Core Extraction Process for Saturated Oil Recovery (CEPSatTM)

Régi Damien Giroux, RG Consultant Chimie Inc, Francois Ollivier, Kirk Petrophysics, Scott Parker, Kirk Petrophysics, Jean-Valery Garcia, Kirk Petrophysics

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ABSTRACT

This paper presents a core analytical instrument developed as a means of rapid and economical oil extraction from ore samples, named here as CEPSat. Described herein is an innovative automated multi-sample solvent extraction technique capable of isolating and quantifying petroleum products out of any core sample. The kinetics of oil sand (ore) elution by CEPSat using DiChloroMethane (DCM) revealed a similar and low partition elution coefficient (Kd), of 0.057 ± 0.022 ml/g, for the medium to high ore oil sands (>10 wt%) and a Kd of 0.163 ± 0.022 ml/g for the low ore oil sands (< 10 wt%) at n=5, where n is defined as the number of elution cycles. The oil recovery statistical mean was high and measured at 99.92 ± 0.05 wt% at n=5 elution of 5 ml DCM per gram of ore. Individual oil sand sample Kd coefficient was obtained as a primary objective of determining if a common partition coefficient existed for oil sands in general and secondly to determine its value. For oil sand's Kd coefficient, the key variables were revealed as its clay content, inorganic ions content (i.e., calcium, carbonates) and principally its organic content. A bank of geologically diversified ore samples was collected from various regions such as Alberta, Utah, California and Madagascar to determine their elution Kd value, hence its efficiency as an oil sand laboratory extraction tool. The CEPSat's Kd results were well within the three sigma standard deviation when grouping the high/medium ores and the low ores at n=5. The tool also demonstrates a time saving by more than 10 times that of the Dean Stark, more accurate than the Centrifuge, less work than the Distillation and less costly than the HNMR with the possibility of recovering the eluted oil. The tool has shown to be capable of handling over 200 core samples in a single day revealing to be a powerful tool for the oil exploration industry. This oil recovery automated multi-sample space-saving workstation may represent the highest economical throughput systems currently available on the market.

INTRODUCTION

The oil sands are soon to be the world's largest heavy oil and bitumen deposits. Approximately 35% of these bitumen reserves are found in unconsolidated deposits where numerous companies have invested billions of dollars in oil-sands mine-development projects. Being able to predict oil properties and fluid saturation in situ

and process optimization of bitumen extraction is therefore of considerable value to the industry. Because Kd value is necessarily empirical and highly dependent on the matrix where they are measured, a brief introduction of the oil sands micro-structure is described herein as a reference to this study. The sand grains are surrounded by a water film of uniform thickness, 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. The water film around the grains, only a few micrometers thick, formed a physically continuous sheath that prevented direct contact between bitumen and quartz (Mossop, 1980).



Fig. 1 - The refined structure model of Athabasca oil sands proposed by Takamura (1982).

THEORY AND PRINCIPLE:

The CEPSat[™] is a solid phase extraction tool by eluting and involves the 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 will concentrate on extracts of oil from the solid phase where the liquid phase is dichloromethane (DCM). Because *Kd* values are necessarily empirical and highly dependent on the system where they are measured, the CEPSatTM (DCM) kinetics needs to be revealed while taking into account the following assumptions:

- 1. The interactions between solvents and the solid phase can be neglected.
- 2. During one elute, all solvent is collected in the test tube (no loss).
- 3. No sample loss occurs during the experiment.

From Plate Elution Theory (Martin and Synge, 1941) we can define the CEPSatTM (DCM) function as:

f(n) = mextr/mt = 1/(1+((Kd/n)msample/Vsolv)))Therefore Kd is defined as: Kd = n ((mt/mext) - 1) Vsolv/msample

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

- n = number of elutions
- F(n) Function of n
- Mextr/mt Mass of oil extracted by the solvent during the whole experiment
- m/sample initial sample mass
- V/solv volume of solvent

EXPERIMENTAL:

Ore from different locations around the world namely Alberta, Utah, California and Madagascar were obtained for this study. A total of 21 samples were taken from each

ore to perform the CEPSatTM analytical tests in determining the mass of oil extracted, their standard deviations and subsequently the partition coefficients (*Kd*). A total of 3 samples were also taken from each ore to obtain the total oil mass by DS.

