

# Heavy Oil Identification and Exploitation



Presented by Jean-Valery GARCIA

SPE London Evening Meeting

30<sup>th</sup> of April 2013



Society of Petroleum Engineers

# Acknowledgement

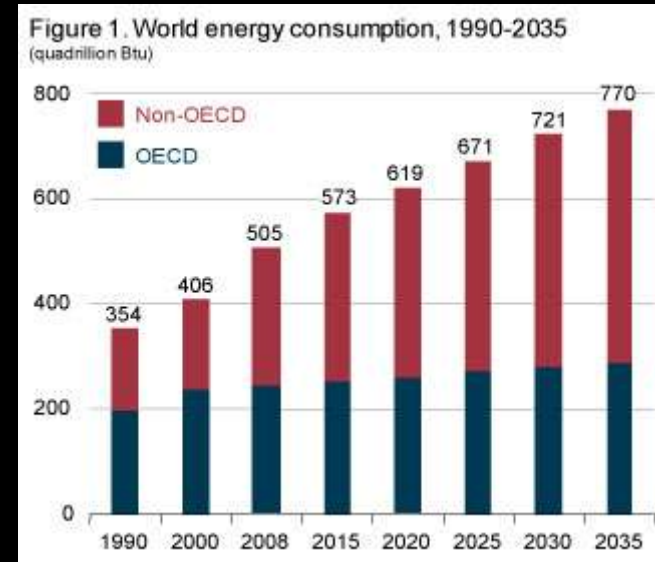
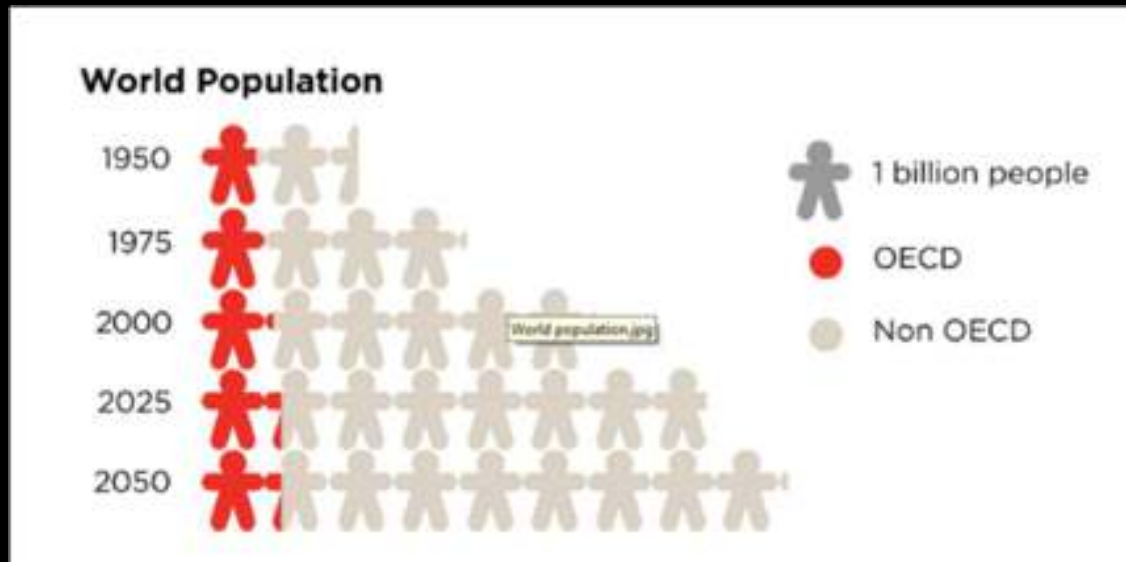
- Regi GIROUX - RG Consultant Chimie Inc (CANADA)
  - Francois OLLIVIER – Kirk Petrophysics UK
  - Scott PARKER – Kirk Petrophysics UK
  - Ony RATIANARIVO – Kirk Petrophysics Madagascar
- 
- TOTAL E&P

