

Biological Filtration of Poor Quality Brackish Water Reducing Reverse Osmosis Membrane Fouling

Authors: *Hans Peterson, Robert Pratt, Roberta Neapetung, Ole Sortehaug*

Presenter: *Dr. Hans Peterson*
Executive Director – Safe Drinking Water Foundation – Canada

Abstract

A primary limitation in applying Reverse Osmosis (RO) is loss of performance caused by membrane fouling resulting from compounds that bacteria can use as energy or nutrient sources. When these compounds enter RO membranes, they are capable of sustaining extensive bacterial growths on the membrane sheets as well as within feed channel spacers. This leads to the entrapment of particles and incorporation of dissolved substances into biological matrices exacerbating the biological fouling. Treating the water with oxidizing chemicals such as chlorine, ozone and potassium permanganate, increase the quantities of compounds that bacteria can use thereby increasing the membrane fouling potential. Also, traces of oxidants reaching the membranes can cause membrane damage decreasing the capability to reject both dissolved and particulate material (including viruses). It is also disconcerting that some organic compounds with relatively high molecular weights are able to pass through even tight RO membranes causing microbial growth in distribution systems. Therefore, even when using RO membranes, quality distributed water cannot be assured. If no corrective action is taken microbes can grow in the RO membranes as well as in the distribution lines.

The solution to this dilemma is to grow microbes in biological filters ahead of the RO membranes. If a high quality filtration material, such as Filtralite[®] expanded clay, is used for microbial attachment, it is possible to effectively remove both microbial energy and nutrient compounds even at low temperatures (6°C). Pilot and full-scale plant experiences from the Canadian prairies using biological filtration have advanced these treatment processes from experimental to proven technologies and are currently being evaluated as potentially becoming “best available technology” in the treatment of extremely poor quality brackish groundwater. The first Integrated Biological and RO Treatment Plant was commissioned in December 2003, and after two years of full-scale testing, two more plants were commissioned in December 2005. At one of these plants, conventional manganese greensand treatment was followed by RO treatment resulting in frequent chemical RO cleanings as well as membrane replacements every eight months. Removing the manganese greensand in the existing filters and replacing them with Filtralite[®] material resulted in a rapid improvement of treated water quality and a literal stop to frequent RO cleanings. The biological filters need to be backwashed 36 times less than the manganese greensand filters (100 filter backwashes per year vs. 3,600). Backwash water use decreased to 0.4 million L from 23 million L and backwash labor decreased to 40 hours from 1,440 hours per year. Combining these savings with decreased RO cleanings, no need for frequent membrane replacements, and decreased chemical costs, it has been estimated that this water treatment plant serving 1,200 people will save more than \$100,000 per year.

I. INTRODUCTION

The Canadian prairie is a semi-arid area in central Canada. However, below the earth's surface there are vast underground rivers and lakes ranging from surficial to 300 m below ground. While surficial aquifers can contain relatively high quality water, although frequently under the influence of surface water, the aquifers below 100 m are typically of extremely poor quality. Part of the problem is that this area of Canada used to be an inland sea and when the sea retracted, it left behind vast tracts of salty deposits that are now making many groundwater supplies high in salt. It is rare to find groundwater in this region that would meet Canadian or international guidelines for the content of Total Dissolved Solids (TDS) of less than 500 mg/L. Indeed, the Saskatchewan Government realized this dilemma and changed its provincial drinking water quality guideline to 1,500 mg/L for TDS, thereby making some of these supplies "meet" guidelines without the application of desalination technologies.

However, associated with the higher salt levels are frequently high levels of other compounds that present problems in drinking water treatment including iron, manganese, ammonium, arsenic, and dissolved organic material. Not only are these compounds problematic in terms of drinking water treatment, they can act as energy/nutrient sources for bacteria causing severe biofouling of RO membranes. In addition, ions presenting problems for desalination techniques include high magnesium, calcium and sulphate concentrations. Both scaling and biofouling issues must therefore be dealt with to treat this water in a sustainable manner. Coupled with these challenges are low temperatures (5-10°C) in the groundwater with low (1-2°C) or no seasonal variations.

Treatment of these challenging water supplies has typically been by the use of various conventional oxidation strategies, such as manganese greensand filtration with potassium permanganate additions. While this is frequently used, close examination of data generated by such water treatment plants reveal that it is very difficult to maintain optimum treated water quality for extended periods of time. In addition, these plants are typically small with limited financial and personnel resources. Even larger plants treating better quality water have been shown to experience failures when using conventional technologies to remove iron and manganese containing waters [1]. The use of oxidants, such as chlorine or potassium permanganate, is not effective in oxidizing the targeted ions when competing ions including dissolved organic material is present in large quantities.

While Canada has Drinking Water Quality Guidelines [2,3] containing more than 50 health parameters, the on-site implementation of those guidelines in small communities has frequently been limited to a select few, typically total and free chlorine, *E. coli* and total coliforms as well as nitrate. Compliance with four of these may be achieved by chlorination alone and failures of the water treatment processes may go unnoticed. Health Canada is carrying out water testing in aboriginal communities on distributed water only and not raw water making it impossible to assess the effectiveness of in-plant treatment processes. Water plant operators will carry out some limited additional tests on the distributed water, such as pH, manganese, iron and turbidity.

