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CAUSTIC RECOVERY USING MEMBRANE FILTRATION

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ABSTRACT

Food and beverage processors that use dilute caustic solutions for cleaning process equipment have shown increased interest in recovering the used caustic. The primary reason is that the price of caustic has increased significantly in the past year or so. Membrane filtration technology can be used to remove suspended solids (clarify with microfiltration) and/or dissolved solids (purify with nanofiltration) from these used caustic solutions. These treated caustic solutions are suitable for reuse within the processing plant as cleaning solutions. While an end-user's specific process, performance, capital and operating cost parameters will require pilot testing and process design evaluations to determine, the existing body of information from commercial and process development work allows for an evaluation of a "typical" caustic recovery application.

INTRODUCTION

Membrane technology is widely used in the food, beverage and dairy industries for process applications directly generating commercial products. Membrane technology is also used and increasingly under consideration for by-product or waste stream applications in these same industries.

Membrane technology has four general classifications, microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). The membrane pore sizes (or alternately described by molecular weight cut-offs, MWCO) range up to a couple microns for the most open MF membrane to less than one thousandth of a micron (or ~60 MWCO) for reverse osmosis membranes. Membrane applications can classified as: clarifications (separating suspended and colloidal components from dissolved components), component separations based on molecular size or other parameter, and concentration (removal of water or other solvent from all other components).

A membrane's composition is usually described as being either polymeric or inorganic. While more than a hundred polymers have been used for membranes, there are five to ten polymer types that make up most of the polymeric membranes widely used and available today. The different polymeric membranes have different membrane capabilities (pore sizes, flux rates, etc.) and also process stream capabilities and compatibilities (pH and temperature ranges, solvent stability, oxidizer stability, etc.). Polymeric membranes cover the complete range of pore sizes from MF to RO. Polymeric membranes can be configured as spiral, tubular, hollow fiber, and flat sheets, with spiral being the most widely used configuration. Inorganic membranes predominantly have supporting layers that are either ceramic or stainless steel in composition. The actual membrane layer is usually a ceramic material. The inorganic membranes are limited to MF and UF pore sizes. The inorganic membranes can be described as robust, capable of tolerating pH extremes, temperature extremes, organic solvents, and oxidizers well. Inorganic membranes are almost always configured as a tubular membrane.

Membrane technology is well suited to treating point-source effluent streams. Point-source effluent streams are usually composed of a few components and have a relatively consistent composition and stream characteristics (volumetric flows, temperature, pH, etc.), especially when compared to combined or total plant effluent streams. Because of these factors application of technologies to purify these point-sources for reuse is much more viable than treating combined or total plant effluent.

Point-source streams that are treated for reuse with membrane technology include: contaminated (or dirty) chemical streams like CIP or cleaning caustics and acids, regeneration chemicals, brine solutions, washing/peeling solutions, condensates and permeates, and treated wastewaters.

CAUSTIC RECOVERY USING MEMBRANE TECHNOLOGY

One of the more widely commercialized point-source treatment applications is the clarification/purification of dirty CIP/cleaning caustics in food and beverage processing plants. Caustic solutions (either sodium hydroxide or potassium hydroxide) are widely used in the cleaning procedures for process equipment, piping, storage tanks, etc. Typically the caustic concentration is about 1-2% but varies from <1% to >5% caustic. The caustic used may or may not contain additives like surfactants, chelating agents, buffers, etc. The equipment cleaned with caustic solutions includes: centrifuges, juicing equipment, evaporators, drying equipment, storage tanks, piping, etc. The dirty caustic typically contains both suspended/colloidal and dissolved contaminants.

The primary justifications for caustic recovery are: (1) reduction in purchase costs for fresh caustic; (2) reduction in waste treatment costs; and (3) achieve or maintain regulatory compliance on plant discharges. There can be additional justifications for implementing caustic recovery (concentration of by-products, reduction in plant water usage, thermal energy recovery) but these tend to have only minor value.