# INTRODUCTION



Society of Petroleum Engineers

# The need for Energy



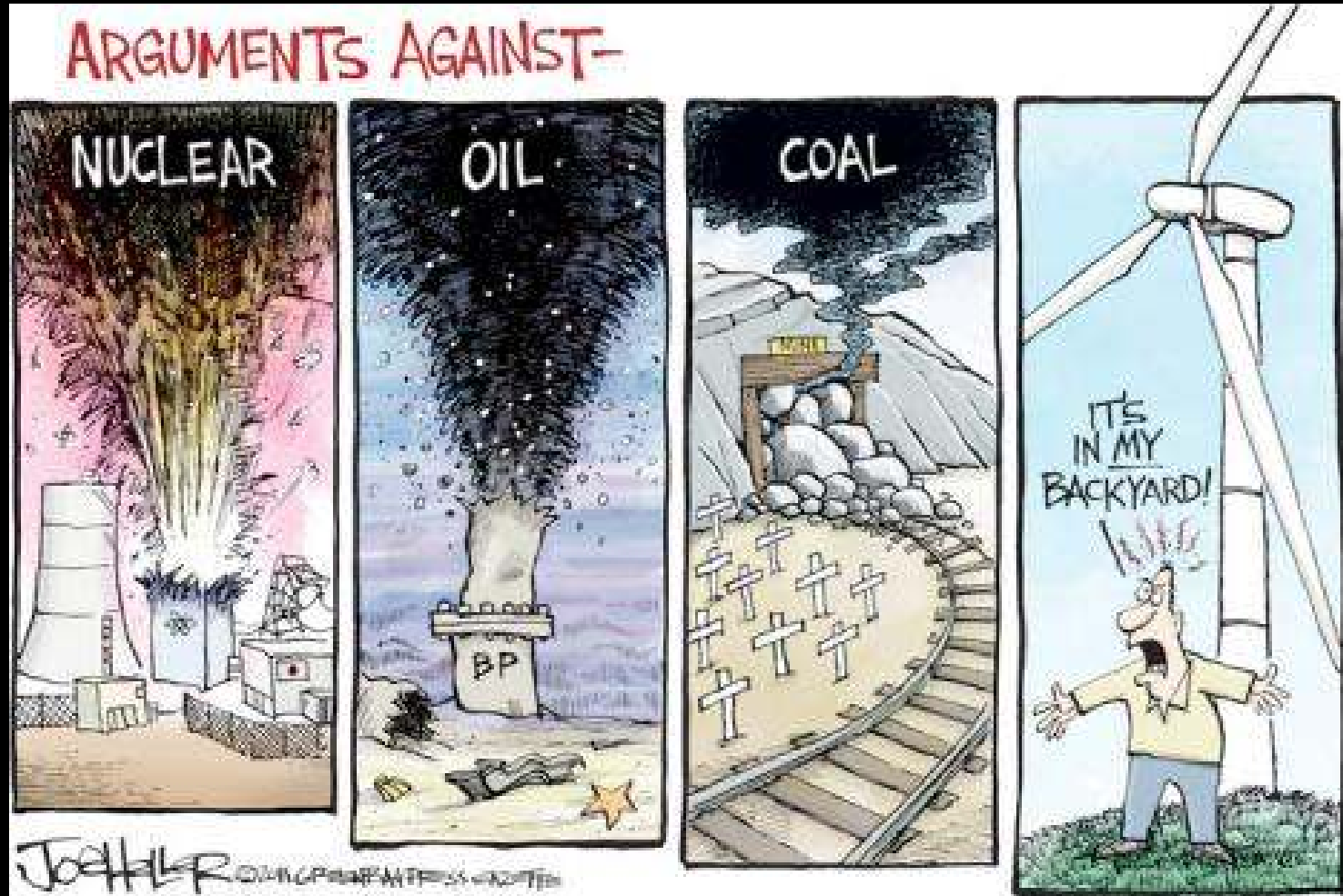
World Marketed Energy  
Consumption

Continued population growth – a Key driver for energy demand

Source: Shell Energy Scenarios to 2050

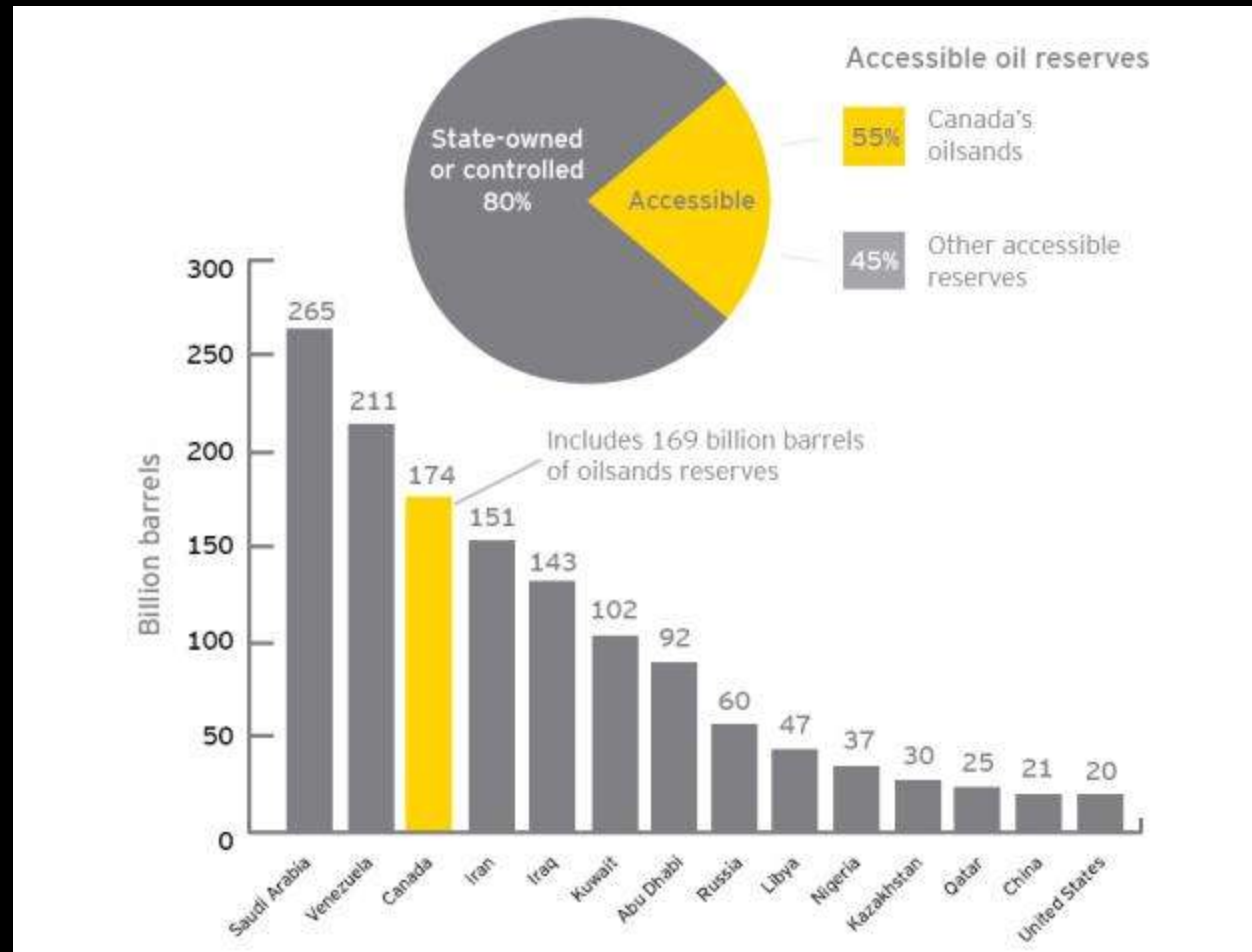
<http://www.eia.gov/forecasts/ieo/index.cfm>

