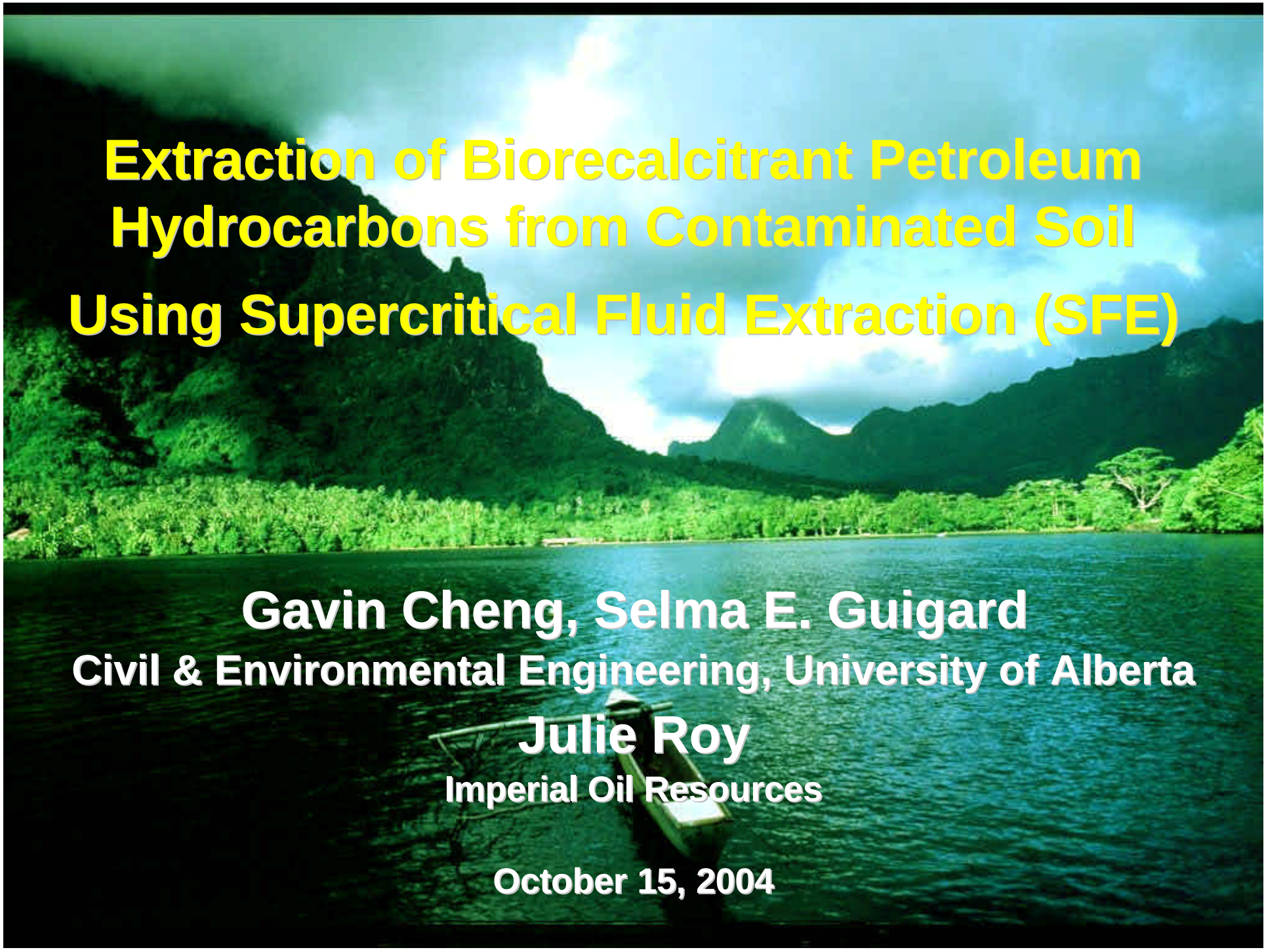

Extraction of Biorecalcitrant Petroleum Hydrocarbons from Contaminated Soil Using Supercritical Fluid Extraction (SFE)

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Outline

- Introduction
- Supercritical Fluid Extraction
- Objectives
- Materials and Methods
- Progress and Results
- Future Work

Introduction

- **Issue:**

  Flare pits were once commonly used to store and burn disposed petroleum hydrocarbons (PHCs) and other oilfield waste

  Migration of some of these compounds may contaminate the surrounding environment.

  Current remediation methods are not able to remediate these sites effectively and efficiently.

