Nanoflotation - using EDL collapse to increase the efficiency of flotation and submerged membrane filtration.

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Extended Abstract:
With most industrial water and wastewater treatment requirements, the objectives for treatment are relatively consistent. Typically they are separation and removal of colloidal particles, removal of free oil and grease and reduction in the parameters that either cause scaling when water is reused or injected in disposal wells or have an effect when released to the environment. We will review water treatment challenges for oil and metal mining industries and provide a case study that deploys flotation followed by ultrafiltration as a treatment solution. In this case study we demonstrate removal of suspended and colloidal solids to 0.01 µm in size at efficiencies that are 10-times the industry norm and at costs that make in-line treatment of tailings economically achievable. The case study will be used to review the science behind microflocculation through use of electric double layer (EDL) compression (the DLVO theory) and how this can enhance traditional coagulation using charge neutralization. Colloidal solids, no matter their charge, will repel each other because of the EDL on each solid. However once the solid enters a highly ionized/charged environment, the EDL collapses and van der waal attraction forces take over such that the solids attach to each other. Individual charge on the solids, in both cases, has no bearing on whether a solid repels or attracts one another. The use of microflocculation requires a novel design that can provide fixed microzones of high ionic charge and a reliable mechanism to capture the small colloids that are rapidly formed in these microzones; membrane treatment partially provides for these needs. Loss of flux rates due to fouling, the nemesis of membrane treatment, had to be solved to take advantage of microflocculation, a challenge overcome by the Nanoflotation system reviewed in this case study. Solids removed from the water can immediately be placed as reclamation fill as long as they pass soil criteria.

Flotation

Flotation has been used extensively in oilsands and metal mining for primary resource recovery. In oilsands, it represents the first stages of oil recovery and subsequent oil-water separation in the treatment of water for reuse. In metal mining it is the most widely used process for ore beneficiation. Flotation systems take on many forms, the simplest of which are tanks with or without settling plates (clarifiers) and a froth skimming system. Loading rates are expressed as the flow rate (m3/hr) divided by the tank cross sectional area (m2) and expressed as meters/hr (m/hr). Typical design loading rates range from 1-2 m/hr for simple clarifiers to 5-10 m/hr for dissolved air flotation systems. High rate DAFs where bubble density and attachment properties are enhanced with frothers is enhanced have more than doubled loading rates to 10- 20 m/hr. Despite these improvements, typical design rates for industrial waste waters remain 5 to 10 m/hr. Nanoflotation improves on these industrial design rates by allowing for designs in the range of 10 -20 m/hr using a surfactant-collector combination and a patent pending high intensity mixing system to enhance bubble surface attachment and rapid froth rise rates.

We tuned the surfactant-collector chemistry for optimal organic and total suspended solids (TSS) removal in a one-year trial treating oilsands tailings waters. The TSS in these waters consists of stable “gel” suspensions of primarily small (< 5 µm) aluminosilicate clays. Better than 97% removal of TSS was achieved in flotation consistently over a 4 month 24-7 run period at dosing rates of 0.028 mL/L of feed water for lower turbidity waters (<100 mg/L TSS) to 0.25 mL/L for higher turbidity conditions (900 mg/L TSS). Additional trials on water containing high concentrations of primarily colloidal silica (20,000 mg/L) did not demonstrate the same performance in the flotation system due to the low ionic charge of the silica colloids. These colloids were, however, efficiently removed in the subsequent ultrafiltration stage (see below).

Bubble density and size influence froth separation efficiency. Typical high rate DAF systems produce bubble densities of 1% and diameters < 0.1 µm. In Nanoflotation we focus on generating high bubble concentrations of 3% and larger bubble sizes in the 1 to 2 µm diameter range. In Nanoflotation, we achieve three features critical to efficiency; high bubble surface area, a highly charged bubble surface and larger bubbles. The charged surface of the bubble causes EDL collapse and better surface attachment while larger bubbles increase the rise rate to values exceeding 16 cm/s. A doubling of bubble size in this range (up to 2 µm) results in 3 to 4 times greater rise rates, with greater efficiencies achieved at higher temperatures.