# No impact free source of Energy



Today, all forms of energy are needed

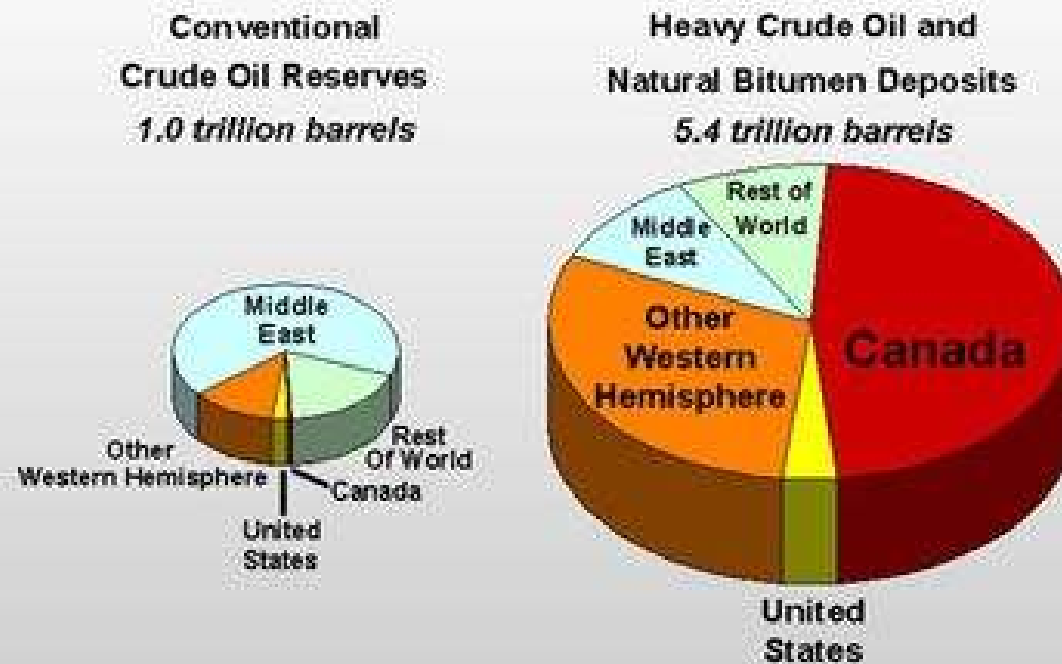
# Oil sands... a significant resource



## World oil reserves

Source: Oil & Gas Journal – Dec 2011

# Heavy Oil



**Figure 1. Worldwide Distribution of Conventional Crude Oil and Heavy Hydrocarbons**

# Summary



1. Dean Stark Method
2. Low field Nuclear Magnetic Resonance
3. Solid Phase Extraction Method (Cepsat™)
4. COMPARISON: The Dean Stark is reviewed as a comparison method to the CEPSat™.
5. A full Study has been carried out to define if it exists a common constant between oil sands samples tested

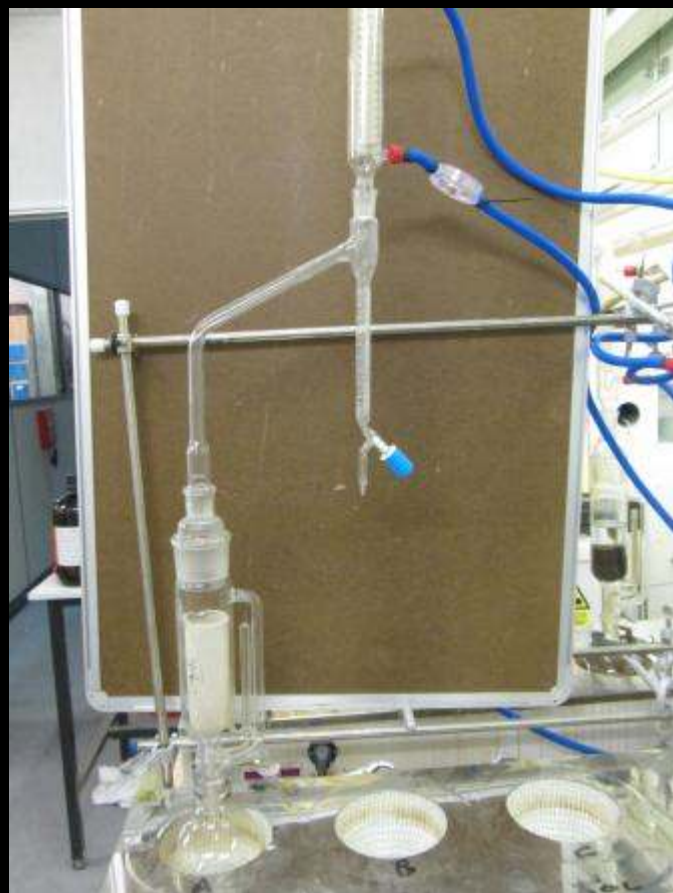




# 1. Dean Stark

- It is the most common most know method to the Canada Oil Sand industry
- The DS is a relatively large piece of equipment. A single DS occupies a fume hood space of approximately 20 x 20 cm including its heating mantle, water tubing, support stand and electrical cord.
- It would be normal for an Oil Sands laboratory in Canada to perform 200 DS per day. These would mostly be done by two different work shift of 12 hours. The laboratories would be equipped with 100 of these DS setup in their laboratory.

# DS apparatus



The sample to be eluted is first weighed before being placed in a cellulose thimble. Solvent (Toluene) evaporated from the heated flask passes through the outer wide-bore side tube and condenses onto the sample, and condenser. Water drop in the side arms.

An efficient extraction can take from 5 to 10 hours. As one night is required to dry the sample after the bitumen extraction, the total time for the analysis, starting from sample preparation to final data acquisition, takes around 24 hours.

**The water % is directly measured from what is collected on the side tube.  
Oil content can be obtained by difference or filter paper technique**

# Dean Stark - Video

VIDEO MISSING



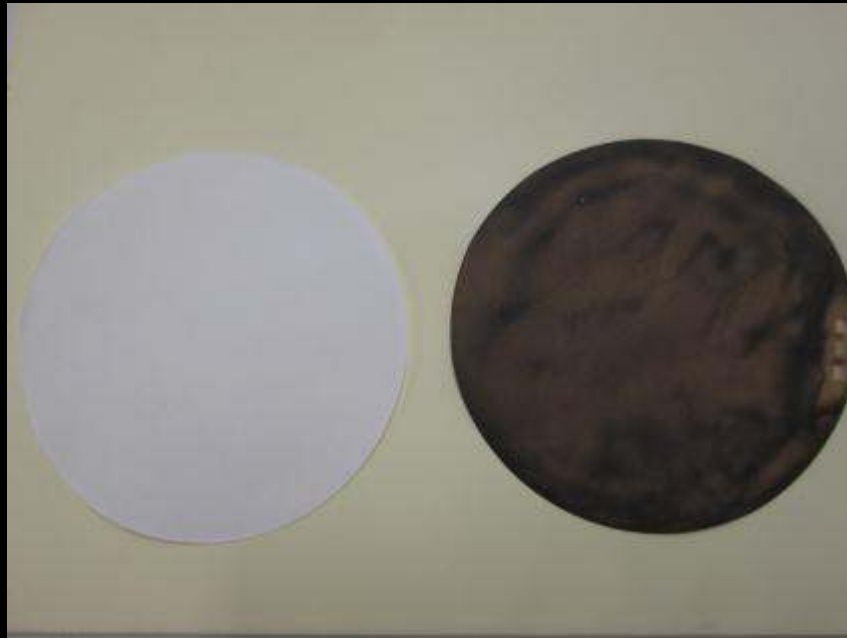
Method with the sample fully immersed providing a faster and more efficient cleaning

