ALBERTA INNOVATES

SOLVENT ASSISTED AND SOLVENT-BASED EXTRACTION FOR SURFACE MINED OIL SANDS: WORKSHOP 2

SOLVENT LEADERSHIP SERIES

July 13, 2017

SOLVENT LEADERSHIP SERIES

WORKSHOP 2

Candice Paton | July 13 2017
Director, Recovery Technologies

Solvent Leadership Series

WORKSHOP 2: SOLVENT ASSISTED AND SOLVENT-BASED EXTRACTION FOR SURFACE MINED OIL SANDS

July 13 2017, Alberta Innovates

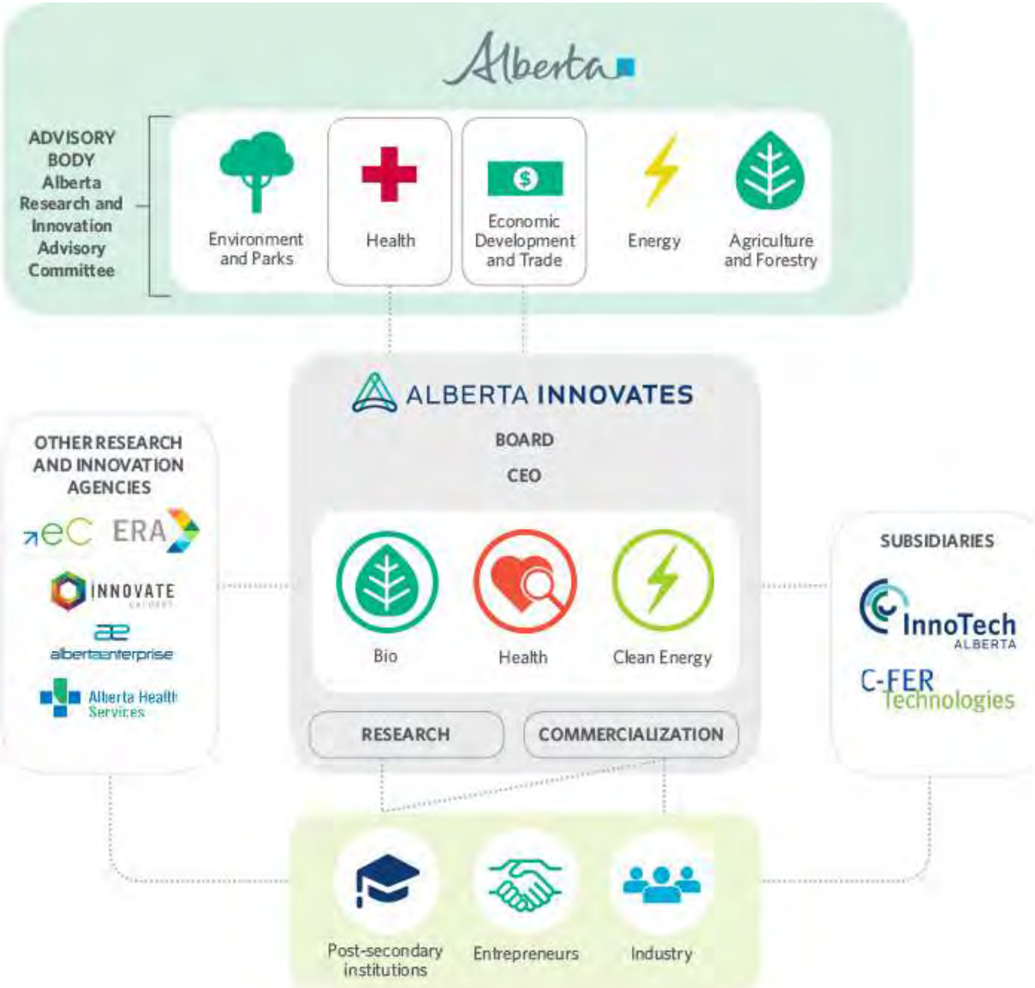
Riverview Room, Floor 26, 801 6 Ave SW, Calgary, Alberta

AGENDA

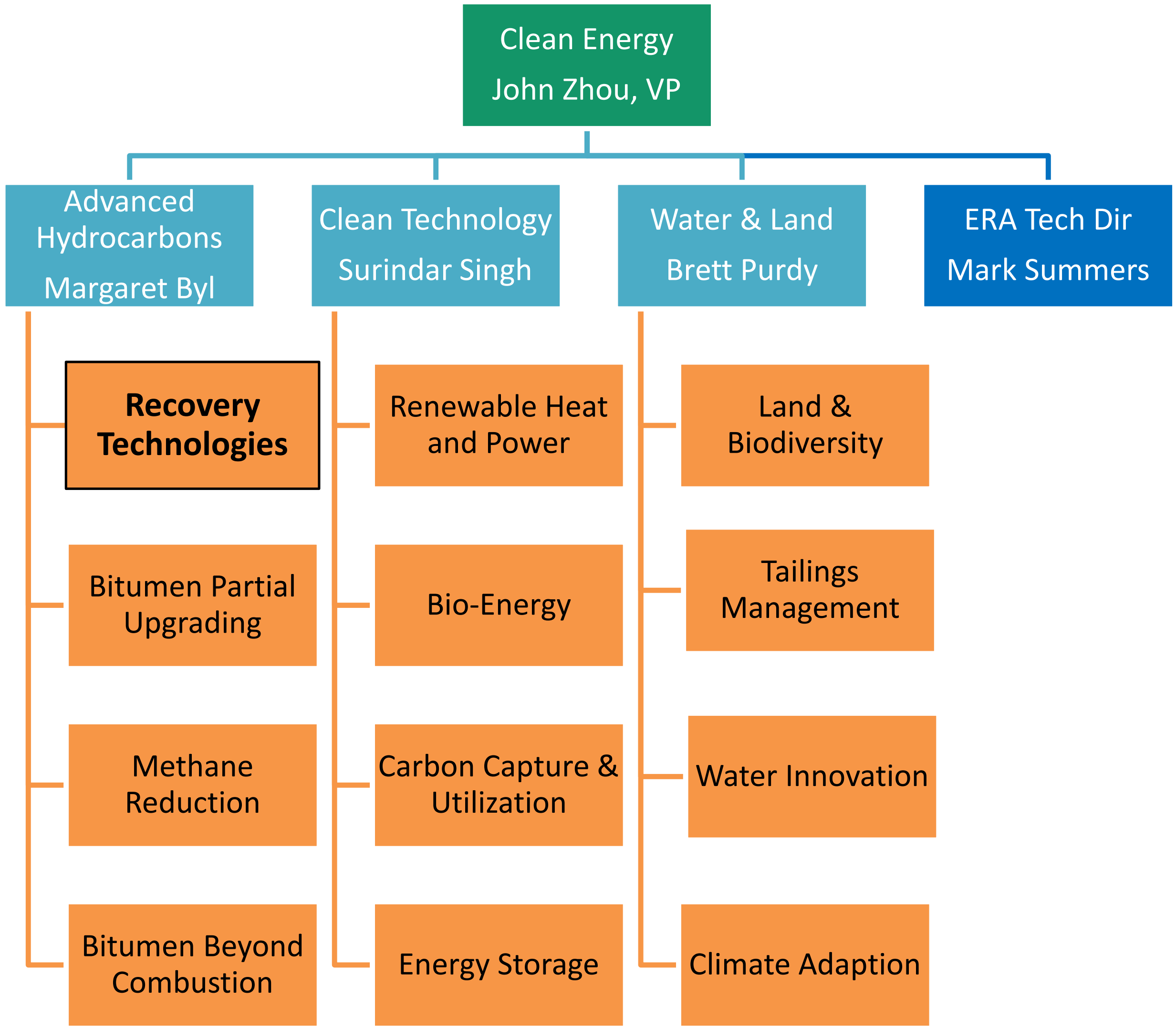
	Sign in and Coffee	8:45 to 9:00 a.m.
1.	Welcome remarks - John Zhou, VP, Clean Energy and Candice Paton, Director, Recovery technologies	9:00 to 9:15 a.m.
2.	Key Presenter: Zhenghe Xu – NSERC Industry Research Chair in Oil Sands Engineering; Canada Research Chair in Mineral Processing.	9:15 to 10:15 a.m.
3.	Key Presenter: Yuming Xu – Senior Research Scientist, CanmetENERGY, NRCan; Scale up and piloting of solvent processes.	10:15 to 11:15 a.m.
	Coffee Break	11:15 to 11:30 a.m.
4.	Key Presenter: Qi Liu – Professor and Scientific Director of IOSI. From research outcomes to opportunities for field pilots in solvent technologies.	11:30 to 12:30 p.m.
5.	"Fireside Chat" Interviews and Discussion with presenters	12:30 to 1:00 p.m.
	Networking Lunch and Closing Remarks	1:00 p.m.

Alberta's Research and Innovation System

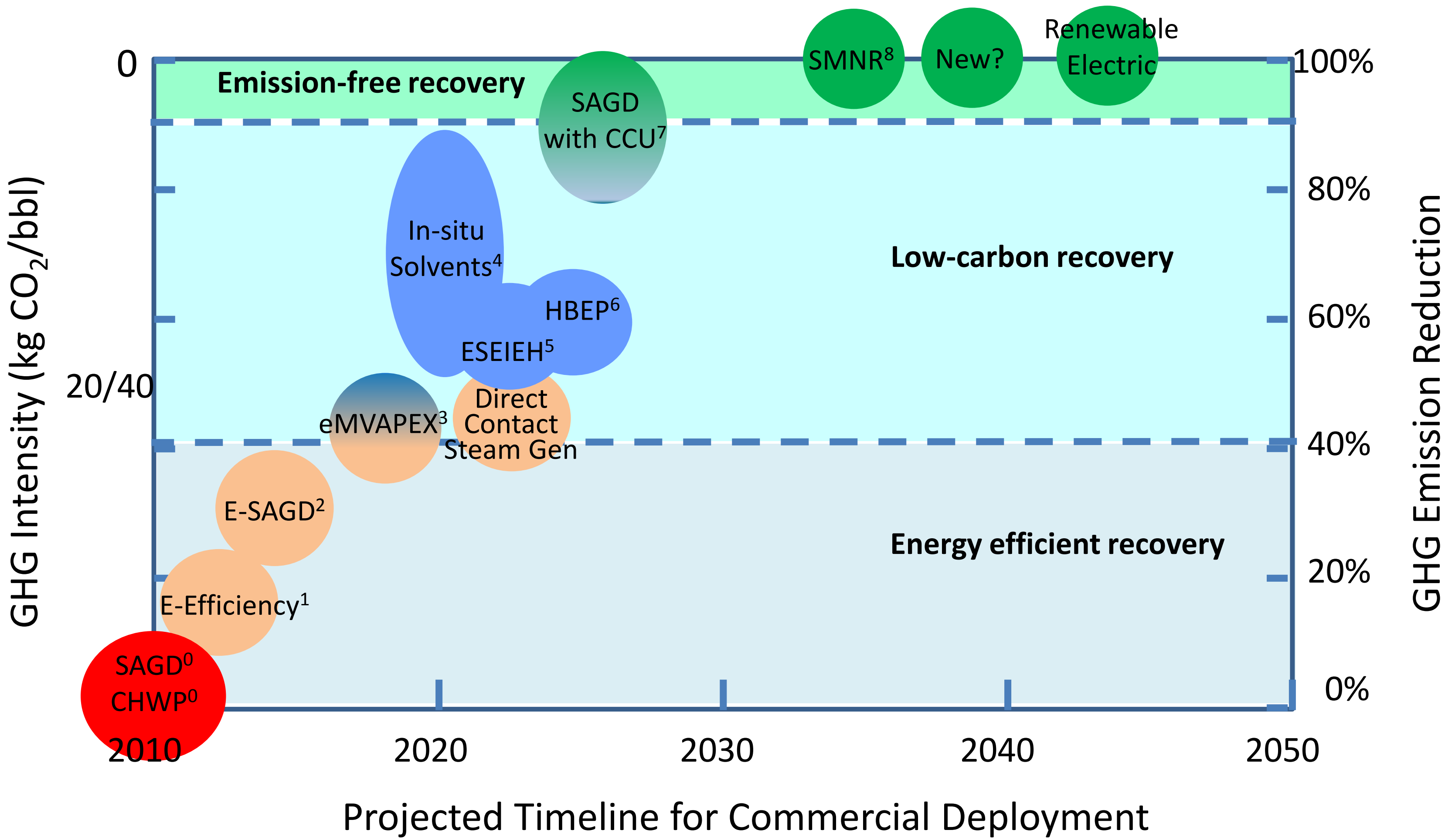
Working together – Cross-Ministry & Cross-Sector



Clean Energy: CORE PROGRAM AREAS



Recovery Technologies (AB's oil: cost & carbon competitive)



[0] SAGD: Steam assisted gravity drainage; CHWP: Clark hot water process; [1]Efficient H_2O treatment, heat recovery, infills, etc.; [2]Various solvent-assisted SAGD processes, and eMSAGP; [3]Enhanced modified VAPour EXtraction (AER 2016); [4]Pure solvent processes: N-Solv, CSP, etc.; [5]Enhanced Solvent Extraction Incorporating Electromagnetic Heating; [6]HBEP = Hybrid bitumen extraction process (surface mining); [7]SAGD with carbon capture and utilization; [8]Small modular nuclear reactors

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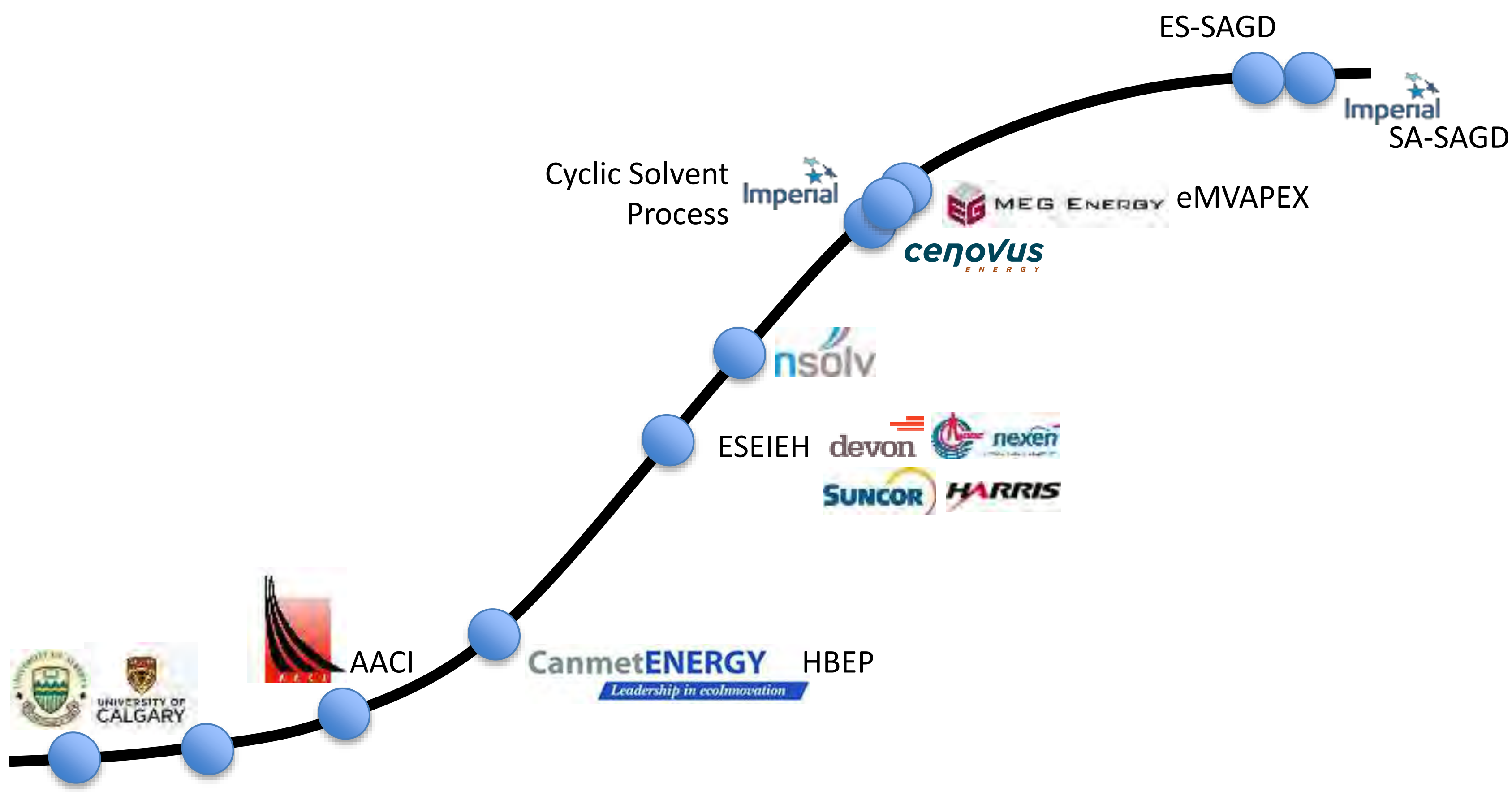
EMISSIONS REDUCTION ALBERTA

Recovery Technologies: SOLVENTS

R & D → **Piloting** → **Demonstration** → **Commercial**

* Illustrative for Selected Technologies



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Progress of Hybrid Extraction of Bitumen at Ambient Temperature from Alberta Mineable Oil Sands

Dr Zhenghe Xu, Yeling (Yale) Zhu, Derek Russell, Qingxia (Chad) Liu, Jacob Masliyah

"uplifting the whole people"

— HENRY MARSHALL TORY, FOUNDING PRESIDENT, 1908

CBC news posted on May 17, 2017

http://www.cbc.ca/news/politics/carbon-price-tax-discussion-paper-1.4120135

Liberals provide details of plan for national carbon tax

Proposed federal rules will only apply in provinces without their own carbon tax

By Susan Lunn and Margo McDiarmid, CBC News Posted: May 17, 2017

The 26-page document released today outlines in detail how a federal carbon tax would be implemented, including how the levy would be applied to fossil fuels, such as gasoline, diesel and natural gas, starting in 2018.

Ottawa has set a starting price of $10 a tonne on carbon dioxide emissions in 2018, increasing to $50 a tonne by 2022.

So, for example, a tax of $10 a tonne on gasoline would require an extra 2.33 cents per litre added at the pumps. That rises to 11.63 cents per litre by 2022. Some provinces already have a carbon tax on gasoline ...at meets the federal requirement.

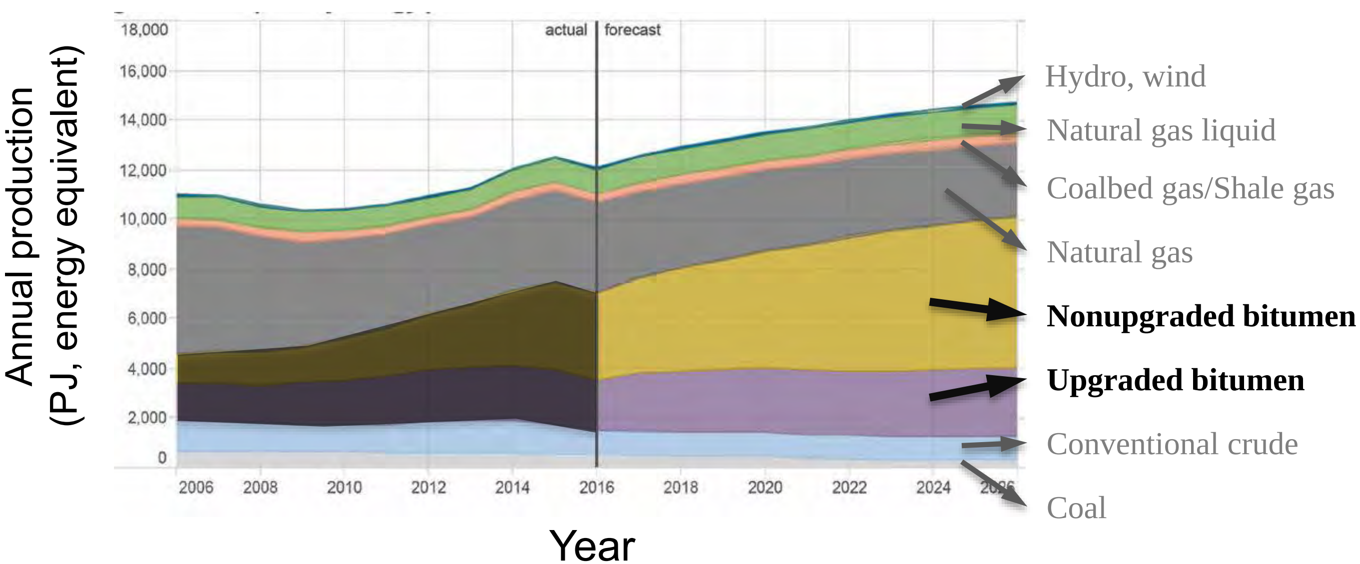
...e levy on emissions from industrial facilities will not start before Jan. 2, ...19, and will only apply to facilities that emit more than 50 kilotonnes

Background

Alberta mineable oil sands (OS)…

- **~1 million bbl/d** production of bitumen; **~40 %** of total OS bitumen production in Alberta.
- Only **CHWE** (Clark's hot water extraction) technology used in current industry.

Total Primary Energy Production in Alberta (AER-2017)

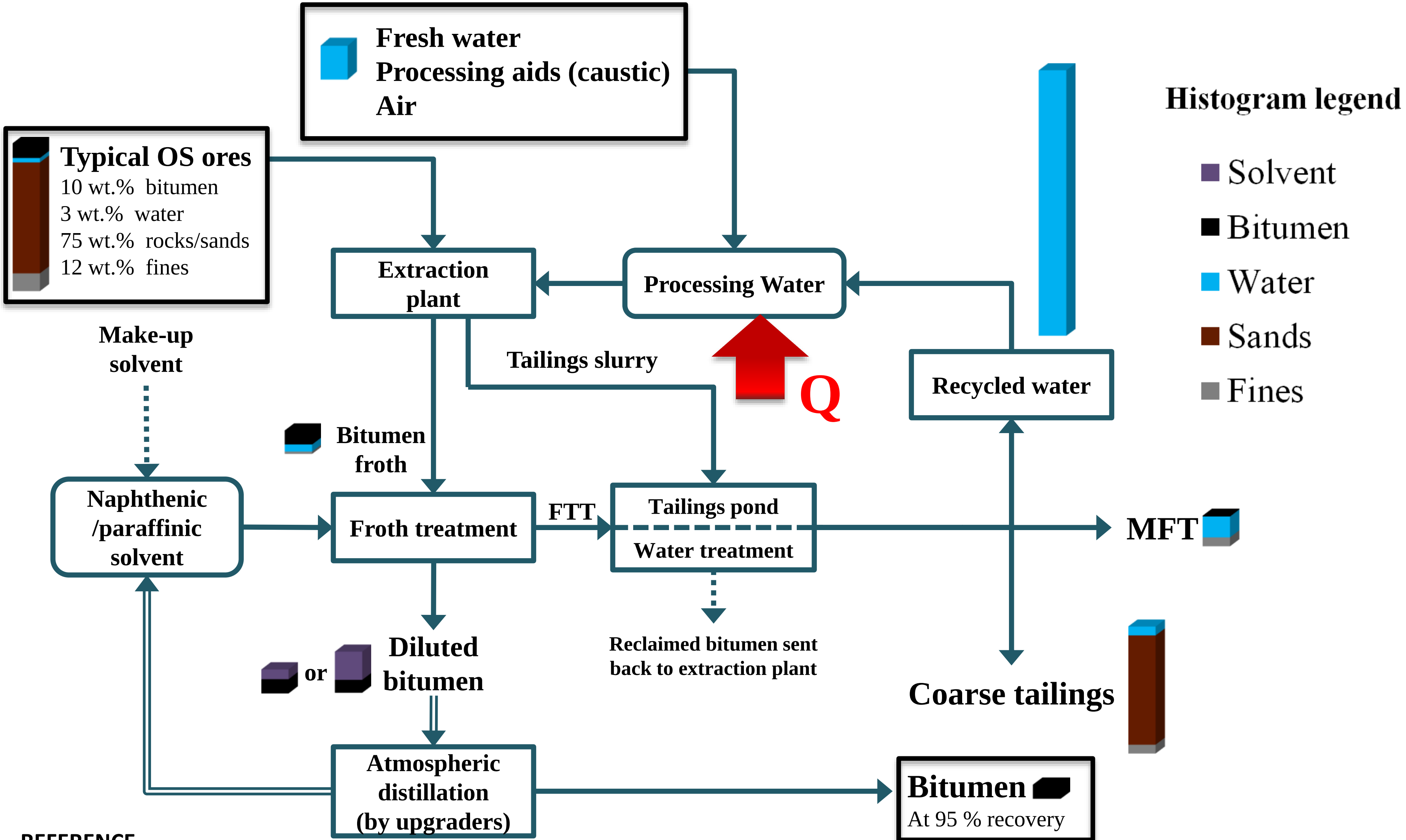


REFERENCE

[1] P. Gosselin, S. E. Hrudey, M. A. Naeth, A. Plourde, R. Therrien, G. Van Der Kraak*, et al.*, "Environmental and health impacts of Canada's oil sands industry," **2010**.

[2] M. Teare, S. Miller, S. Overland, R. March, C. Tamblyn, M. Yemane*, et al.*, "ST98-2017: Alberta's energy reserves and supply/demand outlook," Alberta Energy Regulator **2017**.

CHWE Process



REFERENCE

[1] J. Masliyah, Z. J. Zhou, Z. Xu, J. Czarnecki, and H. Hamza, "Understanding water-based bitumen extraction from Athabasca oil sands," *The Canadian Journal of Chemical Engineering*, vol. 82, pp. 628-654, 2004.

Challenges with CHWE

Energy intensity and GHG emission

- High operation temperature (40-45 °C)

EROEI of different energy sources

Source	EROEI value
Hydro-elect	11 – 267
Conventional oil	19 – 100
Coal	50
Wind	18
Mineable OS (NFT)	**14**
Mineable OS (PFT)	**8.5**
In-situ OS (SAGD)	5.5

HIGH

LOW

What could we achieve for **every 1 °C** reduction in operation temperature? ??

~0.0147 CDN$/bbl bitumen incentive in energy use

Another ~0.0169 CDN$/bbl bitumen incentive in carbon tax by 2022

If temperature drops from **45 °C** to **25 °C**, cost for **1 million** bbl/day bitumen will reduce by:

~294,000 CDN$/day in energy use

~338,000 CDN$/day in carbon tax

~632,000 CDN$/day

REFERENCE

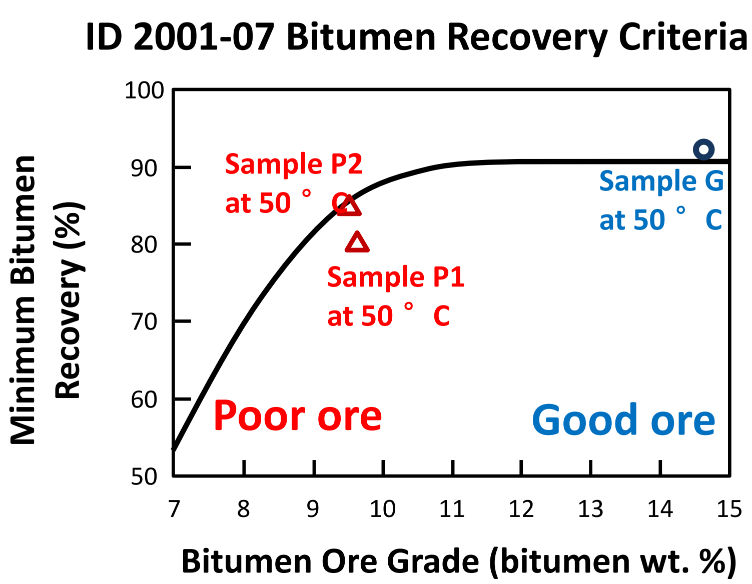
[1] F.A. Seyer, and G. W. Gyte. Viscosity. In *AOSTRA technical handbook on oil sands, bitumen and heavy oils, AOSTRA technical publication series No. 6,* Alberta Oil Sands Technology and Research Authority (AOSTRA), 1989

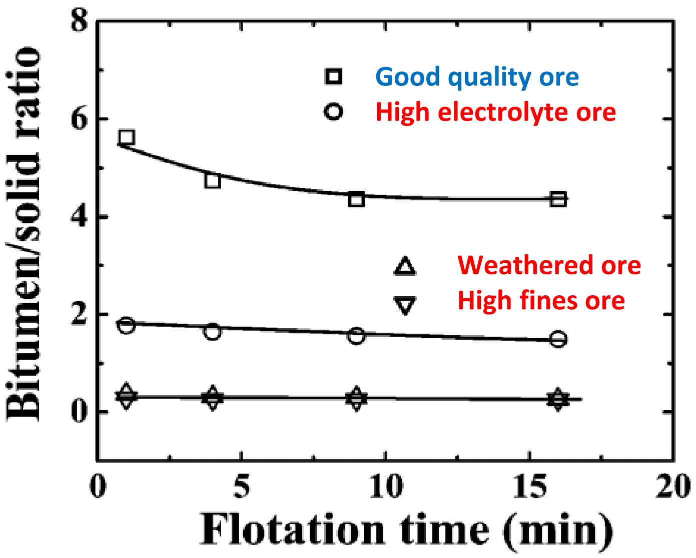
[2] CHE 522 "*Fundamentals of oil sands upgrading*", Course handouts. University of Alberta, Feb 2015.

Challenges with CHWE

Poor processability of poor-quality ores

- Reduced bitumen recovery.
- Increased unwanted contents (water/solids) in bitumen froth.
- Large impurities (electrolyte/fine clay) contamination in diluted bitumen product, especially in naphthenic froth treatment (NFT).





REFERENCE

[1] CHE 534 “*Fundamentals of oil sands extraction*”, Course handouts. University of Alberta, Jan 2015.

[2] S. K. Harjai, C. Flury, J. Masliyah, J. Drelich, and Z. Xu, "Robust aqueous–nonaqueous hybrid process for bitumen extraction from mineable Athabasca oil sands," *Energy & Fuels,* vol. 26, pp. 2920-2927, 2012.

[3] Jianjun Liu, Zhenghe Xu, and Jacob MasliyahDOI: 10.1021/ef050091r

Challenges with CHWE

Fresh water usage

- ~2.8 bbl fresh water are required for 1 bbl bitumen production.

Tailings management

- ~2 bbl MFT are produced for 1 bbl bitumen production.
- Diluent loss, water pollution, land reclamation and safety concern.

REFERENCE
[1] J. Masliyah, Z. J. Zhou, Z. Xu, J. Czarnecki, and H. Hamza, "Understanding water-based bitumen extraction from Athabasca oil sands," *The Canadian Journal of Chemical Engineering,* vol. 82, pp. 628-654, 2004.

Alternative Technology for Recovery

What we want?

