

# **Amended and Restated Study on Lithium Recovery from Oilfield Produced Water Brine & Wastewater Treatment**

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## ***Introduction***

Lithium is a relatively common element that retains high market value because recovery of a pure lithium product is difficult. Some of the properties that make lithium an exceptional element for electric storage contribute to the difficulty in its recovery; lithium has a low density (0.543 g/cm<sup>3</sup>), a high electrochemical standard potential (-3.04 V) and high solubility when in the presence of oxyanions such as lithium chlorate (3.7 Kg/L). Commercial production is dominated by recovery from brines concentrated through solar evaporation. These brines achieve concentrations of >4000 mg/L [Li] (Choubey et al. 2016) for sequential precipitative removal of contaminating ions to a commercial product of lithium carbonate or lithium chloride.

Brines from oil and gas production can contain high concentrations of dissolved ions (>100,000 mg/L) including lithium concentrations exceeding 100 mg/L. These brines have largely been ignored as commercial sources of lithium, in part because of the low ratio of lithium relative to other ions and the difficulty these ions pose for recovery. However, these brines are an increasing environmental liability in many areas of North America. The increasing need to treat these brines for reuse or even for sustainable disposal changes the financials making them a potential source for economic lithium recovery.

MGX developed a theoretical approach to lithium recovery from oilfield brine that drew heavily from existing sequential precipitative methods deployed with solar evaporation. This method required the evaporation of 98% of the water from the brine, an energy intensive and costly approach. Purlucid was asked to test the method but also made the case that other methods should be evaluated for possible efficiencies with the Purlucid ultrafiltration technology.

This report summarizes results of this testing, provides a general overview of the process for lithium recovery and an estimate of recovery cost and revenue based on the MGX brine holdings known as the Sturgeon Property Brines, just one of the many brine sources in MGX's holdings.

## Sturgeon Property Brine & Lithium Recovery

Lithium recovery testing focused on brines from the Sturgeon Lake Property held by MGX. Sturgeon Lake produced water is primarily a calcium and sodium chloride brine (Table 1).

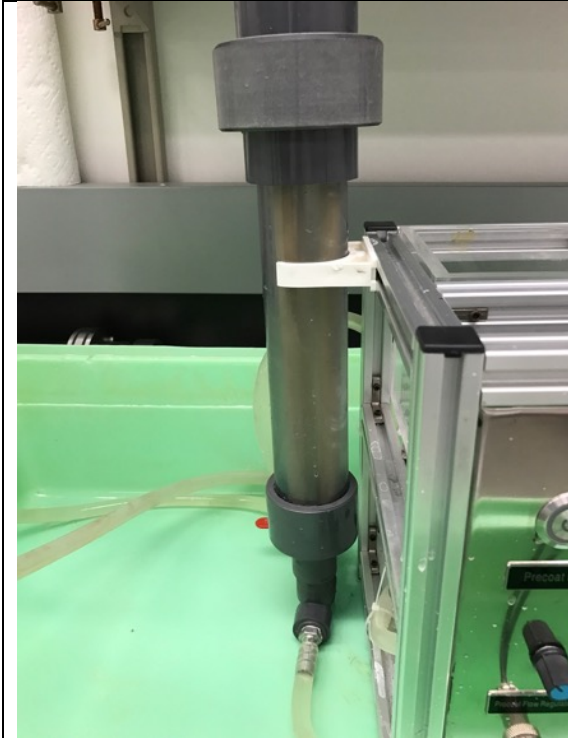
Several aspects of oil field brine contribute to the complexities of lithium recovery. The first is that these brines have very high salinities with relatively low hardness. Sturgeon Lake produced water (PW) has several critical differences that make extraction using a sequential precipitative process difficult; low initial lithium concentration and higher sulfate and chloride concentrations. When we processed Sturgeon Lake PW for the first time, available analytical data was typical for the oil industry and lacked most of the analyses required to determine the stoichiometric ratios and solubility appropriately. This lack of data or, conversely, the wide fluctuations in chemistry that occur on a daily basis as water is sourced from different wells within a property is common for oilfield produced water. It is therefore vital that the lithium recovery process be able to work effectively across variable brine chemistries and with limited real-time analytical data. This is challenging with a sequential precipitation process on its own. We therefore created a combination of processes that may provide MGX with a lithium recovery system that will recover commercial grade lithium products while remaining robust to fluctuations in source chemistry and treatment costs.

*Table 1: Feed chemistries for a hypothetical brine used in previous planning and two oilfield brines tested for lithium extraction.*

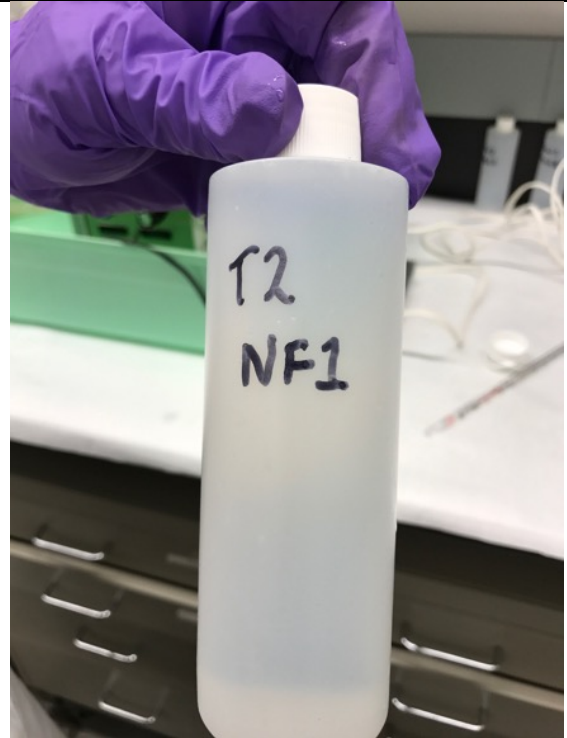
	Ca	Mg	Na	K	SO4	HCO 3	Cl	Sr	B	Br	Li		
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L		
Hypothetical Brine	1590	0	2010	54000	5100	155	232	12500	0	630	260	426	130
Heavy Oil Brine				11340									
Sturgeon Lake Brine	76.65	1	0	4343	270	8601	3						87
	2450				337.		15260						
	0	2760	59900	4230	7	350	0	1050	106	330	60.7		

### Lithium Recovery

The first step in lithium recovery was to evaluate pre-treatment with Nanoflotation. Oilfield brines contain high concentrations of ions as well as oil that would cause any recovery technology to fail if not removed in a pre-treatment step. Nanoflotation is a combination of two separate technologies operating on a similar principle using highly charged nano-environments to destabilize chemicals in the water, making them suitable for removal by flotation or filtration. More information is provided on Nanoflotation in subsequent sections reviewing this technology and its application to the additional revenue stream of wastewater treatment while recovering lithium.