Introduction

(Alberta Environment, 2001)

Flare Pit

- Earthen pits
- 30,000 in Alberta
- Decades old (20-30 years)
- Operation of flare pits banned in 1996
- Both active and inactive sites require remediation

Contaminants

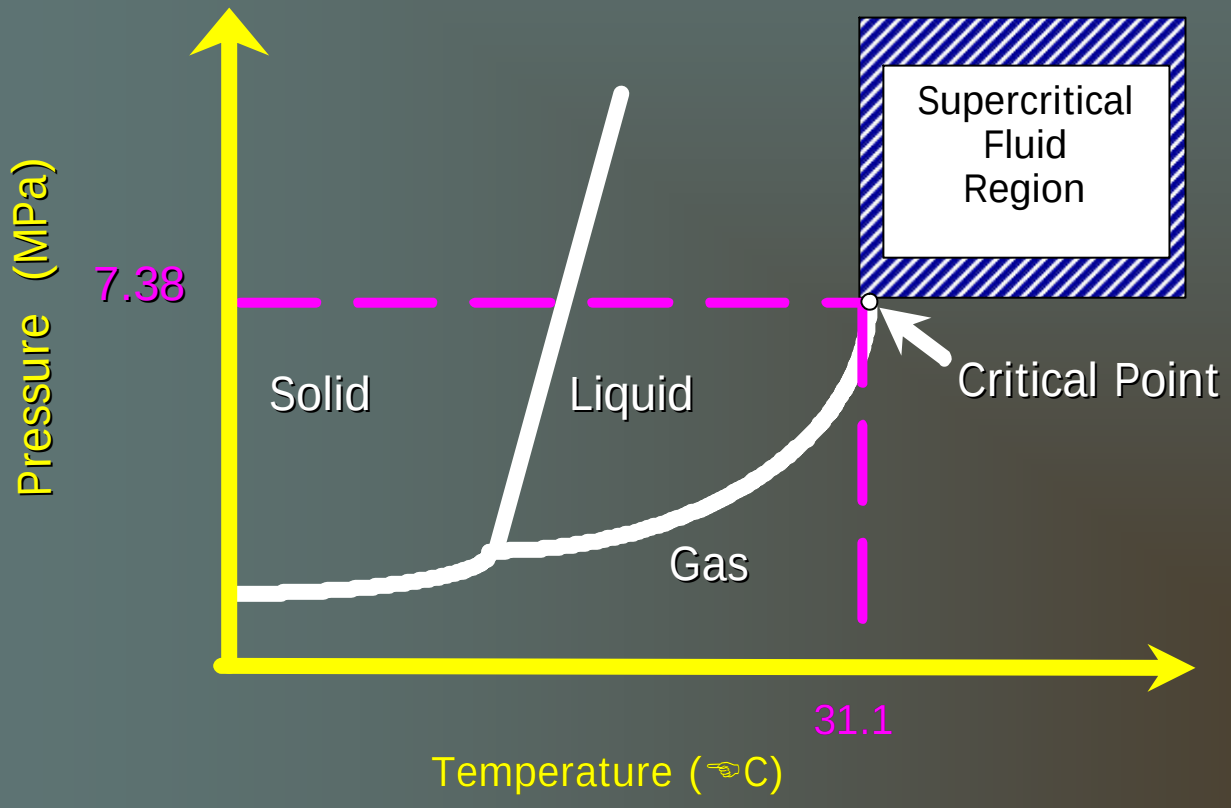
- P
- C
  p
  w
- F
  o

CCME (2001)	
Fraction	**Range**
F1 (C6 to C10)	Gasoline
F2 (C10 to C16)	Diesel
F3 (C16 to C34)	Lubricants
F4 (C34 to C50)	Tars, waxes

Current Remediation Methods

- Excavation / Landfilling
  - transportation, solid waste disposal, waste of natural resources
- Thermal Treatment
  - destroy natural organics, variable results, high cost
- Bioremediation and Composting
  - slow process, not effective for certain soils

Supercritical Fluid



Supercritical Fluid

- CO_2 has critical point of 31°C and 7.4 MPa
- Non-toxic, non-flammable, chemically inert, low cost, readily available
- High diffusivities, low viscosities and zero surface tensions
- rapid and effective matrix penetration

Supercritical Fluid Extraction

- Used extensively in food and other industrial sectors
- Rapid and effective matrix penetration and hence better extraction than conventional solvent extraction
- Previous studies showed promising results

Supercritical Fluid Extraction

- 95% diesel fuel removal from contaminated soil (Lee and Gongaware, 1997)
- Complete removal of C_{20} to C_{38} HCs at 15MPa and 40ºC (Lopez-Avila et al. 1992)
- 70-100% recoveries of aromatic fractions from crude oil in clayey-sandy soil at 22.7MPa and 80ºC (Morselli et al. 1999)

Supercritical Fluid Extraction

- Pilot-scale tests have shown that SFE can remove PCBs from contaminated sediments for $150 to $450 per tonne
- Economic analysis suggests that SFE for soil remediation will range from $60 to $300 per cubic meter
- The technology may be competitive if the cost is less than $200 per tonne under certain circumstances

Objectives

- Investigate the use of lab-scale SFE to extract PHCs from flare pit soils with supercritical carbon dioxide
- Identify the operating conditions that produce the highest extraction efficiencies across soils and hydrocarbon fractions.