Membrane filtration

Membrane filtration has not been used commercially in oilsands solids removal and dewatering primarily due to the high capital cost and an inability to control fouling. In metal mining, filtration is common in dewatering and water treatment. In dewatering, filter presses, belt presses and other non-submerged systems are common whereas in water treatment, submerged membrane filtration is increasingly more common.

Membrane strength, longevity and fouling negatively impact submerged membrane applications. This is particularly the case in oilsands applications where high organic and scale forming ion concentrations seriously curtail performance. Advances in membrane technology to overcome these issues have focused on a fixed precoat that both protects the membrane and repels charged ions that would otherwise foul the membrane and skin layer. The electorstatic repulsion is countered by the trans-membrane pressure (TMP) driving the solids and ions into the skin layer surface. When TMP exceeds a critical threshold (~1 bar), fouling rates can increase substantially.

Cross flow, where a volume of water is passed tangentially over the skin layer surface, is extensively deployed in conventional membrane systems to reduce fouling by removing accumulated solids. Cross-flow systems must have substantially higher tangential flow compared to the flow through the membrane such that pumping flow exceeds permeate (treated) water production by 10 to 20 times or more. In addition to high pumping volumes, cross-flow systems eventually foul.. Once the membrane skin layer fouls in situ cleaning using highly acidic and caustic solutions is required to recover flux rates resulting in reduced longevity and in some cases delamination of the skin layer and failure of the membranes themselves.

An alternate approach is to promote fouling of a temporary filter barrier similar to a skin layer with subsequent replacement *in situ*. These “dynamic membrane” systems use an inert material such as diatomaceous earth and are extensively used in removal of unreactive solids as a mud cake. Nanoflotation improves on the dynamic membrane concept with the patented replaceable skin layer (RSL) design (Fig. 1). We apply a precoat skin layer *in situ,* that creates highly charged microzones in the pore spaces. The skin layer is allowed to foul over an extended period and removed once TMP approaches 1 bar. The RSL technology allows for specific precoat chemistries that promote the agglomeration of ions and small colloidal particles within the precoat material. One formulation of the RSL targets the removal of fine tailings clays in the highly charged pore spaces within the precoat through EDL compression as proposed by the DVLO theory.