*Fig. 1a: Bench scale RSL Membrane™ system filtering Sturgeon brine. Solids accumulation on the membrane tubes is clearly visible*



*Fig. 1b: Permeate post filtration. Note clarity of brine.*

As general overview, the method for lithium recovery consists of a chemical treatment followed by ultrafiltration using the RSL Membrane™ system, which is then followed by lithium concentration and recovery. The first two stages of treatment of Sturgeon Lake brine has been completed on increasingly larger volumes in four consecutive bench-scale tests. The bench-scale RSL Membrane™ system replicates commercial scale systems at 0.2% with a single filtration manifold containing four 16% sized membranes, feed and slurry pumps and flow and pressure control systems (Fig 1a &b). A pilot unit has also been built that operates at up to 5 m<sup>3</sup>/hr, representing the smallest commercial scale membrane bundle. Pre-treatment was done successfully with no reduction in lithium concentration in the post treatment permeate. The Nanoflotation system performed remarkably well for pre-treatment without being limited by trans-membrane pressure build up (<0.07 mPa) over extended run times.

Initially, the brine is subjected to a chemical manipulation that results in a high suspended solids feed to the RSL Membrane™ system. On filtration, these solids and all dissolved oil is removed resulting in a clean permeate with very little to no loss of lithium. The permeate has substantively reduced magnesium concentrations making it suitable for subsequent steps in lithium concentration and recovery. The lithium concentration step uses a trade secret process that results in a 25-fold and higher increase in concentration. For the Sturgeon brines, we achieved clean brine concentrations of 1600

mg/L when starting with 65 mg/L and 1951 mg/L when starting with 70 mg/L. Example data are provided in the table below.

*Table 2: Example results from lithium recovery trials. Metals that are below detection in feed water have been removed for presentation purposes.*

	Units	Sturg. Raw	Step 1 permeate	Concentrate 1	Concentrate 4
Total Aluminum (Al)	mg/L	0.97	0.030	10	1.3
Total Barium (Ba)	mg/L	10	8.6	1.7	0.94
Total Boron (B)	mg/L	110	100	3.7	6.0
Total Calcium (Ca)	mg/L	23000	17000	370	420
Total Lithium (Li)	mg/L	67	65	1600	1951
Total Magnesium (Mg)	mg/L	2800	5.7	13	40
Total Potassium (K)	mg/L	4500	4400	12	8.8
Total Sodium (Na)	mg/L	57000	61000	68	49
Total Strontium (Sr)	mg/L	840	780	30	23
Total Sulphur (S)	mg/L	96	89	6.9	9.9

The final step is production of a lithium solid either as lithium chloride or lithium carbonate (Fig. 2). Both have been successfully created and analyzed for crystallinity and purity.



*Fig. 2: Lithium carbonate and lithium chloride solids recovered from processing Sturgeon Lake brine.*

### *Lithium Carbonate*

Production of lithium carbonate was highly successful. The compact solid that was produced was easily filtered and dried. This solid contained 55% carrier compounds from excess soda ash addition and the filtration media as well as a small amount of calcium carbonates. These will be optimized to limit their carry over to the final product and will be further processed for recovery and reuse in the treatment and recovery steps. The remaining product contained 74% lithium carbonate with some evidence of carbide and

24% sodium chloride salt with trace amounts of magnesium, aluminum, silicon and sulfur. The process recovered 86% of the lithium into the final carbonate product.

With respect to future improvements, particularly the removal of sodium chloride, we expect rinsing may be sufficient in future production runs. This will increase the purity of the lithium product substantively. In these trials our focus was on total lithium recovery so we did not rinse the solid products for two reasons; to provide for the highest possible total lithium recovery and to simplify mass balance calculations which are complicated by the addition of rinse water. Calcium appears to have been present from process contamination in the membrane housing, again which will be solved by rinsing the solids in the backwash cycles.

### *Lithium Chloride*

Recovery of lithium chloride resulted in a solid with moderate crystallinity, 38% of which were hydrated lithium salts and 27% sodium chloride. Total lithium recovery was high, exceeding 95%. This is possible given this process is largely evaporative after removal of contaminating ions in the initial treatment steps.

The remaining 34% of the salts were products from the treatment system as well as unexpected contamination from aluminum and copper. In all, calcium chloride, aluminum oxide and copper chloride salts accounted for 7.1%, 6.7% and 7.7% of the product mass. The aluminum and copper likely derived from the evaporation pans used to crystalize the salts as feed to the evaporation step contained low concentrations of aluminum (1 mg/L) and copper (0.2 mg/L). Better pH control will correct the leaching of metals from evaporative surfaces in the commercial system.

### *Tools Developed for Lithium Recovery*

Optimizing a lithium recovery process is difficult given the variability of brine feed likely to occur at commercial scale. A tool to assist in this optimization process was required and was developed that will substantively contribute to commercial lithium recovery. The tool, a chemical assessment modelling approach was developed using the USGS open source PHREEQC (Parkhurst & Appelo, 2013) as a backbone aqueous model. A standardized data entry and run parameter interface was created to adapt the model specifically for lithium recovery. Within minutes we are able to predict solubility products given introduction of reagents and concentrating steps. The model is performing very well but requires expertise both to run and to interpret the results. Further development will occur to make it more generally user friendly and to integrate it into the programmable logic controller (PLC) for the lithium recovery commercial systems.