# Dean Stark

## *Filter Method*



- Flask of 250ml of mixed oil & Toluene
- 5ml of organic liquid poured into a weighed filter paper
- Mass of bitumen = 50 x increase in weight



# Example of Lab Setup with DS



Example: One side of the laboratory wall covering 50 DS – Picture also shows multi electrical outlets required



The other side of the same laboratory wall covering the remaining 50 DS – Picture also showing a large chiller required to cool down the multi condensers

# Example of Lab Setup with DS



Example of another laboratory with a 13 linear meter of DS fume hood – approximate cost of \$250,000 for this setup, include fume hoods.



Installation of DS in rows of three – A practice that has been stopped due to the high level of accident when handling the glassware

*Courtesy of ....*

## 2. NMR

### (Low field Nuclear Magnetic Resonance)

Use of such technique which is said to be fast, non destructive and inexpensive. BUT

- Correction are needed
- It cannot be used as a stand alone device
- Particle size analysis needed for the interpretation of overlap in bitumen and Water NMR signal
- Technical personnel require
- Does not recover the oil as DS or CEPSat

# 3. CEPSat™

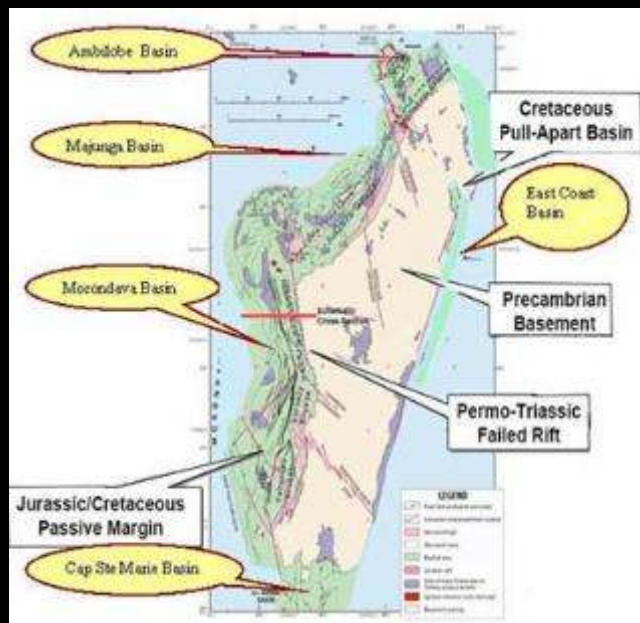


Society of Petroleum Engineers



# Background

- Technique was initially introduced by TOTAL E&P for an heavy oil project onshore.
  1. ASE method (Accelerated Solvent Extraction)
  2. SPE method (Solid Phase Extraction)



17,000 tests were done against 800 DS on 16,000m of core recovered (8000m sampled) (18 months project)

Location Madagascar

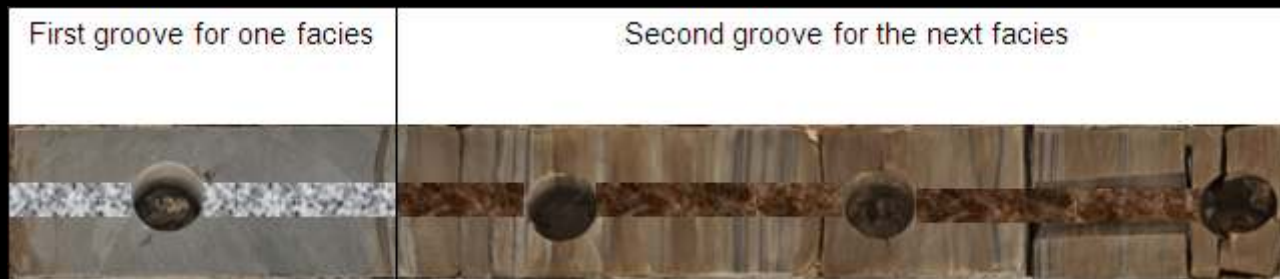
2 fields tested

- Bemolonga tar Sand – Bitumen content between 4 to 6%
- Tsimiroro Heavy Crude Oil

# The process



# Sample Preparation



Example of core scratching and plugging

VIDEO MISSING

# Sample Preparation

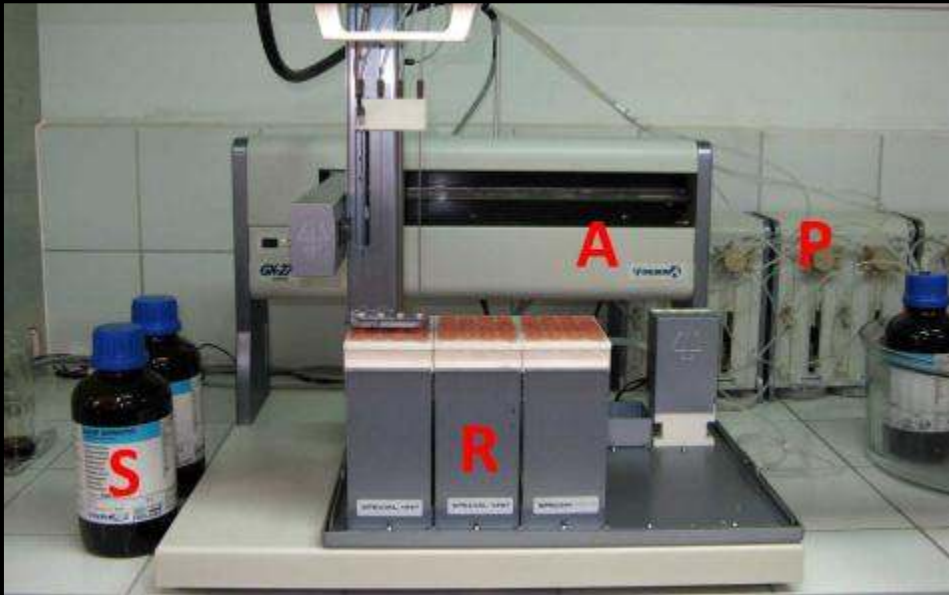
- Each element (cartridge, frits) is weighed and recorded per samples.
- Samples are grinded in a agate mortar or by hand\*
- The extraction cartridges are filled with samples of approximately 1g and compact lightly. A Frits is placed on top and cartridge capped.
- The weighed cartridges and a blank are placed in their well per ID bar code, on the cartridge holder.