However, every one to two years Health Canada is generally doing more extensive distribution system testing where problem compounds in the drinking water have been found. This has led to the implementation in a few communities of RO polishing after manganese greensand treatment of groundwater. After RO implementation, problems with the conventionally treated water have shown up as combinations of membrane fouling and scaling. This sparked a search for treatment methods that could produce high quality water ahead of the RO membranes. The quality of the raw water sources

used and the inability of conventional technologies to produce water suitable for RO polishing are presented together with biological pretreatment solutions.

II. RESEARCH CONDUCTED

Raw water from George Gordon, Pasqua, and Yellow Quill First Nations were analyzed for physical and chemical properties using various analytical techniques including Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, Saskatchewan Research Council Analytical Laboratory and on-site testing). Conventional treatment problems were examined on-site at the George Gordon First Nation and extensive optimization trials were carried out, which all failed. A 15 m mobile trailer equipped with water treatment equipment was moved to the newly constructed wells at Yellow Quill First Nation. Here the trailer was supplied with 200 Lpm directly from one well. This water was distributed to different combinations of treatment including manganese greensand, ozone, UV, different types of biological filtration and membrane units. During the first six months, many different units were piloted, which was followed by another 14 months dedicated to developing the most promising option, biological treatment followed by RO. Different materials, expanded clay and granular activated carbon, and combinations thereof were explored for attachment of microbes in the biological filters. Finally we settled for three filters in series each containing different types of Filtralite[®] expanded clay material. As we were dealing with brackish water, additional desalination was required. While a combination of RO and nano-membranes could meet the treatment objective of having some calcium and magnesium in the finished water, the risk of introducing problem compounds, such as arsenic, manganese and ammonium precluded the use of nanofiltration. Instead, a calcium and magnesium contactor was developed to re-introduce calcium and magnesium to the RO treated water while at the same time producing non-corrosive finished water with a neutral pH. Based on the developed pilot scheme the full-scale plant was designed, and commissioned in December 2003 [4]. Continued full-scale piloting and the commissioning of the same treatment process at Pasqua and George Gordon First Nations have led to further improvements of the Integrated Biological and RO Treatment Process. Cost-reductions in on-site piloting work alone decreased from more than \$500,000 (Canadian dollars) for Yellow Quill to \$75,000 for Pasqua and \$5,000 for George Gordon. Piloting, but not research costs, was paid for by Indian and Northern Affairs Canada (agency responsible for financing water treatment plants in aboriginal communities). The developed knowledge is made available to indigenous communities through Safe Drinking Water Foundation's Advanced Aboriginal Water Treatment Team (AAWTT).

III. RESULTS

3.1 Raw water chemical composition

Groundwater from 100 m depth is used by Yellow Quill, while Gordon and Pasqua First Nations obtain their water from 200 m depth. The depth where the water is collected is important as shallower depths (100 m) are considerably colder (5-6°C) than deeper (200 m) water intakes (9-10°C). The colder the water, the more challenging it is to treat with most processes both for pre-treatment and actual RO treatment. In Table 1 the raw water chemical composition of the three studied groundwater sources are shown.

The alkalinity levels are very high ranging from Pasqua's 380 to Gordon's at 470 mg/L. The aluminum levels are below detection (0.005 mg/L) in all investigated groundwater sources. Ammonium levels, however, are quite high ranging from 1.3 to 4.7 mg/L (as ammonium-N). The arsenic levels are also

well above Canada's current guideline of 0.010 mg/L ranging from Yellow Quill's 0.017 mg/L through Pasqua's 0.036 to Gordon's 0.072 mg/L. Barium is a compound of concern for RO treatment, but all the different groundwater supplies were quite low in this element (0.007-0.009 mg/L). Boron levels were well below the 5 mg/L guideline value at 0.34 to 0.76 mg/L.

The calcium levels were high ranging from Pasqua's 130 mg/L to Yellow Quill's 270 mg/L and Gordon's 360 mg/L with magnesium levels following a similar trend 48 mg/L at Pasqua, 100 mg/L at Yellow Quill and 170 mg/L at Gordon's. Magnesium levels were below the guideline level of 200 mg/L with a low of 48 at Pasqua, and intermediate 100 at Yellow Quill and a high of 170 at Gordon's. The ratio between calcium and magnesium was similar ranging from 2.1 to 2.7. As calcium and magnesium constitute the main part of water hardness a similar trend is shown for this component with Pasqua at 523, Yellow Quill at 1086, and Gordon's at 1599 mg/L. All groundwater sources were above the recommended European Union limit for calcium (100 mg/L) and Yellow Quill and Gordon's were above the Saskatchewan Guideline for hardness (800 mg/L). All the groundwater sources must, however, be classified as extremely hard.

Table 1: Raw water chemical composition of George Gordon's, Pasqua's and Yellow Quill's ground water sources (bolded and italicized, compounds that bacteria can use as either energy or nutrient sources) with Guideline values indicated.