Real-time determination of lithium concentration is another important factor in process control. Using a commercially available ion half-cell, a method for determination of

lithium concentration was created based on electrical potential. While lithium half-cells are available on the market, these are highly sensitive to the typical chemistries of oilfield brines and the membranes themselves are easily destroyed by these brines. We have overcome these limitations such that calibration and data collection are more reliable. Results compared favorably with laboratory analytical results for 10 samples. Resulting lithium concentrations were returned within 15 seconds and were within 10% of laboratory reported values that require over a week to be returned from a commercial lab. The creation of this in-line lithium sensor will allow commercial systems to have real-time continuous concentration information that will control reagent dosing, substantively reducing chemical costs and enhancing the efficiency of lithium recovery. A research program is currently being established at a university lab specializing in micro-sensor development to further advance this product over the next two years.

***Lithium Recovery Conclusions:***

- 1) *Long run times can be achieved in the filtration step. Solids loading up to 6.5 Kg/m<sup>2</sup> of membrane area was demonstrated. This would mean a typical 50 m<sup>3</sup>/hr system could process approximately 1.3 tonnes of solids between each full backwash cycle.*
- 2) *There are many alternative approaches for removing contaminating ions from the feed brine without evaporation. Given the high concentration of divalent cations as permanent hardness countered primarily by the anion chloride, pre-treatment is necessary and results in a less energy intensive recovery process.*
- 3) *A magnesium-free brine was produced in one simple and reliable process. This process has been repeated in four separate trial runs with Sturgeon Lake Produced Water.*
- 4) *The subsequent concentration and recovery steps have been demonstrated on increasingly large volumes of the cleaned brine. In the most recent trials, concentrations of lithium reached 2000 mg/L with very low energy requirements (<0.5 kwh/m<sup>3</sup> of feed water).*
- 5) *Lithium solids have been created successfully on each of the four trials to date. Purity and crystal composition are currently being evaluated by XRD and EDS methods.*



## ***Wastewater Treatment as a primary source of Revenue and Feed for Lithium Recovery***

Oil production brines including produced water, frac flowback and both upstream and downstream wastewaters from thermal processes are a massive industrial and environmental liability as well as revenue for those companies able to manage these brines for producers. Disposal of these waters underground, either by injection into porous formations (deep well disposal) or in salt caverns is the current industry norm, typically at costs from \$10/m<sup>3</sup> to as high as \$150/m<sup>3</sup> for the most difficult and environmentally challenging waters.

Critical to lithium recovery is initial treatment to remove free and emulsified oil which otherwise would foul any of the lithium recovery processes. The following sections contain text excerpted from a report commissioned as a third-party review of Nanoflotation (ATSI 2017).

### **Nanoflotation to Remove Oil**

The Nanoflotation technology was deployed at a refinery in China to demonstrate its ability to remove oil in 24/7 operation at commercial scale. This test occurred over a six week period on site at the Jinan refinery. Backwashing of the RSL membranes occurred at least once a day. The video link provides an overview of the testing and the pilot plant used in these tests. [Jinan Refinery -oil and solid separation](#)

For this application, H<sub>2</sub>S was a concern. The Nanoflotation pilot plant had to be built with a vapour recovery system that allowed gases to be collected in the refinery's vapour recovery system. Sinopec would not allow the pilot to operate with the froth flotation component of the Nanoflotation technology. Sinopec was concerned with the use of a surfactant, which is a key component of the Nanoflotation froth flotation system. As a result, the plant operated with an induced gas flotation (IGF) system using nitrogen gas. This is typical for induced gas flotation systems used to treat produced waters for oil and gas operations in North America and specifically the SAGD (Steam Assisted Gravity Drainage) produced waters from Canada's oil sands.

Figure 3 provides a visual sample of the water before the IGF, after the IGF and after the RSL membranes. As indicated the oil remaining after the IGF was emulsified. The typical concentration of the emulsified oil is approximately 2000 mg/l.



Fig. 3: Jinan Refinery Pilot Test – Raw water into Induced Gas Flotation unit, Treated water with emulsified oil after IGF and treated water after RSL membranes™.

The data shows the high level of treatment provided by the RSL membranes and its ability not only to separate solids but also emulsified oil.

Figure 4 below shows a sample of the data over a 5-day consecutive period. As shown, turbidity levels were good right from the beginning of each filtration run which lasted 6 to 10 hours. Flux rates on the RSL membranes were approximately 400 lmh and backwash consistently resulted in 100% flux rate recovery. Oil levels going into the IGF were not consistent (5000 to 20000 mg/l) yet final effluents after the RSL were relatively consistent with regards to turbidity and oil.

Figure 4: Five Consecutive Days of Test results on oil and turbidity removal from a coker water at the Sinopec Jinan Refinery

IGF and RSL Membrane Test Run Log								IGF and RSL Membrane Test Run Log															
Time	IGF		RSL membrane			Comments	Visitors	Date	2015	21-Jun	Time	IGF		RSL membrane			Comments	Visitors	Date	2015	22-Jun		
	Feed Rate to Flotation	Compressed gas pressure	Water Feed to Compressed Gas	Flow rate to RSL media	Press upstream of Membrane							Press dntstream of Membrane	Feed Rate to Flotation	Compressed gas pressure	Water Feed to Compressed Gas	Flow rate to RSL media						Press upstream of Membrane	Press dntstream of Membrane
	m <sup>3</sup> /h	Mpa	L/h	m <sup>3</sup> /h	Mpa							Mpa	m <sup>3</sup> /h	Mpa	L/h	m <sup>3</sup> /h						Mpa	Mpa
8:00	—	0.57	70	0.65	0.040	0.000					8:00												
9:00	0.59	0.57	70	0.65	0.028	0.000					9:00	replace drain											
10:00	—	0.60	70	0.64	0.045	0.000					10:00												
11:00	—	0.59	70	0.65	0.050	0.000					11:00	0.60	0.60	70	0.68	0.047	0.000						
12:00	0.58	0.59	70	0.65	0.055	0.000					12:00	0.60	0.60	70	0.67	0.053	0.000						
13:00	0.58	0.59	70	0.65	0.060	0.000					13:00	0.59	0.60	70	0.67	0.060	0.000						
14:00	—	0.59	70	0.65	0.075	0.000					14:00	0.60	0.60	70	0.67	0.064	0.000						
15:00	—	0.59	70	0.65	0.028	0.000					15:00	0.60	0.61	70	0.67	0.069	0.000				Automatic B/W		
16:00	—	0.59	70	0.65	0.029	0.000					16:00	0.59	0.60	70	0.67	0.031	0.000						
17:00	—	0.60	70	0.64	0.034	0.000					17:00	0.59	0.60	70	0.67	0.036	0.000						
18:00	—	0.59	70	0.65	0.041	0.000					18:00	0.59	0.60	70	0.67	0.040	0.000						
19:00	—	0.59	70	0.65	0.045	0.000					19:00	0.60	0.60	70	0.67	0.047	0.000						