- Ambient temperature extraction (reduced energy intensity)
- Improved bitumen recovery
- Robust approach capable of dealing with variability of ores
- Low fresh water intake
- Producing dry stackable tailings

Hybrid Extraction Process

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Hybrid Extraction: Introduction

Definition: both solvent and water are used in extraction process.

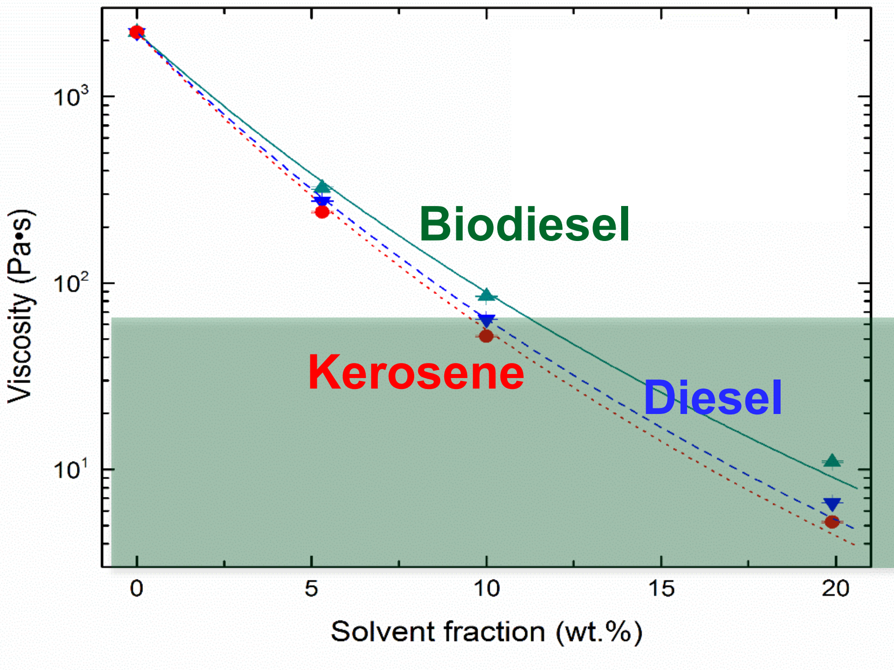
- **Mainly two types**
  - **<u>Early "hybrid" process</u>**
    - Oil sands processed with solvent and water.
    - E.g. *OHWE, LEE, USO's Grande Pairie Pilot*.
  - **<u>True hybrid process</u>**
    - Oil sands pretreated with solvent (viscosity reduction), followed by water extraction process.

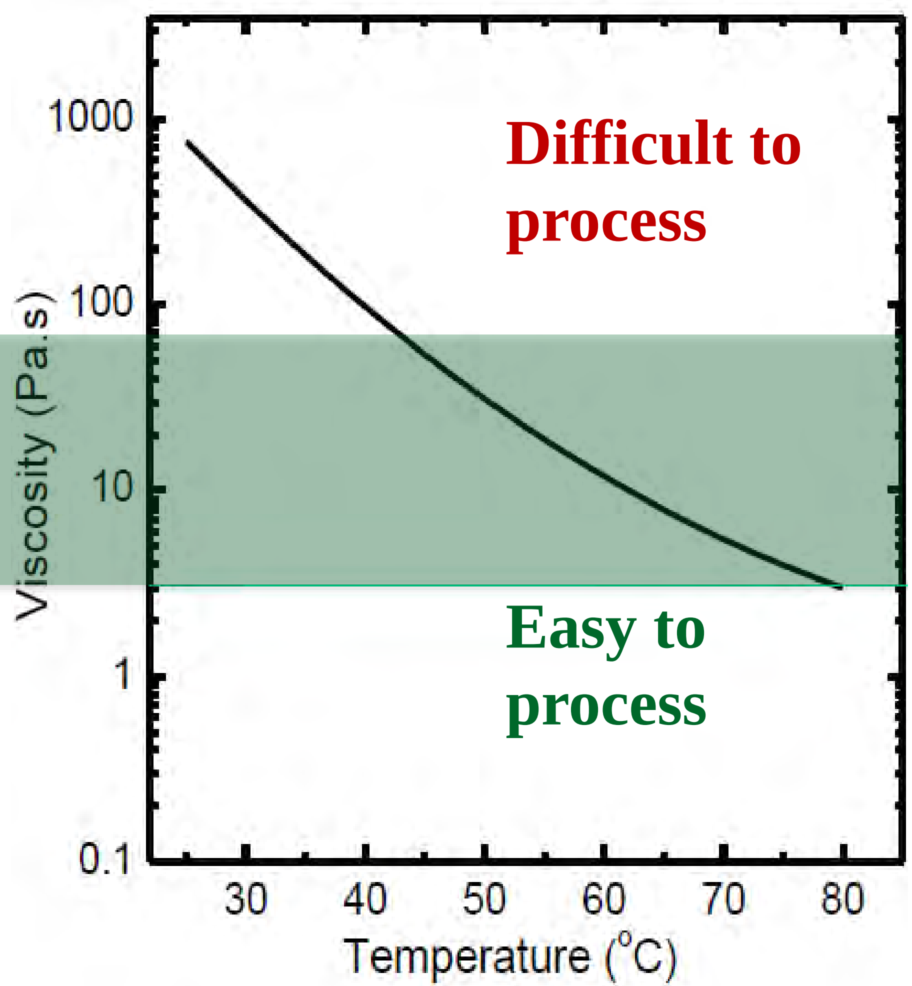
REFERENCE

[1] P. Gosselin, S. E. Hrudey, M. A. Naeth, A. Plourde, R. Therrien, G. Van Der Kraak, *et al.*, "Environmental and health impacts of Canada's oil sands industry," 2010

[2] Harjai, S.K., Flury, C., Masliyah, J., Drelich, J. and Xu, Z., 2012. Robust aqueous–nonaqueous hybrid process for bitumen extraction from mineable Athabasca oil sands. *Energy & Fuels*,*26*(5), pp.2920-2927.

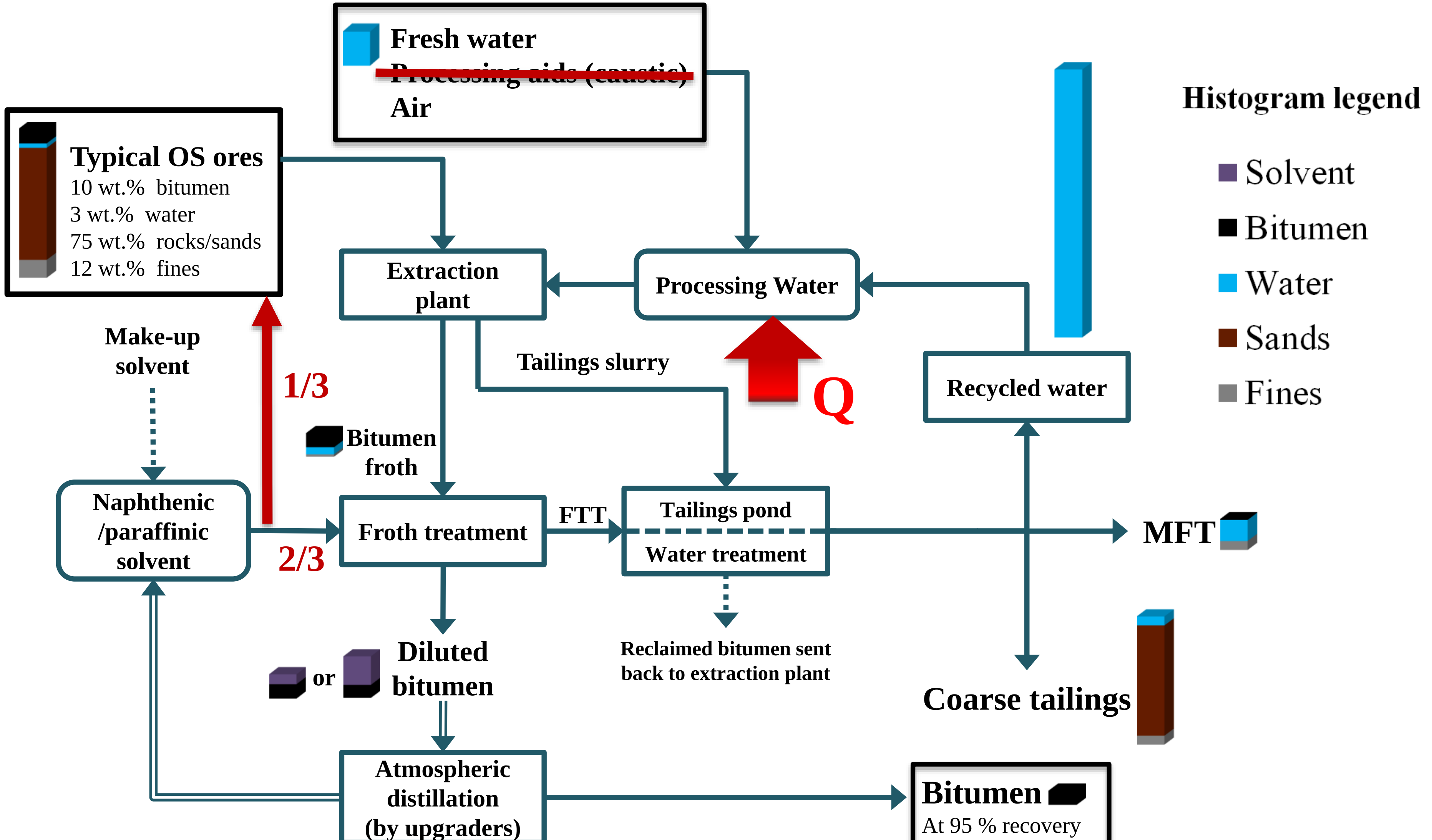
Effect of Solvent on Viscosity of Distillation Feed Bitumen





- Solvent sufficiently dilutes bitumen to the level of 1-10 Pa.s (or 10-100 poise) at 10-20 wt.% case

Hybrid Extraction: Process



REFERENCE

[1] J. Masliyah, Z. J. Zhou, Z. Xu, J. Czarnecki, and H. Hamza, "Understanding water-based bitumen extraction from Athabasca oil sands," *The Canadian Journal of Chemical Engineering*, vol. 82, pp. 628-654, 2004.

Hybrid Extraction: Features

- **Ambient temperature (25 °C)** processing
- Solvent addition at **low dosage**
  - Common solvent: Diesel; Kerosene; Biodiesel.
  - Common dosage: 10-20 wt% of bitumen, or 1-2 wt% of total oil sands.
- **No** caustic addition
- Minimum change to CHWE

Concept approved in lab-scale test at U of A

REFERENCE

[1] P. Gosselin, S. E. Hrudey, M. A. Naeth, A. Plourde, R. Therrien, G. Van Der Kraak, *et al.*, "Environmental and health impacts of Canada's oil sands industry," 2010

[2] Harjai, S.K., Flury, C., Masliyah, J., Drelich, J. and Xu, Z., 2012. Robust aqueous–nonaqueous hybrid process for bitumen extraction from mineable Athabasca oil sands. *Energy & Fuels*,*26*(5), pp.2920-2927.

Fundamental Study

(All experiments conducted at 25 °C)

University of Alberta

Three Solvents on Two Ore Samples

Source	Composition (wt. %)			
	Bitumen	Water	Solids	Fines*
Poor processing ore P	9.2	2.6	88.2	35.6
Medium-grade ore M	11.4	2.3	86.3	8.2

* Fraction of fines (defined as mineral solids less than 44 μm) in solids.

- 0, 5, 10, and 20 wt.% biodiesel, diesel or kerosene with respect to bitumen content as key parameters used in experiments

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Petroleum Diesel on Three Ore Samples

Oil Sands Ores	Bitumen (wt.%)	Water (wt.%)*	Solids (wt.%)*	Fines (wt.%)
AK (2015)	9.20	5.25	85.51	43
AD (2015)	10.00	4.21	85.80	21
AC (2016)	11.40	3.23**	84.86**	22

* Determined experimentally using Dean Stark extraction method
** Averaged values based on two samples

- 0, 5, 10, and 20 wt.% petroleum diesel with respect to bitumen content as key parameters used in experiments
- Dodecane for comparison (tailings analysis)

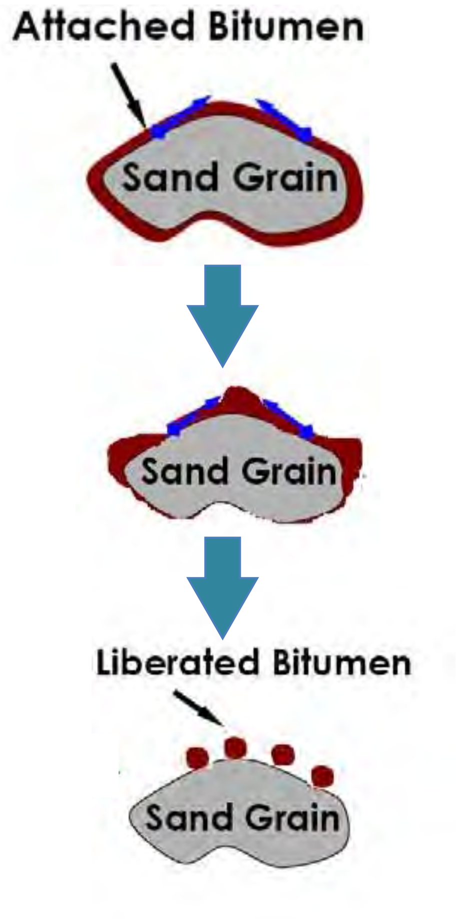
Composition of AURORA Process Water

Ions	Concentration (ppm)
Na^{+}	691
K^{+}	21
Mg^{2+}	19
Ca^{2+}	83
Cl^{-}	444

- The temperature and the pH of the Aurora process water were set at 25 ± 0.5 ºC and 7.52 ± 0.05, respectively

Thanks to Jie Ru and Yi Lu for preparing sample and conducting ion chromatography experiment

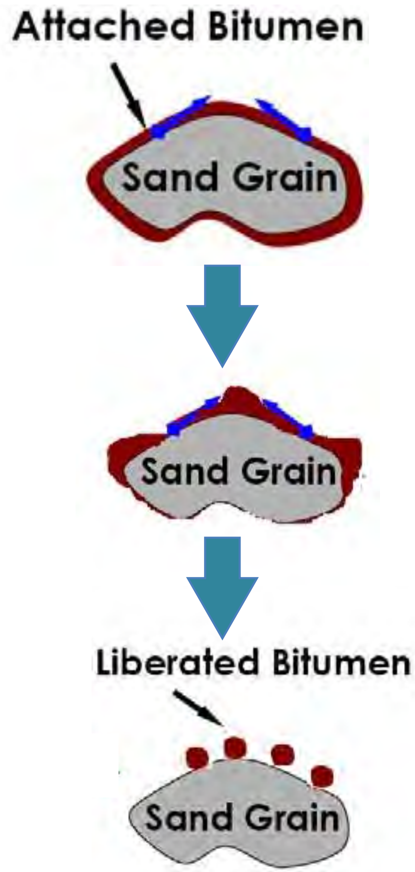
Liberation Visualization Technique



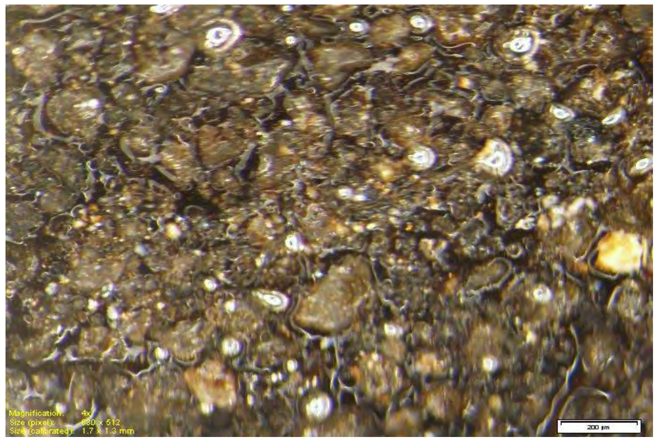
REFERENCE

S. Rajagopalan: Study of Bitumen Liberation from Oil Sands Ore

Still Images of Bitumen Liberation



Blank, 0 s



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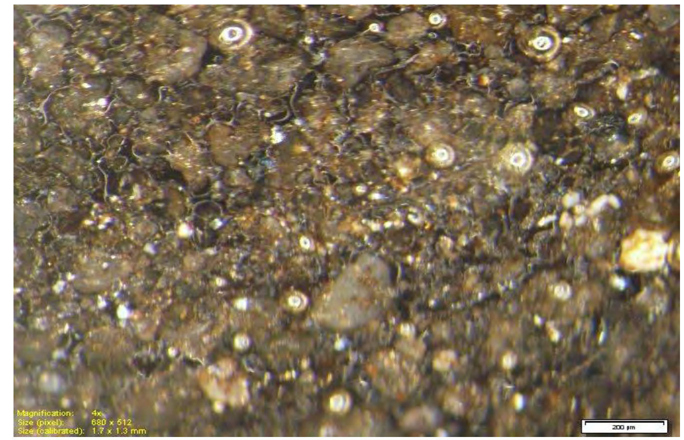
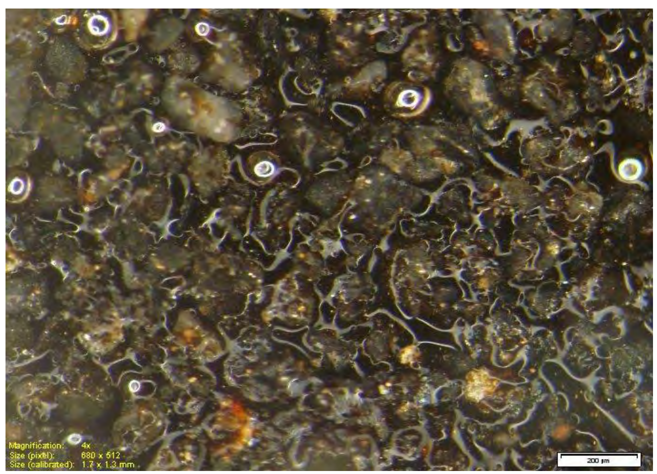
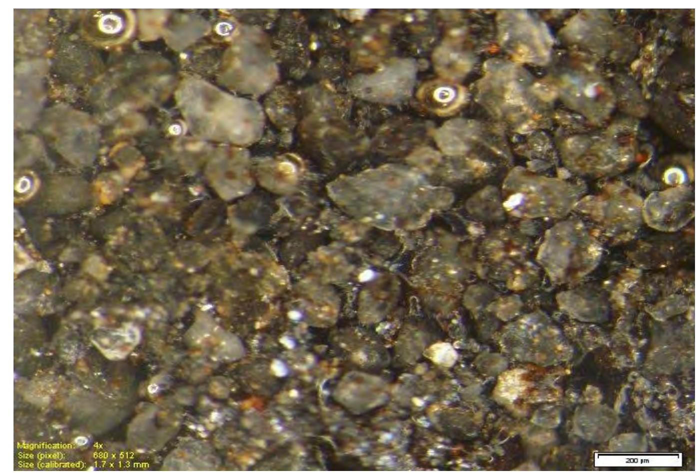


20 wt.% Petroleum Diesel, 0 s

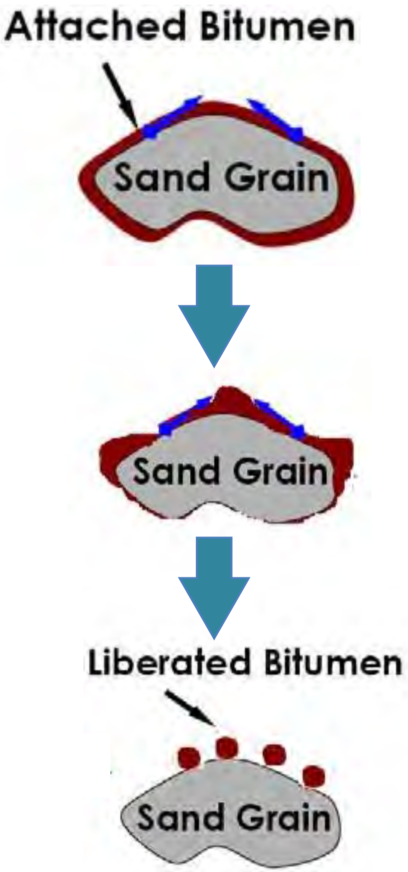


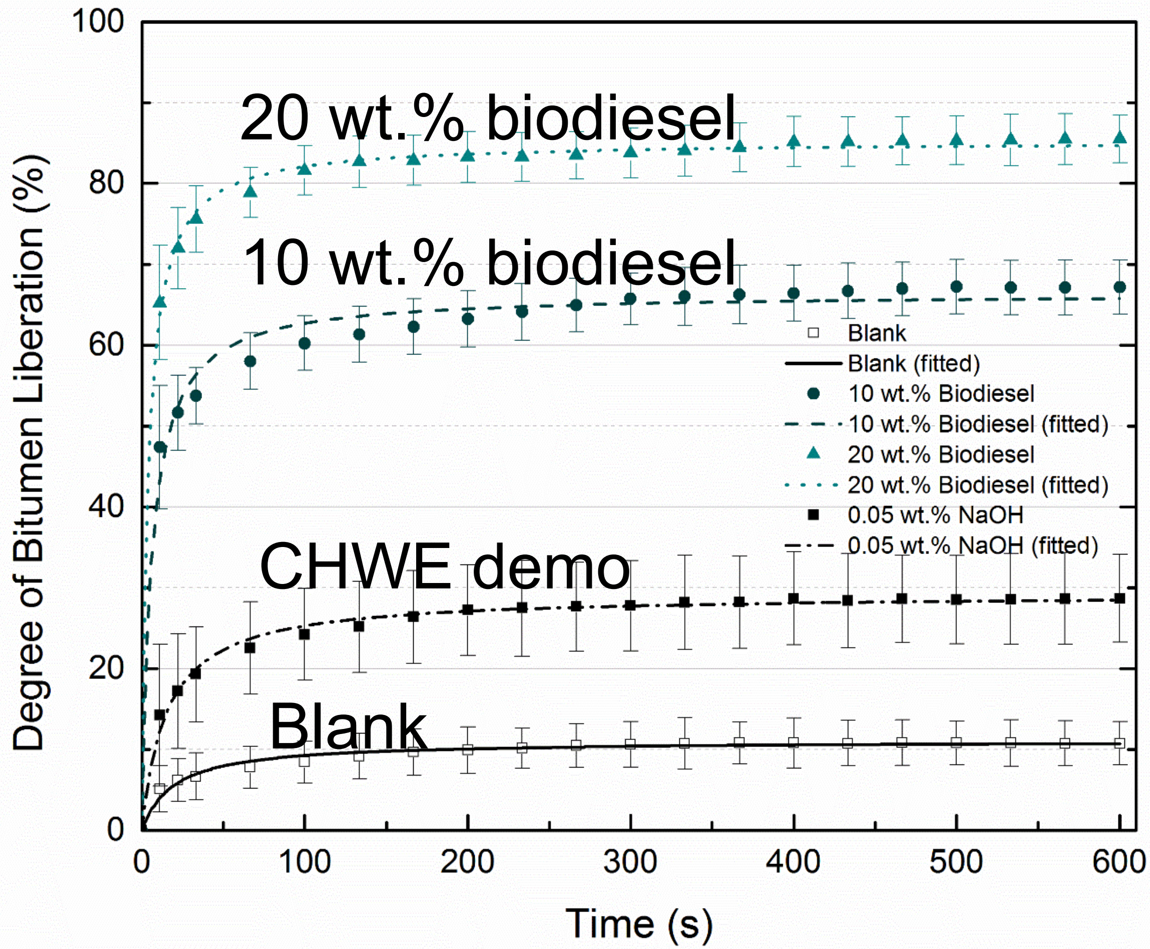
20 wt.% Petroleum Diesel, 100 s



REFERENCE
S. Rajagopalan: Study of Bitumen Liberation from Oil Sands Ore

Effect of Solvent on Bitumen Liberation

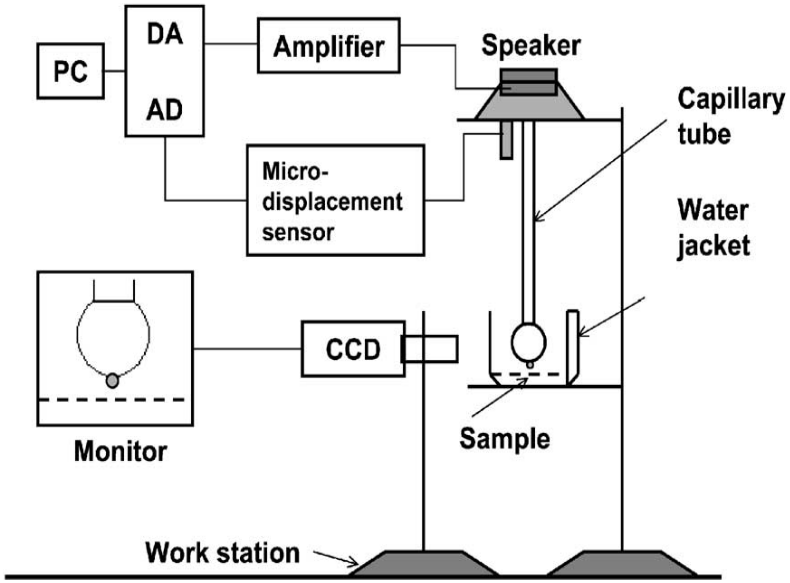


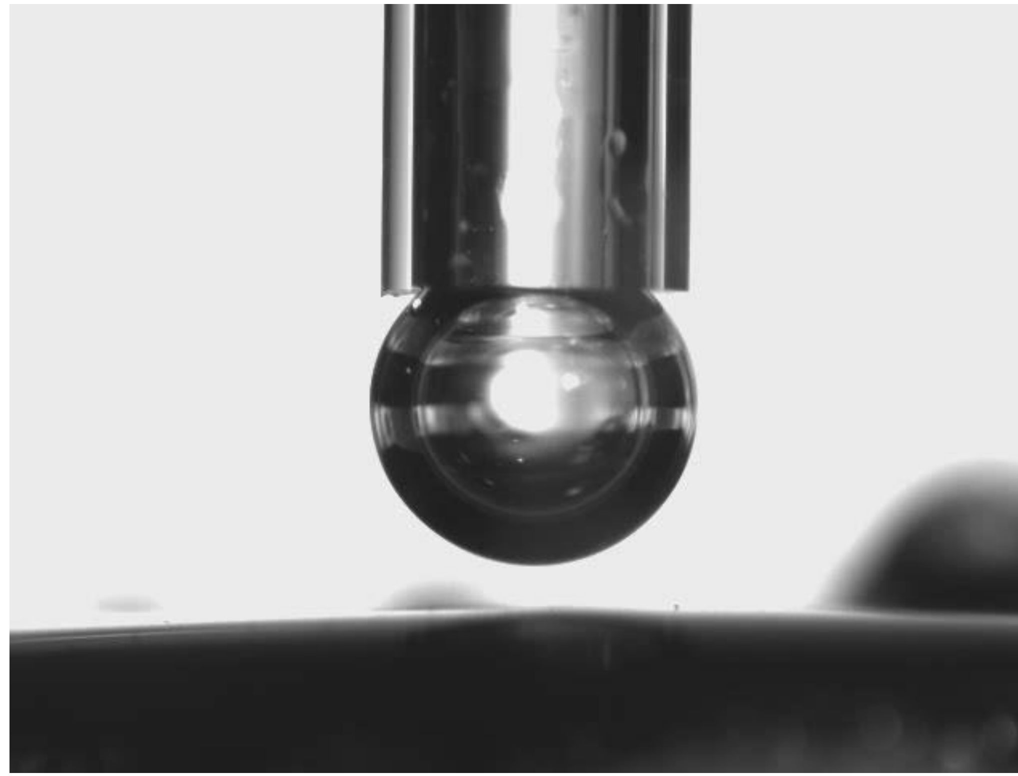


Sample: ore P

REFERENCE
S. Rajagopalan: Study of Bitumen Liberation from Oil Sands Ore

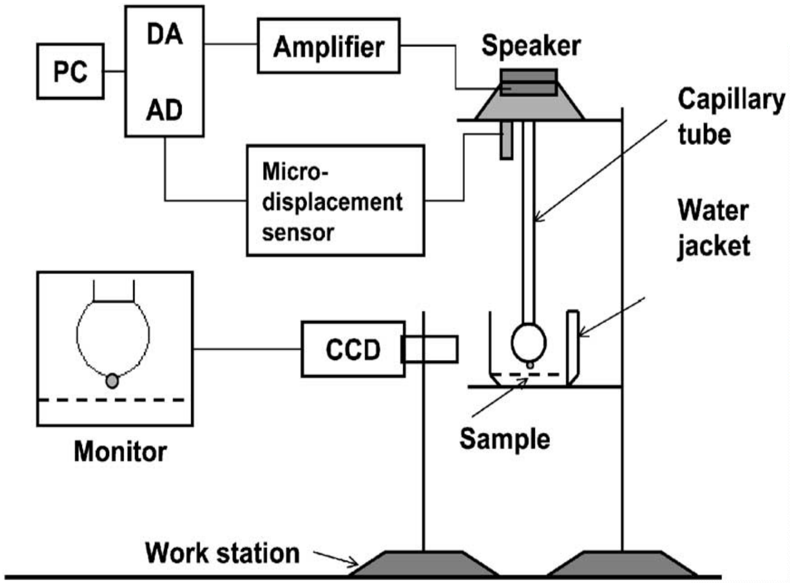
Effect of Solvent on Bitumen Aeration

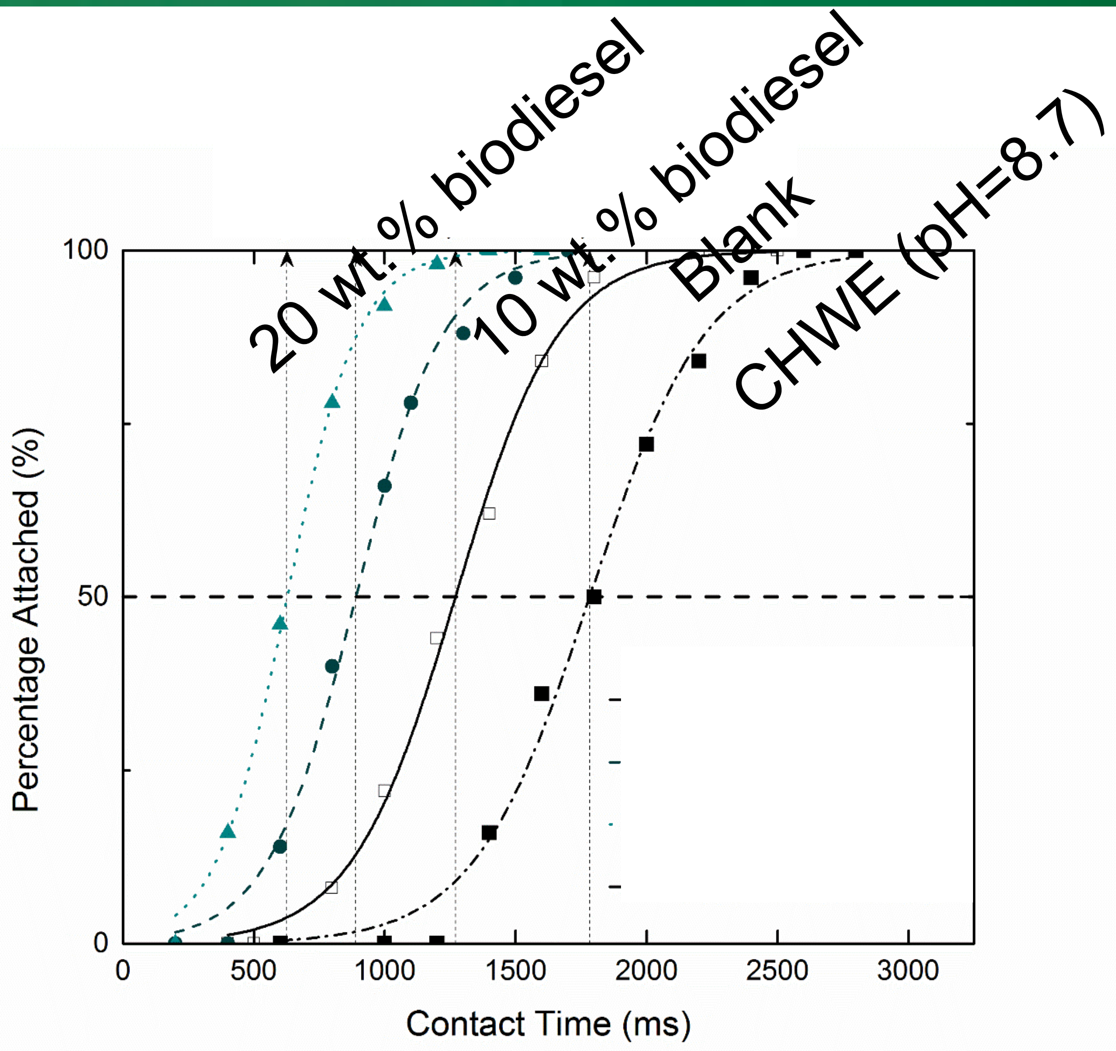




REFERENCE
G. Gu et al. / Int. J. Miner. Process. 69 (2003) 235–250

Effect of Solvent on Bitumen Aeration





REFERENCE
G. Gu et al. / Int. J. Miner. Process. 69 (2003) 235–250

Sample: ore P

Lab Extraction Test

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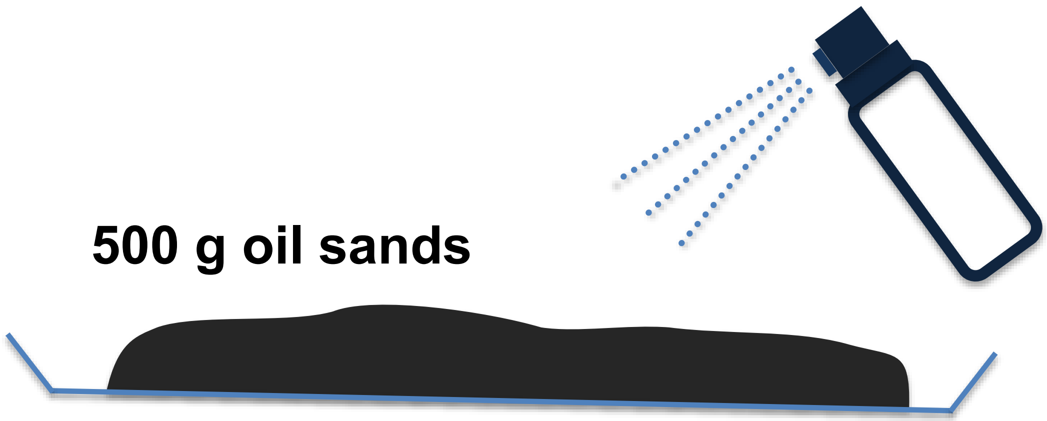
Lab Test Procedures