Parameter	Guideline value	Gordon	Pasqua	Yellow Quill
Alkalinity (mg/L)	<500 (SK)	470	380	460
Aluminum (mg/L)	<0.1 (operational)	<0.005	<0.005	<0.005
Ammonium-N (mg/L)	<5 (EU)	1.3	2.2	4.7
Arsenic (mg/L)	<0.010	0.072	0.036	0.017
Barium	1.0	0.009	0.008	0.007
Boron (mg/L)	<5	0.34	0.74	0.76
Calcium (mg/L)	<100 (EU)	360	130	270
Chloride (mg/L)	<250	67	72	46
Copper (mg/L)	<1	<0.001	<0.001	0.014
Dissolved Organic Carbon (mg/L)	<5 (SDWF)	5.5	4.9	11
Fluoride (mg/L)	<1.5	0.46	0.40	0.18
Iron (mg/L)	<0.3 (AO)	1.41	2.41	8.49
Hardness (mg/L)	<800 (SK)	1599	523	1086
Lead (mg/L)	<0.01	<0.002	<0.002	<0.002
Magnesium (mg/L)	<200	170	48	100
Manganese (mg/L)	<0.05 (AO)	1.59	0.13	0.25
Nitrate-N (mg/L)	<10	<0.01	<0.04	<0.04
pH	6.5-8.5	7.2	7.7	7.5
Phosphate (mg/L)	No guideline	0.060	0.150	0.23
Redox (ORP) (mV)	No guideline	<-100	<-150	<150
Selenium (mg/L)	<0.01	<0.005	<0.005	<0.005
Silicon (mg/L)	No guideline	11.1	12.8	11.8
Sodium (mg/L)	<200 (SK <300) (AO)	110	420	230
Strontium (mg/L)	No guideline	1.42	1.02	1.17
Sulphate (mg/L)	<500 (AO)	1300	850	1100
Temperature (°C)	<15 (AO)	<10	<10	<6
Total dissolved solids (mg/L)	<500 (SK <1,500) (AO)	2260	1760	2130
Turbidity (for raw water, turbidity after aeration)	<0.3	17	37	102
Zinc (mg/L)	<5	<0.005	<0.005	<0.005

The copper levels were below detection for Gordon's and Pasqua while Yellow Quill raw water contains 0.014 mg/L although that is well below the 1 mg/L drinking water quality guideline. The chloride levels were all below the 250 mg/L guideline ranging from 46 to 72 mg/L. There is no guideline for dissolved organic carbon (DOC), but it is expected that to comply with future guidelines for chlorinated disinfection by-products levels as low as 2 mg/L may need to be achieved and removal of DOC will be required for many raw water sources. To meet current Canadian Drinking Water Quality Guidelines for trihalomethanes (0.1 mg/L) DOC levels below 5 mg/L are required [5]. Both Pasqua and George Gordon are around 5 mg/L with Yellow Quill being double that at 11mg/L. It is quite difficult to get a precise DOC level in anaerobic water containing high levels of iron as some co-precipitation with iron may occur. Normally, DOC is determined on non-preserved water, but for these raw water sources it is recommended that the determination be on sulfuric acid preserved water. Fluoride levels need to be below 1.5 mg/L and all raw water sources were below this level (0.18-0.46 mg/L).

The iron levels were greatly above the Canadian Guideline of 0.3 mg/L with Gordon's at 1.41 through to Pasqua's at 2.41 and Yellow Quill's at 8.49 mg/L. Lead was always below detection (<0.002 mg/L). Manganese levels were close to three times above Guideline at Pasqua (0.13 mg/L), five times at Yellow Quill (0.25 mg/L), and 32 times (1.59 mg/L) above the guideline at Gordon's. These groundwater sources are anaerobic and as could be expected the nitrate levels were all below detection (<0.04 mg/L). Phosphate-phosphorus, an essential bacterial nutrient, ranged in concentration from 0.06 mg/L at Gordon's through Pasqua's 0.15 mg/L to Yellow Quill's 0.23 mg/L. In anaerobic groundwater sources the redox potential will be low and it was always less than -100 mV. This anaerobic water is extremely hard on redox probes and not many determinations can be carried out until the probes malfunction.

Selenium levels were below detection for all raw water sources. Silicon levels were relatively high and almost identical for the different raw water sources hovering around 12 mg/L for all of them. Sodium levels were below the Canadian Guideline of 200 mg/L at Gordon's, but at Pasqua they were twice the guideline (420 mg/L) and at Yellow Quill the level was just above the guideline (230 mg/L). The sulphate levels were all well above the Canadian Guideline level of 500 mg/L ranging from 850 mg/L at Pasqua through 1100 at Yellow Quill and 1300 mg/L at Gordon's. Yellow Quill's colder water (5-6°C) compares with 9-10°C at Pasqua and Gordon's. The total dissolved solids (TDS) were well above guidelines for all water sources (hovering around four times above the Canadian Guideline). If the water was allowed to absorb oxygen the particle levels generated from mainly iron oxidation would translate into a turbidity of 17 NTUs at Gordon's through to 37 at Pasqua and 102 at Yellow Quill. This translates to a particle level of more than 400,000/mL in the 2 to 40 micro-m size range at Yellow Quill. The zinc levels in all the groundwater sources were below detection.

3.2 Conventional treatment failure

At the George Gordon First Nation, a manganese greensand water treatment process was used from 1989 to December 2005 when the manganese greensand was removed and replaced by expanded clay (Filtralite®). From 1987 to 2001 the manganese greensand treated water was supplied to the community without any restrictions. It was, however, shown through daily testing by the water treatment plant operator that manganese levels were almost always above guidelines. The process could not assure the removal of arsenic either, but this is not a test that is carried out by the operator. Health Canada is supposed to test for arsenic and other contaminants every two years and warn communities about discrepancies with the Guidelines for Canadian Drinking Water Quality [2,3. But, it was not until 2000

that the community knew about its arsenic problems, at which time Indian and Northern Affairs Canada set aside funds to correct this.