Sinopec Jinan Refinery Coker Wastewater						
Time	Oil mg/L		Turbidity NTU		pH	
	Inlet	after PCM	Inlet	after RSL	Inlet	after RSL
	8:00	10725.20	41.11		0.65	8.50
10:00				0.39	8.50	8.50
12:00				0.40	8.50	8.50
14:00				0.48	8.50	8.50
16:00				0.53	8.50	8.50
18:00				0.47	8.50	8.50

Sinopec Jinan Refinery Coker Wastewater						
Time	Oil mg/L		Turbidity NTU		pH	
	Inlet	after RSL	Inlet	after RSL	Inlet	after RSL
	8:00	20106.00	146.10			
10:00						
12:00				0.31	8.50	8.50
14:00				0.43	8.50	8.50
16:00				0.39	8.50	8.50
18:00				0.46	8.50	8.50



IGF and RSL Membrane Test Run Log									
Time	IGF		RSL membrane				Comments	Visitors	
	Feed Rate to Flotation	Compressed gas pressure	Water Feed to Compressed Gas	Flow rate to RSL media	Press upstream of Membrane	Press dntstream of Membrane			
	m <sup>3</sup> /h	Mpa	L/h	m <sup>3</sup> /h	Mpa	Mpa			
	8:00	0.57	0.59	70	0.69	0.041			0.000
9:00	0.60	0.59	70	0.69	0.047	0.000			
10:00	0.60	0.59	70	0.69	0.051	0.000			
11:00	0.60	0.59	70	0.69	0.055	0.000			
12:00	0.60	0.59	70	0.69	0.060	0.000			
13:00	0.59	0.59	70	0.69	0.066	0.000			
14:00	0.60	0.59	70	0.68	0.069	0.000	Automatic R/W		
15:00	0.60	0.58	70	0.68	0.023	0.000			
16:00	0.60	0.60	70	0.68	0.029	0.000			
17:00	0.60	0.60	70	0.68	0.034	0.000			
18:00	0.61	0.61	70	0.68	0.038	0.000			
19:00	0.60	0.60	70	0.68	0.040	0.000			

IGF and RSL Membrane Test Run Log									
Time	IGF		RSL membrane				Comments	Visitors	
	Feed Rate to Flotation	Compressed gas pressure	Water Feed to Compressed Gas	Flow rate to RSL media	Press upstream of Membrane	Press dntstream of Membrane			
	m <sup>3</sup> /h	Mpa	L/h	m <sup>3</sup> /h	Mpa	Mpa			
	8:00								
9:00	Installation of nitrogen pipe valve								
10:00									
11:00	0.59	0.56	70	0.62	0.040	0.000			
12:00	0.60	0.57	70	0.69	0.041	0.000			
13:00	0.60	0.57	70	0.69	0.045	0.000			
14:00	0.60	0.57	70	0.69	0.052	0.000			
15:00	0.60	0.57	70	0.69	0.056	0.000			
16:00	0.60	0.57	70	0.69	0.062	0.000			
17:00	0.60	0.57	70	0.69	0.067	0.000			
18:00	0.61	0.57	70	0.69	0.073	0.000	Automatic R/W		
19:00	0.60	0.57	70	0.69	0.027	0.000			

Sinopec Jinan Refinery Coker Wastewater						
Time	Oil mg/L		Turbidity NTU		pH	
	Inlet	after RSL	Inlet	after RSL	Inlet	after RSL
	8:00	5373.00	32.00		0.68	8.50
10:00				0.53	8.50	8.50
12:00				0.48	8.50	8.50
14:00				0.47	8.50	8.50
16:00				0.51	8.50	8.50
18:00				0.55	8.50	8.50

Sinopec Jinan Refinery Coker Wastewater						
Time	Oil mg/L		Turbidity NTU		pH	
	Inlet	after RSL	Inlet	after RSL	Inlet	after RSL
	8:00	14894.00	45.20			
10:00						
12:00						
14:00				0.35	8.50	8.50
16:00				0.44	8.50	8.50
18:00				0.51	8.50	8.50
				0.59	8.50	8.50

Sinopec Jinan Refinery Coker						
				Date	2015	25-Jun
Time	Oil mg/L		Turbidity NTU		pH	
	Inlet	after RSL	Inlet	after RSL	Inlet	after RSL
8:00	20189.00	29.30				
10:00						
12:00				0.49	8.50	8.50
14:00				0.55	8.50	8.50
16:00				0.63	8.50	8.50
18:00				0.78	8.50	8.50

Precoat Test Run Log								
						Date	2015	25-Jun
Time	DAF			Precoated membrane			Comments	Visitors
	Feed Rate to Flotation	Compressed gas pressure	Water Feed to Compressed Gas	Flow rate to RSL media	Press upstream of Membrane	Press dntstream of Membrane		
	m <sup>3</sup> /h	Mpa	L/h	m <sup>3</sup> /h	Mpa	Mpa		
8:00	0.61	0.59	70	0.68	0.033	0.000		
9:00	0.60	0.60	70	0.67	0.034	0.000		
10:00	0.60	0.59	70	0.67	0.035	0.000		
11:00	0.60	0.59	70	0.67	0.042	0.000		
12:00	0.60	0.59	70	0.67	0.049	0.000		
13:00	0.60	0.60	70	0.67	0.051	0.000		
14:00	0.61	0.61	70	0.67	0.050	0.000		
15:00	0.60	0.59	70	0.67	0.052	0.000		
16:00	0.60	0.59	70	0.67	0.053	0.000		
17:00	0.60	0.59	70	0.67	0.060	0.000		
18:00	0.59	0.59	70	0.69	0.069	0.000	Automatic R/W	
19:00	0.60	0.59	70	0.68	0.028	0.000		

The data shows that the RSL membranes were capable of handling initial oil concentrations into the IGF that exceeded 2% yet after the membrane the oil concentration was <30 mg/l and turbidity was less than 0.8.