Step 1: Ore Pretreatment with Specified Solvents

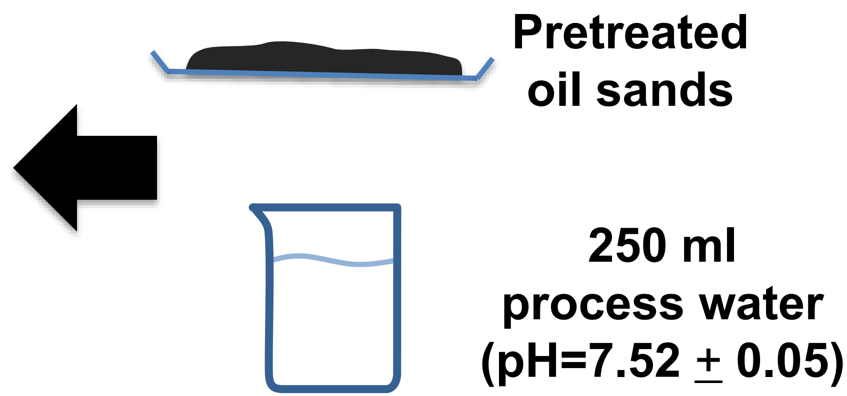
- Solvent spread on 500 g oil sands by spray bottle/atomizer.
- Soaking for 20 min.

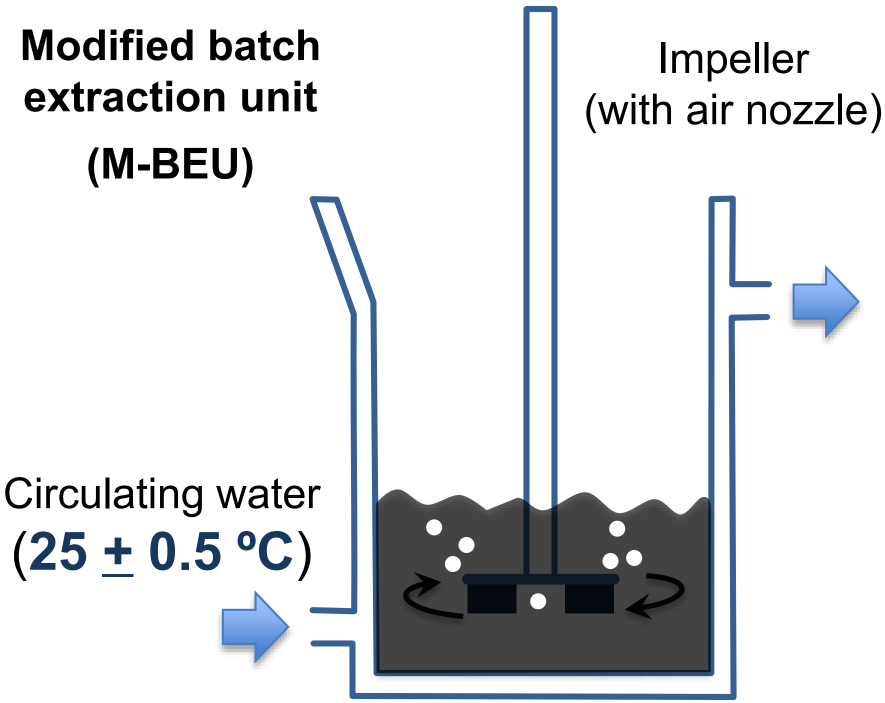


Lab Test Procedures

Step 2: Slurry conditioning

- Agitation rate 800 rpm; air inlet: 150 ml/min.
- Slurry conditioning lasts 10 min.

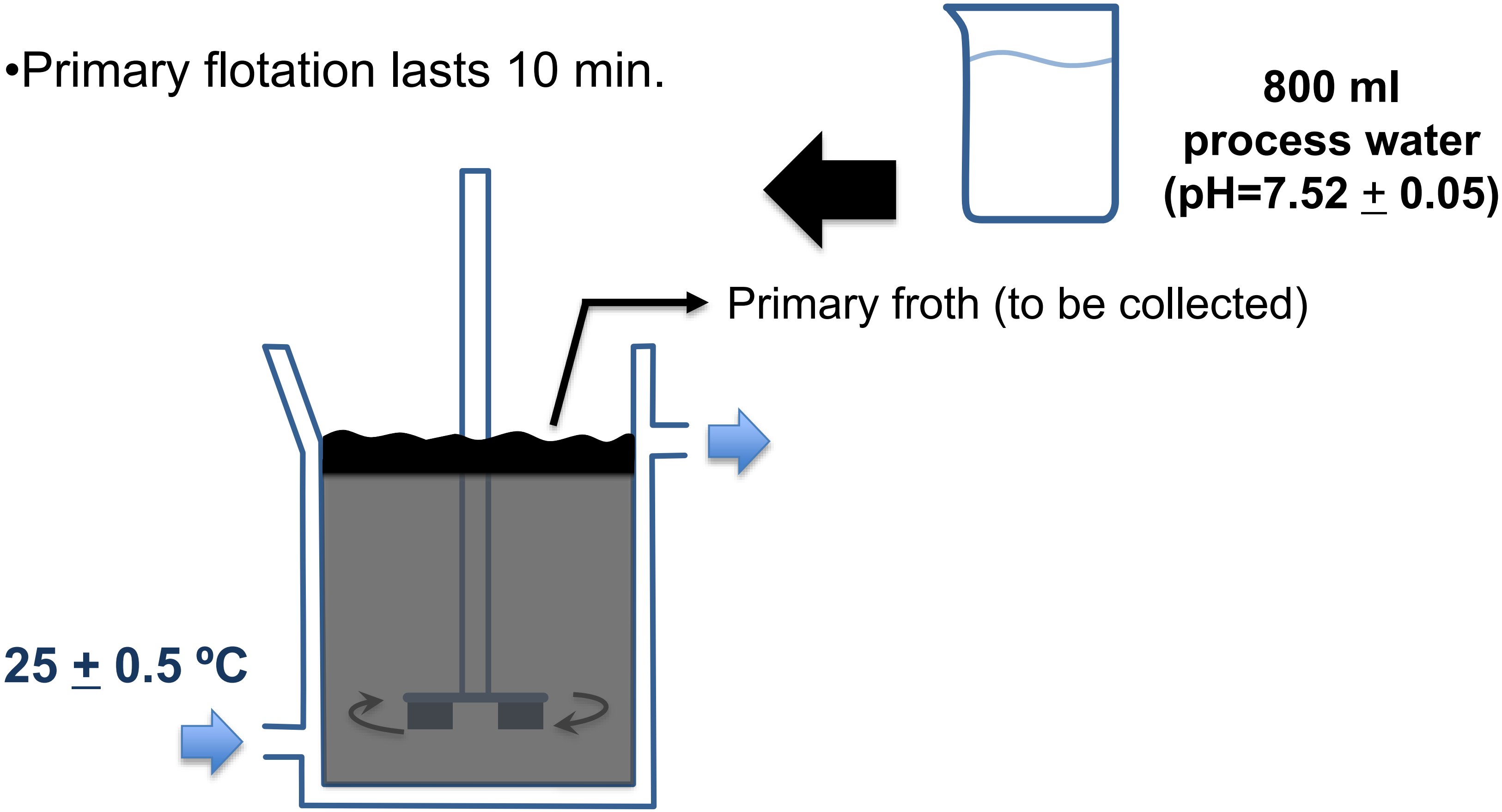




Lab-Based Tests: Procedure

Step 3: Primary flotation

- Agitation rate 600 rpm; no air inlet.
- Primary flotation lasts 10 min.

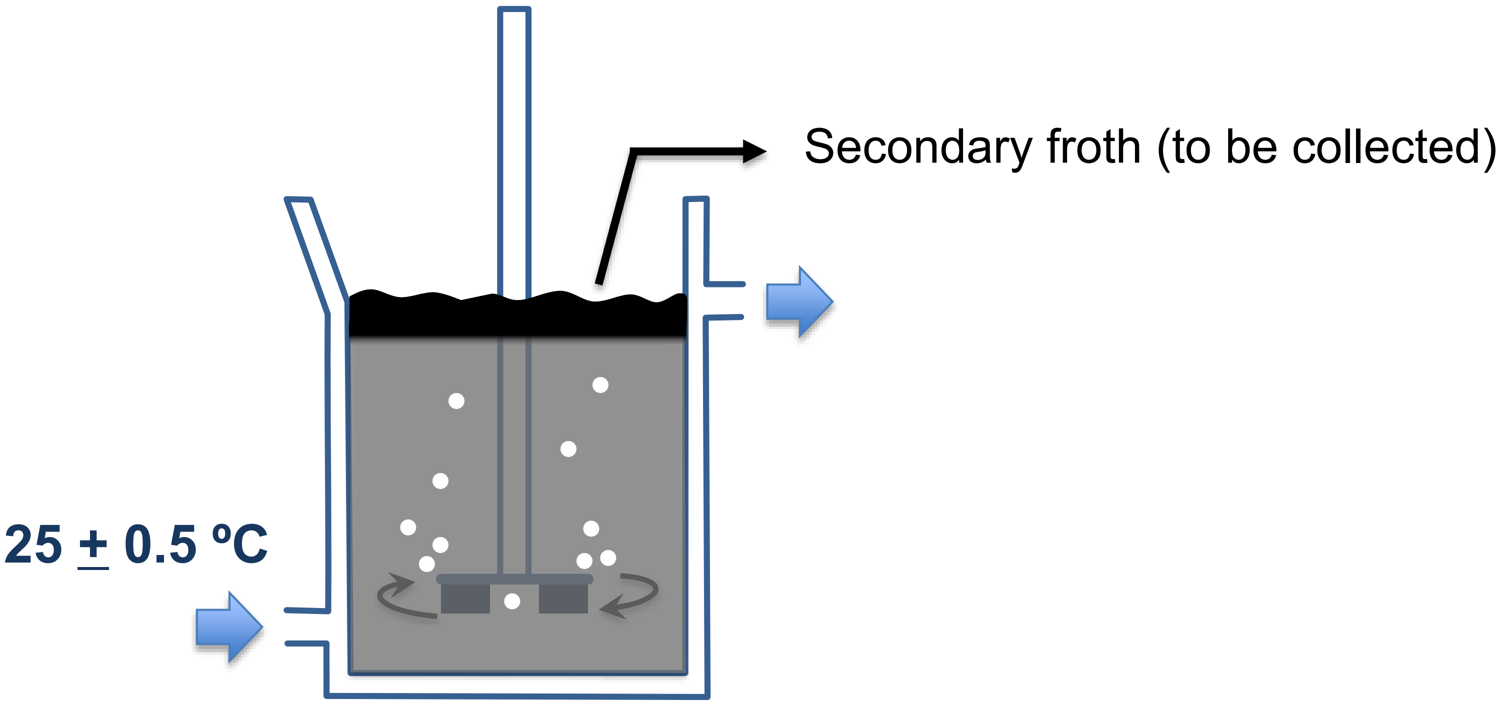


Lab-Based Tests: Procedure

Step 3: Secondary flotation

- Agitation rate 800 rpm; air inlet: 150 ml/min.

- Secondary flotation lasts 10 min.



Lab-Based Tests Video

Primary Flotation (first ~60 seconds out of 10 min)

Blank

10 wt% Diesel

10 wt% Dodecane

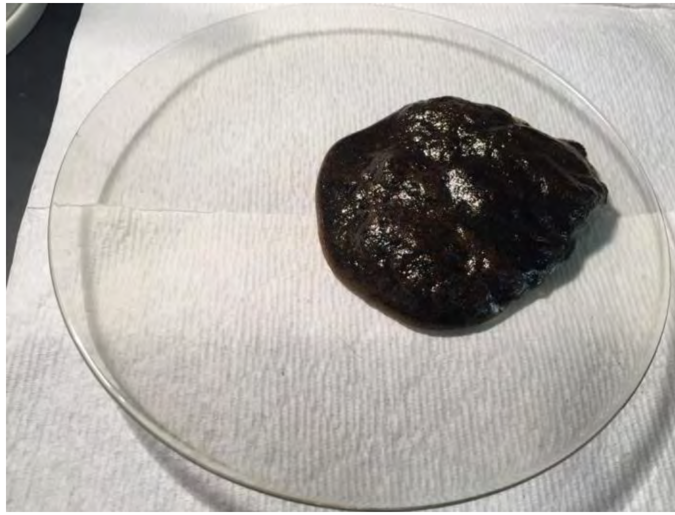
Lab-Based Tests Video

Secondary Flotation (first ~60 seconds out of 10 min)

Blank **10 wt% Diesel** **10 wt% Dodecane**

Froth Quality (Primary Froth)

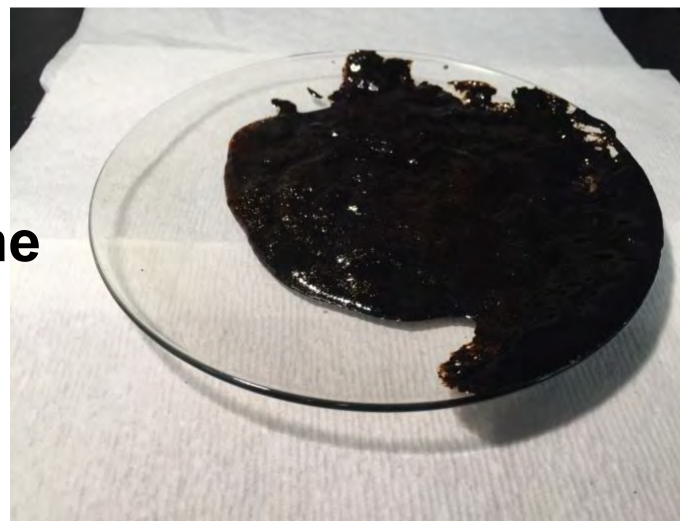
Blank

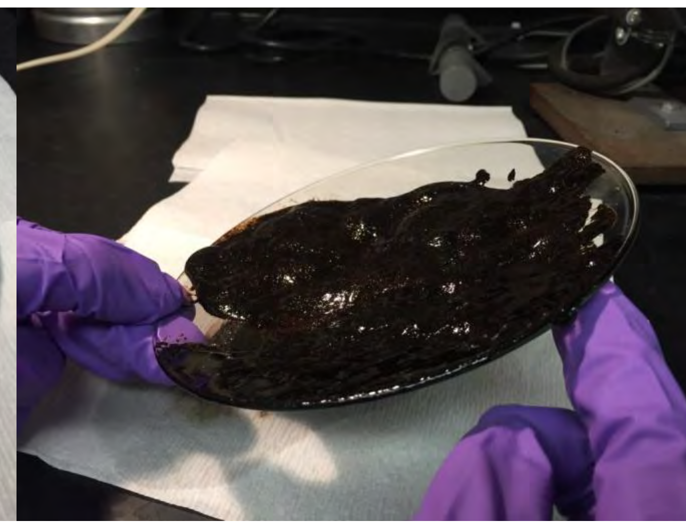


10 wt% Diesel

or

10 wt% Dodecane





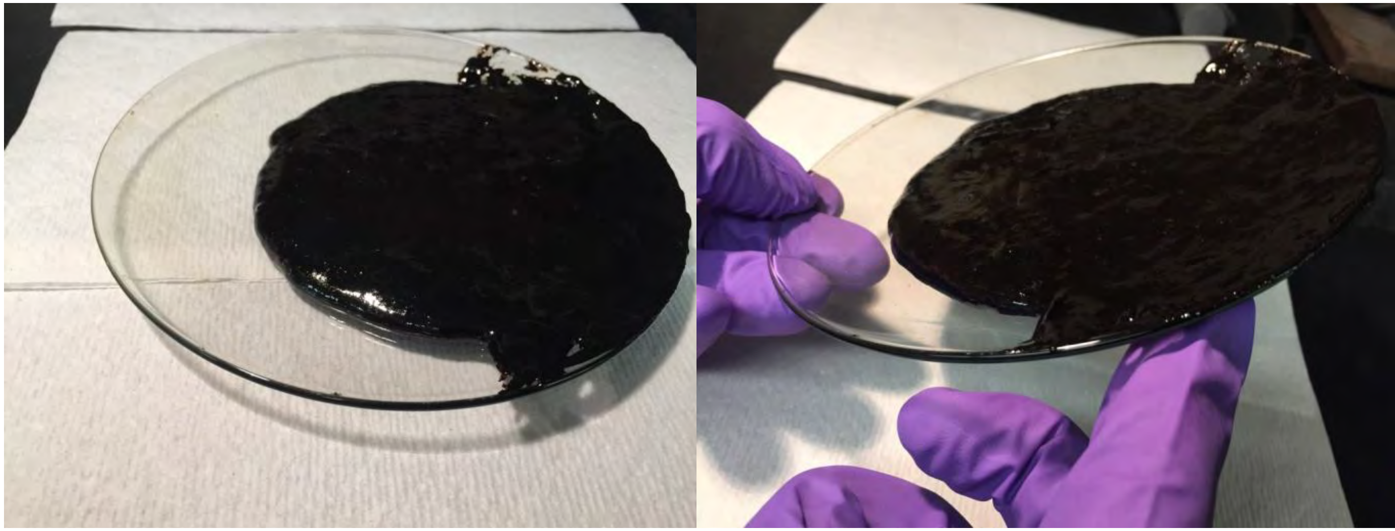
Froth Quality (Secondary Froth)

Blank

10 wt% Diesel

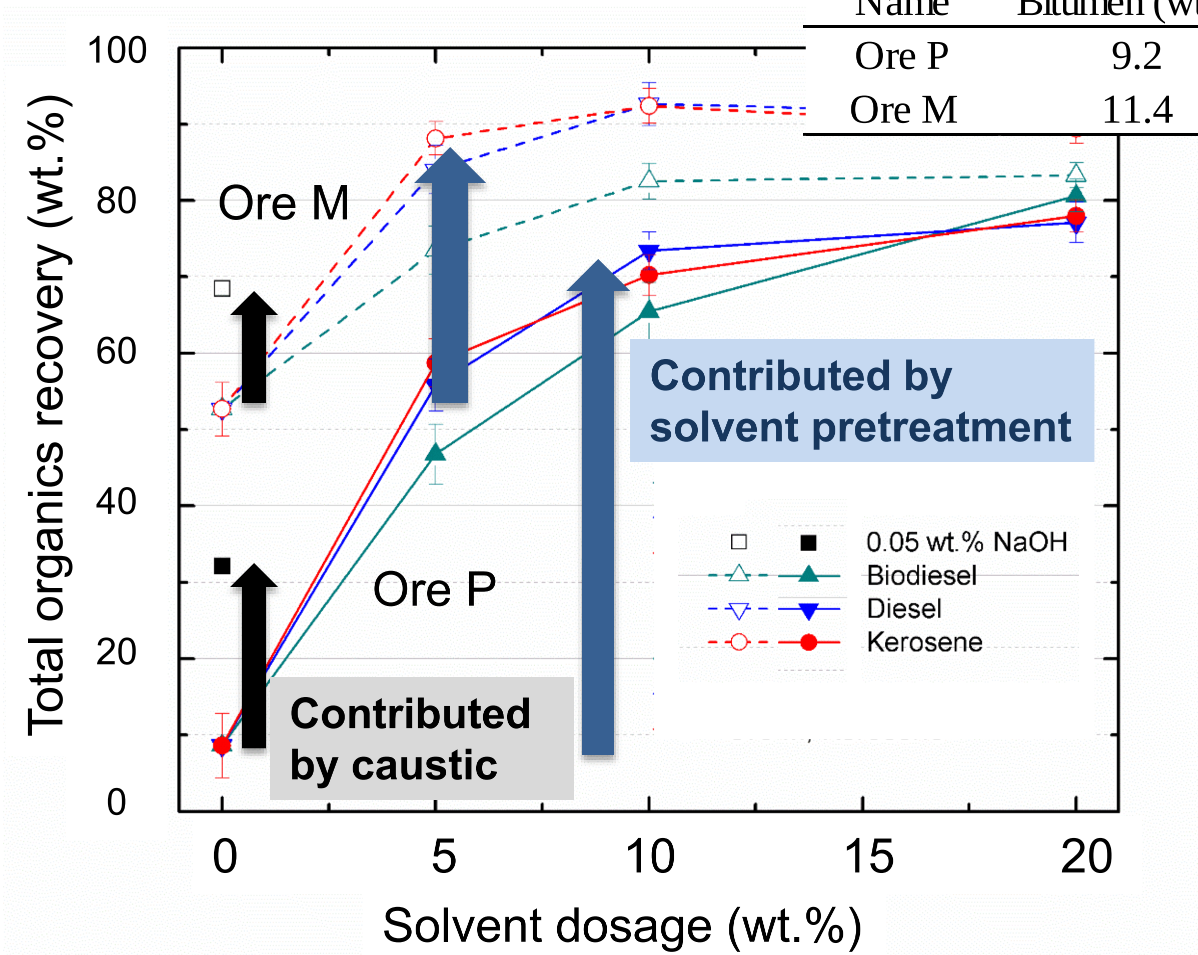
or

10 wt% Dodecane



Effect of Solvent Types on Bitumen Recovery (3 Key Solvent Cases)

Name	Bitumen (wt.%)	Fines (wt.% of Solids)
Ore P	9.2	35.6
Ore M	11.4	8.2

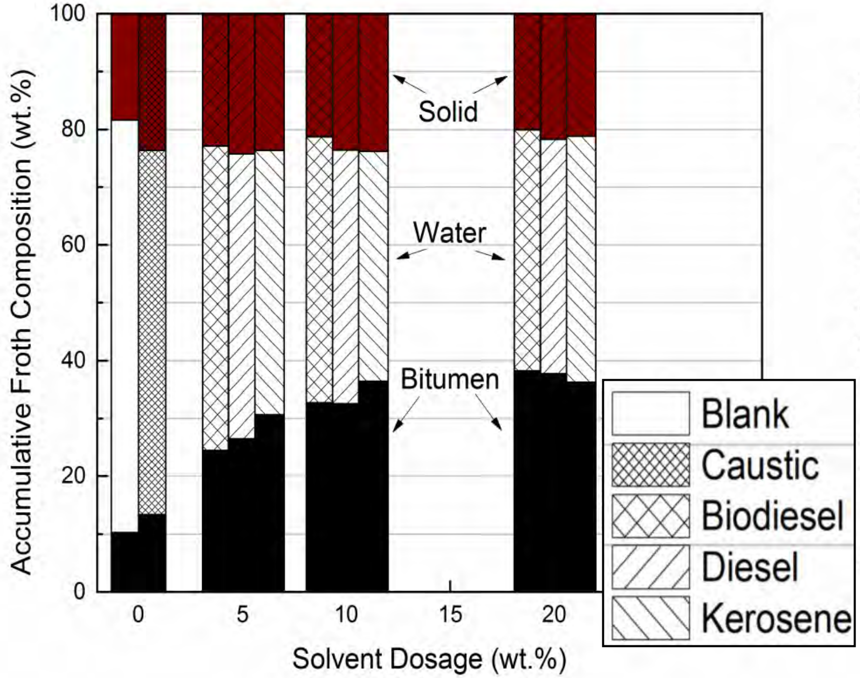


- Solvent addition generally improves bitumen extraction regardless of the types of ores

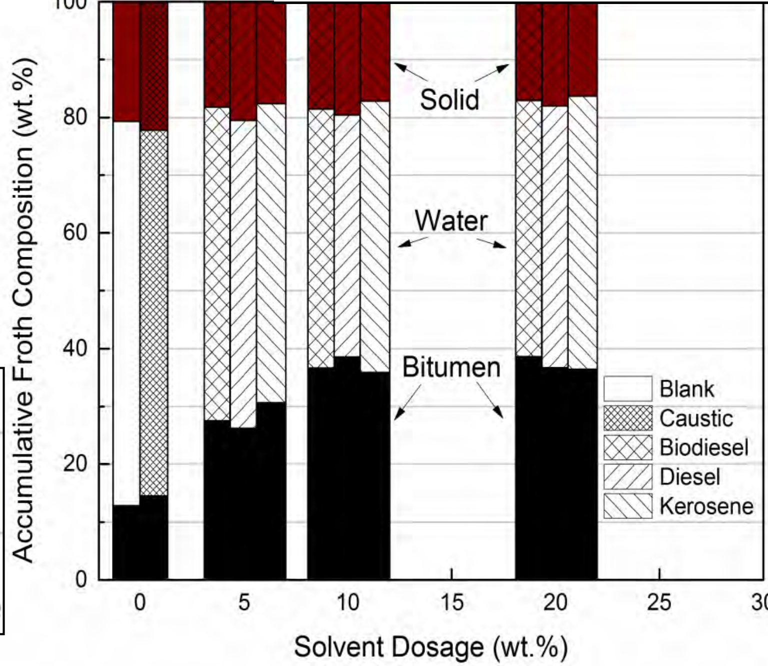
Effect of Solvent Types on Froth Quality (3 Key Solvent Cases)

Name	Bitumen (wt.%)	Fines (wt.% of Solids)
Ore P	9.2	35.6
Ore M	11.4	8.2

Ore P

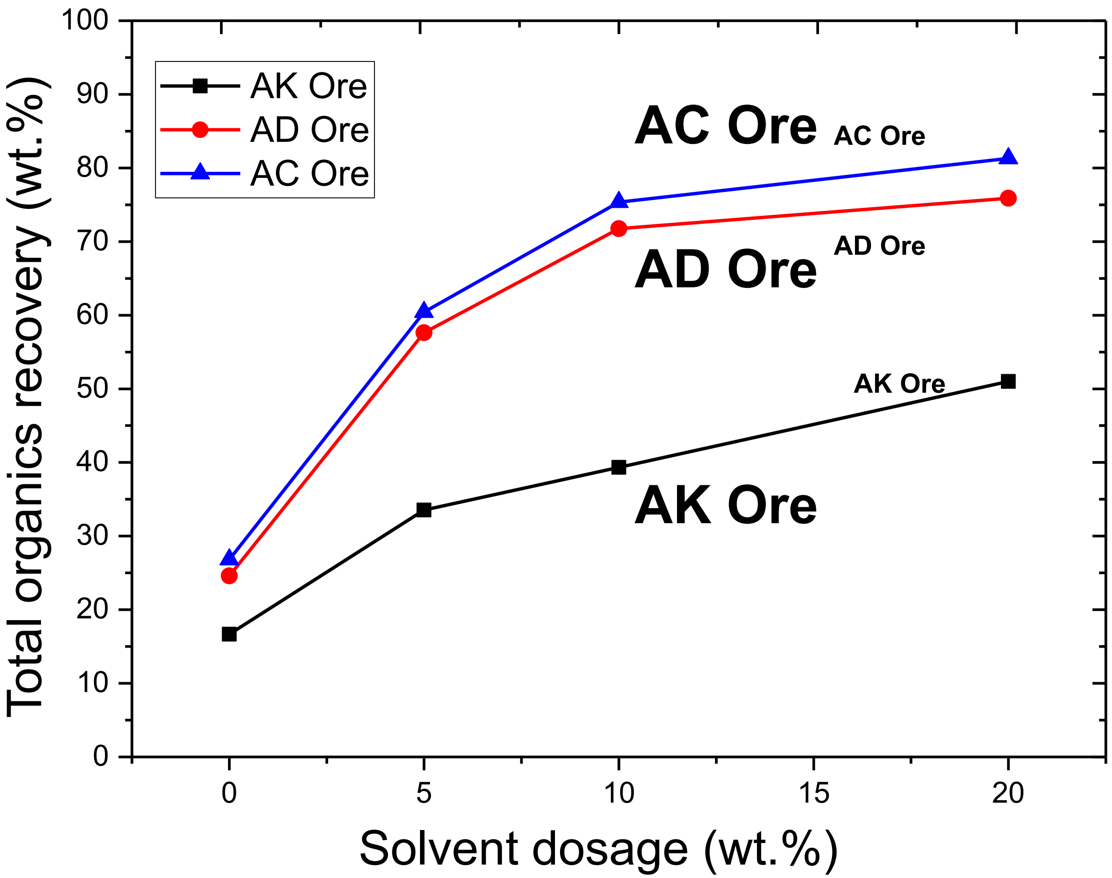


Ore M



- Total extraction process time of 30 min.
- Marginal difference in froth quality at 20 wt.% solvent case between three solvents for both ores.