There are other approaches and technologies for caustic recovery, including: (1) setting and decanting; (2) screening; and, (3) centrifugation. These methods remove to varying degrees the suspended solids in the dirty caustic. In comparison MF membrane technology with defined pore sizes can produce a clarified caustic with essentially no suspended matter. In addition, none of these alternatives offers a way to separate the dissolved contaminants from caustic, in the way the suitable NF membranes can.

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The use of membrane technology for caustic recovery started to become wide-spread in the early 1990's, driven by the then increasing cost of caustic and stricter regulatory environment, and made possible by membranes stable in and capable of performing well with dirty caustic. The first widely used membrane type for caustic recovery was ceramic membranes. Ceramic membranes are not degraded by the pH and temperature of the dirty caustic stream. Their tubular configuration is suitable for removing and concentrating suspended solids. While ceramic membranes can concentrate suspended solids to thick slurries the commercial maximum suspended solids concentration is usually somewhat lower, depending on operational and cost considerations. Ceramic membranes then (as now) were limited to MF and UF pore sizes. The process development work done at the time showed that a ceramic membrane with a pore size of 0.1 micron to 0.02 micron produced a clarified caustic without any suspended or colloidal solids. The membrane is not tight enough to remove dissolved contaminants (sugars, acids, low molecular weight carbohydrates, proteins, peptides, color compounds, etc.) so they will stay with the clarified caustic. This quality of caustic for reuse was acceptable to many food and beverage processing facilities and was commercially implemented.

While ceramic (and stainless steel membranes) offer an excellent solution for removing suspended and colloidal solids from caustic, and acceptable to many applications, there was still a need for membranes that could both remove the dissolved components from the caustic and tolerate the caustic environment. In the late 1990's polymeric nanofiltration membrane products were developed that met these requirements. Since then a couple of NF membrane products have been commercialized based different membrane chemistries and associated chemical properties. One NF membrane, described here as "Type A", offers excellent rejection of organic contaminants (~200 MWCO pore size) while also being stable at the necessary caustic concentrations, pH values, temperatures, etc. This membrane does not tolerate oxidizers (like hypochlorite). Another NF membrane, described here as "Type B", uses a different membrane chemistry (sulfonated polyethersulfone membrane) which is also quite suitable for typical used caustic streams and has the advantage of being able to tolerate oxidizers. The Type B membrane has a larger pore size than the Type A, which means that the Type B membrane has lower rejection of the low molecular weight organics. Most of the nanofiltration work done on used cleaning caustics is based on the Type A membrane. Both of these types of NF membranes are available only in spiral configurations. Spiral membrane elements have a feed channel spacer which creates turbulence and a tortuous flow path for the feed stream, however suspended and colloidal solids will tend to get caught on and build up around these spacers, eventually plugging the feed channel. Consequently the spiral configuration is generally not suitable if the feed stream has suspended solids. Thus the feed to the spiral NF system must be suitable clarified, with an inorganic, tubular MF often the best clarification technology choice.

The typical caustic recovery process options can be defined as follows:

- The dirty caustic stream or streams are collected and sent to a dirty or spent caustic storage tank.
- Either entering or exiting this storage tank the dirty caustic should be screened to remove the large particulates. The screen size is typically about 400 microns.
- If removal of the suspended solids is desired then the dirty caustic is sent to a MF system to clarify the caustic with the suspended solids concentrated. If this quality of caustic is acceptable for reuse then there are no other processing steps.
- If removal of the dissolved solids is also desired then the clarified caustic from the MF is sent to an NF system. The NF system purifies the clarified caustic and concentrates the dissolved contaminants.
- If the dirty caustic is essentially no suspended solids then the MF clarification step can be by-passed and the dirty caustic sent directly to the spiral NF. This is not the usual process.
- The caustic for reuse (clarified or purified) is sent to a storage tank.

This process is shown in Figure 1 below.

