ds}.

APPARATUS

Figure 1 is a schematic of the experimental set-up. A liquid CO₂ cylinder with a dip tube (1) supplied the CO₂ and the CO₂ passed through a 0.5-micron filter (2) to remove impurities before entering the pump (3), which pressurized the CO₂ to the operating pressure (5.86 MPa to 7.93 MPa depending on the experiment).

From the pump, a preheating coil (5) submerged in a waterbath at a temperature of 43°C heated the CO₂. The relief valve (4) acted as a safety device. A check valve (6) placed after the coil prevented back flow. The line then branched into two lines; one lead directly into the bottom of the vessel and the other line bypassed the vessel. Ball valves (7) allowed flow into or out of the vessel. Glass wool was placed in the carbon dioxide exit of the vessel.

A pressure transducer (9) was positioned in the line close to the exit of the vessel and a computer measured the pressure as well as the flow and pressure delivered by the carbon dioxide pump at a one-second interval. After the pressure transducer, the exiting CO₂ passed through a

heated needle valve (10) heated to 100°C to ensure that the contaminant didn't plug the valve. Following the needle valve, the carbon dioxide entered a cooled U-Tube (12) in a bath of acetone & CO₂ (11) (note: first experiments used an ice bath instead) where the naphthalene was collected and the flow was measured by a wet flowmeter (13).

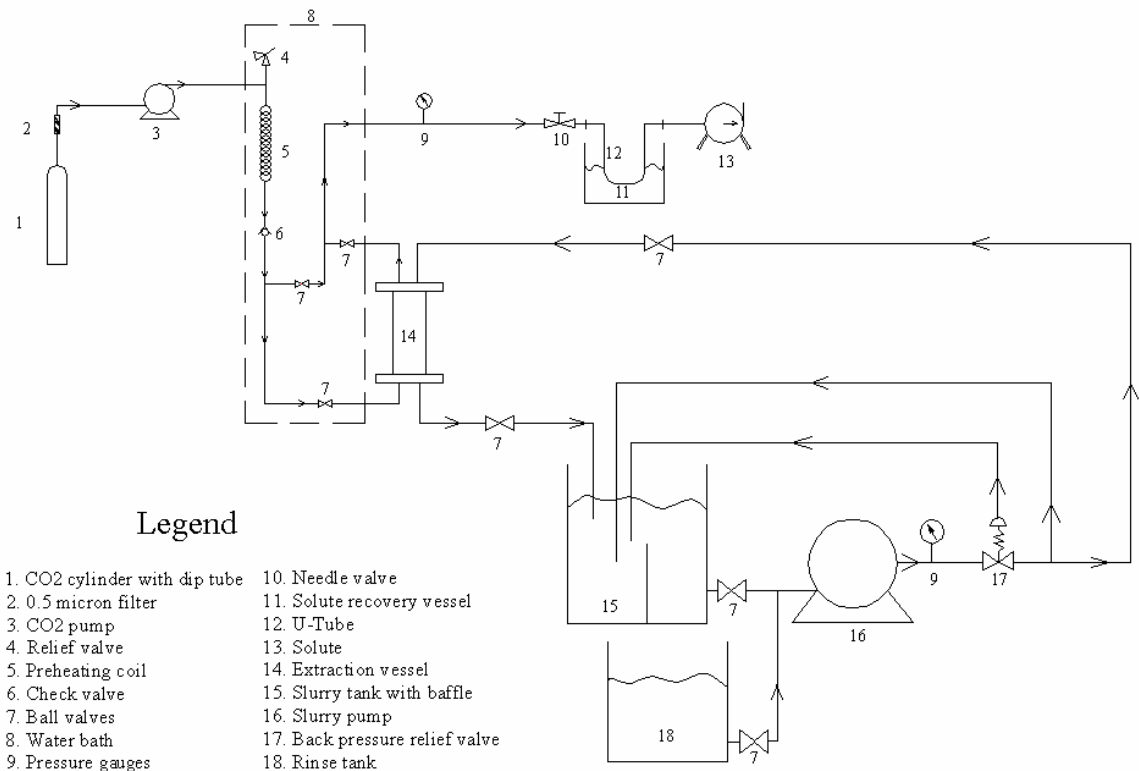


Figure 1: System Diagram

The slurry flow began with a slurry tank (15) as seen on Figure 1 that stored the slurry and a ball valve (7) allowed the intake flow into the high-pressure slurry pump (16). A pressure gauge (9) placed at the discharge of the pump allowed the adjustment of the backpressure relief valve (17) to the desired pressure. The backpressure relief valve redirected excess flow back into the slurry tank.

Next to the backpressure relief valve, a bypass line diverted a portion of the flow. The last line after the relief valve, equipped with a ball valve (7), was the actual feed line to the vessel. Inside the vessel, the slurry contacted the CO₂ and the slurry flowed out of the vessel and was returned to the slurry tank. The rinse tank (18) was used at the end of an experiment to purge the system of soil.

METHODS

The start up of experiments required several adjustments and this was done with running only water and CO₂ through the system. A flow balance was achieved by adjusting the pressure of the CO₂ and sometimes that of the slurry so that the system reached steady state. Once this balance had been reached, the soil was added to the slurry tank. The first U-Tube was replaced after 15 minutes of running the system and the others were removed after 30 minutes. The operating temperatures of the carbon dioxide remained constant at 43°C while the slurry temperature varied from 40 to 80 C.