### Treatment of Concentrated Brines

Large volumes of blowdown are produced daily in Alberta and represent a particularly interesting source for lithium given that these waters have already been concentrated in boilers and evaporators. Nanoflotation, a core PTS technology licensed from DBE, has been successfully applied to many oil wastewaters and concentrates. The most concentrated blowdown in the industry derives from use of evaporators to create boiler feed water.

### *Silica*

In evaporator operation, caustic is added to raise the pH to increase the solubility of the silica present in the produced water. To dispose of the resulting concentrated blowdown the pH has to be lowered to conform to deep well disposal regulations. When the pH is lowered, the silica is precipitated and has to be filtered out to prevent it from plugging the deep well.

Table 3: Summary results from blowdown water treatment trials.

		C1 EBD 1 Raw	C1 EBD 2 Raw	C1 EBD 1 Post RSL	C1 EBD 2 Post RSL	C1 EBD 3 Post RSL	C2 Raw EBD 1	C2 Post RSL	C2 Post RSL	C3 Feed	C3 Post RSL
Dissolved Calcium	mg/L	75.2	78.1	83.6	79.1	77.6	326	294	66	1252	986
Dissolved Magnesium	mg/L	<10.0	<10.0	<10	<10	<10	<10	<10	9.9	109.2	77.6
Hardness	mg/L	184.5	191.8	206	194	191	815	744	206	3570	2780
Reactive Silica	mg/L	20300	19800	196	202	166	5110	136	60.1	20050	27.8
Total Barium	mg/L	0.873	0.885	0.428	0.49	0.54	15.7	7.8	0.80	17.9	2
Total Strontium	mg/L	6.80	6.94	4.69	3.99	3.81	28.1	25.2	2.79	74	51.4
Dissolved Iron	mg/L									2.15	0

Table 3 shows the high levels of silica in the EBD waters (i.e. 20,000 mg/l). After lowering the pH and filtering, the effluent had silica levels less than 200 mg/l. This level of treatment would result in a water quality with regards to silica similar to SAGD produced water. The water can be further treated in a manner similar to SAGD produced water for reuse. The TDS level remains high in permeate (150,000 to 200,000 mg/l) which is beneficial with respect to lithium recovery in that highly soluble ions like lithium remain in the permeate for further recovery. Purlucid has assessed the mass balance and has created a system where treated blowdown water can be blended with the produced water feed to the evaporator or the OTSG making the process suitable for zero liquid discharge (ZLD) or substantively reduced disposal.

In the most recent study at the University of Alberta, an emphasis was placed on maximizing silica removal. In this study, the pH was adjusted to 7.5 and floc formation was enhanced by co-treating with other high total dissolved solids wastewater from the site (demineralizer regeneration water). As shown on the top portion of Table 3, the reactive silica concentrations were reduced to 28 mg/L. In this case the feed water had reactive silica concentrations of 13,000 mg/L (Fig. 5).

#### **Iron, Barium & Strontium**

Iron, barium and strontium are elements that pose scale-forming risk in steam systems. The RSL membranes<sup>TM</sup> provided an effluent with iron below detection limits. Barium and strontium were reduced by 40 to 45%, respectively.

**Carbonates & associated Base Cations (Ca, Mg)**

Despite not targeting calcium removal, 80% removal of calcium has been achieved at a treatment pH of 7 with post treatment calcium concentrations of 15 mg/L from initial concentrations of 76 mg/L. The carbonate balance described below suggests that calcium was precipitated and removed at the lower pH due to carbonate mineral formation.

Bicarbonate is non-detectable in raw EBD as is to be expected at pH 12 where virtually all of the dissolved inorganic carbon should be in the carbonate ion form. Raw EBD had a carbonate ion concentration of 11,709 mg/L and this would convert to 11,572 mg/L of bicarbonate at a pH of 8 with small amounts of carbonic acid and carbonate accounting for the remaining 5 moles. Post treatment bicarbonate concentration was 8,601 mg/L indicating that ~3000 mg/L of the carbonate was removed as colloidal carbonate minerals. This additional floc likely added to the efficiency of targeted ion removal (e.g. Silica) acting as a sweep floc in the overall process.