In 2001 one nano and one RO membrane unit was added with the manganese greensand filtration providing pre-treatment for the membranes. However, as the membrane was put on-line it rapidly built up pressure and very rapidly needed cleaning. Even frequent cleanings could not maintain product flows and pressures within acceptable limits and in July 2003 both the nano and RO membranes were replaced with new RO membranes. Unfortunately, eight months later these membranes had been fouled to an inoperable level and were again replaced (low-pressure membranes reaching >250 psi). In June 2004 a membrane autopsy of one fouled membrane was carried out by the Safe Drinking Water Foundation (SDWF), which is described in Section 3.3.

The primary role of the manganese greensand filters is to remove iron and manganese from the water. A continuous feed of 2 mg/L potassium permanganate was added to the incoming raw water, it was then detained in a chamber for around 30 minutes, after which time it was pumped to five parallel pressure filters. Periodically the manganese greensand needs to be regenerated which is carried out by soaking it in a high concentration of potassium permanganate followed by backwashing before taking back into service. This was carried out on August 31, 2004 for Filter 2 and at 7 a.m. September 1 this filter was backwashed.

At 10 a.m. the manganese (Mn) level reached 0.052 mg/L, 1 p.m. 0.12 mg/L and at 3 p.m. 0.29 mg/L. After having backwashed all filters 7 a.m. on September 2, a raw water Mn level of 1.73 mg/L was injected with potassium permanganate, detained, and then filtered through the five filters. The four filters that had not been regenerated produced Mn levels above 1.0 mg/L (average 1.07 mg/L), while the regenerated filter was at 0.14 mg/L. However, its Mn level peaked at 0.72 mg/L (2 p.m.) and then decreased to 0.49 mg/L at 4 p.m. The filter was backwashed and at 5:30 p.m. after which its filter level was at 0.088 mg/L, but an hour later it had increased to 0.71 mg/L.

It is not possible to raise the feed level of potassium permanganate very much above the 2 mg/L as unreacted potassium permanganate (pink colour) showed up at the filter outlet. But, theoretically 1.06 parts of potassium permanganate is required for 1 part of iron, and 1.92 parts are needed for each part of manganese. Any sulphide will also have a potassium permanganate demand and so will DOC and reduced arsenic (As^{3+}). The actual potassium permanganate demand is therefore more than twice the additions that were made at the plant counting only Fe and Mn. Indeed, when chemically determined it was shown that the potassium permanganate demand was >10 mg/L or five times the actual dose used. But, trying to satisfy a larger portion of the potassium permanganate demand presented a risk for exposing the membranes to an oxidant.

In Figure 1 it can be seen that the potassium permanganate's purplish/red colour does not prevail until after 10 mg/L (24 hour reaction period). During actual plant conditions, however, the pink colour will appear at varying levels starting around 2 mg/L depending on the contact time etc. With such a large potassium permanganate demand it is not surprising that it is difficult to optimize the process to selectively oxidize iron and manganese in a predictable manner.



Figure 1: Potassium permanganate (mg/L) demand of raw water

Manganese greensand treatment was attempted at the Yellow Quill pilot system, but again we were not able to sustainably remove manganese using 0.46 m diameter filter units even at low flow rates (1 gpm/square foot, 2.4 m/hr). Pasqua First Nation employed manganese greensand treatment and was to obtain RO membrane filters as a finishing treatment, but Dan Hogan, Pasqua's engineer, declined to design this process due to the concerns that had been brought to light at Yellow Quill First Nation. Instead, a biological pilot was run at Pasqua and a full-scale Integrated Biological and RO treatment process was built there in 2005.

3.3 RO membrane fouling following failed conventional treatment

The manganese greensand treated water still contained some iron, manganese and arsenic as well as other compounds that can act as either nutrients or energy sources for bacteria. When this water was supplied to the RO membranes frequent cleanings and replacements were required as outlined above. Two fouled membranes were removed from the RO units and two autopsies were carried out. The RO membrane sheets were covered in uniform slime layers (Figure 2) with the chemical composition of the fouling compounds outlined in Table 2. As the redox potential due to the potassium permanganate additions had increased above +400 mV, the conditions in the manganese greensand treated water were ideal for manganese oxidizing bacteria to establish themselves in the membranes. Using the Biolog bacteria identification system, the slime layer was analyzed and a series of *Pseudomonas* species were identified including species similar to *Pseudomonas putida* (formerly *Pseudomonas manganoxidans*).

Therefore the chemically induced increase in redox potential may facilitate manganese oxidizing bacteria to oxidize Mn^{2+} to Mn^{3+} , which require redox potentials above +400 mV. The manganese oxidizing bacteria form extracellular polymeric substances (EPS) making it difficult to remove the fouling layer resulting in rapidly decreasing permeate flows and increased membrane pressures. The chemical composition of the fouling layers show that in order of increasing importance (in terms of amount of material) iron (4.7%) is the major one followed by three elements of almost equal importance, calcium, manganese and phosphorous (around 2.0%) followed by sulfur (1.1%). Magnesium, aluminum and a string of other elements were also present in the fouling material.



Figure 2: Picture of biofouled membrane following pre-treatment using manganese greensand.

Table 2: Chemical composition of fouling material from membrane autopsy (average of outermost and innermost membrane sheets)

<i>Inorganic Chemistry</i>	<i>Foulant concentration (%)</i>	<i>Bacteria content (%)</i>
Aluminum	0.17	
Calcium	2.1	0.5
Iron	4.7	
Magnesium	0.43	0.5
Manganese	2.4	
Phosphorous	2.3	3.0
Potassium	0.11	1.0
Sodium	0.12	1.0
Sulphur	1.1	1.5

A comparison of general content of elements in bacteria has also been included in the above table and the content of magnesium, phosphorus and sulphur is similar to what one would expect in bacterial biomass and is therefore a further indication of the foulant's bacterial characteristics although this data does not allow us to clearly define what is chemical precipitation and biological material. The calcium levels are, however, around four times higher than average bacterial biomass concentrations. Sodium and potassium levels in the fouling layer are low compared with average bacterial levels.