Materials

Materials

- Flare pit soil samples

PARAMETER	FP1	FP2	Alberta Tier 1	
Particle Size Distribution				
Sand (>50µm) (%w)	95.57	41.94		
Silt (2-50µm) (%w)	0.17	43.94		
Clay (<2µm) (%w)	4.27	14.12		
Soil Type	Sand	Loam		
Electrical Conductivity (EC) (dS/m)	3.249	5.67		
Sodium Adsorption Ratio (SAR)	3.31	10.47		
Petroleum Hydrocarbon Content (PHC)			FP1	FP2
F2 (C_{10}-C_{16}) mg/kg	3300	19000	150	900
F3 (C_{16}-C_{34}) mg/kg	17000	64000	400	800
F4 (C_{34}-C_{50}) mg/kg	12000	34000	2800	5600

Materials

-
-

Methodology

- Contaminated soil sample is mixed with SC CO_2 at defined conditions in stainless steel extraction vessel in extended time during **static** mode
- Continuous flow of SC CO_2 carries the extracted PHCs from soil matrix to the outlet during **dynamic** mode

Methodology

- Extracted PHCs separate from SC CO_2 upon change in extraction conditions and contaminants are collected
- Cleaned soil sample is extracted again using Soxhlet extraction to obtain the residual PHC content
- The concentrated extract is analyzed by GC/FID to determine the residual PHCs in the cleaned soil sample

Methodology

- **Extraction Conditions**

Parameter	Level	
	High	Low
Temperature (^{o}C)	80	40
Pressure (MPa / psi)	24.1 / 3500	11.0 / 1600
SC CO_2 flow rate (mL/min)	30	10

Results (FP 1)

Temp.(oC)	Pressure (MPa)	Flow (ml/min)	% Extraction	F2% removal	F3% removal	F4% removal
Initial PHC content (ppm)				3000	17000	12000
Alberta Tier 1 Hydrocarbon guidelines (residential land use) (ppm)				150	400	2800
40	16.1	1	80	97	89	55
40	16	5	77	97	92	46
40	11.1	10	73	94	86	42
40	12.9		74	98	81	53
40	14.8		84	99	92	63
40	16.2		87	96	94	69
40	21.3		89	97	96	72
40	24.1		91	100	98	75
40	16.1	20	79	99	95	46
40	24.1		93	100	98	81
60	13.1	10	51	98	39	43
60	13.9		51	99	44	36
60	14.6		62	95	52	56
60	15.5		79	100	83	62
60	16		83	99	91	62
80	15.1	10	46	99	50	24
Equivalent Removal to meet Alberta Tier 1 Hydrocarbon guidelines				95	98	77

Results (FP 2)

Temp.(oC)	Pressure (MPa)	Flow (ml/min)	% Extraction	F2% removal	F3% removal	F4% removal
Initial PHC content (ppm)				19000	64000	34000
Alberta Tier 1 Hydrocarbon guidelines (residential land use) (ppm)				900	800	5600
40	14.7	10	62	98	69	14
40	15.4		69	99	79	28
40	24.1		82	99	95	40
60	24.1		71	100	80	28
Equivalent Removal to meet Alberta Tier 1 Hydrocarbon guidelines				95	99	83

Results

- Extraction efficiency is directly related to the solvent density
- Higher Pressure increases removal efficiency
- Higher Temperature decreases removal efficiency
- Best extraction conditions at 24.1 MPa and 40ºC

Results

- The effect of SC CO_2 flow rate on removal efficiency is not significant
- Higher SC CO_2 flow rate yield faster extraction
- Soil type affects extraction efficiency

Soil Type	% Extraction	F2% removal	F3% removal	F4% removal
Sand	89	100	98	81
Loam	80	99	95	40

Future Work

- Evaluate the effect of static and dynamic extraction mode which is related to solubility and desorption kinetics
- Evaluate parameters such as temperature, pressure, SC CO_2 flow rate, moisture content, mixing, and soil type
- Potential pilot-scale experiments

Conclusion

- Flare pits are hazardous to the environment
- Preliminary results show SFE is a potential treatment technology to remove PHCs from soil
- Analysis from literature suggests that SFE for soil remediation can be cost effective
- More engineering design and economic analysis are needed to advance the technology

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Questions ?
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