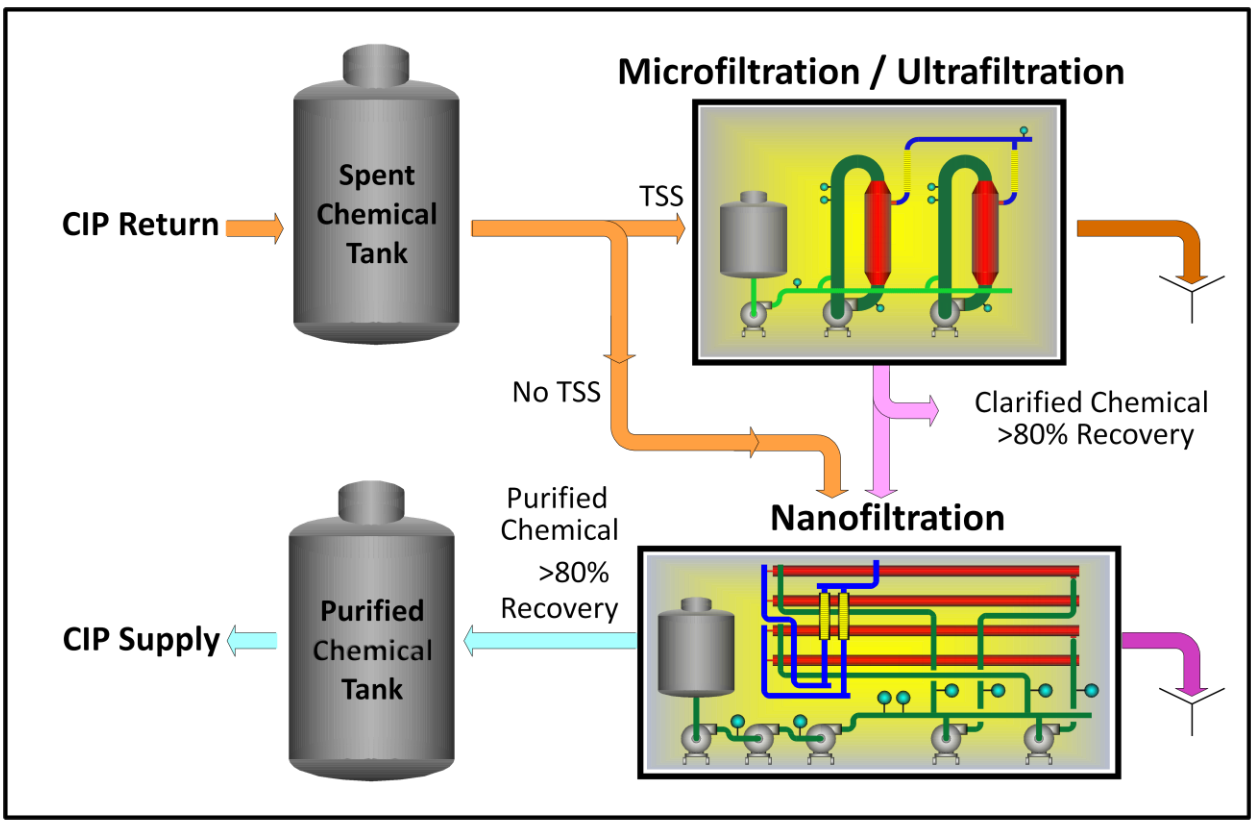

Figure 1: General Caustic Recovery Process Options

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CAUSTIC RECOVERY IN THE CITRUS INDUSTRY

Citrus juice processing plants are utilizing membrane technology for caustic recovery. GEA Filtration has two such installations, one in California and one in Florida. Both of these are ceramic MF membrane filtration systems clarifying spent caustic. GEA Filtration has also done process development work on spent citrus caustic with spiral NF membranes. This section discusses both types of application work.

A good example of the early caustic recovery work as it was applied to the citrus industry is GEA's commercial installation in California. This plant utilized dilute caustic as its primary cleaning solution for most process equipment. At the time of the caustic recovery work (circa 1993) the plant produced primarily juice concentrate (from evaporation) and also had the ability to de-bitter juices. The reasons for considering caustic recovery were: the cost of fresh caustic has recently increased dramatically; concerns over disposal of the spent caustic (land application); and disruptions to production caused by spent caustic handling. About 1/3rd of the spent caustic was applied to citrus peel. The plant wanted to implement a solution which generated a clarified caustic for reuse within the plant with the concentrated solids applied to the peel. This would eliminate discharge of all waste caustic streams.