THEORY/ANALYSIS

The calculation of the overall mass transfer coefficient ($K_{ox}a$) was computed using equations for a packed tower design. In the analysis of a packed tower, the calculations performed lead to a design length based on the following equation:

$$HTU_{ox} = \frac{z}{NTU_{ox}} \quad (1)$$

The HTU_{ox} is the height of transfer units (m), z is the height of the packed tower (m), and the NTU_{ox} is the number of transfer units (unitless). In this case, the height of the vessel was known. The number of transfer units was computed based on the inlet and outlet concentrations as well as from the estimate of the equilibrium relationship. The overall mass transfer coefficient, $K_{ox}a$ (s^{-1}) was computed using Equation 2 where L is the slurry flowrate ($m^3/m^2 \cdot s$).

$$K_{ox}a = \frac{L}{HTU_{ox}} \quad (2)$$

RESULTS AND DISCUSSION

A first level of success was reached since the two flows (SC-CO₂ and slurry) were pumped into the vessel and through the system in a continuous fashion. The system could be kept at steady state for as long as two hours and many times, the system was shut down due to time constraints as opposed to system failure.

The second level of success was that naphthalene was extracted from the soil as proven by a preliminary smell test, followed by gas chromatograph analysis. Six experiments were run and three of those were performed at low pressures (near critical) at around 6 MPa and the others were around 7.5 MPa. The first five experiments are in Table 1. The sixth experiment was performed differently and throughout the run, additional soil was added to the slurry tank and the results of this particular run are summarized in Table 2.

As seen in Table 1, the mass transfer coefficients were as high as $4.6 \cdot 10^{-4} s^{-1}$. These preliminary experiments proved that the balance of continuous flows between slurry and a supercritical fluid was possible and achievable.

In the first three experiments, the U-Tubes were placed in an ice bath and after performing a few calculations it was determined that a cooler bath would result in capturing more naphthalene. The average temperature of the ice bath was around $-4^\circ C$ whereas the acetone and CO₂ could get as cool as $-38^\circ C$, though the temperature was kept at around $-34^\circ C$. The first U-Tube in Experiment #4 (Exp #4) was run in an ice bath and the U-Tubes after that

were in an acetone bath. From Table 1, the effect of a cooler bath is clear and had a greater impact on the recovery and mass transfer coefficient than the increase in pressure.

Table 1: Summary of Results from Experimental Runs

	Exp #1	Exp #2	Exp #3	Exp #4	Exp #5
Average Pressure (MPa)	5.96	5.83	6.03	7.41	7.77
Soil content (g_{ds}/g_{sl})	0.0026	.0027	0.0027	0.0028	0.0027
Naphthalene removed (g_n)	5.12*10 ⁻⁵	2.74*10 ⁻⁵	3.36*10 ⁻⁶	5.10*10 ⁻³	1.52*10 ⁻²
K_{oxa} Range (s⁻¹) Ice bath	1.2–13*10 ⁻⁷	2.0–11*10 ⁻⁷	0.33*10 ⁻⁷	21*10 ⁻⁷	
K_{oxa} Range (s⁻¹) Acetone & CO₂ bath				0.96–2.6*10 ⁻⁴	0.75–4.6*10 ⁻⁴

Table 2: Results from the Experiment #6 with Increasing Soil Content

	Sample 1	Sample 2	Sample 3	Sample 4
Soil content (g_{ds}/g_{sl})	0.0028	0.027	0.027	0.072
Pressure (MPa)	7.78	7.75	7.79	7.2
Naphthalene removed (g_n)	1.50*10 ⁻³	4.28*10 ⁻²	4.13*10 ⁻²	2.18*10 ⁻²
K_{oxa} (s⁻¹)	3.7*10 ⁻⁴	1.5*10 ⁻⁴	1.5*10 ⁻⁴	5.4*10 ⁻⁵

Based on the results in Table 2, it appears that the extraction of naphthalene was dominated by the transfer of naphthalene from the water since with increasing soil content, there was a decrease in the percentage of naphthalene in the water. Further experiments with increasing soil content need to be performed in order to conclusively determine its effect on the extraction.

Although the set-up did extract naphthalene from soil slurries continuously, the mass transfer coefficients are not favourable to full-scale size up. Optimizing the vessel and improving mass transfer are required before a full-scale system is designed.

Conclusion

The ultimate success of this research was designing and constructing an SFE system capable of handling two continuous flows one of which was a slurry. In addition, the fact that the system did remove naphthalene from soil slurry and that mass transfer coefficients were as high as 4.6*10⁻⁴ s⁻¹ is an indication that after some optimizing, a full scale system might be feasible.

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Nomenclature

Subscript _{ds} – dry soil

Subscript _w – water

Subscript _n – naphthalene

Subscript _{sl} – slurry

NTU_{ox} – number of transfer units (unitless)

HTU_{px} – height of transfer units (m)

K_{oxa} – overall mass transfer coefficient (s⁻¹)

z – height of vessel (m)

L – slurry flowrate (m³/m²·s)

SFE – supercritical fluid extraction

SC-CO₂ – supercritical carbon dioxide

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