Procedure:

The cartridges are filled with samples of approximately 1g, a top cap inserted and weighed. The cartridges are placed in their individual holding well, ID (bar code), on the cartridge holder. Samples are dried for 9 hrs at 90°C and weighed to determine the water content. The samples, within their cartridges, are then loaded into the CEPsat[™] and flushed with the dichloromethane solvent. Once the elution is completed, the oil is recovered in the collection tubes, weighed and the DCM is recycled.

RESULTS:

The results of the CEPSatTM are shown here below. A total of 21 CEPSatTM tests were run per ore. Three DS were also run per ore for reference purposes. A statistical mean and deviation were obtained as well as a *Kd* Partition Coefficient per elution.

Canadian Ore - High Grade no.2		18.77 wt% Oil	Kd = n((mt/mext) -1) Vsolv/msample			
Elution Number	Extraction (mext / mt)%	Repeatability	Kd (STD)	mt/mext		
n=1	96.90%	21%	0.160±0.034	1.3199		
n=2	98.74%	17%	0.255±0.043	1.0127		
n=3	99.86%	14%	0.063±0.009	1.0014		
n=4	99.92%	11%	0.088±0.010	1.0008		
n=5	99.93%	8%	0.022±0.002	1.0005		
DS	100.00%	5%				
F						
Canadian Or	e - High Grade	12 60 44 00	Kd = n((mt/m	ext) -1)		
n	0.1	13.60 Wt% OII	Vsolv/msample			
Elution	Extraction	Popostability		mt/movt		
Number	(mext / mt)%	Repeatability	KU (STD)	mymext		
n=1	94.72%	19%	0.279±0.056	1.0557		
n=2	98.99%	12%	0.204±0.022	1.0102		
n=3	99.64%	8%	0.162±0.130	1.0036		
n=4	99.88%	10%	0.096±0.035	1.0012		
n=5	99.95%	7%	0.062±0.021	1.0005		

2%

DS

100.00%

TABLE 1. Results from the different ores.

Canadian Ore - Medium Grade		11.08 wt% Oil	Kd = n((mt/mext) -1) Vsolv/msample	
Elution Number	Extraction (mext / mt)%	Repeatability	Kd (STD)	mt/mext
n=1	79.13%	22%	1.318±0.290	1.2637
n=2	90.30%	19%	2.148±0.408	1.1074
n=3	96.80%	11%	1.487±0.164	1.0331
n=4	99.69%	9%	0.288±0.026	1.0031
n=5	99.94%	8%	0.075±0.007	1.0006
DS	100.00%	3%		

Canadian Ore - Low Grade		6.88 wt% Oil	Kd = n((mt/mext) -1) Vsolv/msample	
Elution Number	Extraction (mext / mt)%	Repeatability	Kd (STD)	mt/mext
n=1	72.01%	27%	1.943±0.524	1.3887
n=2	95.27%	21%	0.993±0.221	1.0496
n=3	99.84%	11%	0.071±0.009	1.0016
n=4	99.88%	8%	0.096±0.008	1.0012
n=5	99.99%	6%	0.125±0.005	1.0010
DS	100.00%	2%		

California Ore - Medium Grade		9.74 wt% Oil	Kd = n((mt/mext) -1) Vsolv/msample	
Elution Number	Extraction (mext / mt)%	Repeatability	Kd (STD)	mt/mext
n=1	75.48%	21%	1.624±0.341	1.3249
n=2	92.55%	26%	1.610±0.419	1.0805
n=3	96.62%	19%	1.574±0.299	1.0349
n=4	99.20%	12%	0.645±0.077	1.0081
n=5	99.83%	9%	0.213±0.019	1.0017
DS	100.00%	3%		

Utah Ore - High Grade		13.82 wt% Oil	Kd = n((mt/mext) -1) Vsolv/msample	
Elution Number	Extraction (mext / mt)%	Repeatability	Kd (STD)	mt/mext
n=1	94.59%	15%	0.286±0.043	1.0572
n=2	99.14%	12%	0.173±0.021	1.0087
n=3	99.71%	8%	0.131±0.010	1.0029
n=4	99.90%	10%	0.080±0.008	1.0016
n=5	99.98%	5%	0.050±0.001	1.0001
DS	100.00%	3%		