The tested and implemented solution was a ceramic MF system, shown in Figure 2. The MF generated a clarified caustic which could be reused everywhere in the plant except for the regeneration of the resin de-bittering system.

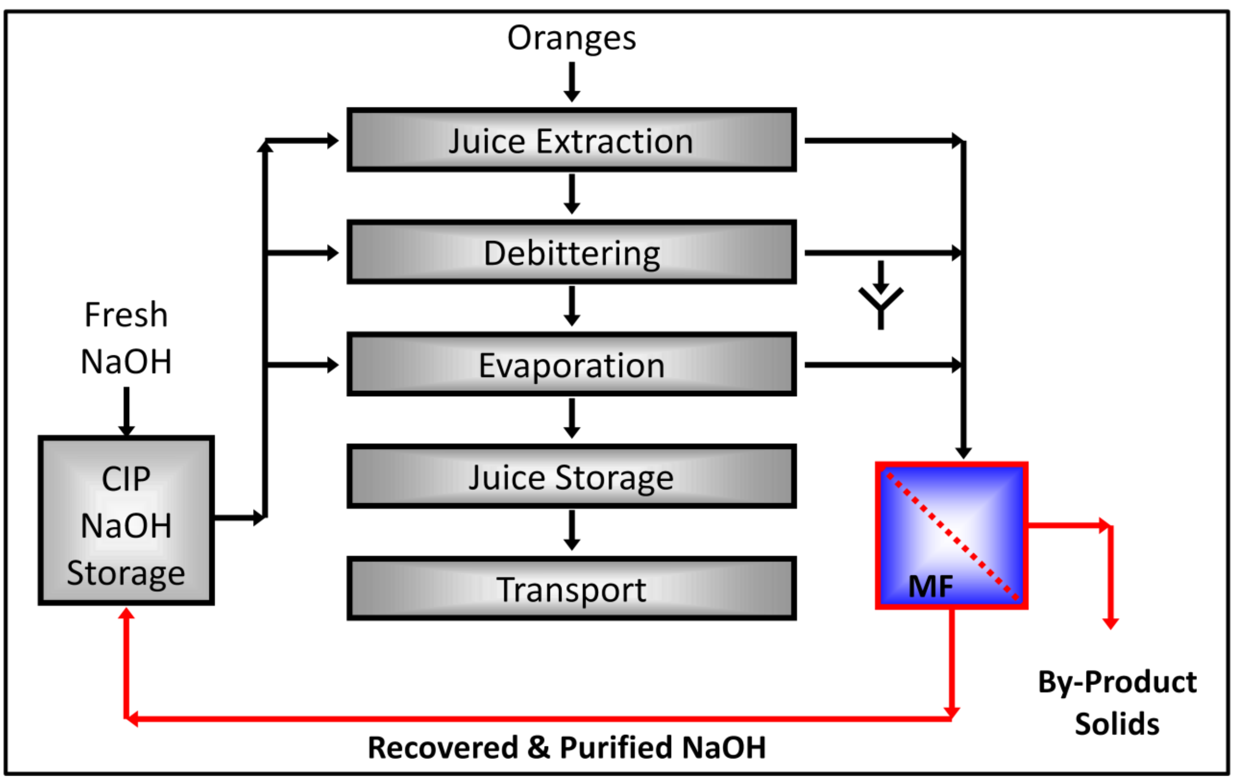
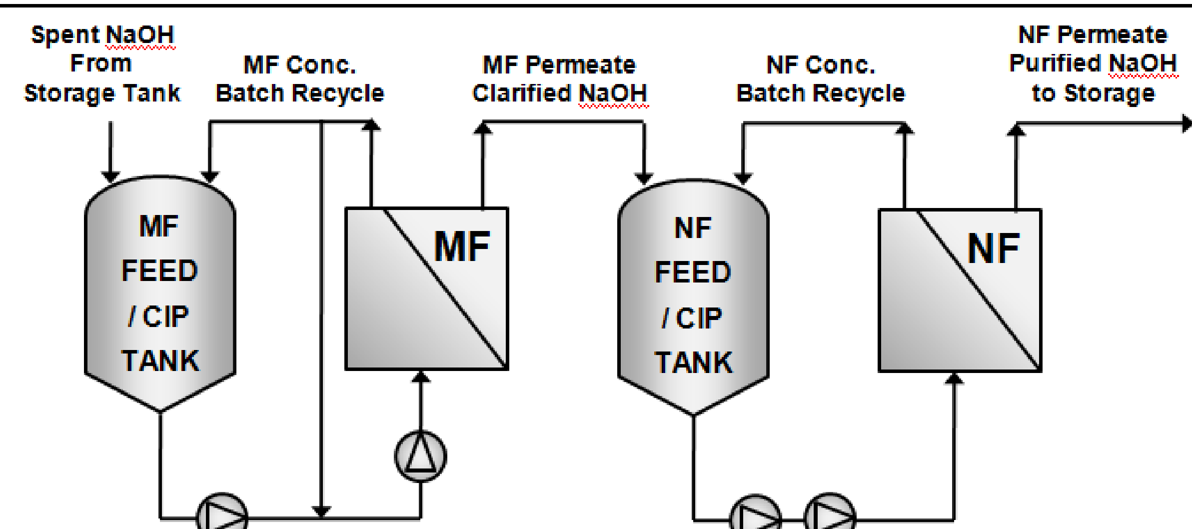