Effect of Petroleum Diesel: Recovery

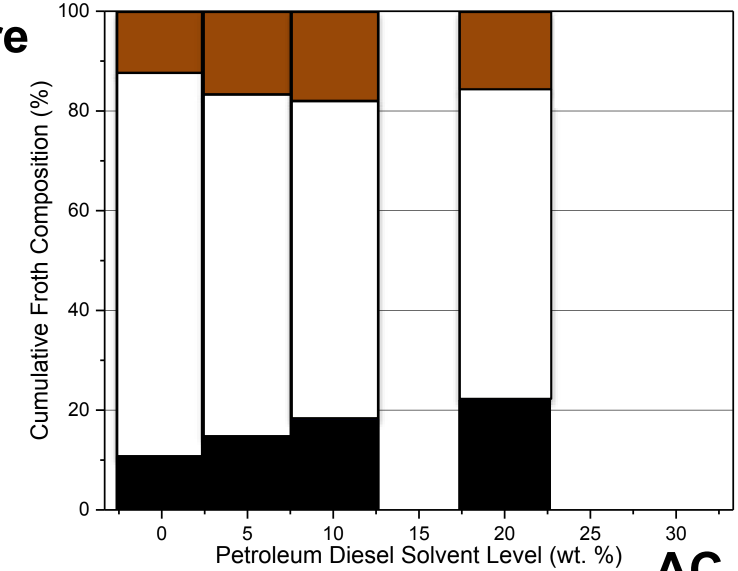


Name	Bitumen (wt.%)	Fines (wt.% of Solids)
AK (2015)	9.20	43
AD (2015)	10.0	21
AC (2016)	11.4	22

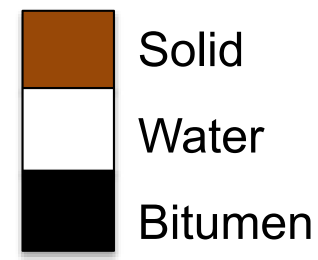
- Marginal improvement in hydrocarbon recovery at 20 wt.% petroleum diesel compare to 10 wt.% dosage for high grade ores

Effect of Petroleum Diesel: Froth Quality

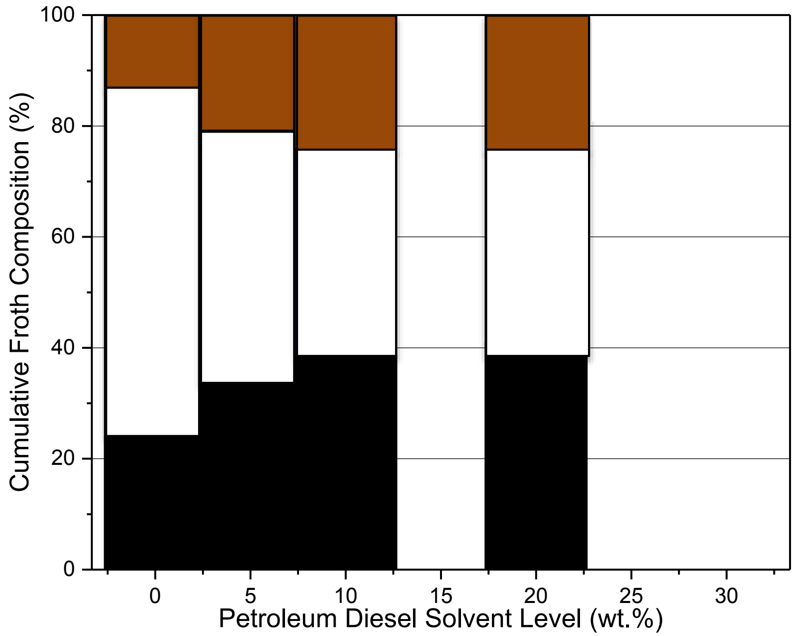
AK Ore



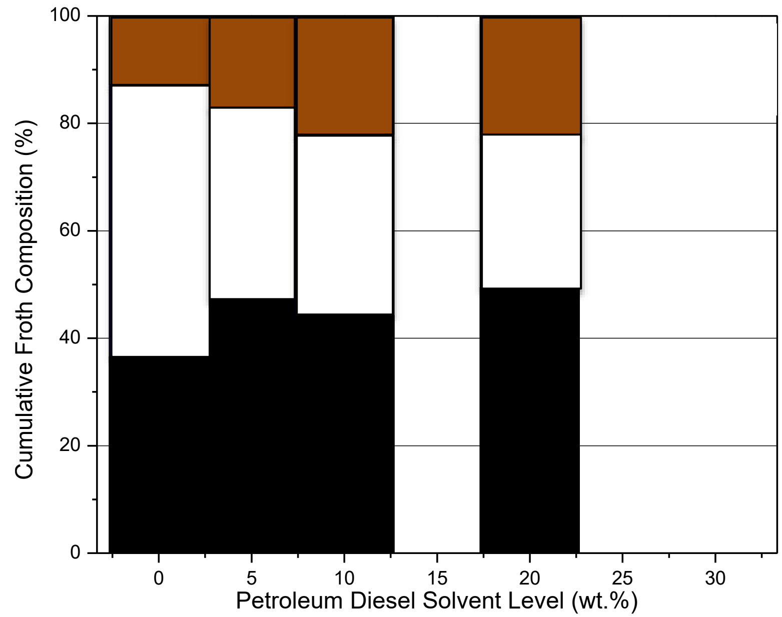
Name	Bitumen (wt.%)	Fines (wt.% of Solids)
AK (2015)	9.20	43
AD (2015)	10.0	21
AC (2016)	11.4	22



AD Ore



AC Ore



Key Findings on Extraction Experiments

- Increasing solvent dosage increases overall organics recovery, the level depending on ore characteristics

- Increasing solvent dosage improves froth quality for all the ores

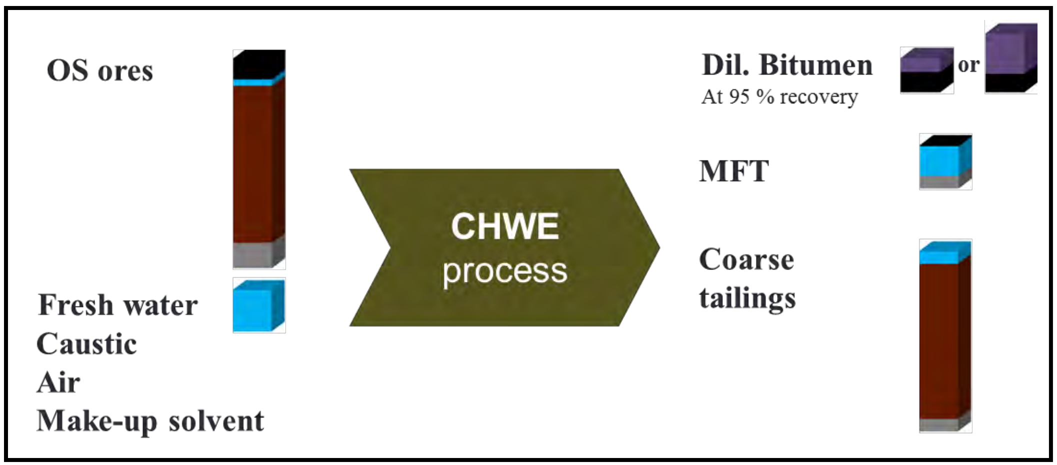
- Petroleum diesel and kerosene perform better than biodiesel for extracting bitumen from ores at ambient temperature and neutral pH conditions

Impact on Tailings Settling

Challenges with CHWE

Tailings management

- ~2 bbl MFT are produced for 1 bbl bitumen production.
- Diluent loss, water pollution, land reclamation and safety concern.



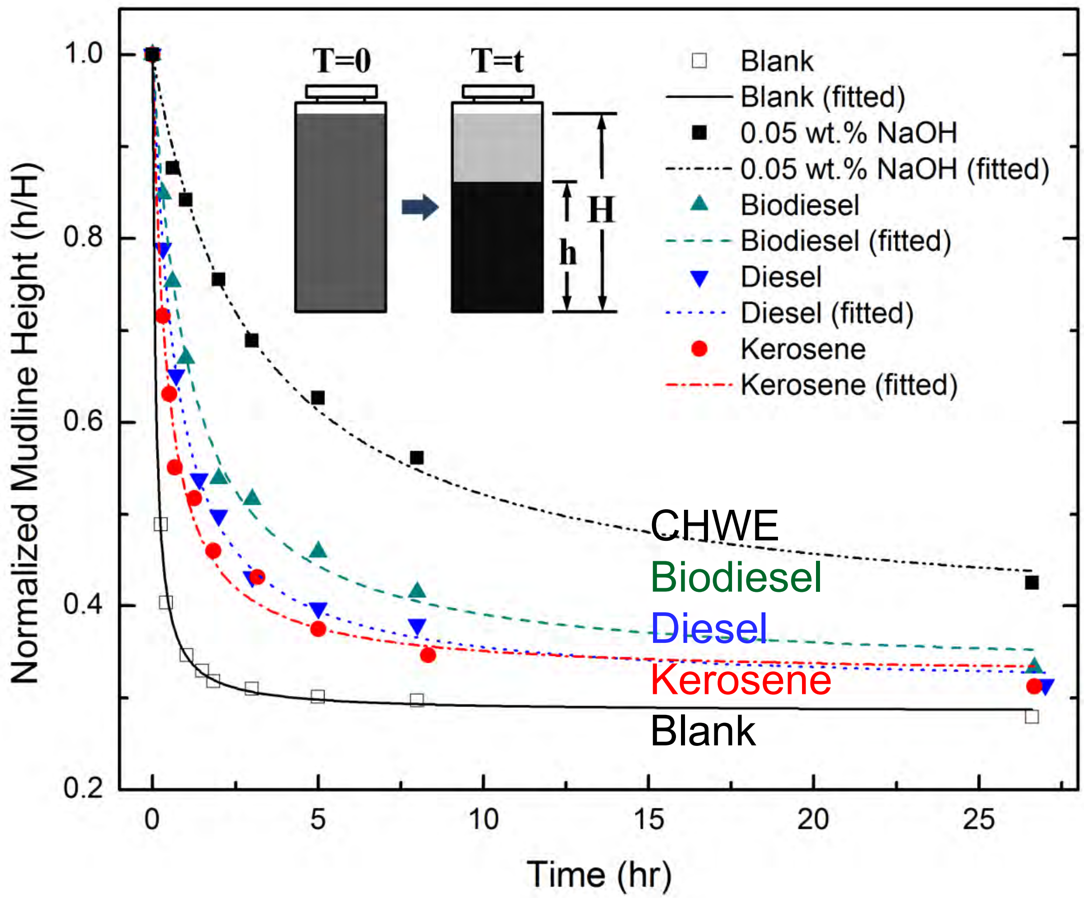
Total area of tailings ponds of Alberta mineable oil sands industry

Year	2008	2015
Area (km^2)	130	176

35.3 %

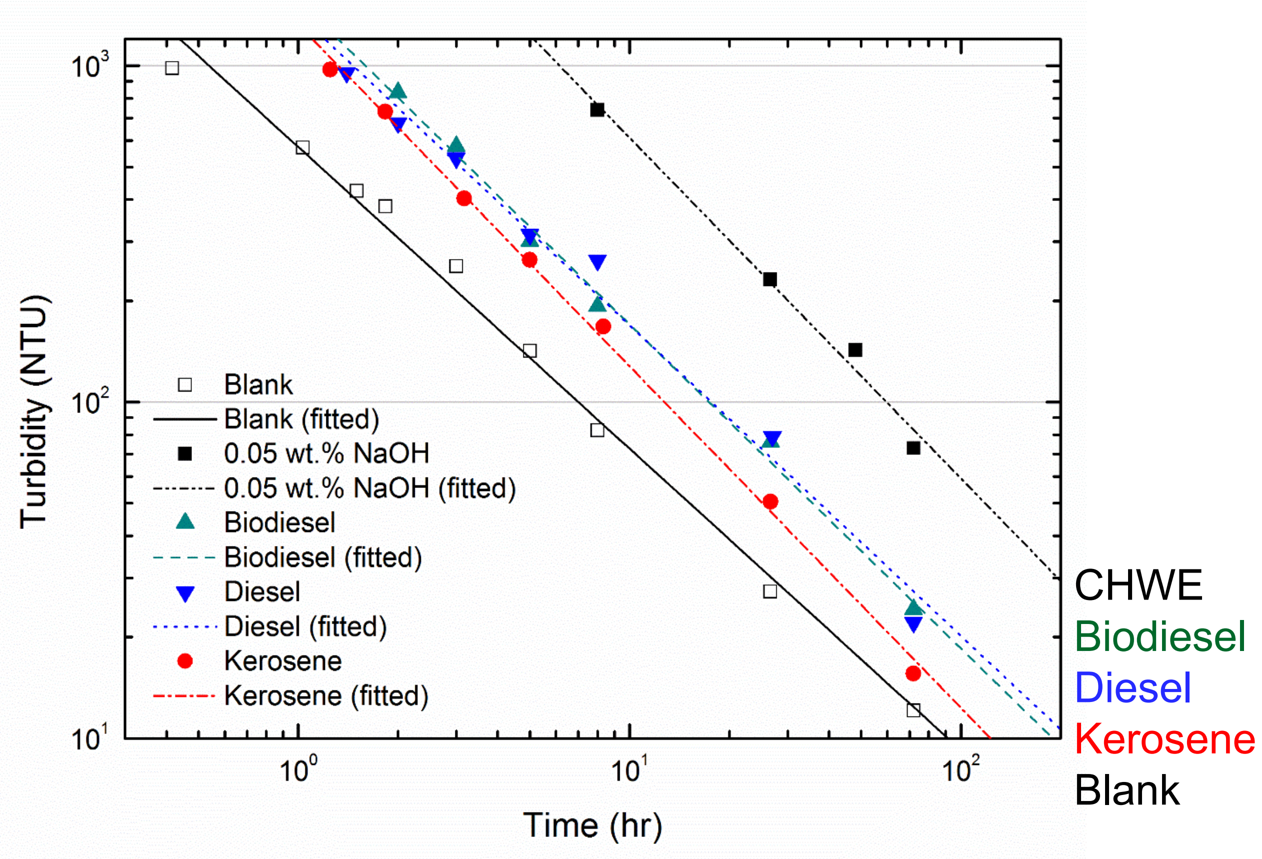
REFERENCE
[1] J. Masliyah, Z. J. Zhou, Z. Xu, J. Czarnecki, and H. Hamza, "Understanding water-based bitumen extraction from Athabasca oil sands," *The Canadian Journal of Chemical Engineering,* vol. 82, pp. 628-654, 2004.
[2] CAPP 2015

Lab Tests: Tailings Settling



- Experimental data fits with hyperbola fitting (lines) for 20 wt.% solvent case using poor processing ore, Ore P
- Solvents improve tailings consolidation and enhance compactness of final sediments

Effect of Solvent Addition on Turbidity of Supernatant (Tailings)



- Experimental data fit with linear in double logarithmic scale for 20 wt.% solvent case using poor processing ore, Ore P

Solvent Partition / Loss to Tailings

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Summary of Dodecane Loss to tailings in MBEU-Based Extraction

	Bitumen (g)	Dodecane (g)	Dodecane / Bitumen Ratio
Initial State	~57 (/500 g OS)	5.70	**~10 %**
Primary Froth	41.8119	4.4781	**10.71%**
Secondary Froth	5.9794	0.5206	**8.71%**
Total Froths	47.7913	4.9987	**10.46 %**
Final Tailings	~9.2714	0.7013	**~7.62%**

- Collected froth underwent Dean-Stark apparatus to remove impurities (solid and water).
- Dodecane / bitumen ratio in total froths is higher than that of initial state, suggesting dodecane preferentially stays with bitumen, rather than solid or water.
- With 84% bitumen recovery, solvent recovery is 88%.

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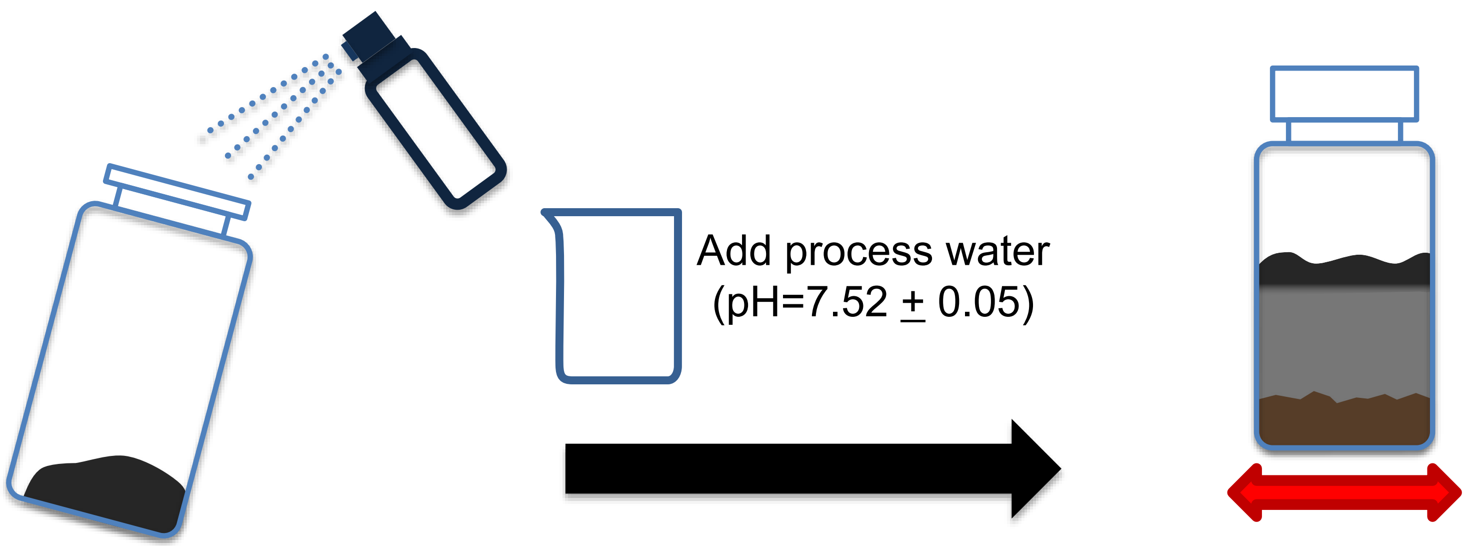
Solvent Partition Test: Procedure

Step 1: Jar-Based Hybrid Extraction Demo

- Weigh 50 g oil sands into glass jar; disperse 10 wt% (of bitumen) atomized solvent onto sample for 20 min pretreatment.

- Adding 100 ml processing water; sealed and homogenized by commercial shaker for 3 hrs at ambient temperature (**<u>25 ºC</u>**).



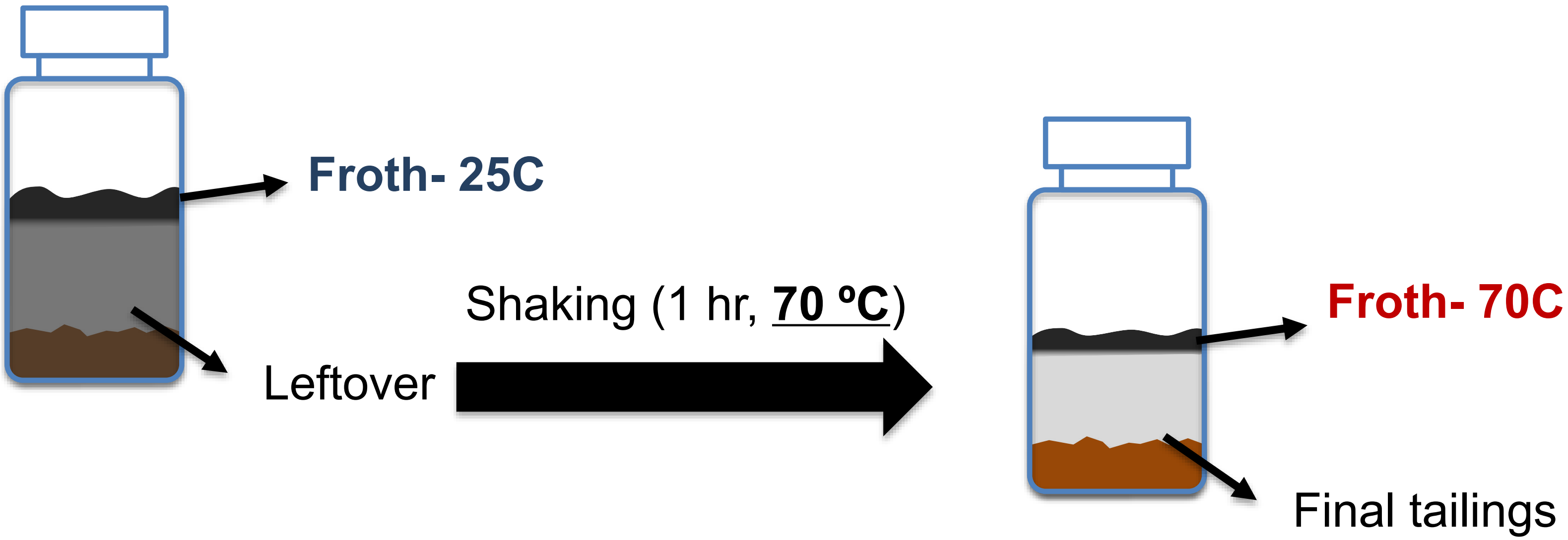
Ore pretreatment (20 min)

Shaking (3 hr, <u>25 ºC</u>)

Solvent Partition Test: Procedure

Step 2: Froth Collection

- Froth was directly collected and named as "**Froth- 25C**", which mainly contains floated bitumen.
- Continue homogenizing the leftover for another 1 hr at an increased temperature of **<u>70 ºC</u>**. Extra froth generated and collected as "**Froth- 70C**".



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Solvent Partition Test: Procedure

Step 3: Froth Cleaning

- "**Froth- 25C**" and "**Froth- 70C**" were treated with cyclo-pentane to reject water/solid impurities; sediment further soaked with adequate amount (not reaching deasphaltening threshold) of cyclo-pentane several times to accumulate all bitumen and solvent.

Froth- 25C
or
Froth- 70C

Cyclo-pentane
→
Sediment wash

→ Cyclo-pentane diluted **Bitumen- 25C** (or diluted **Bitumen- 70C**)

→ Clean impurities (water & fine solids)

Solvent Partition Test: Procedure

Step 4: Solvent Content Quantification

- Remove cyclo-pentane from diluted bitumen at ~50 ºC (B.P.).
- Quantitative analysis of solvent content in product by proper methodology (e.g. FTIR, TGA).

Diluted **Bitumen- 25C**
or
Diluted **Bitumen- 70C**

→ Remove cyclo-pentane →

Solvent-bitumen mixture

→

Solvent content test

Summary of Biodiesel Partition in Jar-Based Procedure

	Bitumen (g)	Biodiesel (g)	Biodiesel / Bitumen Ratio
Initial State	~5.7 (/50 g OS)	0.570	**~10 %**
Froth- 25C	3.3342	0.3501	**10.499 ± 0.024 %**
Froth- 70C	2.2130	0.2086	**9.424 ± 0.005 %**
Total Froths	5.5472	0.5586	**10.07 %**
Final Tailings	~0.1528	0.0114	**~7.46 %**

- Biodiesel / bitumen ratio in froth is close to that of initial state, suggesting biodiesel preferentially stays with bitumen, rather than solid or water.
- Reduced biodiesel concentration (out of bitumen) in froth was observed with increased difficulty in bitumen recovery.

Details of data processing at Page. 61 & 62

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Conclusions

Promoted extraction performance

- Improved overall bitumen recovery (up to 80 % for poor processing ore).
- Improved froth quality.

Feasibility of ambient temperature operation verified

- Reduced energy intensity/GHG emissions.

Improved tailings densification

- Faster tailings densification as compared with CHWE.

Ease of commercialization

- High similarity to the current process.
- Full use of current CHWE facilities.

REFERENCE
[1] Harjai, S.K., Flury, C., Masliyah, J., Drelich, J. and Xu, Z., 2012. Robust aqueous–nonaqueous hybrid process for bitumen extraction from mineable Athabasca oil sands. *Energy & Fuels*,*26*(5), pp.2920-2927.

Research Trends on Hybrid Extraction

Alternative solvents: an ideal solvent for hybrid extraction

Improving bitumen recovery (tailings solvent recovery)

Use of process aids

Enhanced tailings dewatering: dry stackable tailings

- Polymer flocculants, i.e. EO-PO, EC derivatives, etc.
- Advanced polymer flocculant under development in UofA.

REFERENCE

[1] Harjai, S.K., Flury, C., Masliyah, J., Drelich, J. and Xu, Z., 2012. Robust aqueous–nonaqueous hybrid process for bitumen extraction from mineable Athabasca oil sands. *Energy & Fuels*,*26*(5), pp.2920-2927.

Requirement for An Ideal Solvent

- Good extraction performance, i.e. high recovery, high product quality, etc.
- Easy and economic removal/recovery of solvent from tailings.
- Less (negative) environmental impacts, i.e., land, water, air, animals, etc.
- Guaranteed operation safety, i.e., flammability, volatility, toxicity, etc.
- Readily available on site, such as petroleum diesel.

Comparison of Extraction Processes

Process	Medium	Processing Temperature	PROS	CONS
CHWE	Water only with caustic	40-45 °C	• Satisfactory recovery from good/medium grade ore	• High energy intensity • Reduced recovery for poor grade ore • MFT generation; poor tailings dewatering; fresh water intake
Hybrid Extraction	Solvent (O/S: ~1:0.02) with Water similar to CHWE	R.T. or higher	• Enhanced recovery • Enhanced tailings condensation • Good operation safety. • Ease of application	• Solvent loss to tailings.
Solvent Extraction	Solvent only (O/S: 1:1-1:2, commonly) No/little water	R.T. or higher	• Enhanced recovery • Water-induced problems alleviated	• Energy intensive solvent recovery from tailings • Solvent-induced hazards • Safety concerns • Hard to choose proper solvent

Comparison of Extraction Processes

Process	Medium	Processing Temperature	OPEX Evaluation
CHWE	Water with caustic	40-45 °C	• Baseline
Hybrid Extraction	Conventional solvent (O/S: ~1:0.02) Water similar as CHWE	R.T. or higher	• **0.294** CDN$ / bbl bitumen saving in energy use & carbon tax; **But** incentive would gradually increase to **0.632** CDN$ / bbl bitumen by 2022. • Solvent loss could be minimized by increased recovery of bitumen.
Solvent Extraction	Conventional solvent (O/S: 1:1-1:2, commonly) No/little water	R.T. or higher	Set SESA Project as example • CAPEX: 4 times higher than CHWE • OPEX: twice as high

REFERENCE

Godin, M., Review of current non-aqueous extraction technologies. Presentation at CanmetENERGY & AIEES Workshop on Nonaqueous Extraction. Oct 9, 2014

Acknowledgement

- Members of Oil Sands Research Group
- Jim Skwarok and Jie Ru
- Lisa Carreiro and Carl Corbett
- NSERC-IRC in Oil Sands Engineering
- Alberta Innovates – Energy & Environmental Solutions
- Industrial Sponsors

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Acknowledgement

NSERC CRSNG

Outotec
More out of ore

BAKER HUGHES
Baker Petrolite

Alberta Innovates
Energy and Environment Solutions

Champion Technologies

Albian Sands

NALCO

TOTAL

Statoil

Fort Hills Energy L.P.