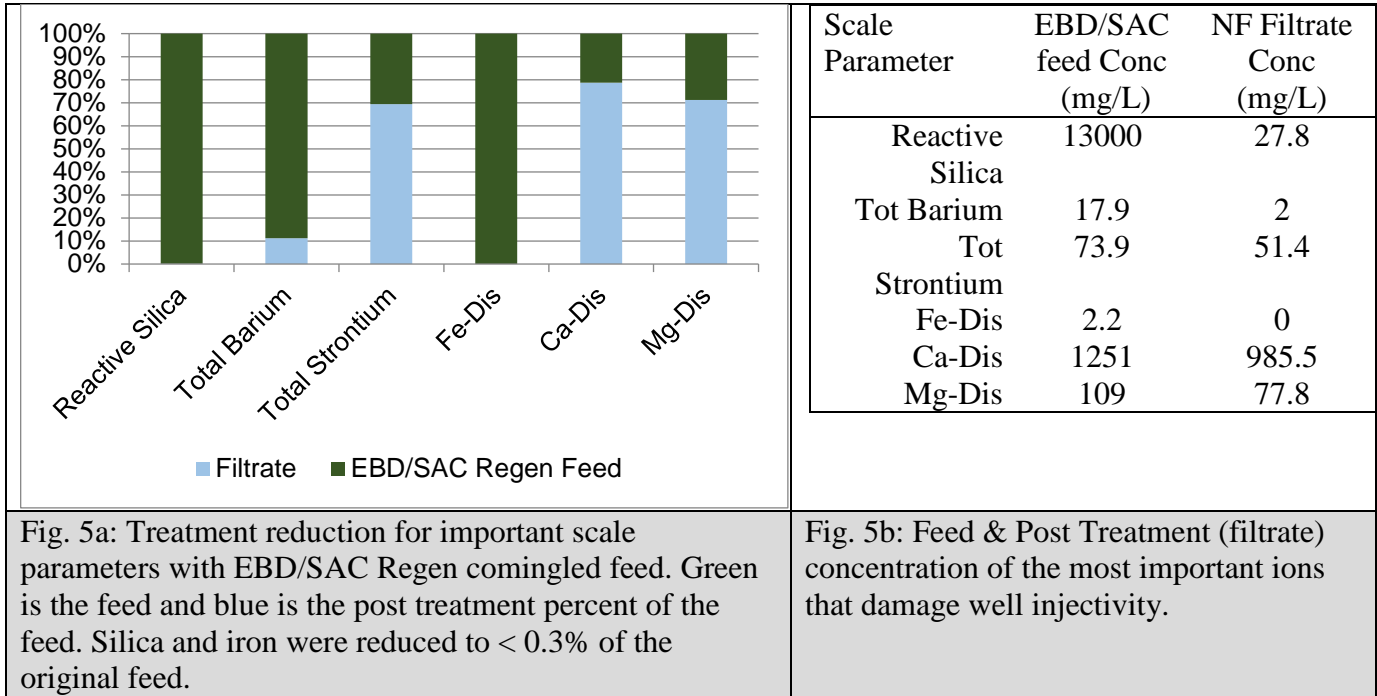


Fig. 5a: Treatment reduction for important scale parameters with EBD/SAC Regen comingled feed. Green is the feed and blue is the post treatment percent of the feed. Silica and iron were reduced to < 0.3% of the original feed.

Fig. 5b: Feed & Post Treatment (filtrate) concentration of the most important ions that damage well injectivity.

## Treatment of SAGD Produced Water

In Steam Assisted Gravity Drainage (SAGD) operations approximately 100% steam quality is injected into the oil sands formation to provide heat to change the viscosity of the bitumen allowing it to be pumped to the surface. Approximately 200 million cubic meters of water was injected in 2016 in Alberta alone, most of which returns to the production facility and requires treatment.

The following slides (Fig. 6) provided by the ATSI author, Mike Rodgers, describe the process.



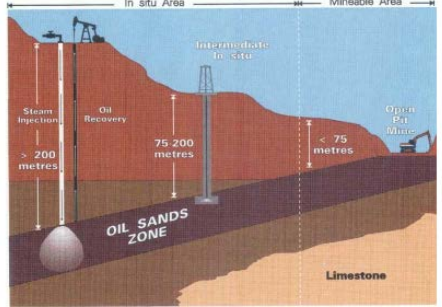

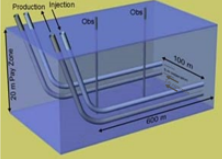
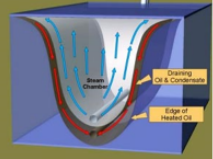

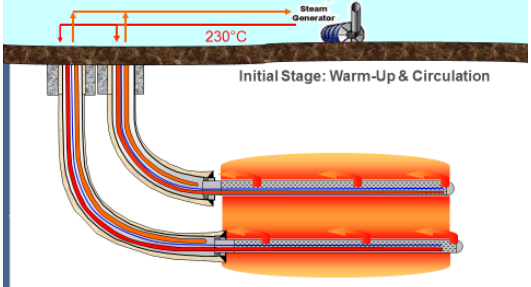

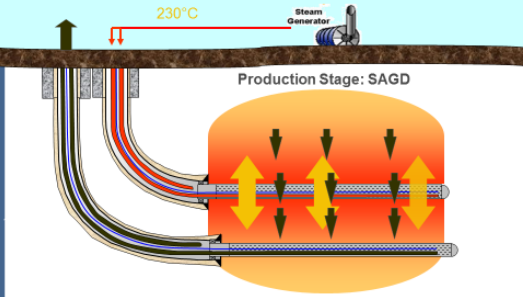

<h3>Water Management Issues at Total's Alberta Facilities</h3>  <p><b>Mike ROGERS</b> Consulting Water Treatment Engineer Thermal Division TOTAL E&amp;P CANADA</p> <p><b>Mark SCHAFFER</b> R&amp;D Engineer Corporate Development Division TOTAL E&amp;P CANADA</p> <p><b>WATER MANAGEMENT SEMINAR</b> Enghien les Bains, France Sept. 27, 2007 (16:50-17:30)</p> 	<h3>Nature of the Oil Sands Resource</h3> <p>Process dictated by depth – different for In situ &amp; Mineable Areas</p>  
<h3>SAGD - Steam Assisted Gravity Drainage</h3> <ul style="list-style-type: none"> <li>• In situ process with stacked pair of horizontal wells</li> <li>• Spaced 5 m apart, 600-1000 m long, 100-125 m lateral spacing</li> <li>• Continuous injection of steam</li> <li>• Bitumen drains under gravity to lower producer</li> <li>• Minimal solids production</li> </ul>   	 <p>Initial Stage: Warm-Up &amp; Circulation</p> 
 <p>Production Stage: SAGD</p> 	

Fig 6: The SAGD Process (Source Mike Rodgers, ATSI)



The bitumen comes to the surface as an emulsion of water and oil. The oil is separated and the remaining water, which is still contaminated with oil, has to be treated and reused in the generation of the steam. The treatment process consists of two distinct sections. The first is de-oiling followed by hardness and silica reduction.

The conventional oil removal process consists of a Skim Tank which is designed to remove 90% of the free oil from the emulsion. This is followed by an Induced Gas Flotation (IGF) unit (additional 90% removal) and then Oil removal Filters.(additional 90% removal) The Nanoflotation can be considered as replacement for any of these or as an addition to improve the quality.

The typical quality of produced water is presented in Table 4.