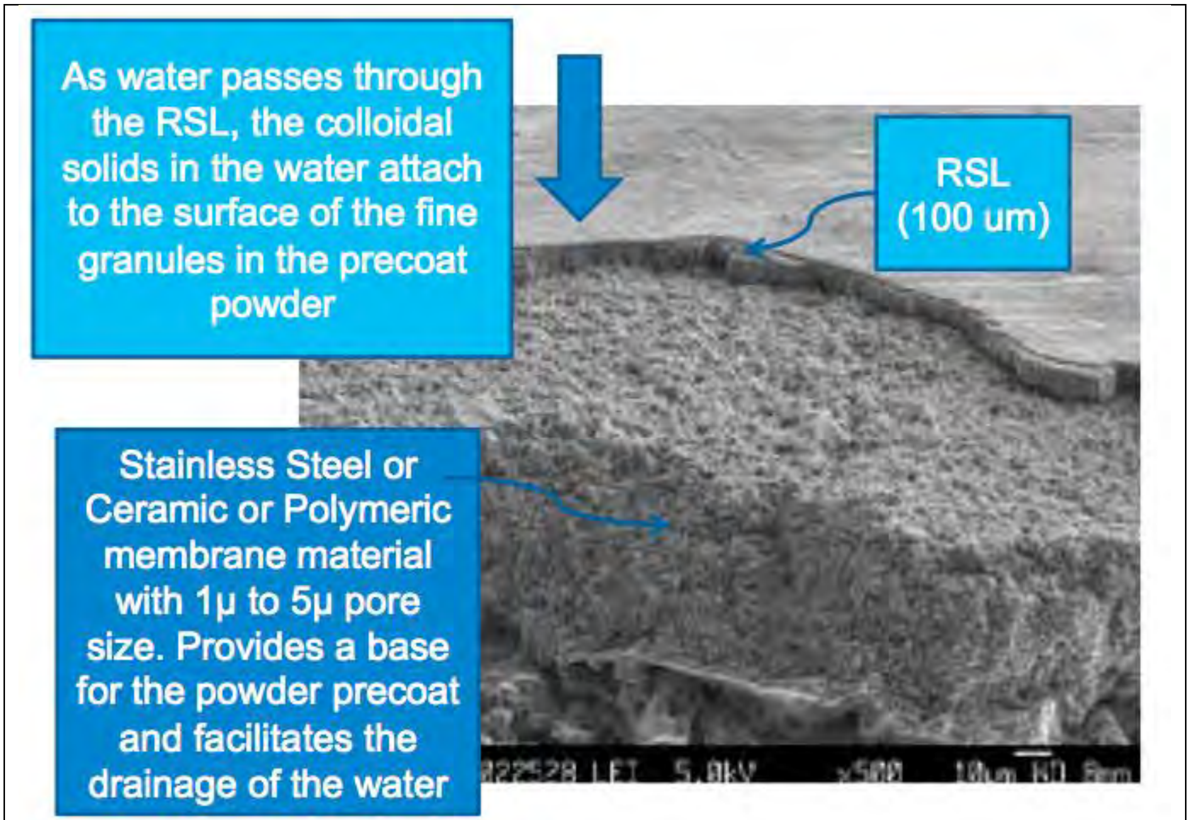

Fig. 1: Electron micrograph of the Nanoflotation RSL able to capture colloids >0.01 μm in size on a stainless steel membrane with a pore size of 1 μm.

The RSL patented technology has been deployed in various oilsands applications including tailings water treatment. In tailings treatment, stable suspensions of ultrafine clay were efficiently removed (Fig. 2) producing similar post treatment water quality of other leading ultrafiltration technologies but at a fraction of the capital cost and footprint.

For example, TSS removal averaged 100% over a four-month continuous treatment operation but was achieved with 10% of the membrane area, no cross-flow requirement, and 30-times fewer backwash cycles when run head-to-head with conventional systems.