Teck

Canadian Natural

SUNCOR ENERGY

Syncrude

On the Move

"Shenzhen is the city that most resembles the Silicon Valley."
--- *Business Week(2014)*

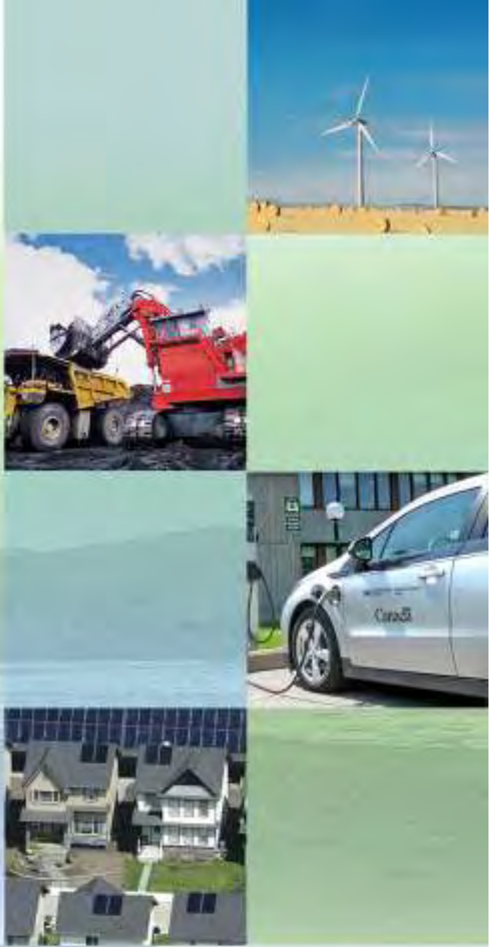
Natural Resources Canada | Ressources naturelles Canada

An overview of Continuous/Pilot-Scale Hybrid Bitumen Extraction Process

Feng Lin and Yuming Xu
Natural Resources Canada, CanmetENERGY -Devon

Presentation at Solvent Leadership workshop, Calgary, Alberta, July 13 2017

CanmetENERGY
Leadership in ecoInnovation



Canada

Outline of Presentation

- ❑ Overview of pilot facilities
- ❑ Pilot hybrid bitumen extraction (HBE)
- ❑ Solvent losses to the tailings
- ❑ Tailings dewatering properties
- ❑ Non aqueous extraction

Nonaqueous Extraction of Oil Sands

Research at the Institute for Oil Sands Innovation

Alberta Innovates Solvent Leadership Series

Workshop 2: Solvent-assisted and Solvent-based Extraction for Surface Mined Oil Sands

July 13, 2017, Alberta Innovates, Calgary, Alberta

Qi Liu
Director, Institute for Oil Sands Innovation

- Institute for Oil Sands Innovation (IOSI)
- Nonaqueous extraction (NAE) flowsheet
- Nonaqueous solvents
- Effect of mineralogy, fines contents, water contents
- Challenges
- Outlook
- Acknowledgements

- An industry-government-university partnership
- Research network extending to 15 universities and government labs
- Annual expenditures of $2-3 million

As of February 2017

Year / Number of	0 **2005**	1 **2006**	2 **2007**	3 **2008**	4 **2009**	5 **2010**	6 **2011**	7 **2012**	8 **2013**	9 **2014**	10 **2015**	11 **2016**	**Sum**
Projects	2	5	6	4	11	10	6	11	6	5	6	12	84
Journal papers	0	0	0	3	5	7	13	15	20	17	17	14	111
Conf. presentations	0	1	5	7	32	20	36	23	29	42	25	19	239
Patent filings	0	0	0	1	1	0	0	10(1)	9(1)	0(1)	2(5)	2(2)	25(10)
Workshops	0	2	3	2	2	3	3	2	2	4	2	3	28
Andrew Main Lecture	0	0	1	1	0	1	1	1	1	1	1	1	9
Researchers	6	25	72	92	148	175	140	167	182	169	144	130	
PDF	0	2	5	5	13	16	14	15	14	17	20	15	
MSc/PhD	0	6	23	28	42	58	45	54	56	48	47	20	
U/G	0	1	2	2	15	21	10	16	9	6	2	1	

Extraction

Originally “Nonaqueous Bitumen Extraction”, started from 2005. Changed from May 2016 to the current name to include both nonaqueous and water-based extraction

Product Cleaning and Partial Upgrading

Originally “Bitumen Upgrading and Characterization”, started from 2005. Changed from May 2016 to the current name to emphasize bitumen transportation and direct feed to refinery

Online Instrumentation for Oil Sands (started 2014)

Tailings Fundamentals

Originally “Tailings Process Fundamentals”, started from 2011. Changed from May 2016 to the current name to include both tailings processes and tailings geotechnics fundamentals

Solvent selection and interfacial chemistry

2006-01 Design of Solvent Use for Bitumen Extraction by Molecular Modeling and Inverse Gas Chromatography
2009-06 Unsticking Bitumen from Kaolinite
2010-01 Interfacial Forces in Solvent Extraction Processes
2010-08 Non-aqueous Bitumen Extraction: Interfacial Science behind the Process
2014-03 Cyclohexane-Adjuvant Systems for Improved Non-aqueous Extraction of Bitumen from Oil Sands

Mineralogy

2006-02 Clay Mineralogy in the Oil Sands
2009-11 Role of Mineralogy and Solids Surface Condition in Separation of Bitumen from Oil Sands using Solvent Extraction and Solids Agglomeration
2010-06 Nano- and Micro-size Minerals in Nonaqueous Bitumen Extraction from Oil Sands

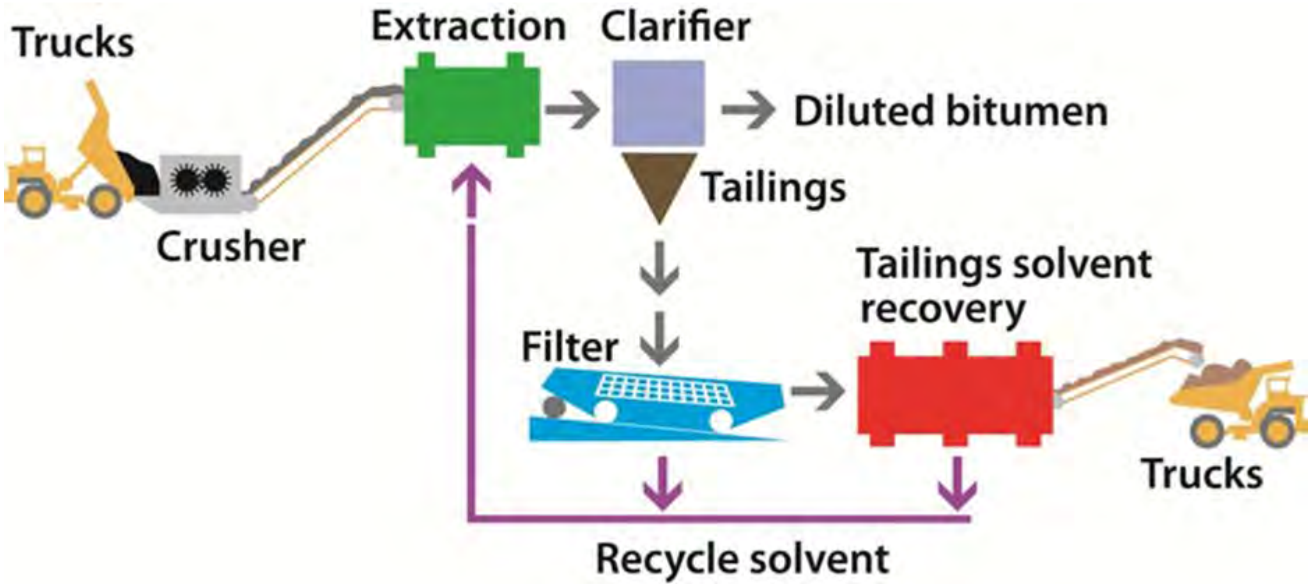
Fine solids removal

2006-05 Attachment and Transport of Particulates at the Oil-Water Interface
2012-11 Optimization of Solids Removal from Solvent-Recovered Bitumen through Asphaltene Precipitation Kinetics
2014-02 Behaviour of Bitumen-Coated Fine Solids in Organic Solvents
2016-03 Surface-functionalized Magnetic Particles for Removal of Suspended Fine Solids from NAE Bitumen
2016-05 Removal of Hydrophobic Bitumen-coated Fine Solids from NAE Bitumen Using Water Droplets with Modified Interfacial Chemistry and Bio-inspired Polymers

Solvent recovery / destruction

2007-04 Recovery of Residual Oil Using Microemulsions
2010-04 Kinetics of Solvent Recovery from Extracted Oil Sands Tailings
2016-04 Biodegradation of Cyclohexane under Different Redox Conditions

Concept


Trucks
Extraction
Clarifier
Diluted bitumen
Tailings
Crusher
Tailings solvent recovery
Filter
Trucks
Recycle solvent

Concept

Ore A: High grade, low fines content

Ore B: Low grade, high fines content

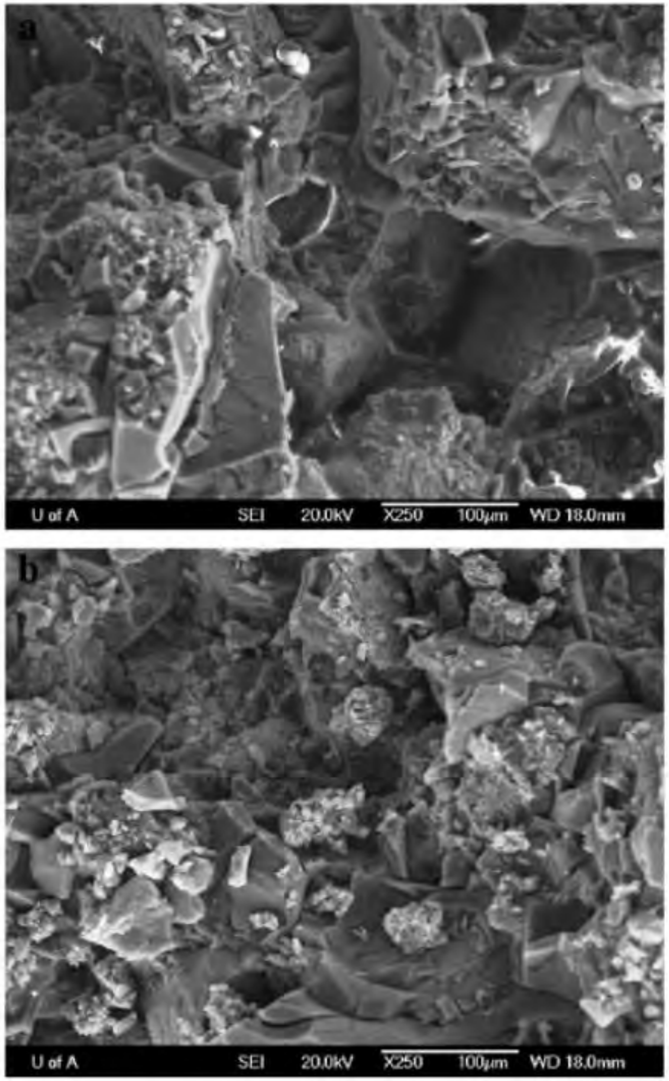


Fig. 2. Cryo-SEM secondary electron images of raw oil sands ores, A and B, showing agglomerates of clay particles in ore B.

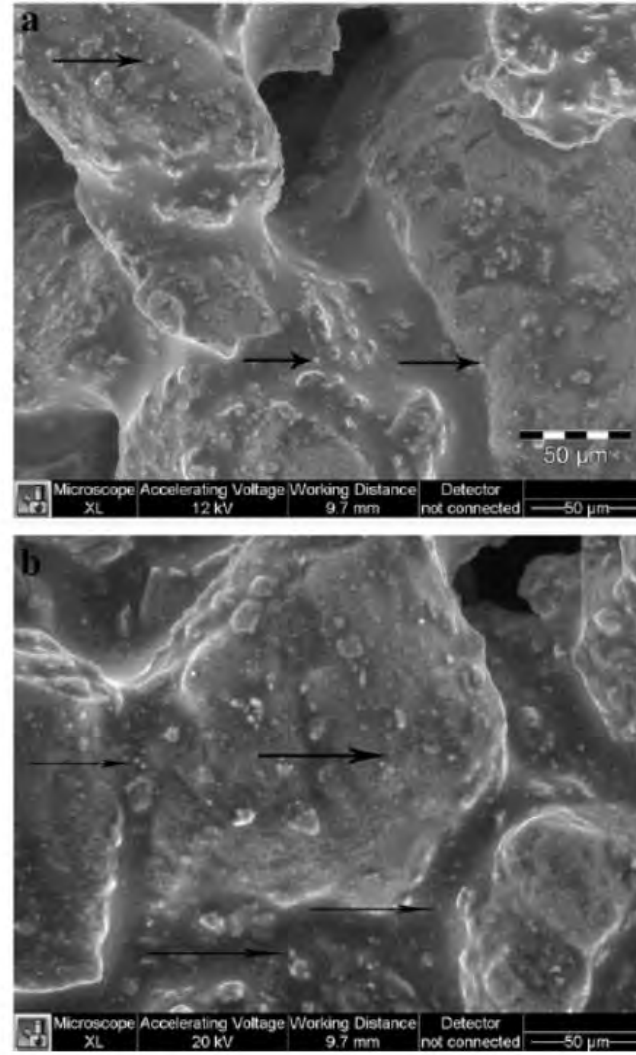
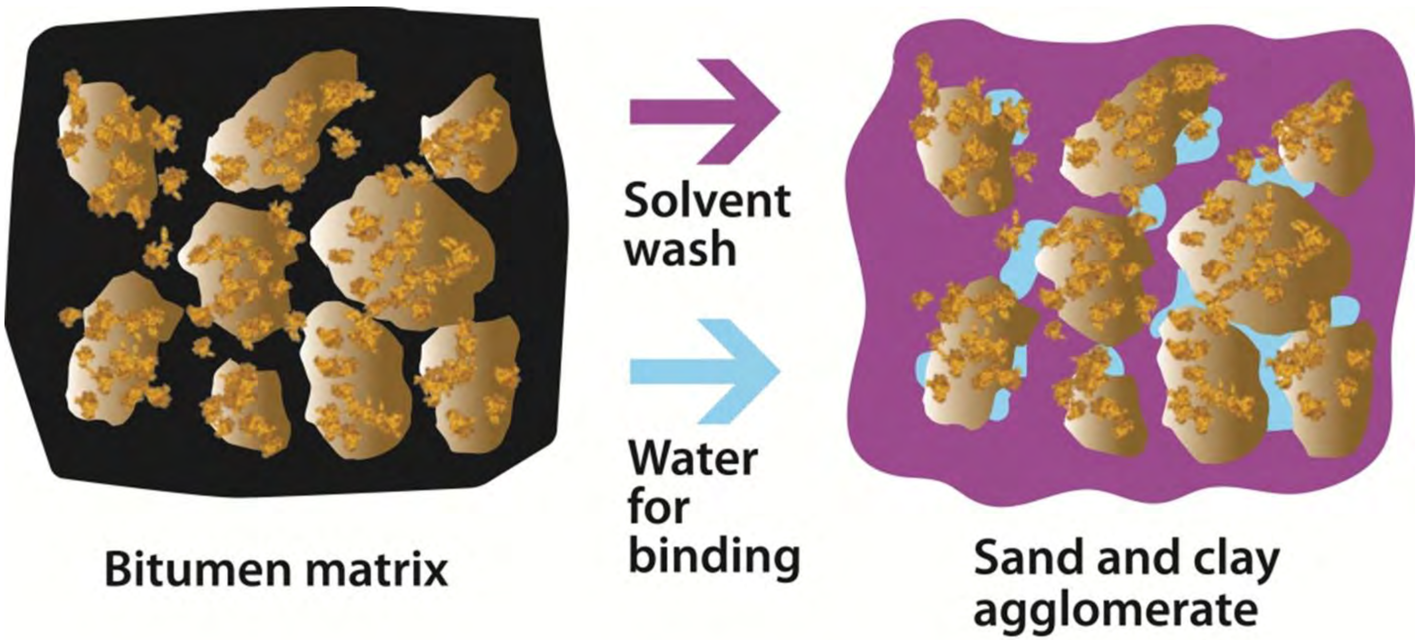


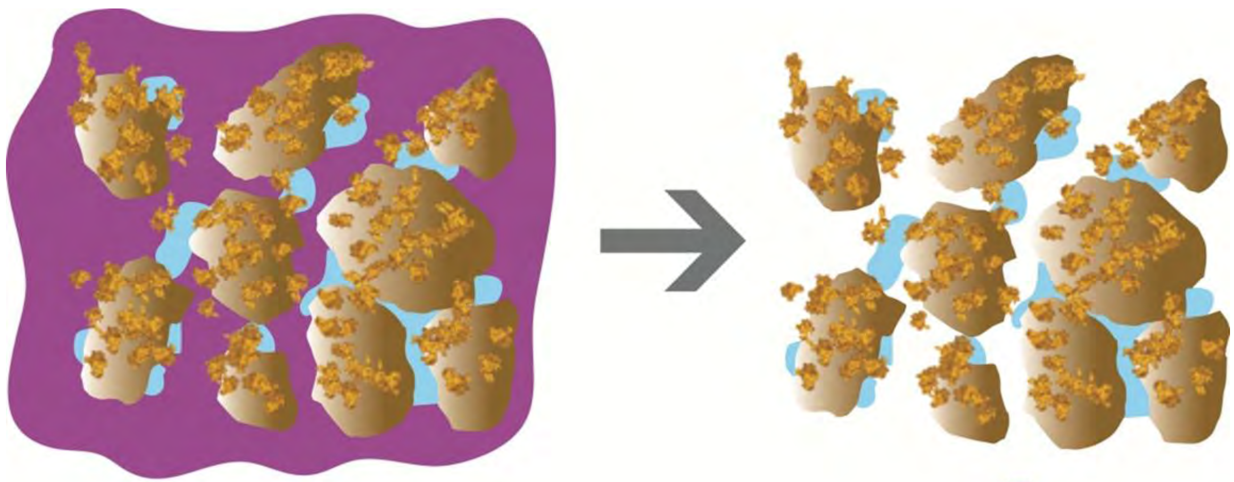
Fig. 1. Environmental SEM images of the good processing raw oil sands ore showing the very fine (clay) particles attached to the large sands grains. Bitumen is most probably present in dark channels among sand grains. Arrows show some small clay particles as an example.

A. Hooshiar, P. Uhlik, D.G. Ivey, Qi Liu, T.H. Etsell, 2011. Clay minerals in nonaqueous extraction of bitumen from Alberta oil sands. Part 1. Nonaqueous extraction procedure. [**Fuel Processing Technology**](), Vol. 94, 80-85.

Concept

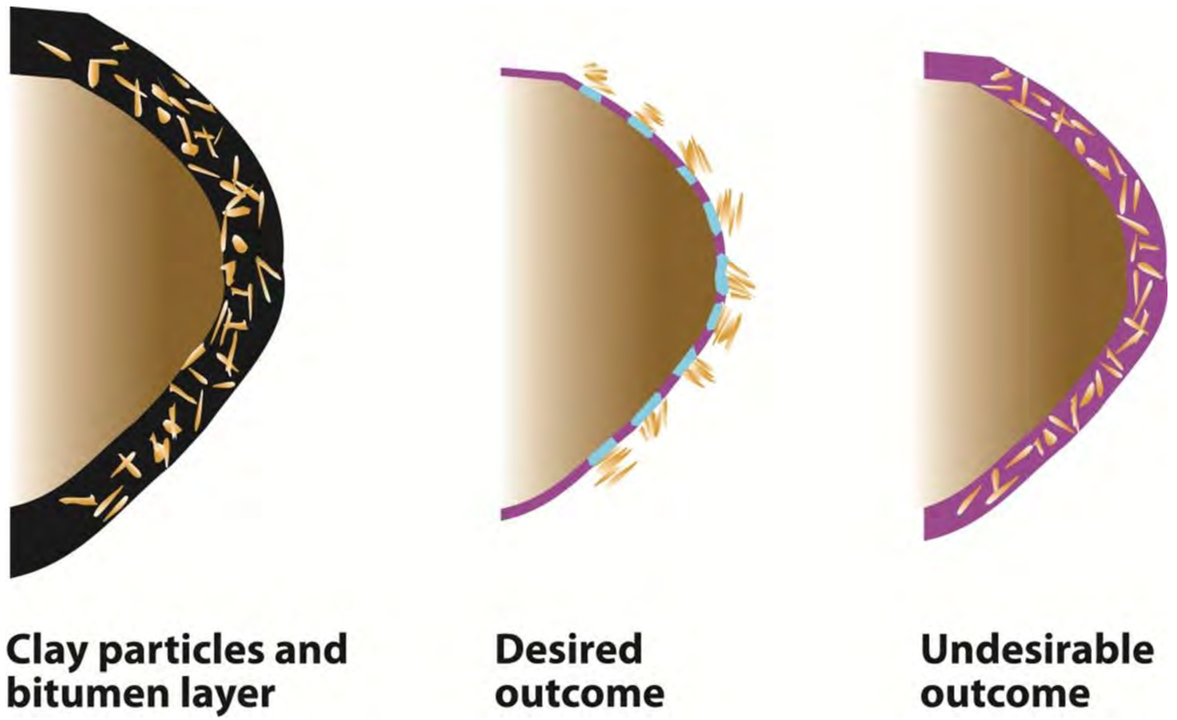

Bitumen matrix
Solvent
wash
Water
for
binding
Sand and clay
agglomerate

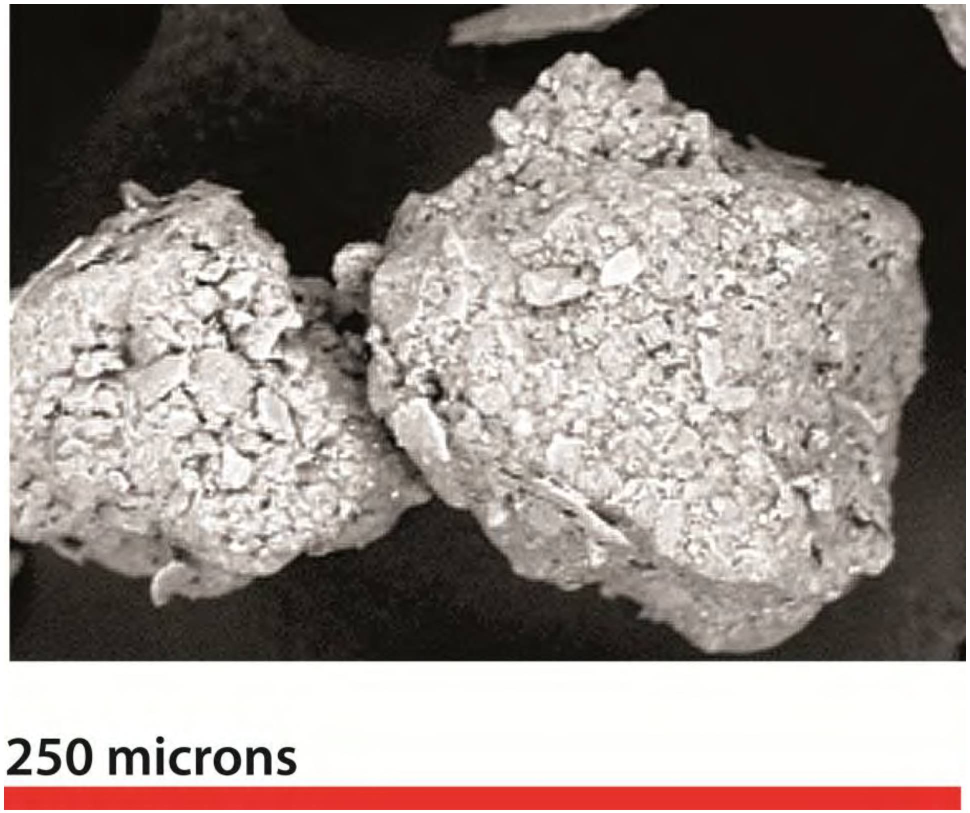
Concept



Need to understand wettability
of sand/clay surfaces

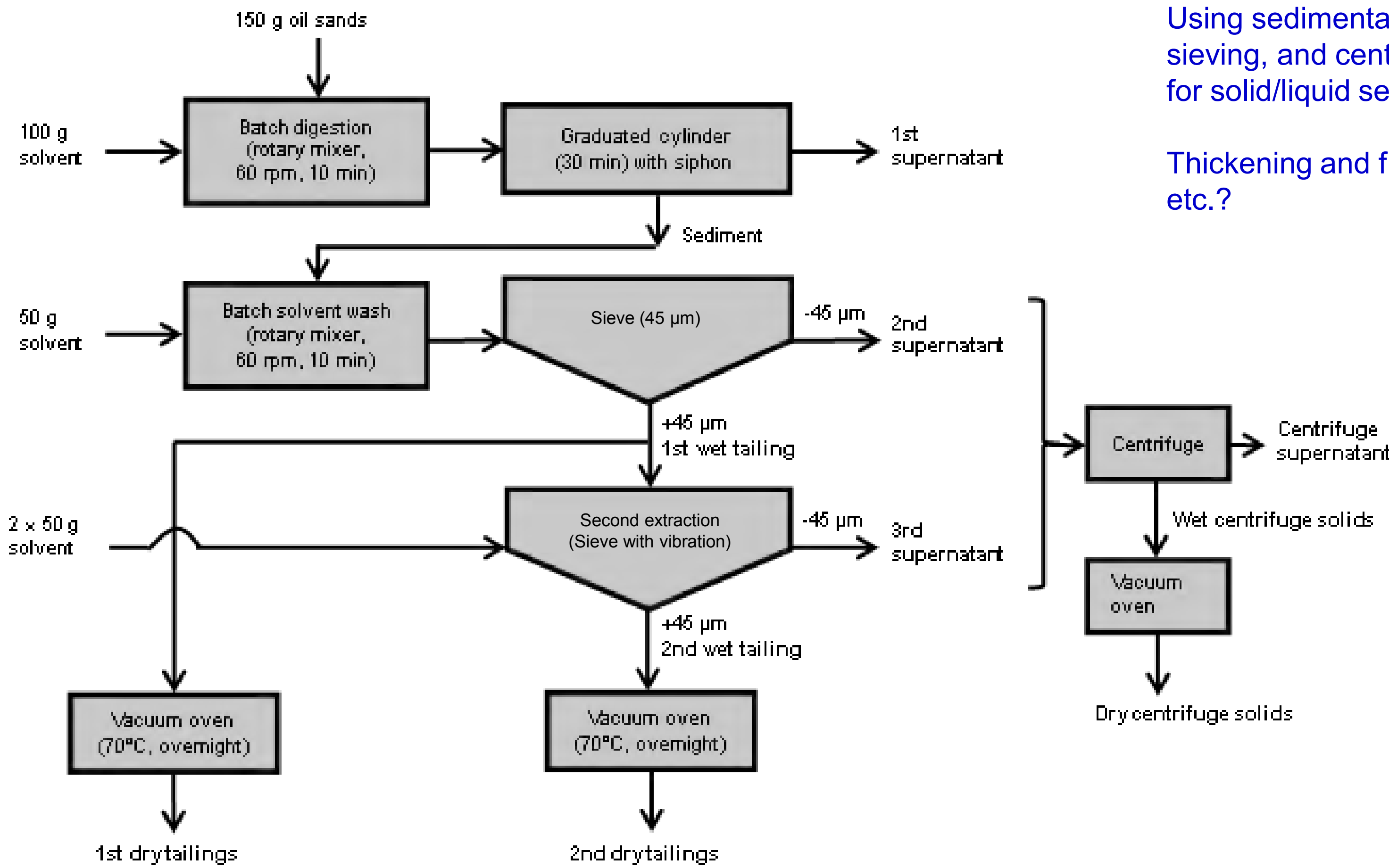
Concept


Clay particles and bitumen layer
Desired outcome
Undesirable outcome



- Fine solids stick on sand grains
- No fines in bitumen
- No wet tailings

Concept **IOSI NAE lab flowsheet**



Using sedimentation, sieving, and centrifugation for solid/liquid separation

Thickening and filtration, etc.?

H. Nikakhtari, L. Vagi, P. Choi, Qi Liu and M. Gray, 2012. Solvent screening for a non-aqueous extraction of Alberta oil sands process. **Canadian Journal of Chemical Engineering**, Vol. 91, 1153-1160.

Extraction

- **Bitumen extraction performance**

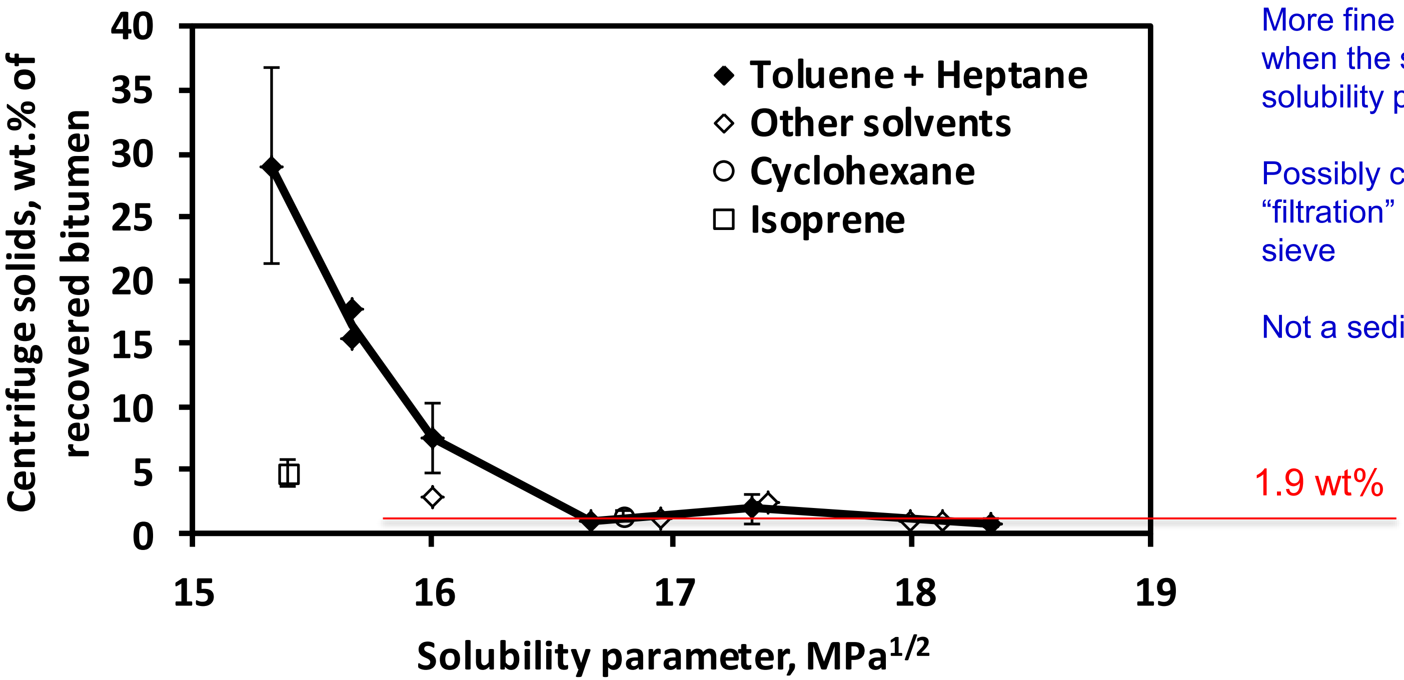
Amount of fine solids through the 45-μm sieve, reflecting tendency of fines aggregation / blockage

Solvent	C % in 2nd Tailing	Bitumen recovery, %	C % in centrifuge solids	Weight of centrifuge solids, % of ore
100% Toluene	0.79	96.3 ± 1.1	20.1 ± 2.8	0.07 ± 0.03
70% Toluene/30% n-Heptane	1.04	94.3 ± 2.3	18.1 ± 6.4	0.16 ± 0.10
50% Toluene/ 50% n-Heptane	0.85	95.9*	23.6	0.07
30% Toluene/ 70% n-Heptane	0.86	95.8 ± 2.5	19.2 ± 6.3	0.63 ± 0.22
20% Toluene/ 80% n-Heptane	0.85	95.9	24.4	1.37
10% Toluene/ 90% n-Heptane	1.27	92.6 ± 3.2	26.9 ± 7.2	2.33 ± 0.64
10% Toluene/ 90% Cyclohexane	1.18	93.2	23.2	0.10
Methyl Cyclohexane	0.97	94.9	17.0	0.24
Cyclohexane	1.05	94.4 ± 1.7	21.9 ± 1.7	0.11 ± 0.04
Ethylbenzene	1.11	93.8	18.6	0.07
Xylenes	1.16	93.4	20.1	0.08
Isoprene	1.40	91.4 ± 1.5	20.6 ± 1.7	0.38 ± 0.09
Limonene	5.87	53.0	22.3	0.11

* No duplicate tests

H. Nikakhtari, L. Vagi, P. Choi, Qi Liu and M. Gray, 2012. Solvent screening for a non-aqueous extraction of Alberta oil sands process. **Canadian Journal of Chemical Engineering**, Vol. 91, 1153-1160.