TarCore Ore 5 - Low Grade		2.52 wt% Oil	Kd = n((mt/mext) -1) Vsolv/msample	
Elution Number	Extraction (mext / mt)%	Repeatability	Kd (STD)	mt/mext
n=1	71.30%	22%	2.013±0.043	1.4025
n=2	78.07%	28%	5.618±0.021	1.2809
n=3	95.02%	17%	2.358±0.010	1.0524
n=4	98.99%	8%	0.816±0.013	1.0102
n=5	99.90%	6%	0.125±0.006	1.0001
DS	100.00%	4%		

TarCore Ore 1 - Medium Grade		5.58 wt% Oil	Kd = n((mt/mext) -1) Vsolv/msample	
Elution Number	Extraction (mext / mt)%	Repeatability	Kd (STD)	mt/mext
n=1	76.62%	26%	1.526±0.040	1.3051
n=2	88.95%	29%	2.485±0.721	1.1242
n=3	95.42%	21%	2.160±0.454	1.0480
n=4	99.04%	12%	0.775±0.119	1.0096
n=5	99.85%	8%	0.188±0.015	1.0150
DS	100.00%	3%		

TarCore Ore 3 - Medium Grade		16.04 wt% Oil	Kd = n((mt/mext) -1) Vsolv/msample	
Elution Number	Extraction (mext / mt)%	Repeatability	Kd (STD)	mt/mext
n=1	90.77%	21%	0.508±0.106	1.1017
n=2	97.04%	20%	0.610±0.122	1.0305
n=3	98.17%	16%	0.839±0.134	1.0186
n=4	99.00%	11%	0.808±0.089	1.0101
n=5	99.94%	7%	0.075±0.005	1.0006
DS	100.00%	3%		

RESULT INTERPRETATIONS:

A *Kd* Partition Coefficient elution value was identified for the CEPSatTM(DCM) extraction in ore for n=5 on high/medium ore and low ore. Ore samples from various different geological locations showed a similar Kd Coefficient when extracted by the CEPSatTM at n=5. The oil recovery statistical mean was high and measured at 99.92 \pm 0.05 wt% for n=5 elution of 5 ml DCM per gram of ore. Various factors caused the Kd to vary. The amount of oil content in the ore played a significant factor in obtaining different *Kd* coefficients.



Fig. 2 - Showing the results from the different ores.

CONCLUSION

The CEPSATTM with the DCM solvent obtains a stronger *Kd* elution coefficient correlation as the number of elution increased. The kinetics of oil sand (ore) elution by CEPSat using DiChloroMethane (DCM) revealed a similar and low partition elution coefficient (*Kd*), of 0.057 ± 0.022 ml/g, for the medium to high ore oil sands (>10 wt%) and a *Kd* of 0.163 ± 0.022 ml/g for the low ore oil sands (< 10 wt%) at n=5. Low ore extracted with greater difficulty than high ore using DCM. Clay and organics may play a large role in this elution kinetic. A *Kd* constant using the Plate Theory at n=5 could be used. The CEPSatTM shows great potential but further study will be carried with different solvents.

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REFERENCES

- 1. Biochem J. 1941, A.J.P.Martin and R.L.M.Synge, A new form of chromatogram, employing two liquid phases, 35(12): 1358-1368)
- Chemistry RG Consultant Inc, Canada <u>www.chemistryrgconsuling.com</u> Alberta Energy and Utilities Board. 2004. Statistical Series (ST) 2004–98: *Alberta's Reserves 2003 and Supply/Demand Outlook 2004–2013* (Calgary, May 2004, Revised June 2004). Bryan, J., Kantzas, A., Badry, R., Emmerson, J., and Hancsicsak, T. 2006.
- 3. Clark, K.A. 1944. *Hot-Water Separation of Alberta Bituminous San*d, Transactions, Canadian Institute of Mining and Metallurgy, Vol47, pp.257
- 4. G.R Coates, Lizhi Xiao, M.G. Prammer, 1999, NMR Logging Principles and Applications. Texas Gulf Publishing Company, Trans. 47: 257–274,
- 5. Houston: Halliburton Energy Services.
- 6. Core Laboratories. 2002. Conventional Core
- 7. Takumura, 1982, *Microscopic structure of Athabasca Oil Sand*, Canadian Journal of Chemical Engineering, 60(4), 538-545, 1982
- 8. Martin, Synge, 1941, A new form of chromatogram employing two liquid phases, Plate Theory, Biochem, December; 35(12): 1358–1368.