- All cartridges are placed in a drying oven for 8 hours\* and weighed to determine their water content. After the drying process all samples + cartridges are placed in the CEPSat™ for extraction which last approximately 15 minutes.



# CEPSat™ model shown here with 4 pumps and needles



5 rack of 16 samples (15 ores + 1 QC per rack)  
TOTAL of 75 samples + 5 QC  
Estimation of 1hrs per rack  
5hrs to process 80 samples with 3 elutions

Each machine comes with two 406 Dual Syringe Pumps (P) able to deliver positive pressure through the syringes. The two instruments are equipped with 5 mobile sample holders racks (R) capable to accommodate up to 16 chromabond cartridges & collection tubes each,

CEPSat™

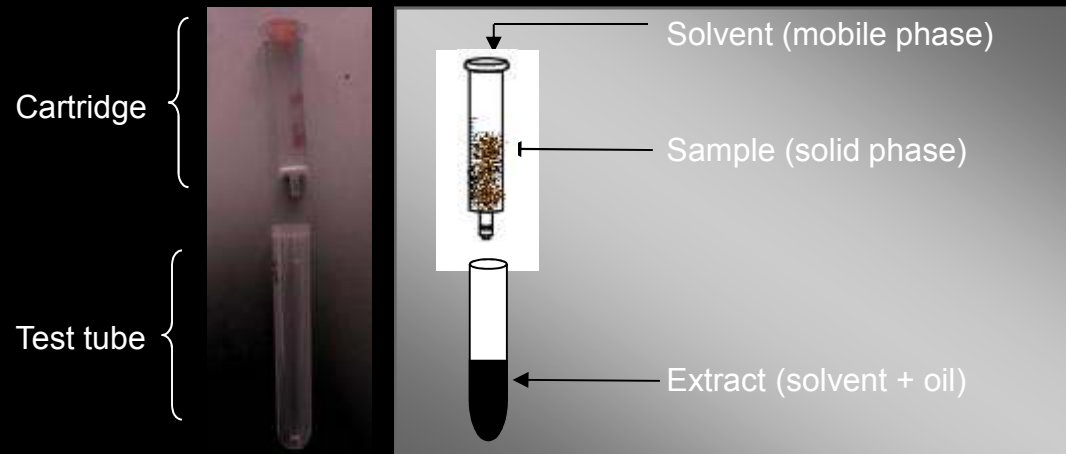
VIDEO MISSING

VIDEO MISSING



# CEPSat™

The CEPSat™ is a solid phase extraction by eluting involves an extraction of solute inside a solid phase during n elutes by a mobile phase, which means the solute is integrated in the solid phase and extracted by a liquid phase



In this study we have concentrated our efforts on extracting heavy crudes i.e., extraction of oil from unconsolidated oil sands samples where the liquid phase is the mobile phase i.e., DiChloroMethane (DCM) solvent.

# CEPSat™



# 4. Comparison



**Vs**



# The downside of Dean Stark method

- Large amount of samples required i.e., 100g each
- Long extraction time i.e., ~6 to 24hrs hours each
- Large amount of solvent required i.e., ~350ml each
- Long preparation time i.e., 8 minutes each
- Initial installation is very expensive i.e., \$250,000 (\$900 equipment per DS)
- Large amount of personnel i.e., 6 per 12 hours shift
- Large amount of solvent waste i.e., 70 liters per day
- Large cost associated to solvent purchase i.e., \$ 2000 per day.
- Large cost associated to solvent disposal i.e., \$ 300 per day.
- Large cost associated to rent space i.e., Fort McMurray Alberta \$10,000 per month for 2000 sq.ft.
  
- And Low margin for the lab (\$15 to \$35 per test/run depending on contract.)

# How DS compares with the CEPSat™

- Small bench space requirement i.e., 1 linear meter of fume hood space compared to 10 linear meter for the DS as discussed
- Small amount of required sample i.e., 1 gram compared to 100 grams for the DS
- Small extraction time i.e., 15 minutes compared to 6 hrs for the DS
- Small amount of solvent i.e., 15 ml each compared to 100 ml for the DS
- Identical preparation time i.e., 8 minutes
- Initial installation is \$90,000 usd instead of \$250,000 usd for the DS
- Small amount of personnel to run the CEPSat™ i.e., 3 technicians to run the CEPSat™ compared the 6 for the DS per shift
- Small amount of solvent waste i.e., 30 liter compared to 70 liter per day for the DS
- Low cost associated with the solvent purchase i.e., \$200 compared to \$2000 per day for the DS (\$56/L) based on 200 samples a day
- Low cost associated to solvent disposal
- Low cost associated to rent space (the whole could fit in a 20ft container if we wanted)

# CEPSat™ Disadvantages

- Require 8 hrs of drying time for water removal + 3 to 6 hrs to dry out the sample and remove the DCM but with correct planning the operation can be continual. DS require 1 drying after the test for 6 to 8HRS
- Requires greater sample handling care due to the small amount of sample use i.e., 1g
- Optimal operating condition – with room temperature control
- Solvent used has to be of good quality, regular control needed, especially if technique used in remote area with potential contamination or impur solvent.

# Comparison

|                                | Dean Stark  | CepSat   |
|--------------------------------|---|--|
| Consumables per Test (USD)     | Thimbles \$ 8<br>Culture Tube, syringes   | \$ 4   |
| Solvents per test (+ disposal) | \$ 13 / 350ml<br>Toluene (\$30/l)   | \$ 1 / 15ml<br>DCM (\$56/l)                        |
| Handling, Electricity, rental  | Highly depending on where you operate   |  |
| Rental space                   | For 2000 sq.ft<br>50\$/sq.ft in Canada \$100,000 annual<br>14\$/sq.ft in UK \$28,000 annual | For 100 sq.ft<br>\$ 5,000 annual<br>\$ 1400 annual |
|                                |   |  |
|                                |   |  |
|                                |   |  |
| AVG charges                    | \$15 to \$35 in Canada<br>> \$50 in UK for DS   | Estimation of \$15 to<br>\$30 per test             |

# 5. Our study

Ore from four different locations around the world namely Alberta, Utah, California and 3 unknown location in Canada were obtained for this study. A total of 21 samples were taken from each ore to perform the CEPsSat™ analytical tests and for repeatability purpose.