- **Amount of centrifuge solids**

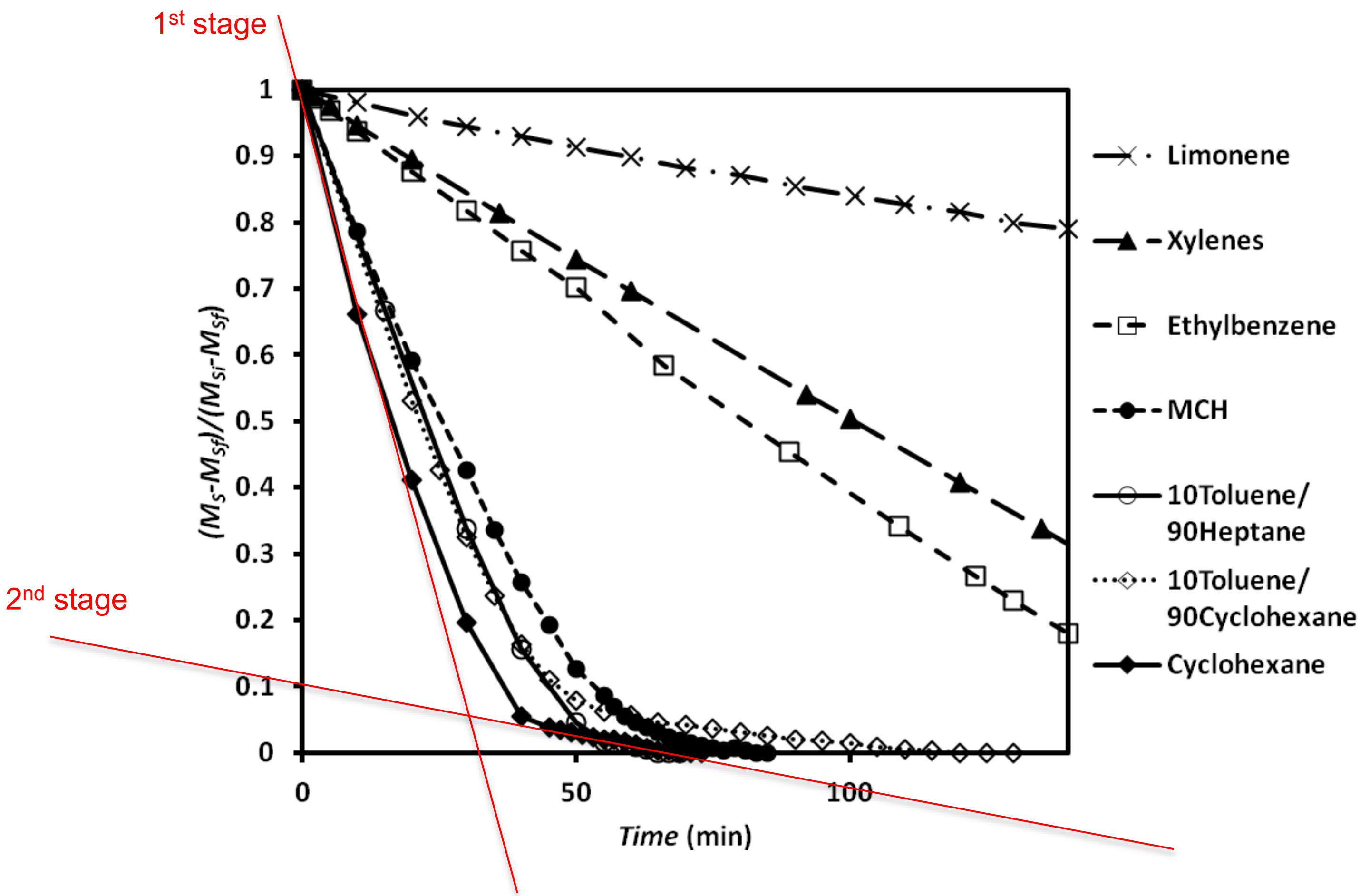


More fine solids in bitumen when the solvent had a low solubility parameter

Possibly caused by the "filtration" effect on the 45-μm sieve

Not a sedimentation process

H. Nikakhtari, L. Vagi, P. Choi, Qi Liu and M. Gray, 2012. Solvent screening for a non-aqueous extraction of Alberta oil sands process. **Canadian Journal of Chemical Engineering,** Vol. 91, 1153-1160.



Two-stage evaporation process.

The 1st stage was solvent evaporation and it was fast

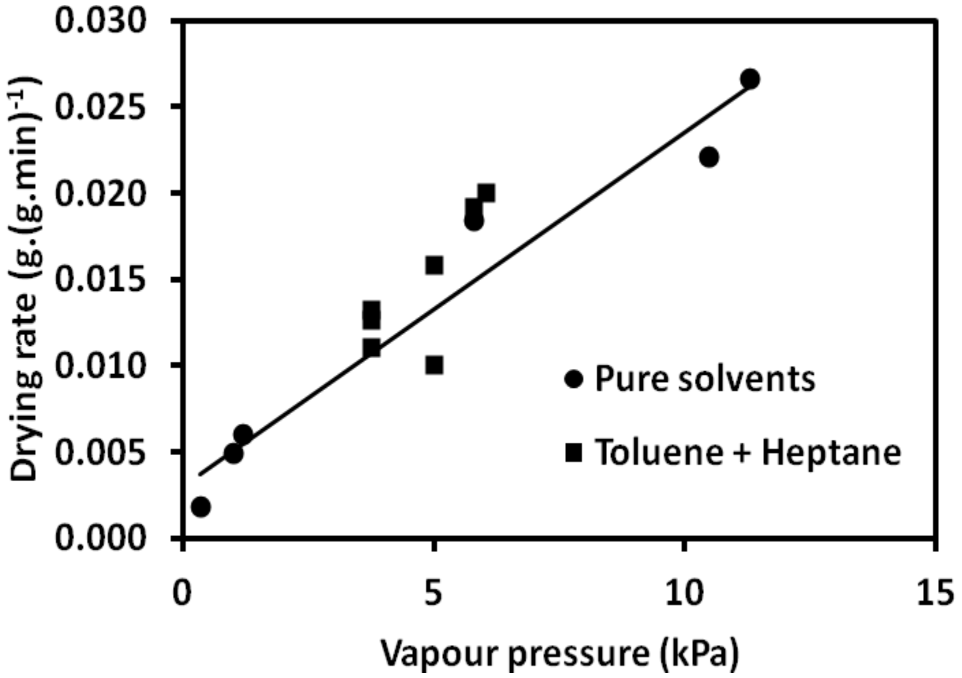
The 2nd stage was water evaporation and it was slow

H. Nikakhtari, L. Vagi, P. Choi, Qi Liu and M. Gray, 2012. Solvent screening for a non-aqueous extraction of Alberta oil sands process. **Canadian Journal of Chemical Engineering**, Vol. 91, 1153-1160.

- **Solvent recovery from the 2nd extraction tailings**

Solvent	Vapour pressure at 297 K	Residual solvent concentration	Total equilibration time	1st evaporation stage equilibration time
	kPa	mg/kg of tailings	min	min
100% Toluene	3.6	210	118	72
70% Toluene/30% n-Heptane	4.2	108	120	66
30% Toluene/ 70% n-Heptane	5.0	93	70	48
10% Toluene/ 90% n-Heptane	5.5	89	69	44
10% Toluene/ 90% Cyclohexane	10.5	20	100	30
Methyl Cyclohexane	5.8	29	85	40
Cyclohexane	11.3	5	61	25
Ethylbenzene	1.2	407	200	123
Xylenes	1.0	448	235	150
Isoprene	70.3	1	130	5.2
Limonene	0.3	370	1400	160

H. Nikakhtari, L. Vagi, P. Choi, Qi Liu and M. Gray, 2012. Solvent screening for a non-aqueous extraction of Alberta oil sands process. **Canadian Journal of Chemical Engineering**, Vol. 91, 1153-1160.



Solvent evaporation rate is linearly related to its vapor pressure

H. Nikakhtari, L. Vagi, P. Choi, Qi Liu and M. Gray, 2012. Solvent screening for a non-aqueous extraction of Alberta oil sands process. **Canadian Journal of Chemical Engineering,** Vol. 91, 1153-1160.

End members

- **Four petrologic end member samples**

Estuarine Clay (EC)
Estuarine Sand (ES)
Marine Clay (MC)
Marine Sand (MS)

Table 3
Mineral composition (in wt%) of the oil sands determined by RockJock.

Sample	Size fraction (μm)	Quartz	K-feldspar	Calcite	Dolomite	Siderite	TiO_2 minerals	Kaolinite	Total 2:1 clays	Chlorite	Pyrite
EC after DS	Bulk	52.3	2.7	0.0	0.3	3.0	0.7	14.4	25.3	1.3	0.0
EC after DS	>45	89.3	3.3	0.0	0.1	0.5	0.2	3.3	3.3	0.0	0.0
EC after DS	2–45	69.0	3.3	0.0	0.1	0.7	0.8	9.5	14.8	1.8	0.0
EC after DS	<2	4.2	1.0	0.8	0.3	1.0	0.3	28.9	58.9	4.6	0.0
EC after DS	0.2–2	6.9	0.6	0.0	0.2	0.1	0.3	37.0	52.6	2.3	0.0
EC after DS	<0.2	1.2	0.9	1.3	0.3	1.1	0.0	21.4	64.8	8.9	0.1
MC after DS	Bulk	72.1	3.9	5.5	1.4	0.1	0.3	8.9	7.5	0.2	0.1
MC after DS	>45	88.5	3.8	1.8	0.8	0.0	0.0	3.0	2.1	0.0	0.0
MC after DS	2–45	55.0	4.6	9.5	2.8	0.4	0.1	14.2	10.9	2.3	0.2
MC after DS	<2	8.2	0.0	13.8	1.2	0.4	0.0	30.4	40.6	5.2	0.2
MC after DS	0.2–2	16.4	1.3	7.7	1.0	0.3	0.0	38.4	33.7	1.2	0.0
MC after DS	<0.2	1.9	2.4	7.4	0.7	0.9	0.0	20.9	54.9	10.7	0.2
ES after DS	Bulk	94.5	3.6	0.0	0.1	0.1	0.0	0.8	0.7	0.2	0.0
ES after DS	>45	94.7	4.0	0.0	0.1	0.1	0.0	1.1	0.0	0.0	0.0
ES after DS	2–45	63.2	8.5	0.0	0.0	0.2	0.5	18.2	7.7	1.3	0.4
MS after DS	Bulk	86.8	3.7	1.4	0.8	0.3	0.2	4.1	2.5	0.0	0.2
MS after DS	>45	93.0	2.8	0.4	0.4	0.3	0.2	1.5	1.2	0.0	0.2
MS after DS	2–45	58.3	4.5	2.9	2.2	0.6	0.2	17.6	10.4	2.4	0.9
MS after DS	<2	18.7	4.1	7.1	1.8	1.6	0.0	30.9	31.8	3.4	0.6

Total 2:1 clays – the sum of illite and illite–smectite.
DS – Dean Stark extraction.

M. Osacky, M. Geramian, D.G. Ivey, Qi Liu and T.H. Etsell, 2013. Characterization of petrologic end members of Alberta oil sands, Part 1: Mineralogical and chemical composition. **Fuel**, Vol. 113, 148-157.

End members

Table 4
Chemical composition (in wt%) of the oil sands determined by ICP-MS.

Sample	Size fraction (μm)	Al	Ca	Na	Mg	K	Fe	Ti
EC after DS	Bulk	6.49	0.22	0.27	0.40	1.44	2.61	0.38
EC after DS	>45	2.13	0.08	0.10	0.10	0.86	0.89	0.15
EC after DS	2–45	5.23	0.14	0.12	0.27	1.46	2.95	0.43
EC after DS	<2	11.54	0.17	1.05	0.68	2.85	3.02	0.71
EC after DS	0.2–2	10.23	0.26	0.15	0.54	2.70	2.86	0.85
EC after DS	<0.2	9.76	0.37	1.34	0.64	2.45	3.61	0.52
MC after DS	Bulk	4.47	4.32	0.17	0.54	0.87	0.64	0.23
MC after DS	>45	1.46	1.31	0.06	0.18	0.64	0.25	0.14
MC after DS	2–45	4.35	5.78	0.09	0.62	1.07	0.82	0.34
MC after DS	<2	7.39	7.71	0.29	0.76	1.35	1.05	0.41
MC after DS	0.2–2	9.39	4.77	0.06	0.42	1.43	0.94	0.36
MC after DS	<0.2	9.36	6.86	0.73	0.75	1.65	1.36	0.52
ES after DS	Bulk	0.60	<0.01	0.03	<0.01	0.47	0.05	0.03
ES after DS	>45	0.77	0.01	0.04	0.01	0.67	0.06	0.04
ES after DS	2–45	5.52	0.04	0.14	0.13	1.85	0.83	0.34
MS after DS	Bulk	1.46	1.16	0.08	0.20	0.55	0.55	0.09
MS after DS	>45	1.35	1.30	0.05	0.22	0.70	0.85	0.09
MS after DS	2–45	3.25	4.69	0.10	0.62	0.99	1.97	0.30

DS – Dean Stark extraction.

M. Osacky, M. Geramian, D.G. Ivey, Qi Liu and T.H. Etsell, 2013. Characterization of petrologic end members of Alberta oil sands, Part 1: Mineralogical and chemical composition. **Fuel**, Vol. 113, 148-157.

End members

Reasonably good correlation between aluminum content and clay mineral content

Correlation of clay minerals to potassium is more scattered

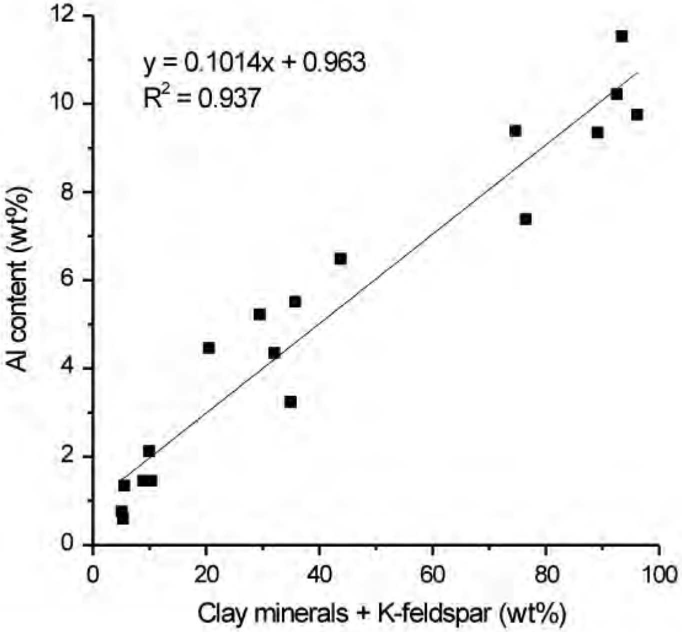


Fig. 8. Al content versus clay minerals (sum of kaolinite, 2:1 clays and chlorite) + K-feldspar content after bitumen removal.

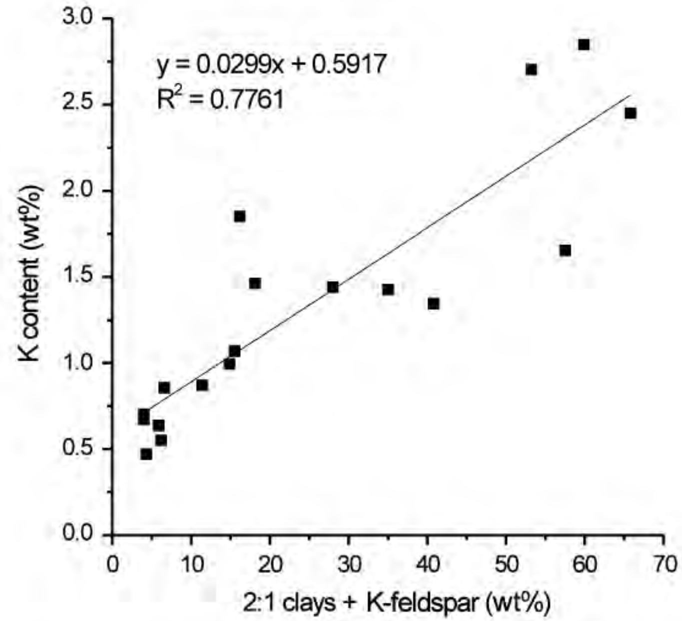


Fig. 9. K content versus 2:1 clays (sum of illite and illite–smectite) + K-feldspar content after bitumen removal.

M. Osacky, M. Geramian, D.G. Ivey, Qi Liu and T.H. Etsell, 2013. Characterization of petrologic end members of Alberta oil sands, Part 1: Mineralogical and chemical composition. **Fuel**, Vol. 113, 148-157.

- **Pure clays (**smectite **Swy-2,** illite-smectite **ISCz-1,** kaolinite **KGa-2,** Illite **IMt-1,** chlorite **CCa-2)**

to examine their tendencies to retain solvent and bitumen

Table 2. Cation Exchange Capacity (CEC), Specific Surface Area (SSA), and Elemental (H, N, S, and C) Analysis

sample	CEC (meq/100g)	SSA (m^2/g)	H (wt %)	N (wt %)	S (wt %)	C (wt %)
Starting Materials						
starting SWy-2	87.1 ± 1.10	28.3 ± 3.69	0.736 ± 0.04	0.053 ± 0.01	0.009 ± 0.00	0.133 ± 0.02
starting ISCz-1	37.5 ± 0.28	50.4 ± 1.24	0.687 ± 0.01	0.045 ± 0.01	0.009 ± 0.00	0.100 ± 0.00
Solvent-Clay Mixtures without Bitumen (Blanks)						
SWy-2 blank 0% RH	85.6 ± 1.24	13.4	1.010 ± 0.06	0.048 ± 0.02	0.049 ± 0.06	0.888 ± 0.01
SWy-2 blank 50% RH	87.5 ± 0.31	12.2	1.114 ± 0.01	0.053 ± 0.01	0.006 ± 0.00	0.750 ± 0.00
SWy-2 blank 95% RH	85.7 ± 1.03	9.3	1.432 ± 0.01	0.120 ± 0.00	0.022 ± 0.00	0.807 ± 0.03
ISCz-1 blank 0% RH	36.9 ± 0.43	38.6	0.774 ± 0.02	0.060 ± 0.01	0.062 ± 0.01	0.898 ± 0.01
ISCz-1 blank 50% RH	37.2 ± 0.63	42.4	0.862 ± 0.02	0.047 ± 0.01	0.021 ± 0.00	0.867 ± 0.02
ISCz-1 blank 95% RH	37.6 ± 0.12	43.9	0.977 ± 0.02	0.120 ± 0.00	0.015 ± 0.00	0.593 ± 0.01
Bitumen-Clay Mixtures after Cyclohexane Extraction						
SWy-2 bitumen 0% RH	82.1 ± 0.80	4.7	1.342 ± 0.08	0.123 ± 0.01	0.038 ± 0.01	4.605 ± 0.03
SWy-2 bitumen 50% RH	79.3 ± 0.14	5.6	1.515 ± 0.01	0.123 ± 0.01	0.536 ± 0.02	5.523 ± 0.19
SWy-2 bitumen 95% RH	76.9 ± 0.08	6.0	2.173 ± 0.01	0.193 ± 0.01	0.031 ± 0.01	8.153 ± 0.15
ISCz-1 bitumen 0% RH	32.3 ± 0.03	6.3	1.368 ± 0.08	0.153 ± 0.01	0.048 ± 0.00	7.083 ± 0.04
ISCz-1 bitumen 50% RH	29.2 ± 0.65	6.3	1.570 ± 0.01	0.160 ± 0.01	0.014 ± 0.00	8.180 ± 0.06
ISCz-1 bitumen 95% RH	30.2 ± 2.16	5.5	1.693 ± 0.01	0.203 ± 0.01	0.037 ± 0.00	8.047 ± 0.11

M. Geramian, M. Osacký, D.G. Ivey, Qi Liu and T.H. Etsell, 2016. Effect of swelling clay minerals (montmorillonite and illite-smectite) on non-aqueous bitumen extraction from Alberta oil sands. **Energy and Fuels**, Vol. 30, 8083−8090.

Table 2. Cation Exchange Capacity (CEC), Specific Surface Area (SSA), Mean Crystallite Thickness (T_{MEAN}), Elemental (H, N, S, and C) Analysis, H/C Atomic Ratios, and the Amounts of Cyclohexane Insoluble Organic Carbon Retained on Clays ($CIOC_{clays}$)[a]

sample	CEC (mequiv/(100 g))	SSA (m^2/g)	T_{MEAN} (nm)	elem anal (wt %) H	N	S	C	H/C	$CIOC_{clays}$ (wt %)
Starting Materials									
starting KGa-2	8.4 ± 1.07	21.1	16.2	1.523 ± 0.04	0.022 ± 0.02	0.016 ± 0.01	0.038 ± 0.00		
starting IMt-1	17.9 ± 0.14	42.0	7.5	0.679 ± 0.02	0.040 ± 0.00	0.021 ± 0.01	0.108 ± 0.00		
starting CCa-2	8.2 ± 0.49	14.7	26.6	1.419 ± 0.02	0.008 ± 0.00	0.003 ± 0.00	0.024 ± 0.01		
starting bitumen				10.734 ± 0.10	0.445 ± 0.01	4.869 ± 0.39	82.850 ± 1.12	1.54	
Solvent–Clay Mixtures without Bitumen (Blanks)									
CIOM + KGa-2 blank 0% RH	8.2 ± 0.15	19.1	16.0	1.472 ± 0.04	0.030 ± 0.01	0.023 ± 0.00	0.490 ± 0.03		
CIOM + KGa-2 blank 50% RH	7.6 ± 0.03	18.6	16.6	1.636 ± 0.03	0.067 ± 0.02	0.025 ± 0.01	0.543 ± 0.02		
CIOM + KGa-2 blank 95% RH	9.1 ± 0.14	20.8	16.1	1.492 ± 0.05	0.047 ± 0.03	0.010 ± 0.01	0.317 ± 0.01		
CIOM + IMt-1 blank 0% RH	17.9 ± 0.21	24.5	7.1	0.751 ± 0.03	0.058 ± 0.02	0.072 ± 0.03	0.885 ± 0.01		
CIOM + IMt-1 blank 50% RH	17.7 ± 0.35	28.9	6.7	0.677 ± 0.01	0.053 ± 0.01	0.000 ± 0.00	0.530 ± 0.00		
CIOM + IMt-1 blank 95% RH	18.4 ± 0.97	31.0	7.1	0.787 ± 0.01	0.110 ± 0.00	0.024 ± 0.00	0.550 ± 0.00		
CIOM + CCa-2 blank 0% RH	8.1 ± 0.20	9.6	28.3	1.476 ± 0.06	0.025 ± 0.01	0.031 ± 0.01	0.758 ± 0.01		
CIOM + CCa-2 blank 50% RH	7.8 ± 0.06	9.7	27.8	1.461 ± 0.04	0.073 ± 0.02	0.023 ± 0.01	0.593 ± 0.01		
CIOM + CCa-2 blank 95% RH	8.5 ± 1.16	10.8	26.8	1.448 ± 0.01	0.030 ± 0.00	0.027 ± 0.01	0.233 ± 0.01		
Bitumen–Clay Mixtures									
CIOM + KGa-2 bitumen 0% RH	4.2 ± 0.27	15.4		1.901 ± 0.01	0.087 ± 0.01	0.540 ± 0.00	5.460 ± 0.01	0.83	2.52
CIOM + KGa-2 bitumen 50% RH	4.4 ± 0.06	17.6		1.875 ± 0.13	0.130 ± 0.03	0.378 ± 0.32	5.357 ± 0.02		2.42
CIOM + KGa-2 bitumen 95% RH	5.8 ± 0.24	17.9		2.109 ± 0.00	0.113 ± 0.01	0.016 ± 0.00	5.660 ± 0.02		2.72
CIOM + IMt-1 bitumen 0% RH	15.6 ± 0.32	11.6		1.254 ± 0.03	0.130 ± 0.01	0.612 ± 0.03	6.588 ± 0.01	1.06	3.58
CIOM + IMt-1 bitumen 50% RH	15.5 ± 0.52	11.2		1.190 ± 0.01	0.140 ± 0.00	0.626 ± 0.03	6.367 ± 0.04		3.36
CIOM + IMt-1 bitumen 95% RH	16.8 ± 1.07	10.2		1.469 ± 0.02	0.163 ± 0.01	0.031 ± 0.01	6.967 ± 0.11		3.96
CIOM + CCa-2 bitumen 0% RH	7.0 ± 2.10	6.5		1.711 ± 0.01	0.050 ± 0.00	0.380 ± 0.00	4.075 ± 0.01	0.86	1.15
CIOM + CCa-2 bitumen 50% RH	7.8 ± 0.35	5.6		1.619 ± 0.01	0.070 ± 0.02	0.370 ± 0.00	3.637 ± 0.01		0.71
CIOM + CCa-2 bitumen 95% RH	7.7 ± 0.07	6.7		1.817 ± 0.01	0.080 ± 0.00	0.031 ± 0.00	3.797 ± 0.02		0.87
CSOM + KGa-2 bitumen 0% RH				10.403 ± 0.04	0.452 ± 0.02	5.290 ± 0.26	83.052 ± 0.19	1.49	
CSOM + IMt-1 bitumen 0% RH				10.369 ± 0.06	0.436 ± 0.03	5.044 ± 0.20	83.166 ± 0.61	1.49	
CSOM + CCa-2 bitumen 0% RH				10.237 ± 0.12	0.440 ± 0.03	5.275 ± 0.07	82.533 ± 0.60	1.48	
Solvent Extraction of Bitumen from Pure Bitumen									
TDB				10.441 ± 0.20	0.480 ± 0.01	5.051 ± 0.12	82.120 ± 0.24	1.52	
CIOM				6.197 ± 0.15	0.900 ± 0.02	6.126 ± 0.09	61.290 ± 0.51	1.20	
CSOM				10.511 ± 0.16	0.380 ± 0.01	3.745 ± 0.06	80.580 ± 0.04	1.55	

[a] TDB, toluene-diluted bitumen; CIOM, cyclohexane insoluble organic matter; CSOM, cyclohexane soluble organic matter.

Clays retained solvent and bitumen

Swelling clays retained more than the non-swelling clays

M. Osacký, M. Geramian, D.G. Ivey, Qi Liu and T.H. Etsell, 2015. Influences of non-swelling clay minerals (kaolinite, illite and chlorite) on non-aqueous solvent bitumen extraction. **Energy and Fuels,** Vol. 29, 4150-4159.

- **Effect of feed grade and fines contents**

Table 1
Composition of oil sands ore samples.

Sample	Characteristics	Bitumen (wt.%)	Solids (wt.%) >45 µm	Solids (wt.%) 2–45 µm	Solids (wt.%) <2 µm	Water (wt.%)
A	High grade, low fines, good processing	13.5	78.7	4.5	0.8	2.5
B	Medium grade, high fines, poor processing	10.5	62.5	15.2	8.1	3.7

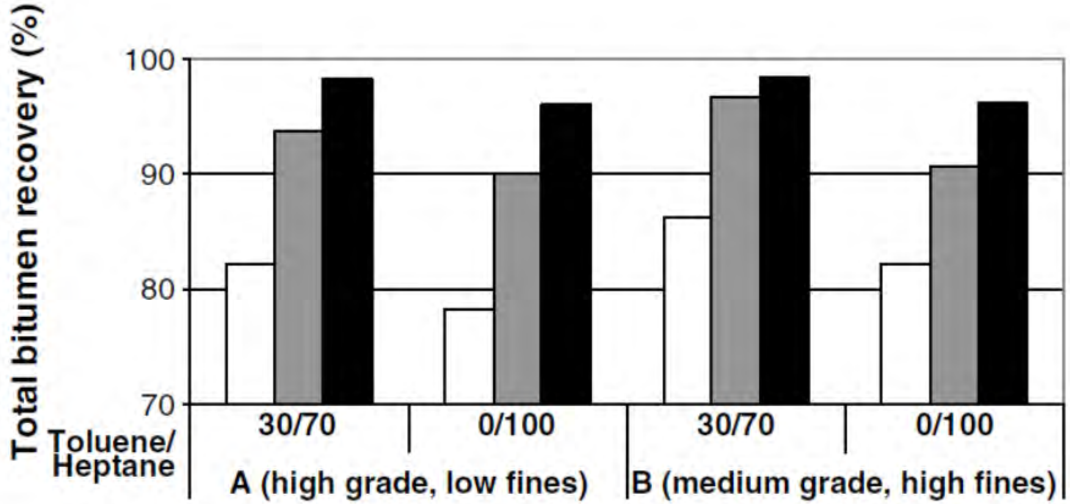


Fig. 4. Total bitumen recovery based on the mass of the remaining bitumen in the tailings after a 2nd wash (primary tailings – white bars, tailings after 1st wash – gray bars, tailings after 2nd wash – black squares).

Good bitumen recovery seemed to have been achieved after 3rd solvent wash using pure heptane, even for the low grade ore with high fines content

But this was possibly due to the bitumen-coated fines in the extracted bitumen product

A. Hooshiar, P. Uhlik, D.G. Ivey, Qi Liu, T.H. Etsell, 2012. Clay minerals in nonaqueous extraction of bitumen from Alberta oil sands. Part 2. Characterization of clay minerals. **Fuel Processing Technology**, Vol. 96, 183-194.

- **Supernatant quality**

Table 2
Supernatant assays based on solvent-free mass balance calculations*.

Ore	Toluene/ heptane	–	Bitumen (wt.%)	Solids (wt.%)	Water (wt.%)
A	70/30	Min–max	99.68–99.75	0.03–0.11	0.21–0.22
		Average	99.72	0.07	0.21
	30/70	Min–max	96.62–99.88	0.02–3.33	0.09–0.10
		Average	98.24	1.67	0.09
	10/90		99.84	0.08	0.08
	0/100	min–max	96.12–97.34	2.63–3.78	0.03–0.04
		Average	96.75	3.21	0.04
B	70/30		99.5	0.13	0.37
	30/70	Min–max	94.76–99.75	0.13–5.14	0.07–0.11
		Average	96.78	3.13	0.09
	10/90		99.72	0.19	0.09
	0/100	Min–max	98.85–94.28	5.65–1.10	0.07–0.05
		Average	96.57	3.37	0.06

* The average values given are from two extractions, except for sample B treated in toluene/heptane = 30/70 which is from three extractions. Only one extraction test was performed on samples without an average value.