3.4 Biological treatment

Compounds present in water can be removed by bacteria providing they are either a nutrient or an energy source for the bacteria. Many compounds can be both a nutrient and an energy source, such as iron. Frequently only a small part of the removal or conversion of a compound that act as an energy source will be to satisfy its nutrient demand. The compounds that can be either a nutrient or an energy source have been highlighted in Table 1. These compounds for the studied groundwater sources include ammonium, arsenic, dissolved organic carbon (DOC), iron, manganese, and phosphate. The redox potential is also important as without a redox increase to around 0 there would be no iron removal, and without a further redox increase to above +100, there would be no oxidation of ammonium to nitrate. Oxidation of manganese requires very high redox levels (>400 mV).

Performance of the biological water treatment processes for the different water sources is shown in Table 3. Pilot data and full-scale data were similar for all plants except for the conversion of ammonium to nitrate (nitrification) at the Yellow Quill water treatment plant. In the Yellow Quill pilot nitrification had to be induced. This was carried out by collecting water from other sources, and incubating with biological attachment material, while no nitrification occurred with Yellow Quill's groundwater alone. The full-scale plant was operated by discouraging nitrification for nine months, but nitrifying bacteria had by then colonized one of the filters and the plant was changed to encourage nitrification and after several modifications to the process it is now operating with excellent ammonium removal similar to the other plants. The biologically treated water at all the plants have redox potentials >200 mV.

Biological filtration achieves almost complete removal of ammonium, a considerable amount of arsenic is removed and what is not removed has been converted from As^{3+} to As^{5+} by the bacteria; As^{5+} is effectively removed by RO membranes while As^{3+} is not [6]. The low level of dissolved organic carbon removal is due to the age of the ground water, which is more than 100 years old resulting in low levels of bioavailable DOC. The process was designed to not encourage manganese removal, which was removed by the RO membranes. A considerable amount of phosphorus was removed biologically with the remainder being removed by the RO membranes. If the raw water was left to become chemically oxidized high levels of turbidity were formed, but instead of allowing this turbidity to form the biological treatment converts dissolved nutrients directly into microbial biomass with very low turbidities following the biological filtration process.

Process problems have almost invariably been caused by the supply of air/oxygen to the filters. One type of nozzle used for the introduction of gas into the process stream has caused problems and has now been replaced by a different set-up. There have also been some challenges in optimizing backwashing for the filters. Both of these problems affect nitrification most and during those times some ammonium has entered the membrane vessels. These challenges were resolved by continued monitoring and experimentation in the full-scale plants. Compared with conventional treatment, biological treatment requires less than 5% of the backwash water and number of backwashes, doesn't use any chemicals, and is very gentle on the membranes (long membrane life) all of which is contributing to lowered material and labor costs.

A detailed cost comparison per year before and after (manganese greensand vs. biological treatment) is currently carried out for the George Gordon First Nation Water Treatment Plant and some preliminary costs include: Membrane replacement (before \$57,000, after, estimated at \$5,000), antiscalant (\$15,600 vs. \$3,900), filter backwashes (3,600 vs. 100), labor for backwashing (1,440 hours vs. 40 hours), and

volumes of water used for backwashing (23 million L vs. 0.41 million L). For the manganese greensand treatment there were also considerable costs for other chemicals (including potassium permanganate), contract membrane cleanings, several optimization assessments by water treatment troubleshooters and engineering companies. Indeed, attempts to optimize the manganese greensand treatment were also carried out through water treatment plant modifications. Unfortunately, these modifications spanning three different engineering companies and equally many process schemes failed to properly address the potassium permanganate/manganese greensand chemistry and for 15 years the engineers did not realize that they attempted to do what was chemically impossible.

Table 3: Effectiveness of biological filtration as percent removals

Parameter	Gordon	Pasqua	Yellow Quill
	Percent removal	Percent removal	Percent removal
Ammonium	>98	>98	>98
Arsenic	>85	>60	>75
Dissolved Organic Carbon	<5	<5	>10
Iron	>98	>98	>98
Manganese	0	0	0
Phosphate	>60	>75	>95
Turbidity (for raw water, turbidity after aeration)	>98	>98	>98

3.5 Reverse Osmosis treatment

The Reverse Osmosis (RO) treatment has operated longest at Yellow Quill First Nation where the water treatment plant was commissioned in December 2003. Only one cleaning of the RO membranes has been carried out since then. After RO treatment the water is going through a calcium and magnesium mineral bed producing both a non-corrosive, healthy and safe drinking water (Table 4). The other plants, Pasqua and Gordon's are producing similar quality treated water with the exception of calcium and magnesium at Gordon's. Instead of the calcium and magnesium mineral bed sodium hydroxide is injected to produce a neutral pH. We are, however, in the process of designing a new mineral bed for Gordon's and it will be implemented later this year.