Despite DS known, from the provider of the samples, DS were re done.



| From             | Grade         | % Oil      |
|------------------|---------------|------------|
| Alberta          | Low           | > 6%       |
| Utha             | High          | > 13%      |
| California       | Medium        | > 9%       |
| Unknow<br>Canada | From LG to HG | 3, 8 & 15% |



# The key driver : The number of elutions

Because  $K_d$  (Partition Elute Coefficient) is a simplification (derived from Plate Theory), the values are necessarily empirical and highly dependent on the **matrix** as well as the **system** where they are measured, therefore the Oil Sand Matrix and CEPSat™ (DCM) kinetics were determined here.

# Microstructure of Oil Sands: Matrix

Structural model for oil sands in terms of solids, water and bitumen is shown below.

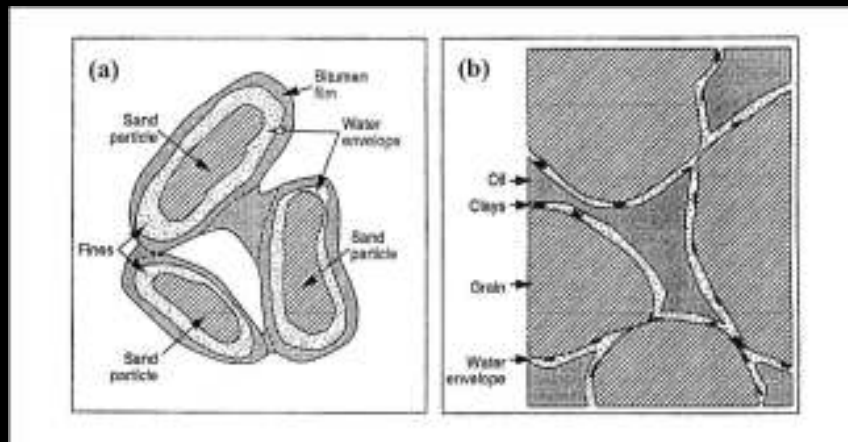


Figure 1: Sketch of model structure of oil sands proposed by (a) J. H. Cottrell (1963), and (b) G. D. Mossop (1980)

- The sand grains are surrounded by a water film, while clay minerals are suspended in the water layer. This film of water was further encased by the bitumen, which filled the voids between the individual sand grains.
- An updated structure model showed that the quartz grains were all in direct contact with each other, and they constituted a stable framework that remained virtually unchanged when the fluids were mobilized.
- The water film around the grains, only a few micrometers thick, formed a physically continuous sheath that prevented direct contact between bitumen and quartz. The bitumen phase was also continuous, linked from one pore to the next through a three-dimensional network of pore throats.
- Clay minerals were attached to the surface of sand grains, and it was unlikely that they protruded through the water envelop (Mossop, 1980).

# Matrix

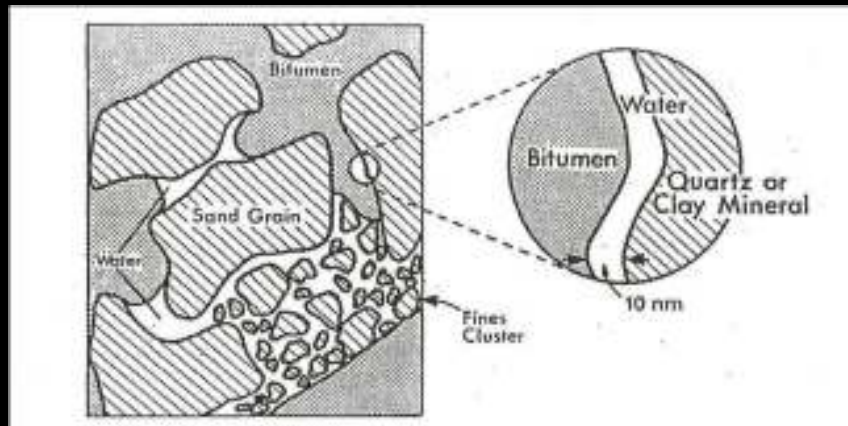


Figure 2: The refined structure model of oil sands proposed by Takamura (1982).

- The water in the oil sands appears as pendular rings at grain-to-grain contact point; as a roughly 10 nm thick film which covers the sand surface; and as water retained in fines clusters. In the case of high grade oil sands, the pore space is filled with bitumen and water. The water occupies between 10-15% of the pore.
- These pendular rings cover roughly 30% of the surface and the remaining 70% of the surface is covered by a thin film of water which is stable because of the double layer repulsive forces acting between the charged sands and the bitumen surfaces.
- In lower grade oil sands, clusters of fine particles ( $<44 \mu\text{m}$ ) exist within the framework formed by coarse sand grains. These clusters of fine particles are saturated with water. Thus it provides an explanation that the amount of formation water in oil sands increases linearly with increasing fines content.
- The formation water in the oil sands is of high salinity which can be at similar level as seawater. The sodium and chloride ion concentrations can vary from 10-100 mg/kg of oil sands. Calcium and magnesium ions can vary up to 40 mg/kg of oil sands (Masliyah, 2007). Other inorganic ions (e.g.  $\text{K}^+$ ) are also present in the formation water.
- It is this layer of water that would allow for a quick or ease of extracting the bitumen from the sand matrix. The kinetics would be greatly different if water was absent. The clay on the other hand ionic charges tend to retain the Bitumen to the sand grain which complicates the extraction in **certain** industrialized process

# System

- Because  $K_d$  is a simplification, its value also depends on the **system** where they are measured, the CEPSat™ (DCM) kinetics also needs to be reveal. To derive the kinetic equation to determine  $K_d$  The Plate Elution Theory was applied.

Define here as the ratio of concentration of oil in a mixture of DCM (mobile) and concentration of oil in the ore matrix (stationary) at equilibrium.