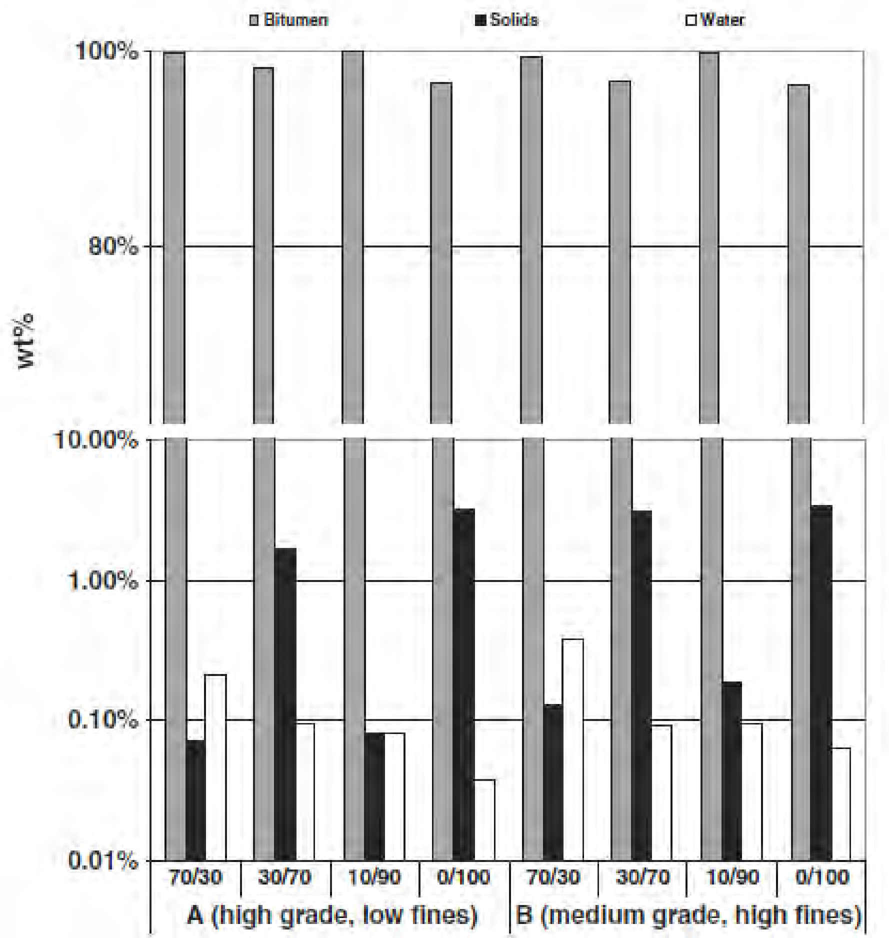


Fig. 5. Supernatant assays from mass balance calculations — average values are from Table 2, using water content values from the KF titration method.

Paraffinic solvent tended to lead to poor supernatant quality (higher fine solids content)

But the 10/90 (toluene/heptane) was a notable exception

A. Hooshiar, P. Uhlik, D.G. Ivey, Qi Liu, T.H. Etsell, 2012. Clay minerals in nonaqueous extraction of bitumen from Alberta oil sands. Part 2. Characterization of clay minerals. **Fuel Processing Technology**, Vol. 96, 183-194.

- **Kaolinite enrichment in supernatant**

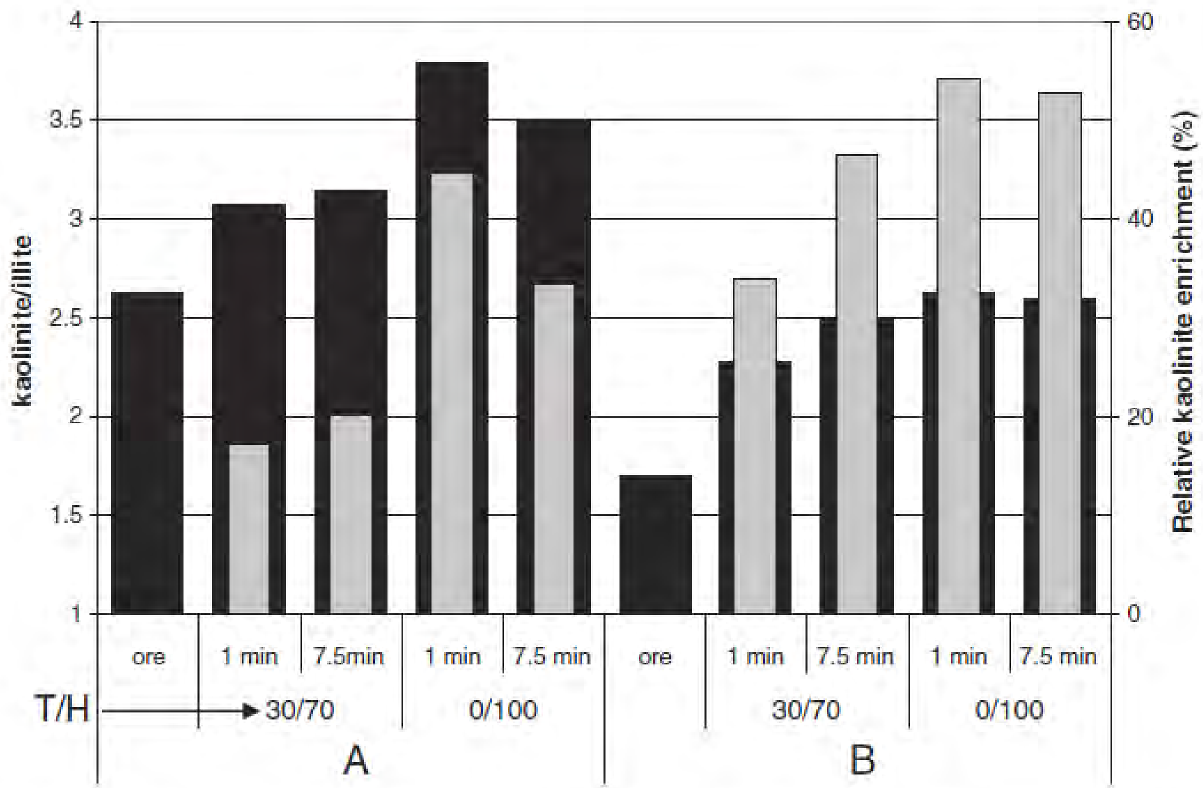


Fig. 5. K/I ratio (black bars) and relative enrichment of kaolinite to the supernatant (gray bars) for the entire clay fraction (<2 μm) from the ore and supernatant after 1 and 7.5 min of settling, based on quantitative XRD analysis. T/H — toluene to heptane ratio.

A. Hooshiar, P. Uhlik, D.G. Ivey, Qi Liu, T.H. Etsell, 2011. Clay minerals in nonaqueous extraction of bitumen from Alberta oil sands. Part 1. Nonaqueous extraction procedure. **Fuel Processing Technology**, Vol. 94, 80-85.

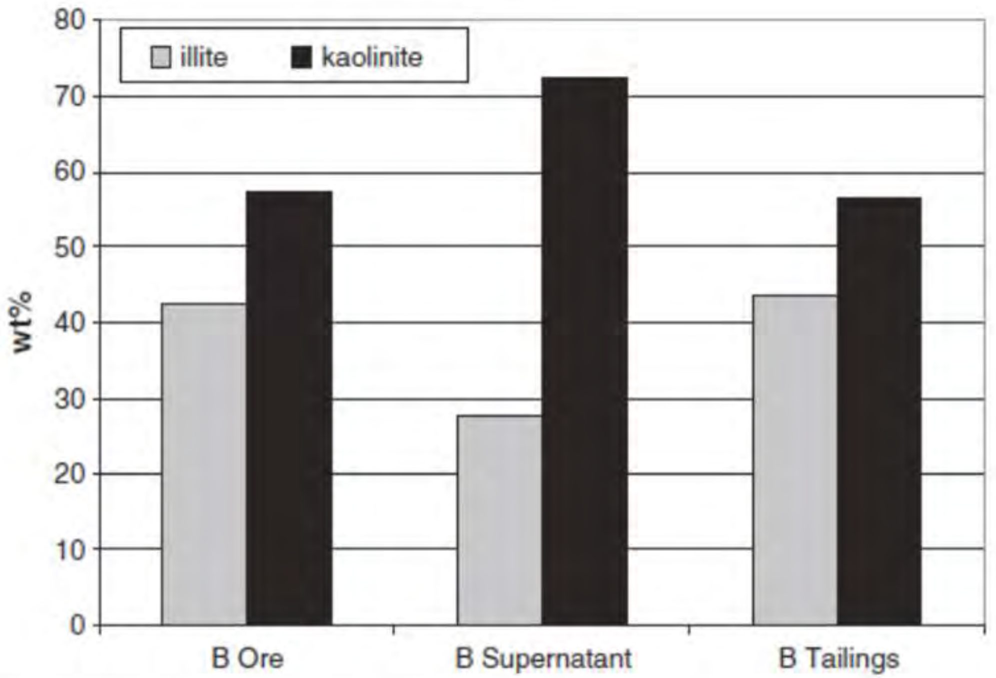


Fig. 14 Comparison of clay fraction (<2 μm) composition of the ore and fractions after nonaqueous extraction (supernatant and tailings) at a toluene to heptane ratio of 0/100, showing the kaolinite enrichment in the supernatant.

Kaolinite was enriched in the supernatant relative to illite

A. Hooshiar, P. Uhlik, D.G. Ivey, Qi Liu, T.H. Etsell, 2011. Clay minerals in nonaqueous extraction of bitumen from Alberta oil sands. Part 1. Nonaqueous extraction procedure. **Fuel Processing Technology**, Vol. 94, 80-85.

- **Effect of water**

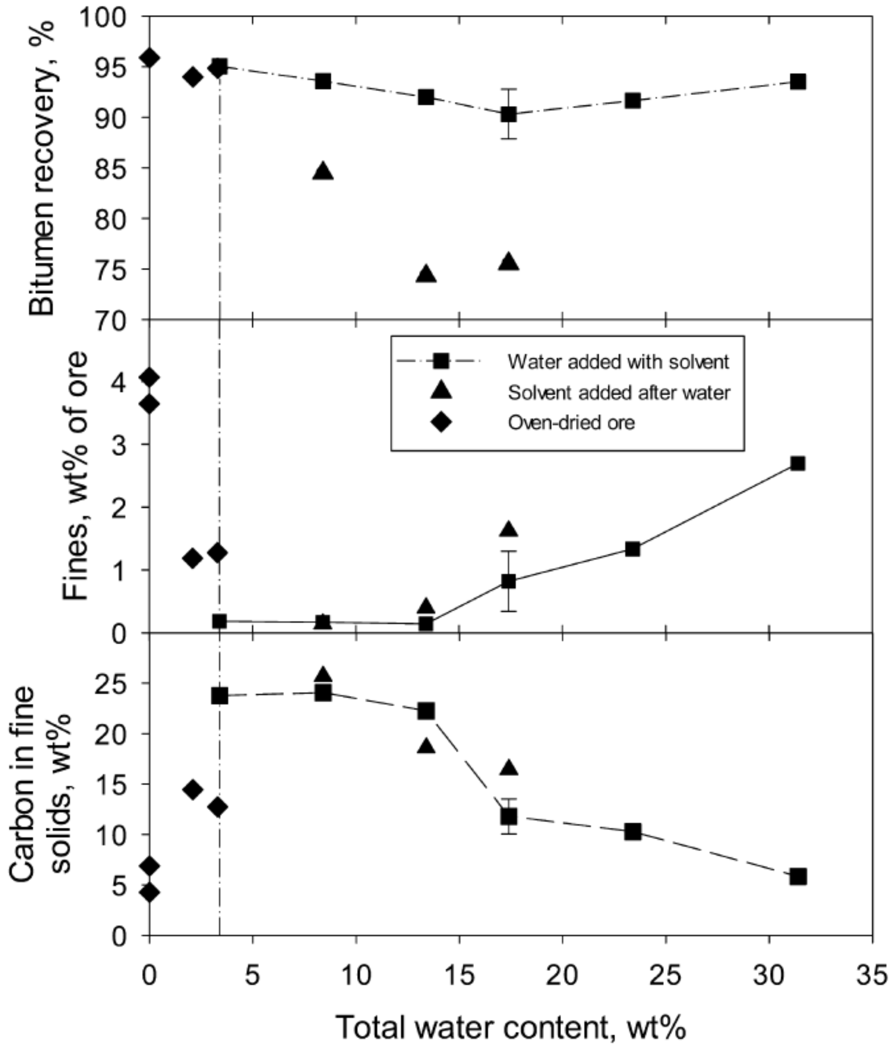


Table 5. Mineralogy of Centrifuge Solids[a]

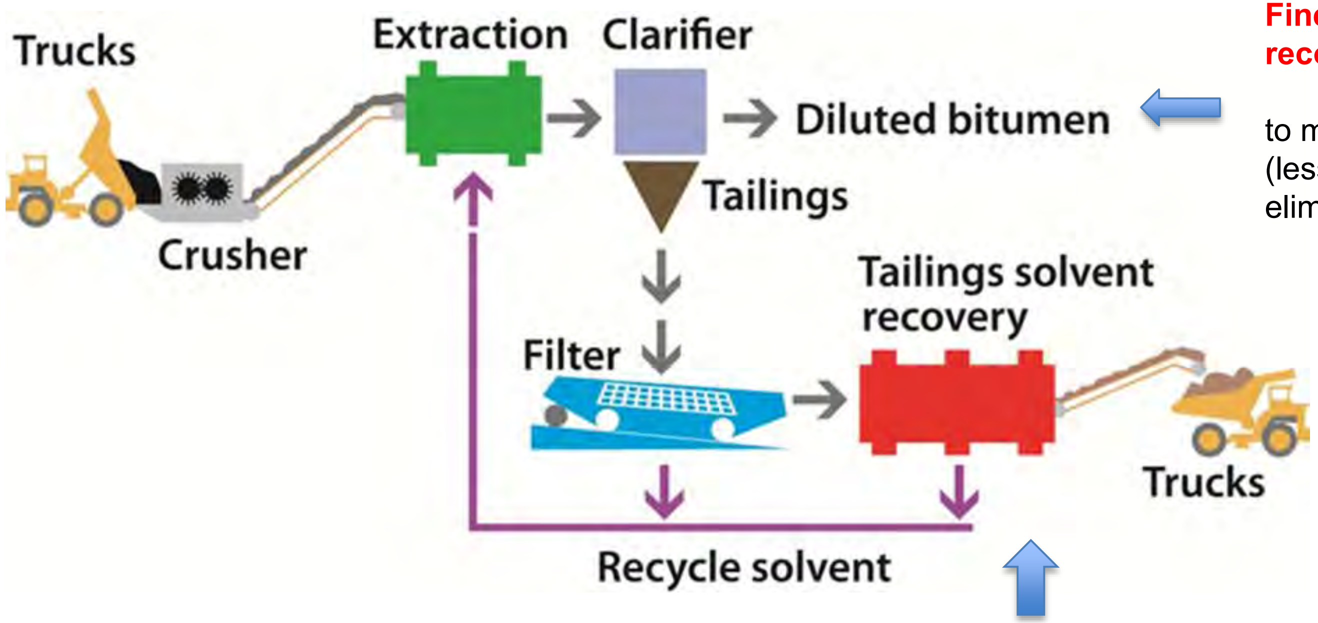
mineral	weight % (normalized)
nonclays	
quartz	38.6
potassium feldspar	8.0
calcite	2.4
dolomite	0.8
siderite	3.2
pyrite	0.7
hematite	0.2
anatase	0.2
total nonclays	**54.1**
clays	
kaolinite (disordered)	27.2
illite	16.8
chlorite	1.8
total clays	**45.9**
total	**100.0**

[a]Low-fines ore, centrifuged solids after filter washing with toluene.

- Add solvent (cyclohexane) after water lowered bitumen recovery
- Low water content (2-12 wt%) helped reduce fine solids content in bitumen
- Too much water or no water increased fines solids content in bitumen, and the fine solids had lower carbon content

H. Nikakhtari, S. Wolf, P. Choi, Qi Liu and M. R. Gray, 2014. Migration of fine solids into bitumen from solvent extraction of Alberta oilsands. **Energy and Fuels**, Vol. 28, n 5, 2925–2932.

Two challenges



Fine solids removal from recovered bitumen

to meet refinery requirements (less than 300 ppm fine solids) to eliminate the need for upgrader

Solvent recovery from extraction tailings

to meet regulation (4 parts solvent in extraction tailings per thousand part of extracted bitumen)

works out to be about 260 ppm for rich ore (~13 wt% bitumen)

low energy intensity in solvent recovery

- **Effect of clay surface bitumen coating**

Clay surface bitumen coating increased the affinity of clays to cyclohexane

Table 3. Equilibrium data and kinetic rate constants for cyclohexane vapour ($p/p^0 = 0.4$) and water vapour ($p/p^0 = 0.5$) on the three samples in the absence and presence of the other vapour at 30 °C

	Kaolinite				FS				ORFS			
	sorbed amount[1]				sorbed amount				sorbed amount			
	mmol/g	g/g	k_{ad} (s^{-1})	k_{des} (s^{-1})	mmol/g	g/g	k_{ad} (s^{-1})	k_{des} (s^{-1})	mmol/g	g/g	k_{ad} (s^{-1})	k_{des} (s^{-1})
cyclohexane alone	0.12	0.0101	0.014	0.003	0.07	0.0059	0.020	0.003	0.22	0.0185	0.008	0.003
cyclohexane after water	0.06	0.005	0.022	0.006	0.05	0.0042	0.022	0.003	0.21	0.0177	0.008	0.003
water alone	0.88	0.0158	0.0009	0.0022	0.63	0.0113	0.0015	0.0018	0.73	0.0131	0.0019	0.0019
water after cyclohexane	0.57	0.0103	0.007	0.0004	0.55	0.0099	0.0009	0.0008	0.66	0.0119	0.0006	0.0006

[1]mmol/g: mmol of adsorbate per gram of adsorbent; g/g: mass of adsorbate on adsorbent

X. Tan, L. Vagi, Qi Liu, P. Choi and M.R. Gray, 2016. Sorption equilibrium and kinetics for cyclohexane, toluene and water on Athabasca oilsands solids. **Canadian Journal of Chemical Engineering**, Vol. 94, 220-23

- **Effect of water content during extraction**

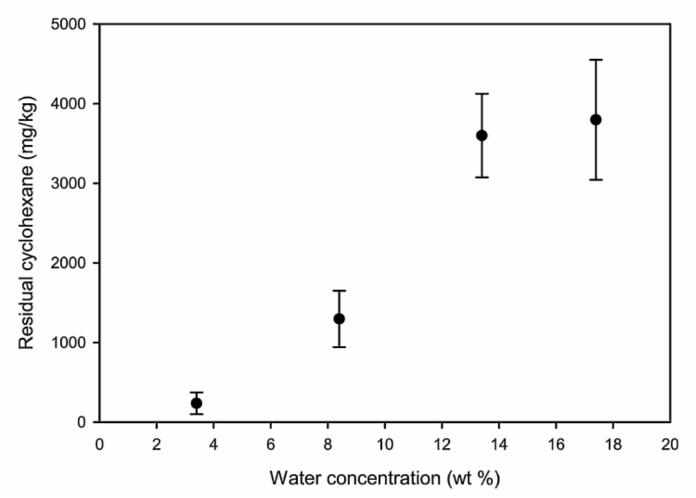
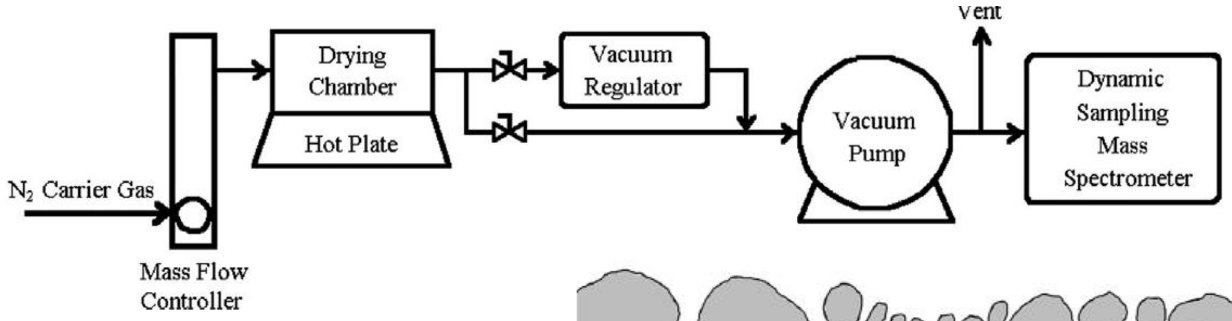


Figure 5. Residual cyclohexane content in the gangue after drying in the environmental chamber at 24ºC for 40 min as a function of water content.

High water content during extraction kept more cyclohexane in the extraction tailings

H. Nikakhtari, S. Wolf, K. Pal, P. Choi, Qi Liu and M.R. Gray, 2016. Solvent removal from cyclohexane-extracted oil sands gangue. **Canadian Journal of Chemical Engineering**, Vol. 94, 408-414.

- **Drying chamber tests**



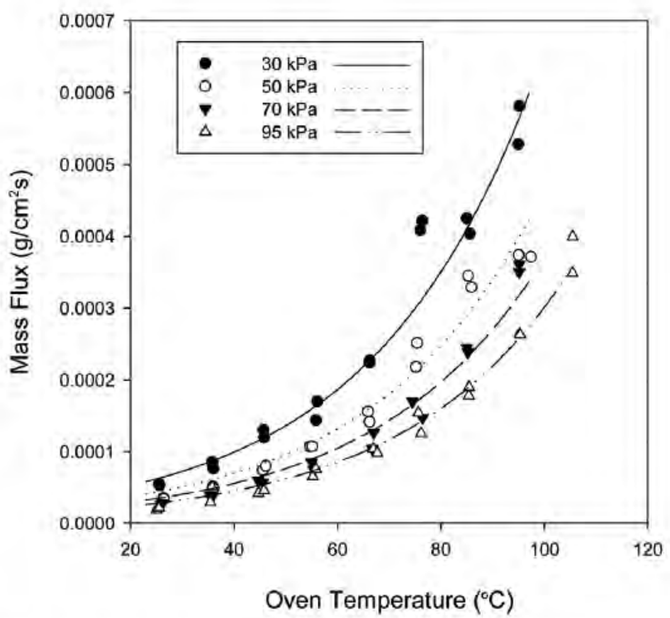
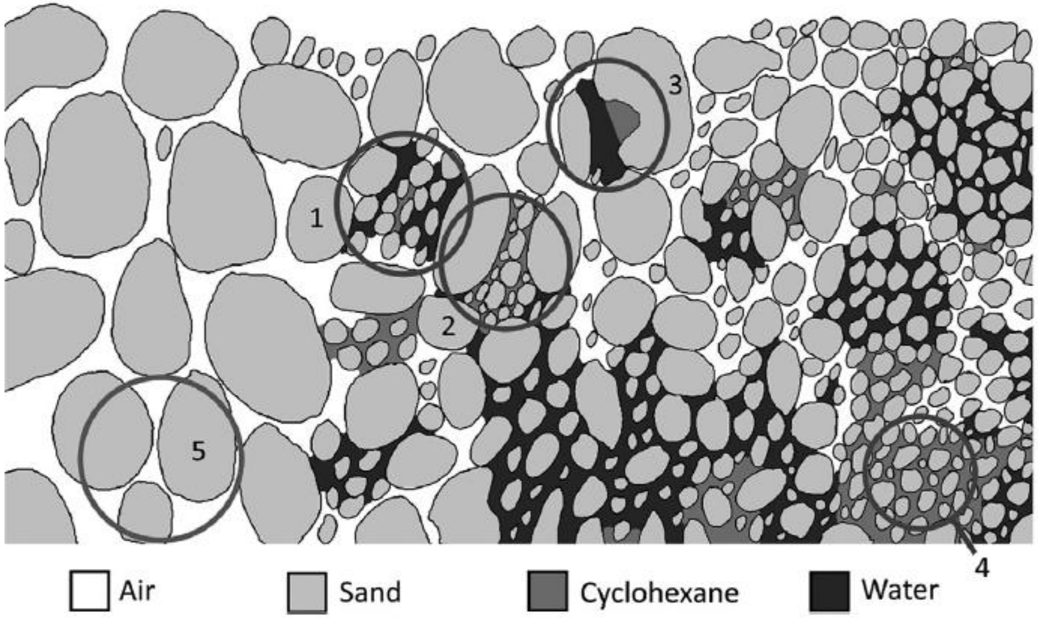


Figure 4. Maximum cyclohexane mass flux for high-grade gangue. Curves represent the best fit of data to Equation (3).



Different modes of cyclohexane transport and evaporation from extraction tailings

R. Renaud, K. Pal, T. Weiss, P. Choi, Qi Liu, and M.R. Gray, 2016. Vacuum drying of cyclohexane from solvent-extracted oil sands gangue. **Canadian Journal of Chemical Engineering**, Vol. 95, 459-466.

- **Cyclohexane evaporation from re-constituted extraction tailings**

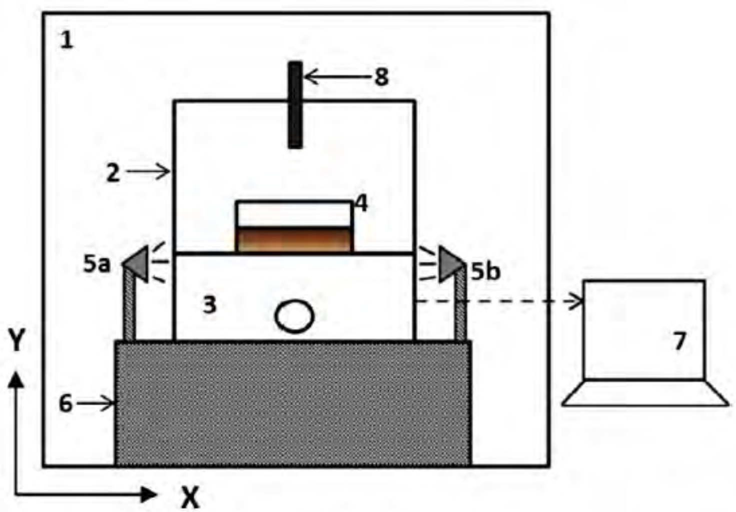


Fig. 1. The drying experiment setup. 1 – Fumehood, 2 – Balance chamber, 3 – Weighing scale, 4 – Glass petri-dish with gangue sample, 5 a, b – Lamps for illumination, 6 – Blackened cardboard, 7 – Continuous monitoring of liquid mass loss in sample, 8 – Temperature/humidity probe.

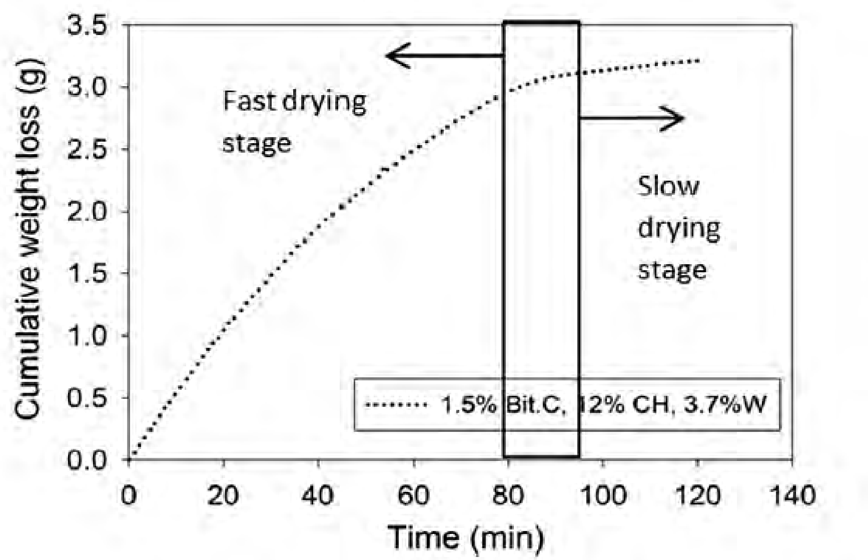
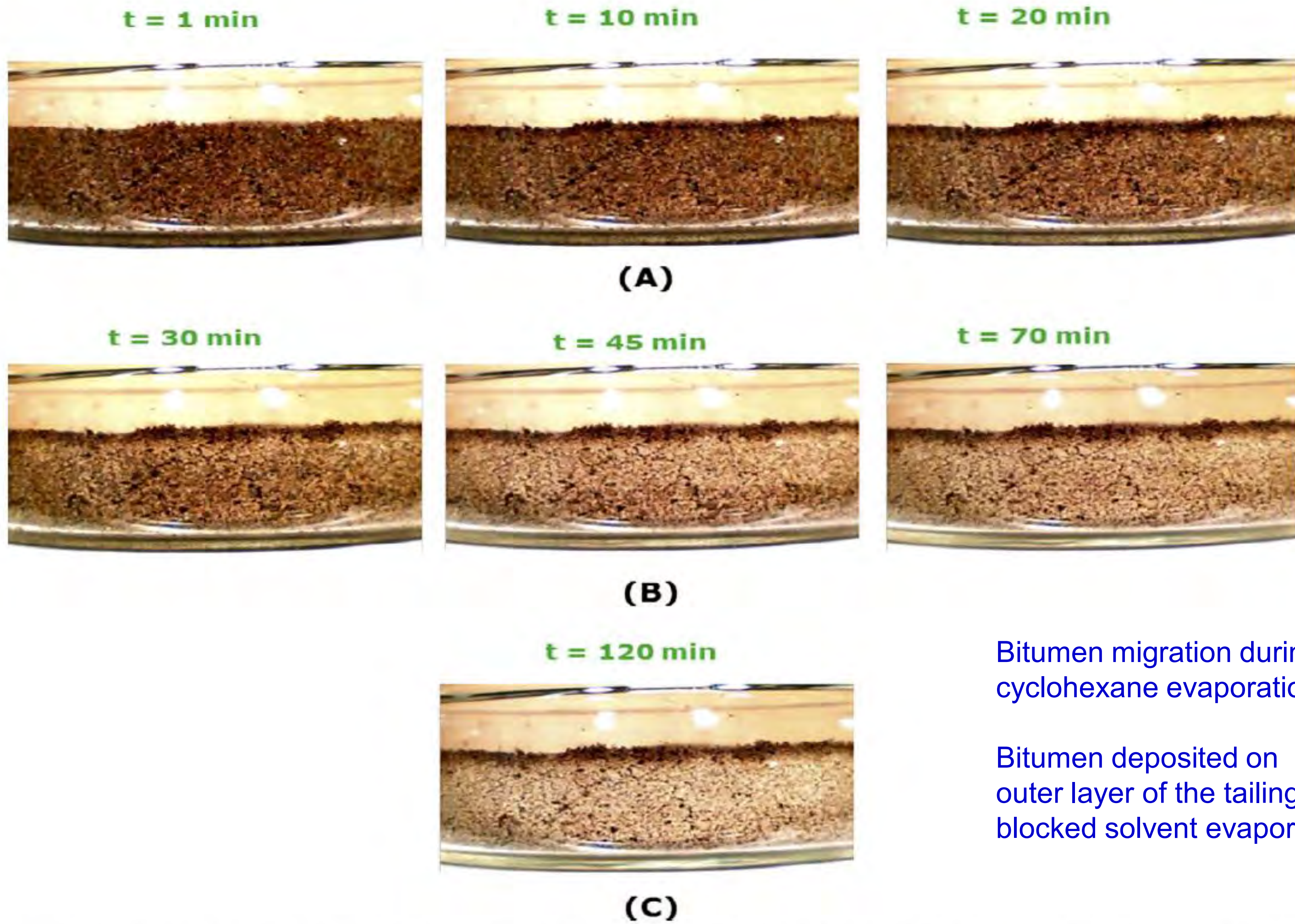


Fig. 2. A typical drying curve with a transition from fast to a slow drying stage. The boxed area is the interval where the transition time lies.