Yellow Quill's treated water is of exceptional quality and far superior to the quality called for by any Guidelines. In addition the distributed water is biologically stable, which can be seen by the stability of the chlorine residuals in the distribution system. The chlorine demand is very low with final total residual chlorine levels around 0.35 mg/L resulting in free chlorine levels being >0.30 mg/L both at the water treatment plant and in the distribution system. The low chlorine demand is also resulting in trihalomethane levels below detection (<0.005 mg/L). Problem compounds, such as ammonium, arsenic, sulphate, dissolved organic carbon, and sodium, have been removed to below or close to detection limits. For some compounds, however, one would like to see elevated levels in the demineralized water. This includes calcium, magnesium, hardness, TDS and alkalinity where in the literature there are various recommendations for minimum levels. Elevated levels of these compounds will limit corrosion of metals, such as copper and lead, from distribution and house pipes, and improve taste. WHO [7] outlined medical problems associated with inadequate calcium intake and listed osteoporosis, kidney stones, colorectal cancer, hypertension and stroke, coronary artery disease, insulin resistance and obesity. Re-adjusting pH after RO treatment is therefore not a trivial matter and will require the careful design of

solutions that will be sustainable both in terms of water treatment and human health. We have put some recommended minimum values in Table 4 with an S (for suggested) after the value. Carrying out pH corrections of RO water with sodium hydroxide will not address the issues discussed above, but the use of a filter containing a calcium and magnesium mineral bed, can solve some of these issues.

Table 4: Yellow Quill distributed water (S is suggested levels in demineralized water)

Parameter	Guideline value	Yellow Quill Tap Water
mg/L	mg/L	mg/L
Alkalinity	>30 (S)	77
Aluminum	<0.1 (operational)	<0.005
Ammonia	<5 (EU)	<0.05
Arsenic	<0.010	<0.002
Barium	1.0	0.001
Boron	<5	0.52
Calcium	>20 (S)	23
Chloride	<250	45
Free chlorine	>0.20	>0.30
Copper	<1	0.028
Dissolved Organic Carbon	<5 (SDWF)	<0.5
Fluoride	<1.5	<0.05
Iron	<0.3 (AO)	0.032
Hardness	>60 (S)	76
Heterotrophic plate count (HPC)	<500 ct/mL	<2
Lead	<0.01	<0.002
Magnesium	>10 (S)	4.6
Manganese	<0.050	0.006
Nitrate (as nitrate-nitrogen) (mg/L)	<10	0.52
pH	6.5-8.5	7.1
Phosphate	No guideline	<0.01
Redox (ORP) (mV)	No guideline	720
Selenium	<0.01	<0.005
Silicon	No guideline	0.40
Sodium	<200 (SK <300)	6.0
Strontium	No guideline	0.044
Sulphate	<500	5.9
Temperature (C)	<15 (AO)	<10
Total dissolved solids	>100 (S)	90
Trihalomethanes	<0.100	<0.005
Zinc	<5	<0.005

Yellow Quill's alkalinity levels were above suggested minimum level (77 vs. 30), the calcium levels were also greater (23 vs. 20, although some recommendations are >30 mg/L) and so were the hardness levels (76 vs. 60), while magnesium was lower (4.6 vs. 10) and TDS (90 vs. 100). Increasing the contact time in the mineral contactor as well as increasing its magnesium content should increase both the low magnesium and TDS levels.

IV. DISCUSSION

4.1 Poor quality raw water sources

Most large communities have been located where there is ample quality raw water sources while many rural communities have grown despite a profound lack of quality water. Many of these smaller communities have not realized the extent of chemical problems nor waterborne illnesses associated with poor quality water sources and inadequate water treatment systems. The current work was prompted by the realization that using water sources tainted by human sewage or naturally occurring problem compounds require far better, rather than inferior, treatment processes than currently used by most large cities.

Water treatment processes capable of achieving truly safe drinking water when compromised raw water sources are used need to be able to deal with both these high levels of problem chemicals and microbes. While conventional treatment has been able to deal to some extent with specific chemicals, such as iron and manganese, other problem compounds, such as arsenic, ammonium and bioavailable dissolved organics as well as many problem microbes including protozoan parasites, bacteria and viruses frequently present challenges for small rural water treatment plants.

Failure to deal appropriately with poor quality water sources is a huge concern in terms of human health. The extent of the problem may be realized from the fact that one person with a viral illness can produce one billion viruses per day and infective dose can be less than 10 viral particles and there can be more than 100 different types of disease-causing viruses in human sewage [8]. Even in jurisdictions with stringent regulations in terms of drinking water quality as well as considerable support to improve small treatment systems, it is still the small communities that have problems meeting even rudimentary requirements, such as complying with the U.S. Environmental Protection Agency's coliform rule. Indeed, 96% of violations of the Total Coliform Rule came from water treatment plants serving 10,000 or fewer people with the highest violations for water plants serving 500 people or less [9]. This prompted the following statement by the National Research Council:

“Current drinking water quality standards are aimed at water obtained from relatively uncontaminated sources and, thus, cannot be relied on as the sole standard of safety”.

The need for more effective water treatment systems especially for small communities is therefore a pressing public health concern.

4.2 Conventional treatment ahead of RO membranes

The use of conventional treatment ahead of RO membranes would be most cost-effective as there are many existing plants with such treatment that are currently considering the addition of RO polishing. One of the world's largest private water suppliers, the Metropolitan Water Quality District of Southern

California, hoped that conventional treatment technologies would work as pre-treatment processes ahead of RO [10] to lessen the costs of RO implementation at its water treatment plants. Gabelich [10] investigated conventional treatment (coagulation, flocculation, sedimentation, multi-media filtration) and conventional treatment with ozone disinfection and biofiltration both in pilot and full-scale experiments. In full-scale testing membrane degradation and inorganic colloidal fouling were caused by both aluminum sulphate (alum) and ferric chloride coagulation making conventional treatment unsuitable as pretreatment for RO technologies. Conventional technologies with ozone disinfection and biofiltration as well as microfiltration produced better quality water at the pilot-stage, but were not implemented full-scale.