The coefficient is a measure of the difference in solubility of these two phases is:

$$K_d = [Tis] / [Aim] \quad (1)$$

**The Plate Theory**

# The Plate Theory

For i extractions:

$$[T_i]msample = [T_t]msample - [A_{extr}]V_{solv} \text{ From (1)}$$

$$K_d[A_{im}]msample = [T_t]msample - [A_{extr}]V_{solv}$$

$$[A_{im}]msample = ([T_t]msample - [A_{extr}]V_{solv}) / K_d$$

For n elutes, we have (1...n):

$$\sum [A_{im}]msample = \sum (([T_t]msample - [A_{extr}]V_{solv}) / K_d)$$

$$[A_{extr}]msample = n (([T_t]msample - [A_{extr}]V_{solv}) / K_d)$$

$$[A_{extr}] = m_{extr} / V_{solv} = n[T_t]msample / (nV_{solv} + K_d msample)$$

Where  $[T_t] = m_t / msample$

$$m_{extr} / V_{solv} = n(m_t / msample)msample / (nV_{solv} + K_d msample)$$

$$f(n) = m_{extr} / m_t = 1 / (1 + ((K_d / n)msample / V_{solv}))$$

# Plate Theory

- Where **A** is the quantity of oil, **m** the mobile phase and **S** the stationary phase, **V<sub>sol</sub>** the total amount of solvent during the whole experiment. The indexes 1, 2, 3,...i,...n are used to indicate the number of elutes. Then, **[A<sub>im</sub>]** indicates the mass concentration of oil during i elute
- **K<sub>d</sub>** is the partition elute coefficient between the DCM and the sample, **[T]** the concentration of oil left on solid sample, **m<sub>sample</sub>** the initial sample mass. Finally, **m<sub>extr</sub>** and **A<sub>extr</sub>** indicate respectively the mass and the concentration of oil extracted by the solvent during the whole experiment.

For our purpose we can derive the  $f(n)$  in terms of  $Kd$  which is:

$$Kd = n ((mt/m_{ext}) - 1) V_{solv}/m_{sample}$$

Where a partition elution coefficient ( $Kd$ ) can be determined for each oil sand sample.

# Example

For example,

If the  $Kd = 0.05$  ml/g  
and  $m_{\text{sample}} = 1$ g and  
 $V_{\text{solv}} = 15$  ml,  $n=3$

then,

we can write:

$$f(n) = m_{\text{ext}}/m_{\text{t}} = 1 / 1 + (1/300n)$$

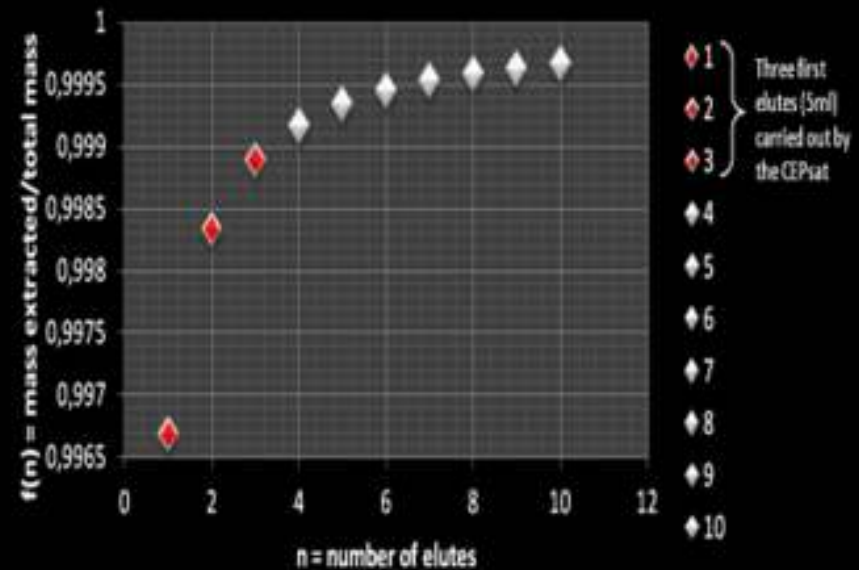


Fig A. Showing  $f(n)$  versus  $n$  elution



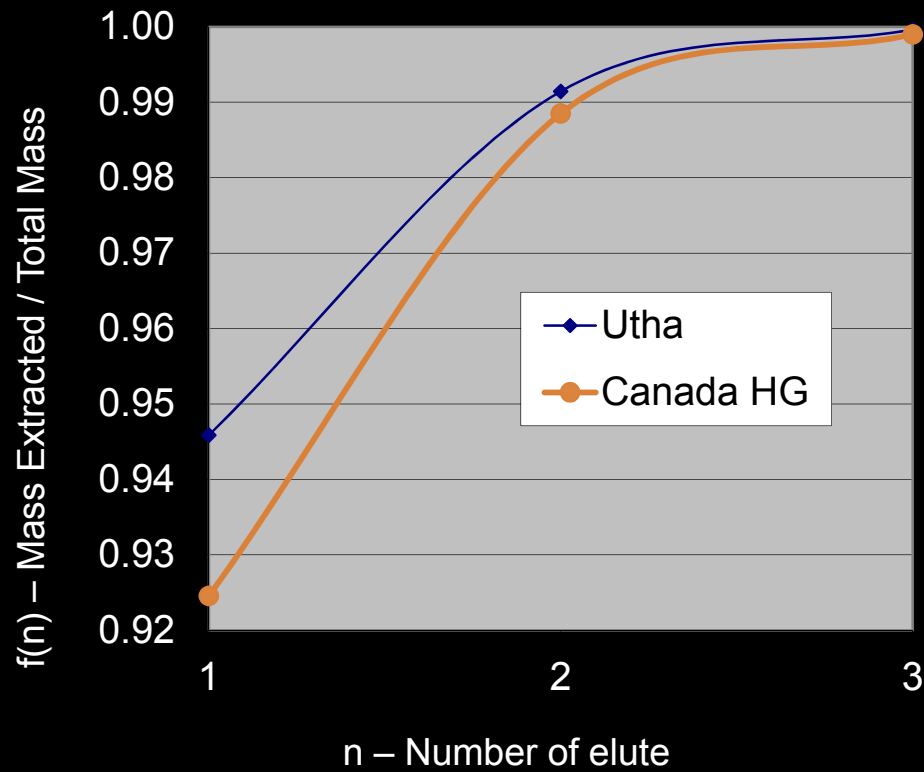
# Our Study

From these tests the following were determined:

- The mass of oil extracted (mext)
  - The total oil mass (mt) by DS
  - The standard deviations, reproducibility and repeatability
  - Hence the partition coefficients ( $K_d$ )
- From the group of different ores obtained, the Canadian, Utah and California ores were all unconsolidated.