S. Panda, K. Pal, S. Merzara, M.R. Gray, Qi Liu, and P. Choi, 2017. Transport and removal of a solvent in porous media in the presence of bitumen, a highly viscous solute. **Chemical Engineering Science**, Vol. 165, 229-239.



Bitumen migration during cyclohexane evaporation

Bitumen deposited on the outer layer of the tailings and blocked solvent evaporation

Fig. 9. (A) Top layer thickness increases due to bitumen migration. (B) A middle lighter layer is seen which increases in thickness. (C) The gangue bed finally. Sample: 1% BitC %, 12 wt% cyclohexane, 3.7 wt% water, bed height = 1 cm.

S. Panda, K. Pal, S. Merzara, M.R. Gray, Qi Liu, and P. Choi, 2017. Transport and removal of a solvent in porous media in the presence of bitumen, a highly viscous solute. **Chemical Engineering Science**, Vol. 165, 229-239.

Two challenges **Solvent recovery**

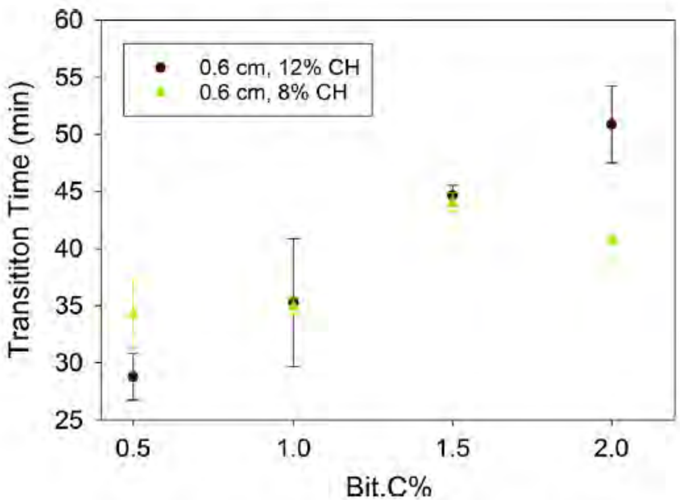


Fig. 7. Transition time of samples, bed height – 0.6 cm.

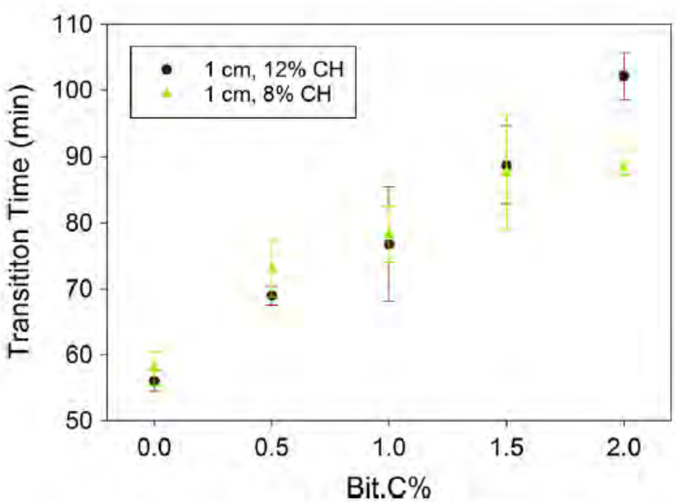


Fig. 8. Transition time of samples, bed height – 1 cm.

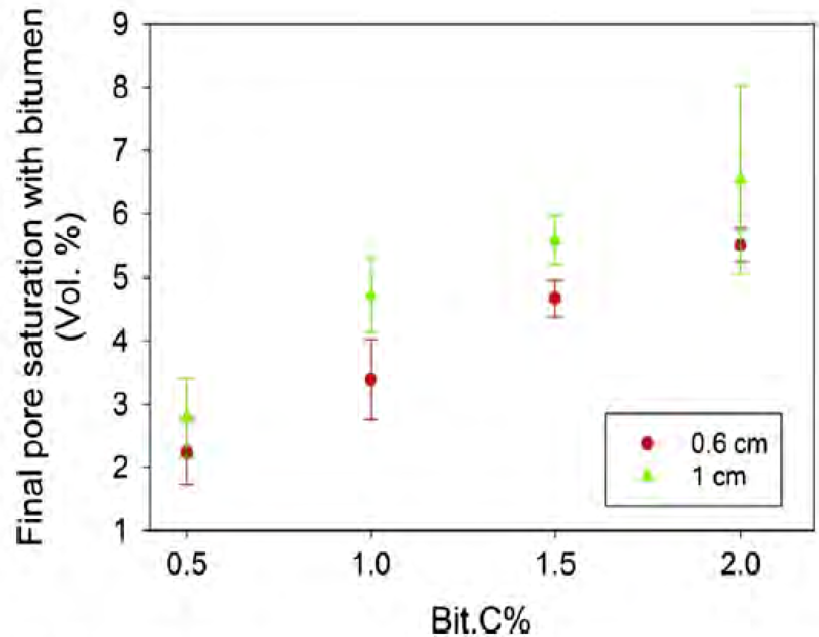


Fig. 13. Final pore saturation with bitumen (vol%) in the top layer for reconstituted gangue samples containing 12 wt% cyclohexane.

Residual bitumen in the extraction tailings extended the time required to evaporate cyclohexane, mainly due to its gradual accumulation on the particle bed surface

S. Panda, K. Pal, S. Merzara, M.R. Gray, Qi Liu, and P. Choi, 2017. Transport and removal of a solvent in porous media in the presence of bitumen, a highly viscous solute. **Chemical Engineering Science**, Vol. 165, 229-239.

- **Effect of surface bitumen coating, and solvent**

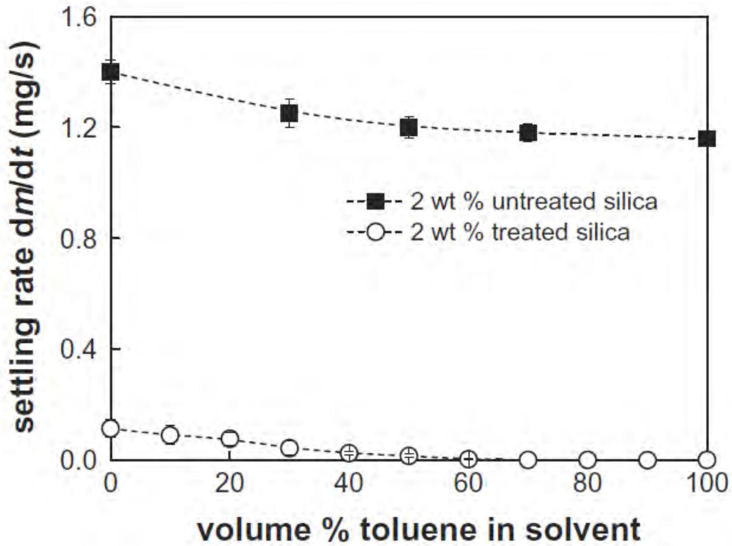


Fig. 3. Sedimentation of clean (i.e. untreated) and bitumen-treated silica in hydrocarbon solvents. The solvents were mixtures of *n*-heptane and toluene at various ratios.

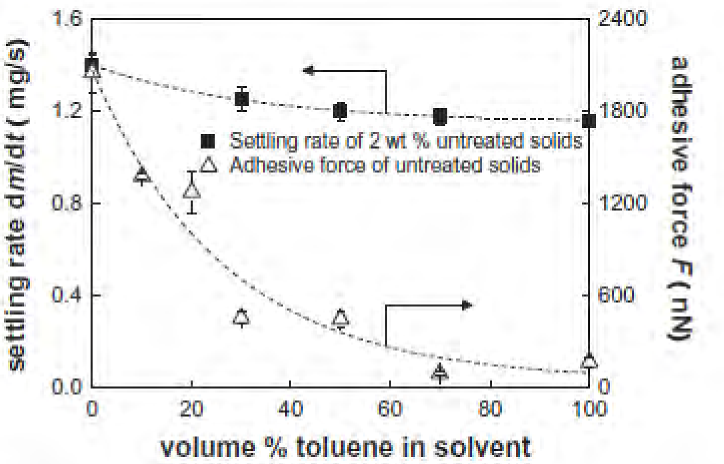


Fig. 6. Settling rate (re-plotted from Fig. 3) and the corresponding interparticle adhesive forces for clean (i.e. untreated) solids. It is seen that the settling rate is not much affected by the magnitude of interparticle adhesion.

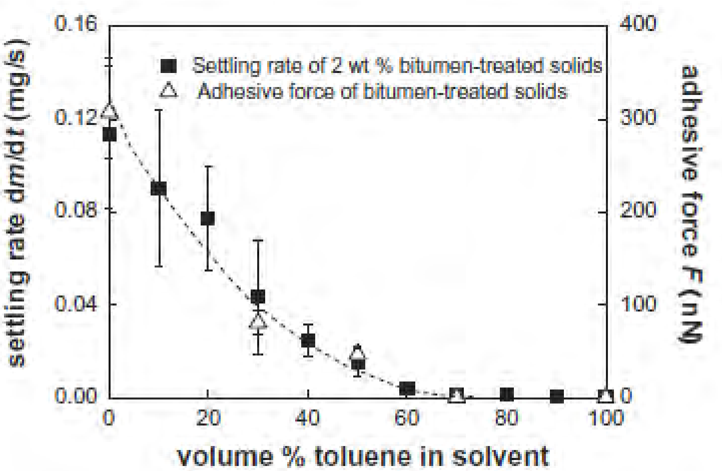


Fig. 7. Settling rate (re-plotted from Fig. 3) and the corresponding interparticle adhesive forces for bitumen-treated solids. Here, strong correlation is seen between settling rate and interparticle adhesion.

- Pure silica settled fast in heptol
- Bitumen-coated silica settled slower in heptol. The more the toluene, the slower the settling rate
- The settling rate correlated well with attraction force

Y. Jin, W. Liu, Qi Liu and A. Yeung, 2011. Aggregation of silica particles in non-aqueous media. **Fuel,** Vol. 90, 2592-2597.

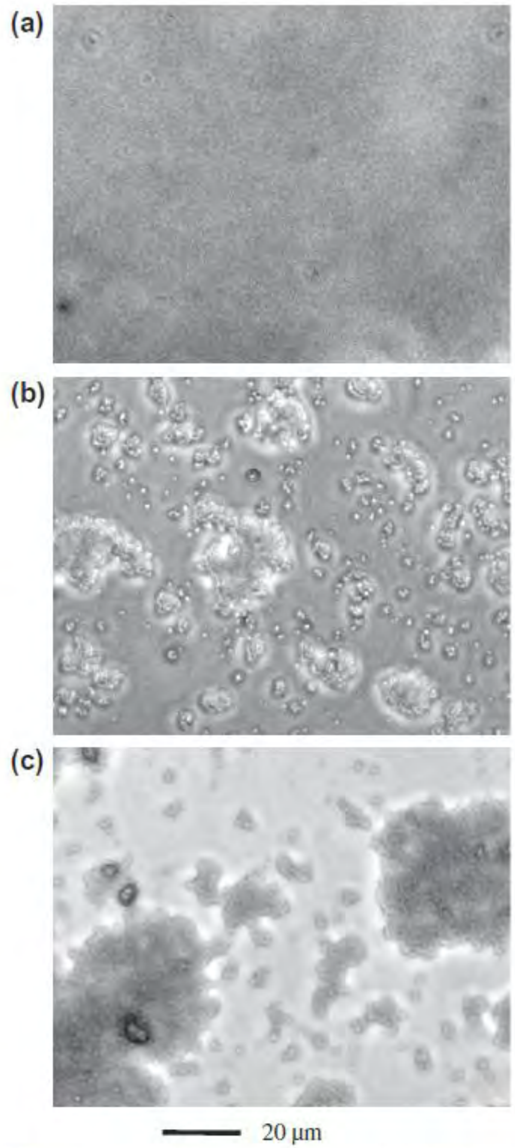


Fig. 5. Microscope images of bitumen-treated silica in mixtures of toluene and *n*-heptane at various ratios: (a) 100% toluene. (b) Equal volumes of toluene and heptane. (c) 100% heptane.

100% toluene

50% toluene, 50% heptane

100% heptane

Fast settling was due to aggregation of bitumen-coated silica in a paraffinic solvent

Y. Jin, W. Liu, Qi Liu and A. Yeung, 2011. Aggregation of silica particles in non-aqueous media. **Fuel,** Vol. 90, 2592-2597.

- **Effect of solvent blend**

Table 1. Properties of Solvents in Descending Order of Solubility Parameter

solvent	boiling point (°C)	density (g cm^{-3})	solubility parameter (MPa$^{1/2}$)[14]
cyclohexane	80.7	0.78	16.8
cyclopentane	49	0.75	16.6
methylcyclopentane	71.8	0.75	16.2
n-heptane	98.4	0.68	15.34
n-hexane	68.7	0.66	14.93
n-pentane	36.1	0.63	14.32

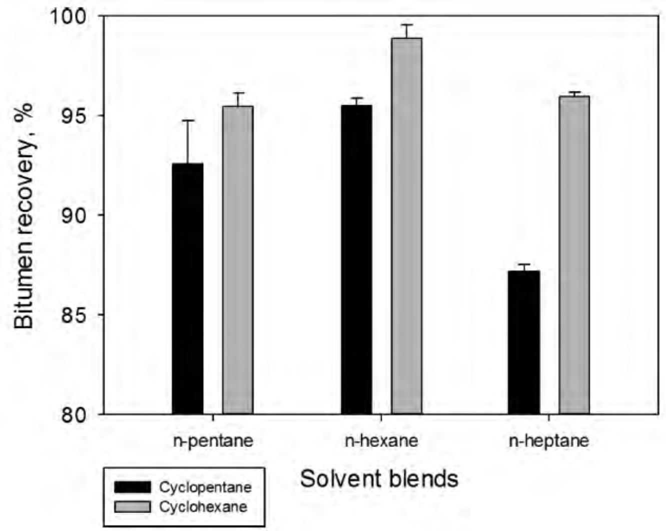


Figure 3. Comparison of bitumen recovery (fines-free basis) for mixtures of cyclopentane and cyclohexane with paraffinic solvents at a constant value of the solubility parameter of 16.45 MPa$^{1/2}$.

Table 2. Performance of Single Solvents for Non-aqueous Extraction of a High Grade Oil Sands Ore Sample

solvent	bitumen recovery (%)	centrifuged solid fines (wt % in bitumen product)[a]	centrifuged solid fines carbon (wt %)	bitumen recovery (fines-free basis)
cyclohexane	97.9 ± 0.8	5.8 ± 0.1	8 ± 0.3	97.4 ± 0.8
cyclopentane	91.6 ± 0.8	5.5 ± 0.8	11.6 ± 1.6	90.8 ± 1.0
methylcyclopentane	84.8 ± 1.2	8.9 ± 1.2	9.2 ± 0.5	83.9 ± 1.2
n-heptane	96.0 ± 0.63	32.6 ± 0.3	30.0 ± 0.8	81.5 ± 0.02

[a]Mass percent of recovered bitumen on a solvent-free basis.

K. Pal, L. da Paz Nogueira Branco, A. Heintz, P. Choi, Qi Liu, P.R. Seidl and M.R. Gray, 2015. Performance of solvent mixtures for non-aqueous extraction of Alberta oil sands. **Energy and Fuels**, Vol. 29, n 4, 2261−2267.

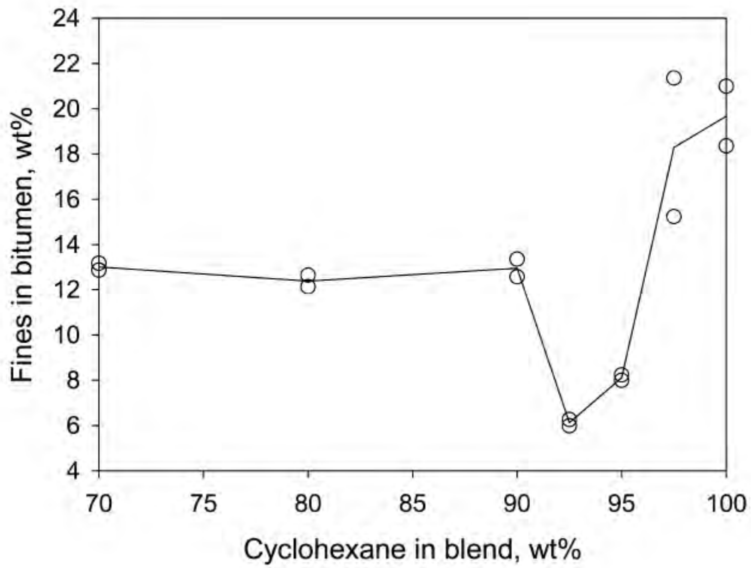


Figure 2. Percentage of centrifuged fine solids in the bitumen product using solvent mixtures of cyclohexane and *n*-heptane. The line shows the trend for mean values of duplicated experiments.

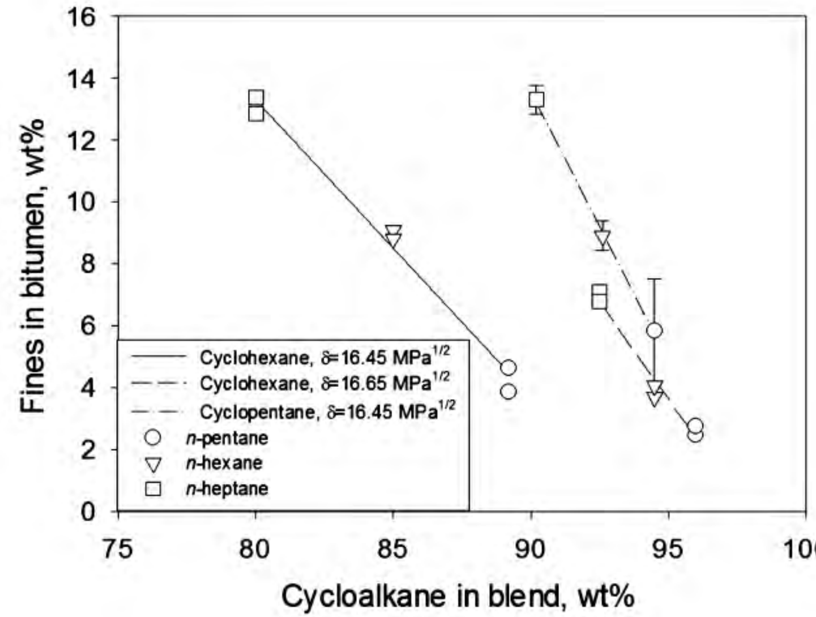


Figure 4. Percentage of centrifuged fine solids in extracted bitumen using cyclohexane and cyclopentane in mixtures with different paraffinic solvents. Where indicated, error bars are standard deviations of experiments in triplicate. The lines show linear regression for data of blends of constant solubility parameter.

- Some particular combination of cyclohexane/heptane seems to cause lower find solids content in NAE bitumen
- Higher cycloalkane content caused lower fine solids content
- Shorter chain alkane caused lower fine solids content

K. Pal, L. da Paz Nogueira Branco, A. Heintz, P. Choi, Qi Liu, P.R. Seidl and M.R. Gray, 2015. Performance of solvent mixtures for non-aqueous extraction of Alberta oil sands. **Energy and Fuels**, Vol. 29, n 4, 2261−2267.

- **Hydrothermal treatment + water venting + hot filtration** (tested on bitumen froth)

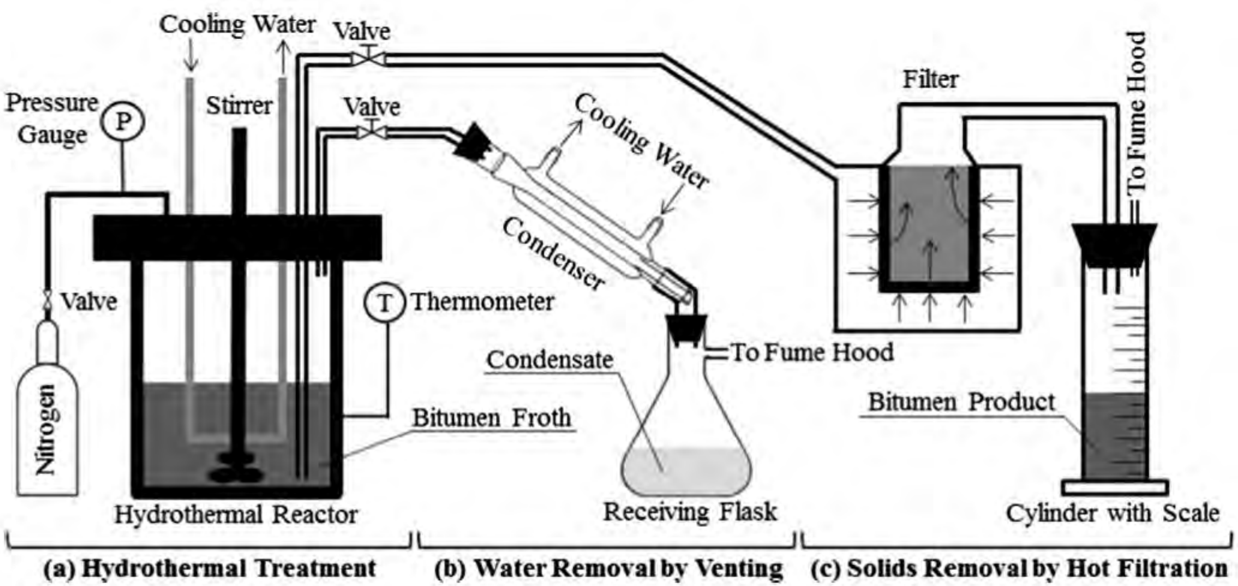


Fig. 2. Schematics for laboratory-scale hydrothermal bitumen froth cleaning test set up. The schematics show the hydrothermal treatment (a), venting (b) and solids hot filtration (c).

Q. Chen, I. Stricek, M. Cao, M. Gray, Qi Liu, 2016. Influence of hydrothermal treatment on filterability of fine solids in bitumen froth. **Fuel**, Vol. 180, 314-323.

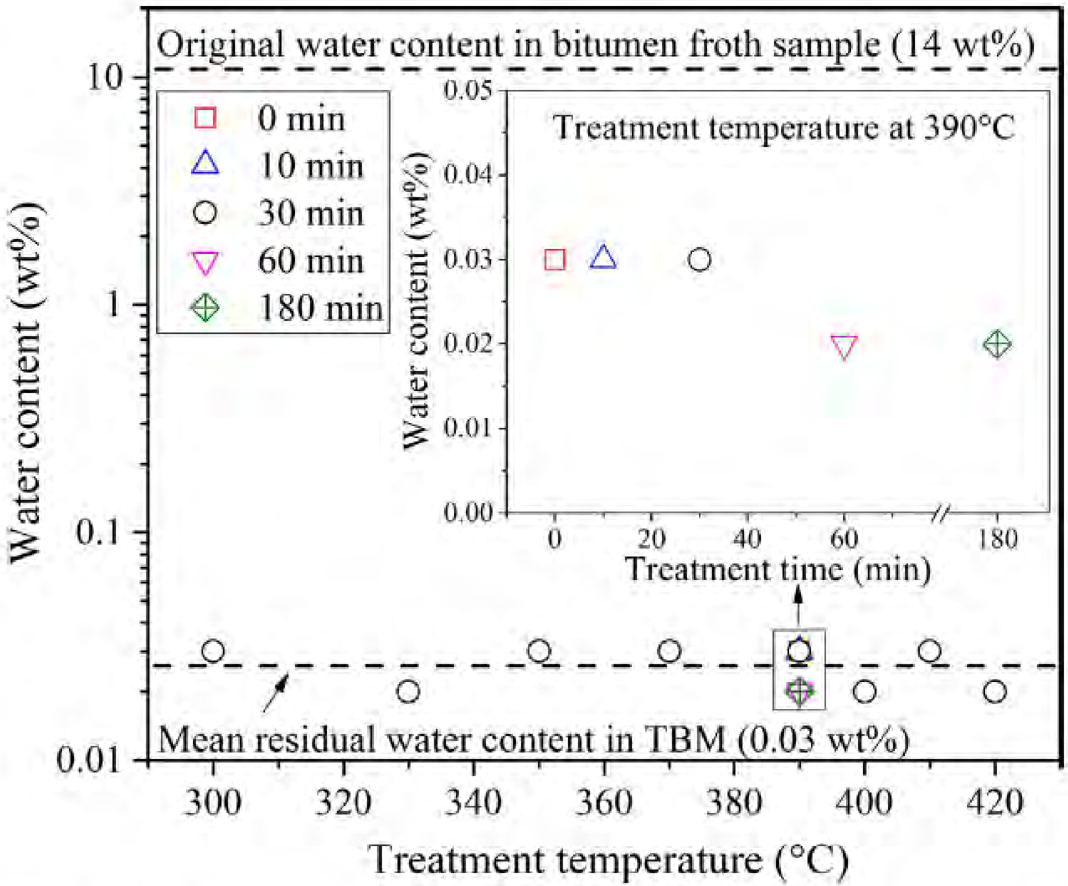


Fig. 3. Residual water contents in TBM as a function of temperature for a treatment time of 30 min. The inset figure shows the water contents under different treatment times at 390 °C.

Venting at 270ºC removed all the emulsified water from bitumen froth

Without venting, about half of the emulsified water was demulsified and phase-separated out

Q. Chen, I. Stricek, M. Cao, M. Gray, Qi Liu, 2016. Influence of hydrothermal treatment on filterability of fine solids in bitumen froth. **Fuel**, Vol. 180, 314-323.

Hydrothermal treatment at 390ºC significantly improved the filtration removal of fine solids from bitumen froth

The bitumen froth became filterable whether by room-temperature filtration (after toluene dilution) or hot filtration (200ºC) without solvent dilution

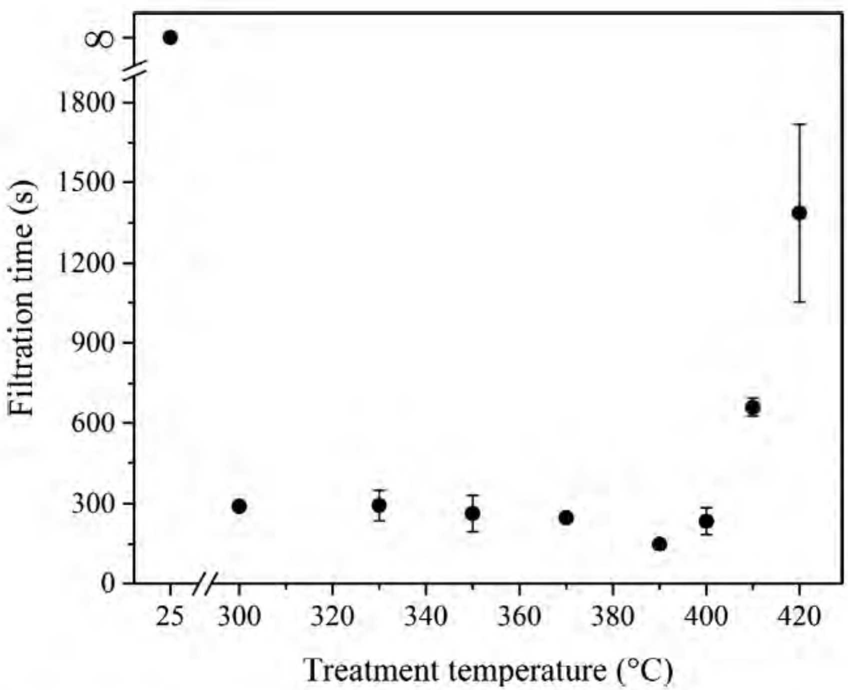


Fig. 5. Effect of treatment temperature on the room-temperature filtration behavior (hydrothermal treatment time 30 min).

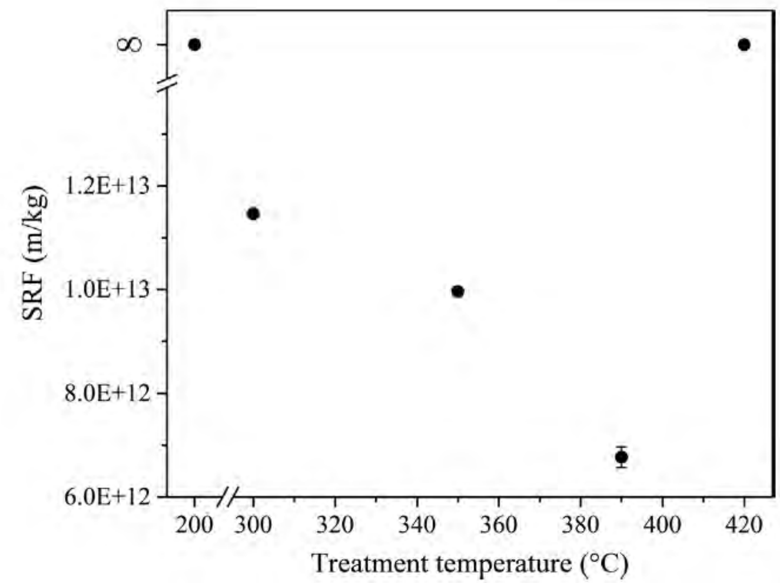


Fig. 7. Effect of treatment temperature on the hot filtration behavior (hydrothermal treatment time 30 min). The error bar at 390 °C indicates the standard deviation from three repeat tests.

Q. Chen, I. Stricek, M. Cao, M. Gray, Qi Liu, 2016. Influence of hydrothermal treatment on filterability of fine solids in bitumen froth. Fuel, Vol. 180, 314-323.

What we know

- Solvent
- Swelling and non-swelling clays
- Bitumen coating on the fine solids and clays
- Water
- Solvent recovery: thermodynamics and kinetics
- Fine solids removal

What we don't know

- Energy consumption in solvent recovery, GHG emission
- Feasible fine solids removal method(s)
- How to build a NAE plant

ACKNOWLEDGEMENTS

- Financial support to the research program on NAE within IOSI is provided by
    - Imperial Oil
    - Alberta Innovates
    - NSERC
    - NRCan

- Imperial Oil technical personnel, esp Keith Abel, have been providing technical consultation and advices to the NAE research in IOSI

Thanks for your attention