There are a host of reasons why neutralization of negative particles (including colloids) during the coagulation process can cause problems for RO membranes. Particles are normally negatively charged similar to membrane surfaces and the entire charge characteristics of water is changed during the coagulation process in favour of neutral or positively charged particles with the intended result of the particles clumping together and forming larger agglomerations that can be filtered, or sedimented out of solution. This coagulation can be carried out with cationic polymers, inorganic salts, and aluminum and iron salts. A major problem with using coagulation ahead of RO membranes is the difficulty in removing traces of coagulation chemicals, which if they reach the membranes can be deposited on the membrane surface.

Adding chelators, such as 5 mg/L of citric acid, ahead of the membranes to complex residual metal from the coagulant has been partly successful, but further increases chemical additions and cost of the pre-treatment [11]. In addition, when aluminum is used reactions with silicates, hydroxides and phosphates generate combined foulants with the aluminum as well as interacting with antiscalants [10]. Moreover while aluminum chlorohydrate and ferric chloride coagulants minimized colloidal fouling, the potential for causing oxidative damage on the membranes was increased [10]. It is therefore extremely challenging to include conventional coagulation strategies in combination with RO membrane treatment. Treatment processes that are more suited to work well with RO membranes have to be developed. Biological treatment can resolve most RO pretreatment challenges although attention must be paid to the optimization of the biological processes and limiting the shedding of particulate fines prevalent with some biological attachment materials.

4.3 Biological treatment of water ahead of RO membranes

Drinking water meeting all current regulatory requirements at the water treatment plant may still deliver unacceptable quality water at the kitchen tap. Compounds capable of causing microbial growth can cause the formation of slime layers in the distribution system, which can harbor and shed disease-causing microorganisms, such as *Mycobacterium* and *Legionella*, which are slow-growing organisms ideally suited for life in water distribution pipelines [12]. This microbial growth can cause loss of chlorine residuals and the generation of taste and odour in the water. Some treatment practices increase these problems. Ozonation is well known for splitting larger molecular weight organic compounds into smaller and more bioavailable pieces, but even chlorination before distribution has the same effect producing more bioavailable organic material [13]. It is therefore likely that all oxidation practices increase bioavailability, and while many planktonic microorganisms cannot make use of the bioavailable compounds, biofilm forming bacteria with their extensive mucilage secretions, such as *Mycobacterium*, are able to overcome toxicity of residual disinfectants.

While oxidative treatments increase bioavailability, filtration processes including RO cannot assure treated water without microbial nutrients. Indeed, there are virtually no currently used water treatment processes that are capable of effectively removing all compounds capable of causing microbial growth. Conventional technologies, such as sandfiltration, microfiltration and ultrafiltration technologies can only remove dissolved organic material if adsorbed onto Powdered Activated Carbon (PAC), coagulated by coagulation chemicals or otherwise modified from its dissolved state. Even nanofiltration is a poor barrier for bioavailable organics causing proliferation of microbes in the treated water [14]. In addition, tight RO membranes that remove 99% of sodium have been shown to remove only 42% of material causing Biological Oxygen Demand [15].

There are no regulatory requirements to deal with all of the different compounds that can act as energy or nutrient sources for bacteria. While there are aesthetic guidelines for both iron and manganese the levels at which these compounds can trigger microbial growth is much lower than the aesthetically suggested upper levels. Only arsenic and nitrate are included in regulatory health requirements while others including ammonium, phosphorus, and dissolved organic material have no health or aesthetic guidelines associated with them at least not at the concentrations that are of concern for microbial growth.

Therefore, if the water contains microbial energy and nutrient sources, or such compounds are generated in the treatment process, then it can be expected that microbial growth will occur to the extent that many of those compounds will be removed before reaching the customer's tap. But, during this process both chemical and microbial problem issues are developed negatively affecting the treated water quality. These compounds will also generate microbial growth on RO membranes causing biofouling. This biofouling of RO membranes is a major limiting factor in RO treatment decreasing quality of the produced water and increasing the need for membrane cleanings and increased risk for premature membrane failures [16].

There is only one currently available solution for the above dilemma. Remove the microbial energy and nutrient compounds before they enter the distribution system. This is most easily carried out in the water treatment plant where conditions suitable for microbial growth need to be established for optimum removal of these growth stimulating microbial compounds.

In practice, in-plant removal of microbial nutrient and energy compounds, rely on the establishment of biofilm forming bacteria on a high-surface area bacterial attachment material, such as granular activated carbon (GAC) or inert expanded clay material. The use of biological treatment to treat water is commonly occurring for specific compounds, such as ammonium, iron, manganese and bioavailable organic compounds. However, the poor quality water sources used on the Canadian prairies require the biological removal of multiple compounds including ammonium, arsenic, bioavailable DOC, iron and phosphorus in the same treatment plant. The process that has been developed here is capable of doing this.