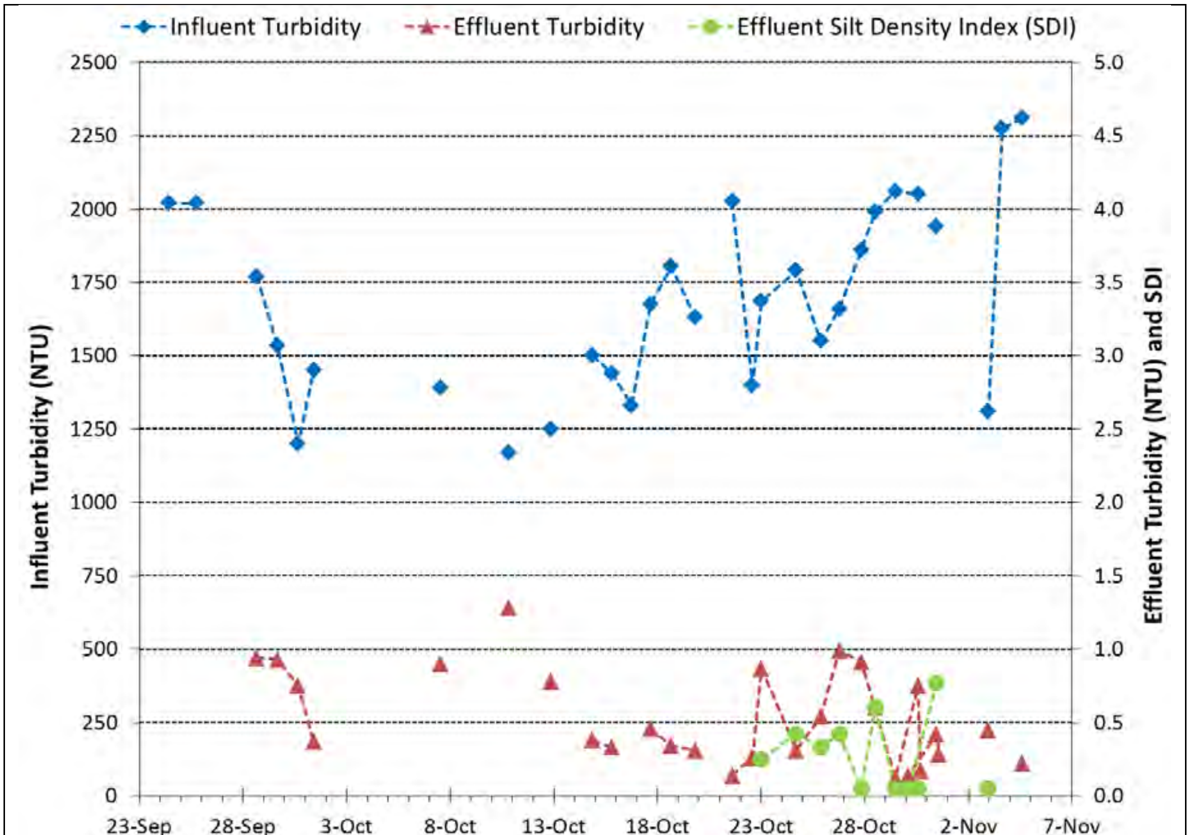

Fig. 2: Example of feed and permeate water quality during continuous treatment of oilsands mine tailings release water after the Nanoflotation RSL.

When applied to highly concentrated brines such as those from produced water and evaporative water treatment, the RSL membranes performed well with nearly 100% removal of dissolved silica, dissolved iron and colloidal particles including polymerized and unreactive silica (Table 1). For this to occur, it is necessary to convert the dissolved parameters to colloidal or suspended solids using targeted chemical manipulation which can be as simple as pH adjustment.

Table 1: Example performance of Nanoflotation treatment of a highly concentrated brine wastewater.

Scale Parameter	EBD/SAC feed concentration (mg/L)	NF Filtrate Concentration (mg/L)
Reactive Silica	13000	27.8
Total Barium	17.9	2
Total Strontium	73.9	51.4
Fe-Dis	2.2	0
Ca-Dis	1251	985.5
Mg-Dis	109	77.8

Table 2: Operational performance summary

Nanoflotation/ Replaceable Membrane Skin Layer vs Conventional Membrane Technology			Conventional Membranes	RSL Membranes
Why is Nanoflotation better than conventional technology?				
1. Very low material requirement per litre of water treated for membrane skin layer replacement			will add coagulant for pretreatment - 15 to 100 mg/l	Powder for precoat is 10 to 15 mg/l
2. Delta pressure (trans membrane pressure)-very low at 20 to 70 kpa (2 to 10 psi)		Note 3	No difference	No difference
3. Full H_2S operation if necessary			No difference	No difference
4. Can operate at high temperatures and pressure			Yes but high cost	Yes but low cost
5. Fully automated back wash and skin layer replacement			No	Yes
6. Back wash intervals			15 sec	6 to 15 hrs
7. Oil removal	99 to 99.9%		poor	excellent
8. Turbidity removal	99.9 to 99.99%		excellent	excellent
9. Average loading (flux) rate between backwashes (lph)	325 to 600	Note 1		10x higher
10. Flux recovery after b/w	98 to 99%		92%	99%
11. Max TSS application (mg/l)	150,000	Note 2	6000 mg/l	150.000 mg/l
12. Anticipated life of membrane	20 years		5 to 10 years	10 to 20 years
13. Pumping requirements vs conventional UF crossflow membranes	10%	Note 3	high energy	low energy 90% reduction
Note 1 Result: Significantly reduced footprint and membrane requirements				
Note 2 Result : Can be applied to sludges				
Note 3 Result : Very low energy requirements				

Summary

The Nanoflotation technology provides an effluent similar to other ultrafiltration membrane technologies but requires significantly less energy and capital costs (Table

2). In addition, the use of the RSL increases flux rates on the membrane significantly (10 to 15 times when it was compared against conventional ceramic membranes). The design allows for the use of heat and corrosive resistant membrane substrates such as stainless steel. With the significantly improved flux rates, the cost of using temperature resistant material results in an overall cost similar to or less than the typically low cost polymeric membranes that are limited to a temperature of 40^{o} C. The ability to treat at very high temperatures or in corrosive environments removes the need for energy intensive steps in the treatment process such as cooling or neutralization. For a facility that is dependent on steam generation, the Nanoflotation technology provides significant energy savings and correspondingly excellent CO_2 reductions.

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