# Results – High Grade

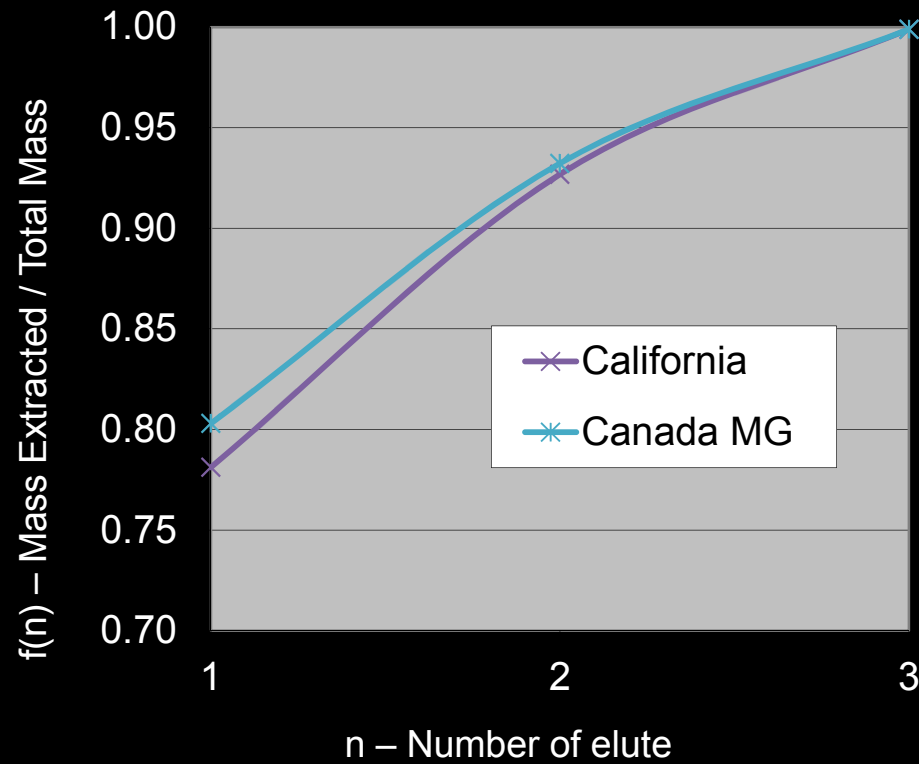
## High Grade Sample



Data Protected

# Results - Medium

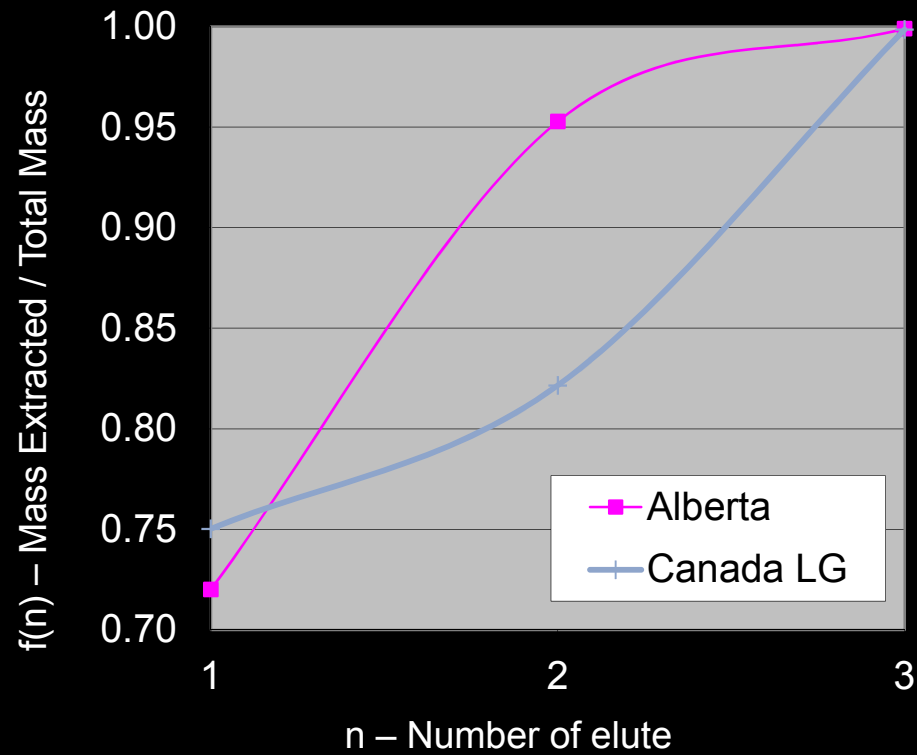
## Medium Grade



Data Protected

# Results – Low Grade

## Low Grade



Data Protected

# Conclusion

- A common *Kd* Partition Coefficient elution value was NOT identified for the **CEPSat™** (DCM) extraction of all oil sands.
- The plate Theory using DCM is therefore not usable. The low or high clay from the bitumen matrix influence the results.
- The **CEPSat™** showed to efficiently extract 99.9 wt% of the bitumen out of core samples when compared to the Dean Stark technique after 3 elutions for all 6 samples tested. The *Kd* (Partition Elution Coefficient) indicated a high extraction capability kinetics for all measured ore samples independent of their origins after  $n=3$

# Conclusion

- The CEPSat™ method for oil extraction is a powerful tool for the oil exploration industry.
- Its main goal is its capability to run multiple analyses in a relatively short time allowing, thus, a strict control on the exploration operations.
- We have demonstrated that a lab equipped with 2 units can run up to 400 samples per day.

# What's next

- The existing affinity between the oil and the sands matrix is such that the DCM  $n=1$  and  $n=2$  is different for different oil sands.
- In another study we are to define a solvent that has a greater affinity for the oil whereby an Elution Constant ( $K_d$ ) can be determined.
- The system parameter such as the amount of solvent eluted, air purge and solvents all play a large role in obtaining the  $K_d$  Constant. The DCM optimizes its affinity after  $n=3$  but we believe that an optimisation could be reached at  $n=1$  by selecting the right parameters.

# Technical Publication

- Study to be presented at the Symposium of Core Analysis.  
September 2013 –  
Nappa Valley



Thanks

Questions