4.4 Reverse Osmosis treatment

RO treatment of water that contains high levels of some compounds, such as dissolved organic carbon, has previously been considered to cause too many problems. Recommendations from RO membrane manufacturers have therefore typically been to restrict DOC levels to below 3 mg/L. This excludes the use of RO treatment on most poor quality raw water sources. For example, the average DOC level in

Saskatchewan groundwater is around 7 mg/L [17] and Saskatchewan surface water is 11 mg/L [18]. Saddle Lake Cree Nation in Alberta is using a water source with around 25 mg/L of DOC, where we have also successfully applied RO treatment following biological treatment.

The Yellow Quill water treatment plant has operated since December 2003 with DOC levels of 10-11 mg/L with the first membrane cleaning after 18 months. Pasqua First Nation has operated for 20 months at 5 mg/L of DOC without any cleaning requirement. The DOC that is really causing problems on RO membranes is bioavailable DOC and removal of this component, however small, is crucial to minimize fouling. This needs to be coupled with the removal of other nutrient and energy sources that are present in the raw water source. Biological pre-treatment to ensure that food and nutrient compounds for bacteria are restricted in the RO supply water is therefore essential to trouble-free RO treatment.

4.5 pH adjustment of RO treated acid water

When intact RO membranes are used to treat fresh and brackish raw water sources high removals of calcium, magnesium and alkalinity generate low pH (<pH 6) and highly corrosive treated water. Chemically or physically damaged RO membranes can, however, produce water with low TDS rejection and pH levels >6.0, but unfortunately the microbial protection offered by RO membranes is lost and problem compounds, such as arsenic, ammonium, manganese, and increased levels of bioavailable compounds (if not removed biologically) may not be rejected by the membrane. Inappropriate chemical cleanings and pre-treatment using oxidizers are generally to blame for these conditions in RO plants in western Canada. Using nanofiltration membranes on poor quality water sources also typically will result in elevated levels of problem compounds. While blending pre-treated water with RO water was recommended earlier, problems with chemical and microbial contaminants have now limited these practices in aboriginal communities. It should also be noted that if anaerobic water is treated with RO membranes, the rejection of trivalent arsenic (As^{3+}) can be well below 50% and this RO treatment process is not recommended for arsenic-containing water sources [6].

With blending not being acceptable any longer for the reduction of corrosivity and stabilizing the water, other means of carrying out this have to be used. A common practice in western Canada is pH adjustment with sodium hydroxide or soda ash (although the most commonly used soda ash product used here has not been certified for drinking water use). Unfortunately, this does not produce non-corrosive water as there is no calcium present, and while a positive Langmuir index may be obtained in this manner, the water can still be corrosive and corrosion control inhibitors may have to be added [19]. Water that is corrosive will potentially leach out copper and lead from distribution and house pipes. Elevation of sodium levels in the treated water is also not desirable because there are health concerns rather than benefits from this compound.

Instead of adding sodium, as in the above pH adjustment strategy, calcium and magnesium is added at Pasqua and Yellow Quill. We designed a mineral contactor consisting of calcium and magnesium carbonate salts that can be run 24 hours per day without backwashing. This produced corrosion free water that in addition is providing some health benefits. WHO [7] outlined medical problems associated with inadequate calcium intake and listed osteoporosis, kidney stones, colorectal cancer, hypertension and stroke, coronary artery disease, insulin resistance and obesity. Re-adjusting pH after RO treatment is therefore not a trivial matter and will require the careful design of solutions that will be sustainable both in terms of water treatment and human health.

V. CONCLUSIONS AND RECOMMENDATIONS

The development of an Integrated Biological and RO Treatment Process has made it possible to treat water sources that previously were unusable for human consumption in a sustainable manner. While attempts on the Canadian prairies to treat similar types of water with conventional pretreatment, and indeed direct treatment of anaerobic water, problems with RO membrane fouling and damage have been obstacles that have now been overcome with the developed process. A key difference in the developed process is that no chemicals are used during pre-treatment generating a high quality of pre-treated water with low levels of compounds that bacteria can use as energy or nutrient sources. These quality traits result in low membrane fouling, retained membrane integrity, and expected long membrane life. The addition of calcium and magnesium through a continuously operated mineral bed contactor is also making the RO treated water non-corrosive and healthy.

Operator interventions with the developed process are also fewer, while at the same time costs are being decreased. On-going efforts in the full-scale plants are geared towards further improving both the biological and RO process. Through the Advanced Aboriginal Water Treatment Team it is our intention to have the most affordable, yet best quality water anywhere, even in remote aboriginal communities across Canada. Many of these communities, including Yellow Quill and George Gordon First Nations, in the past before the current process, distributed water unsuitable for human consumption; removing drinking water as a source of disease is the ultimate goal.

Aboriginal beliefs are centered on taking care of nature with water being the main concern. The heavy use of chemistry in conventional treatment is very much against this view of life and using natural biological filtration processes to deal with contaminants has the blessing of Aboriginal Elders that provide spiritual guidance of these communities.

It is our hope that government agencies will realize the benefits of using science to characterize raw and treated water so that effective treatment strategies can be developed at low costs so that the current poor state of treatment processes in aboriginal communities across Canada can be remedied in a foreseeable future. Adoption of new processes, including those described in this paper face formidable challenges with both engineering companies and government agencies. These entities have done the same things for so long that accepting change and moving towards truly safe drinking water appears to be quite difficult. SDWF estimates that more than 90% of aboriginal communities in Canada cannot meet the current Canadian Drinking Water Quality Guidelines; this is, unfortunately, the result of lack of water quality knowledge in aboriginal communities, and lack of federal government desire to truly fix aboriginal water quality problems, which it has the fiduciary duty to do.

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