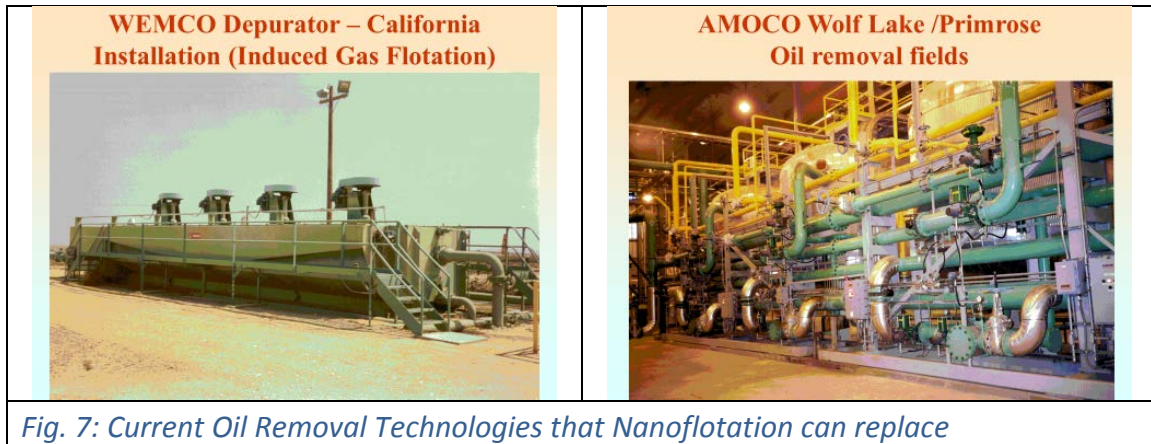
*Table 4: Produced Water Quality and Boiler Feedwater Requirements*

<b>Parameter</b>	<b>Units</b>	<b>Typical Produced Water</b>	<b>Boiler Feedwater Requirements</b>
Oil	mg/L	1000 to 10000	2
Suspended Solids	mg/L	1000 to 10000	2
Hardness	mg/L as CaCO <sub>3</sub>	150 to 300	0.1
Silica	mg/L as SiO <sub>2</sub>	150 to 400	50
TDS	mg/L	2000-3500	7000
Total Alkalinity	mg/L as CaCO <sub>3</sub>	500 to 1100	2000
Iron	mg/L	0.2 to 0.5	0.05
Oxygen	mg/L	0.05	0.05
pH	Units	7.0 to 7.8	7.0 to 11.0

Silica is reduced by co-precipitation with magnesium hydroxide, a product created from subsequent lithium recovery. When the pH is elevated by the addition of caustic or lime, the solubility of magnesium and calcium salts is reduced and the magnesium is precipitated as magnesium hydroxide. The addition of magnesium oxide ensures that there is sufficient magnesium present to allow for the co-precipitation of the silica. At the elevated pH the calcium is precipitated as calcium carbonate. In conventional systems these reactions take place in either a Warm Lime Softener (WLS) or a Hot Lime Softener (HLS). In either case there is some carryover of particulates which must be filtered out before the water goes into the final boiler feedwater treatment consisting of an ion exchange system. The Nanoflotation technology is proposing to carryout the hardness and silica reduction in-line and use its surface filtering technology to replace the WLS/HLS and the traditional media after filters (AF) used to polish the carryover. The effluent from the AF's is treated in an ion exchange treatment train to further reduce the residual hardness.

The current oil removal technologies of Skim Tank, IGF and ORF are bulky and expensive installations (Fig. 7) with limited oil removal efficiency. The industry continues to search for other solutions and have considered and have extensively tested the use of ceramic UF membranes in the conventional way.





Because of the limited efficiency and large foot print of the existing treatment train described above for deoiling, development work has been undertaken to evaluate the use of membranes instead of the Skim Tank/IGF/ORF flow sheet. The results from the Sinopec Jinan Refinery study supports the proposal that the RSL technology can be used for SAGD produced water to evaluate its effectiveness as a replacement to either the conventional Skim Tank/IGF/ORF or the ceramic membrane. Effectiveness would include standard parameters as CAPEX, OPEX, and ease of operation, maintainability and quality of de-oiled effluent. It is important to understand that the comparison will be between the RSL technologies and ceramic membranes.

### ***Silica and Hardness Reduction***

The role of the WLS/HLS is to provide for sedimentation of the precipitated silica and hardness salts. The effluent which contains some particulates is filtered in an after filter (AF) and sent to the ion exchange train. The use of either a ceramic UF filter or the RSL technology has the potential to do away with the necessity of the WLS/HLS. This can be accomplished by feeding the treatment chemicals in line, allowing the precipitation to take place and be followed by the RSL filter.

### ***Evaporator Flowsheet***

An alternative exists to the WLS/HLS/Ion Exchange/OTSG flowsheet. The alternative is to replace the WLS/HLS/Ion Exchange with an evaporator which produces a boiler feedwater quality suitable for either the OTSG or a drum boiler. The use of the evaporator for both boiler types requires the injection of caustic into the evaporator to raise the pH and solubilize the silica and precipitate the hardness. The other option is to add the caustic and magnesium oxide outside of the evaporator and send the entire water with precipitate into the evaporator. Application of the RSL technology to the precipitated mixture would relieve the load of solids on the evaporator. The solids which enter the evaporator without the application of the RSL filter will end up in the evaporator blowdown which presents treatment issues in the disposal of the blowdown.

The opportunity therefore to prevent the entry of the precipitates into the evaporator is a worthwhile operational improvement.

In bench-scale testing performed in Q1 – 2017 produced waters from two SAGD facilities was treated and evaluated for further lithium recovery. Treatment of produced water from SAGD was proven with successful reductions in dissolved ions, particularly silica, to target concentrations for a SAGD water treatment plant (Table 5). These produced waters typically contain low lithium concentrations. Given their large revenue potential from treatment alone, these dilute but high volume waters may be an economic source of lithium and an evaluation is on-going.

*Table 5: Treatment results using produced water from two clients.*

	Client 1 Raw Water	Client 1 Post Treatment	Client 2 Raw Water	Client 2 Post Treatment
pH	7.78	9.84	7.83	9.92
Na	480	500	500	410
K	<15	<15	16	<15
Ca	<15	<15	5.9	<15
Mg	<10	49	<2	45
Cl	740	630	480	450
SO <sub>4</sub>	<10	<10	<10	<10
Reactive SiO <sub>2</sub>	140	21	120	5.2
TOC	270	220	190	160

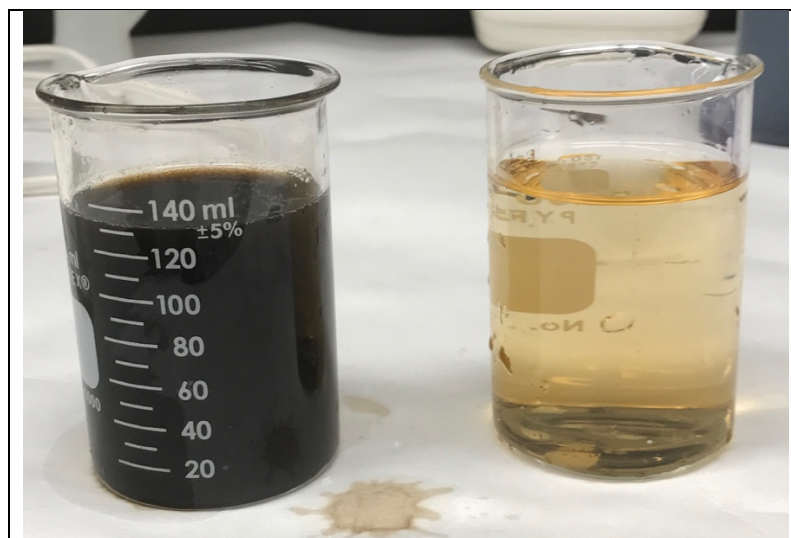
#### OTSG Blowdown

Roughly 20% of the water treated for steam generation becomes OTSG Blowdown and hence is concentrated up to 5-fold. Treatment of these waters was also proven with results that exceeded the performance on produced water alone. Reactive silica was surprisingly low in the blowdown feed (70 mg/L), however, this was also reduced by 70% to 22 mg/L making the water potentially suitable for reuse.

Exceptional reductions were achieved in selected parameters with better than expected reduction in TOC and colour (Table 6). TOC was reduced by 73% from 660 mg/L to 180 mg/L. The results for TOC are intriguing in that they suggest a treatment alternative for their removal using acidification which further implies that the majority of these compounds are large molecular weight acids with humic-humin characteristics. From a qualitative perspective, this is consistent with visual observation (Fig. 8) where lower molecular weight organic acids are typically yellow in colour (and soluble in acid) while large organic acids are grey to black with decreasing solubility with decreasing pH. Lithium concentrations at this client site were not high enough for subsequent commercial recovery but remained unchanged by the treatment process. Higher lithium concentrations in the source waters and subsequently the blowdown for SAGD operations are likely across the geographic scale of SAGD operations in Alberta.

*Table 6: Treatment results from OTSG blowdown supplied by a client.*

	UNITS	BD RAW	BD PERMEATE Post Treatment
Reactive Silica	mg/L	70	22
Total Organic Carbon (C)	mg/L	660	180
Turbidity	NTU	8.5	2.2
Total Calcium (Ca)	mg/L	100	46
Total Magnesium (Mg)	mg/L	<20	12
Total Sodium (Na)	mg/L	5600	2300
Total Potassium (K)	mg/L	61	29
Dissolved Chloride (Cl)	mg/L	7200	2700
Dissolved Sulphate (SO4)	mg/L	67	750
Alkalinity (Total as CaCO3)	mg/L	1700	220



*Fig. 8: Client 1 OTSG blowdown (left) and permeate following RSL Membrane™ treatment (right).*

### Evaporator Blowdown

Very high removals of silica have been achieved consistently across trials with three SAGD clients. A summary from the most recent trials (Table 7) demonstrates the exceptional treatment efficiency of the RSL Membranes™ in this application. Reducing silica concentration further is likely possible with a secondary magnesium treatment and re-filtration, however, given the exceptional results with total silica < 80 mg/L, these waters may be suitable for blending and reuse with produced water with the only challenge being the residual calcium concentration of 160 mg/L. Magnesium, iron and

other problematic ions were substantively reduced or undetectable. Lithium is in relatively good concentrations for recovery and remain so after treatment.

*Table 7: Summary of treatment results for client 3 Evaporator Blowdown.*

	CON EBD RAW	CON EBD	CON EBD	CON EBD	Mean Conc.	Final removal
Time (min)	0	20	35	55		
Reactive Silica	9200	79	74	61	71	99%
Total Organic Carbon	4800	3900		3200	3550	33%
Total Suspended Solids	12000 (1)			<1		

1) After floc formation

### Treatment of Wastewater Summary

The oil industry has a high level of interest in finding an alternative to the bulky, operationally difficult and energy consuming oil, silica and hardness removal systems now being used to treat both upstream and downstream wastewaters. Ultrafiltration ceramic membranes are considered as a viable alternative to replace existing processes. Nanoflotation represents a lower cost, smaller footprint and lower energy alternative to ceramic UF membranes. Purlucid, with MGX, will deploy RSL membranes™ in the following applications:

- Replace conventional ultra-filtration ceramic membranes as pretreatment for RO.
- Replace the conventional de-oiling for SAGD produced water
- Replace conventional HLS/WLS silica and hardness reduction
- Pretreat SAGD produced waters to reduce silica loading on evaporators and treat evaporator blowdown waters to improve evaporator blowdown management.

Following treatment through which revenues of approximately \$2/m<sup>3</sup> are projected, these very high volume waters will be a source of lithium in subsequent extraction. Once treated and marketable minerals such as lithium are removed, the water is returned to the boiler for further oil extraction by the client producer.

## ***References***

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## ***About the Author***

Dr. McEachern started Purlucid to bring new technologies to the problems of water treatment and solids control. Prior to Purlucid, he was the VP of Research and Development for Tervita and the head of Science Research and Innovation for oil sands in Alberta Environment. Dr. McEachern received his PhD from the University of Alberta modeling industrial impacts on northern hydrology and water quality. Dr. McEachern is active in research with an appointment to the Biorefining Research Institute and adjunct professor appointments at the University of Alberta in Civil and Environmental Engineering where he supervises graduate students in water quality and water treatment, and at Lakehead supervising students in forest hydrology and chemical mass transport. He is a Qualified Environmental Professional (QEP) with the Institute of Professional Environmental Practice (IPEP) which is CESB certified.