Figure 2: Commercial Caustic Recovery Process in the Citrus Industry, 1993

The ceramic MF process was installed in 1994. The annual savings on all factors led to a calculated Return-On-Investment (ROI) of about 2 years for the project. The system has been operating at the design parameters without any significant interruption since 1994. The original membranes are still in the system, which while not unheard of for ceramic membranes, is now almost 4 times the membrane life value used in the original ROI calculations.

While clarifying caustic for reuse has proven to be a good choice for many plants, the initial and increasing concentrations of dissolved solids in reused caustic may make it unacceptable for reuse at some points in the plant and also limit the recovery of caustic. In addition there may be a desire to standardize throughout the plant on a quality of reuse caustic better than what microfiltration can produce. NF membrane technology can be used to meet these plant criteria.

A good way to illustrate the process and engineering criteria and parameters for caustic recovery is to go through a typical example. In this example two filtration solutions will be examined: (1) Clarification with ceramic MF membranes only; and (2) adding spiral NF to purify the clarified caustic. The block flow diagram and parameters are shown in Figure 3. The process is assumed to operate in the production mode 20 hours per day and allows for up to four hours or cleaning (CIP) per day.



STREAM PARAMETER	MF FEED	MF CONC.	MF PERM.	NF CONC.	NF PERM
% NaOH	1.5%	1.5%	1.5%	1.5%	1.5%
% TSS	0.5%	5%	0%		
Gal. / day	20,000	2,000	18,000	900	17,100
Unit Op Recovery, %			90%		95%
Process Total Recovery, %	100%		90%		85.5%

Figure 3: Block Flow Diagram & Parameters for Caustic Recovery Application

The block flow diagram in Figure 3 shows GEA's typical scope of supply for this process. GEA's typical scope of supply of supply is to provide all necessary component (membranes, pumps, valves, gauges, instruments, piping, framing, controls hardware, etc.) and engineering services (project management, engineering, design, onsite commissioning). The system would utilize a PLC controls system with LCD interface. The Customer is responsible for: installation, field wiring and utility connections, storage tanks and transfer equipment, pre-screening equipment, etc. Based on this information the capital and operating costs can be calculated, as shown in Table 1:

PARAMETER	ASSUMPTIONS	OPTION 1A	OPTION 1B	OPTION 2A	OPTION 2B
Unit Operations		MF	MF	MF+NF	MF+NF
$, Capital Cost		**$ 269,900**	**$ 269,900**	**$ 516,200**	**$ 516,200**
Operating Costs / Year		High $$	**Lower $$**	High $$	**Lower $$**
Power Consumption	$0.07 / kW-Hr	$ 18,679	$ 18,679	$ 43,953	$ 43,953
Cleaning Chemicals	MF&NF=$120 ea.	$ 43,800	**$ 6,350**	$ 87,600	**$ 12,700**
Membrane Replacement		$ 5,000	**$ 1,667**	$ 59,000	**$ 28,667**
Steam	$5 / 1,000#	$ 1,414	**$ 0**	$ 3,274	**$ 0**
CIP Water	$0.20 / 1,000 gal.	$ 107	$ 107	$ 206	$ 206
Cooling Water	$0.07 / kW-Hr	$ 18,007	$18,007	$ 37,883	$ 37,883
Labor	$50,000/man-yr	$ 50,000	**$ 0**	$ 50,000	**$ 0**
$, TOTAL		**$ 137,007**	**$ 42,840**	**$ 281,916**	**$ 123,409**

Table 1: Capital and Operating Cost Parameters for Caustic Recovery Example

Comments about Table 1:

- Option 1A is the ceramic MF clarification only solution with high operating cost parameters – ceramic membrane life of 5 years
- Option 1B is the ceramic MF clarification only solution with lower and more likely operating cost parameters – 15 year ceramic membrane life, no addition operators required, recovery of CIP chemicals, use of warm water for CIP.
- Option 2A is the ceramic MF clarification + spiral NF solution with high operating cost parameters – ceramic membrane life of 5 years, NF life of 6 months
- Option 2B is the ceramic MF clarification only solution with lower and more likely operating cost parameters – 15 year ceramic membrane life, NF life of 12 months, no addition operators required, recovery of CIP chemicals, use of warm water for CIP.
- The capital cost parameters are budgetary and the operating costs will vary with specific plant site parameters.
- The process performance parameters represent the typical performance in citrus caustic applications. Any specific plant application requires pilot testing to determine scale-up parameters.

Based on the capital and operating cost information in Table 1 and value of $4.50 / gallon for 50% bulk NaOH (tanker car cost), the value of the recovered caustic can be calculated, as shown in Table 2.

PARAMETER	UNITS	MF	MF+NF
Volume of Recovered NaOH	gallons / day	18,000	17,100
Mass of Recovered NaOH	Kg / day	1035	983
Equivalent Volume of 50% NaOH	gallons / day	357.7	340
Cost of Purchased 50% NaOH	$ / gal	$ 4.50	$ 4.50
Value of Recovered NaOH (Equ.Vol.) x (Cost of 50%)	$ / day	$ 1,610	$ 1,530
	$ / 365 days	**$ 587,650**	**$ 558,450**

PARAMETER	OPTION 1A	OPTION 1B	OPTION 2A	OPTION 2B
Unit Operations	MF	MF	MF+NF	MF+NF
$, Capital Cost	$ 269,900	$ 269,900	$ 516,200	$ 516,200
Operating Costs / Year	$ 137,007	$ 42,840	$ 281,916	$ 123,409
Capital + 1st Year's Ops. Costs	$ 406,907	$ 312,740	$ 798,116	$ 639,609

Table 2: Value of the Recovered Caustic for the Caustic Recovery Example

Table 2 accurately condenses the cost values of membrane filtration solutions for the selected application and cost parameters. Besides what has already been mentioned as being outside GEA's system scope (storage tanks, transfer equipment, etc.), an often important consideration is the plant modification costs to collect and transport spent caustic to the system. In more modern plants this may not be an expensive cost because it was either planned for or relatively inexpensive to modify. In older or heavily modified or expanded plants this cost may be quite significant.

The throughput selected for this example (20,000 gallons per day) represents a value similar to our commercial application work, but it is less than the spent caustic volume generated in many citrus processing facilities. Larger throughput applications will have a better payback because the cost does not scale exactly with throughput as some costs are relatively fixed (engineering, etc.) and some cost increase more slowly (larger or more components, etc.).

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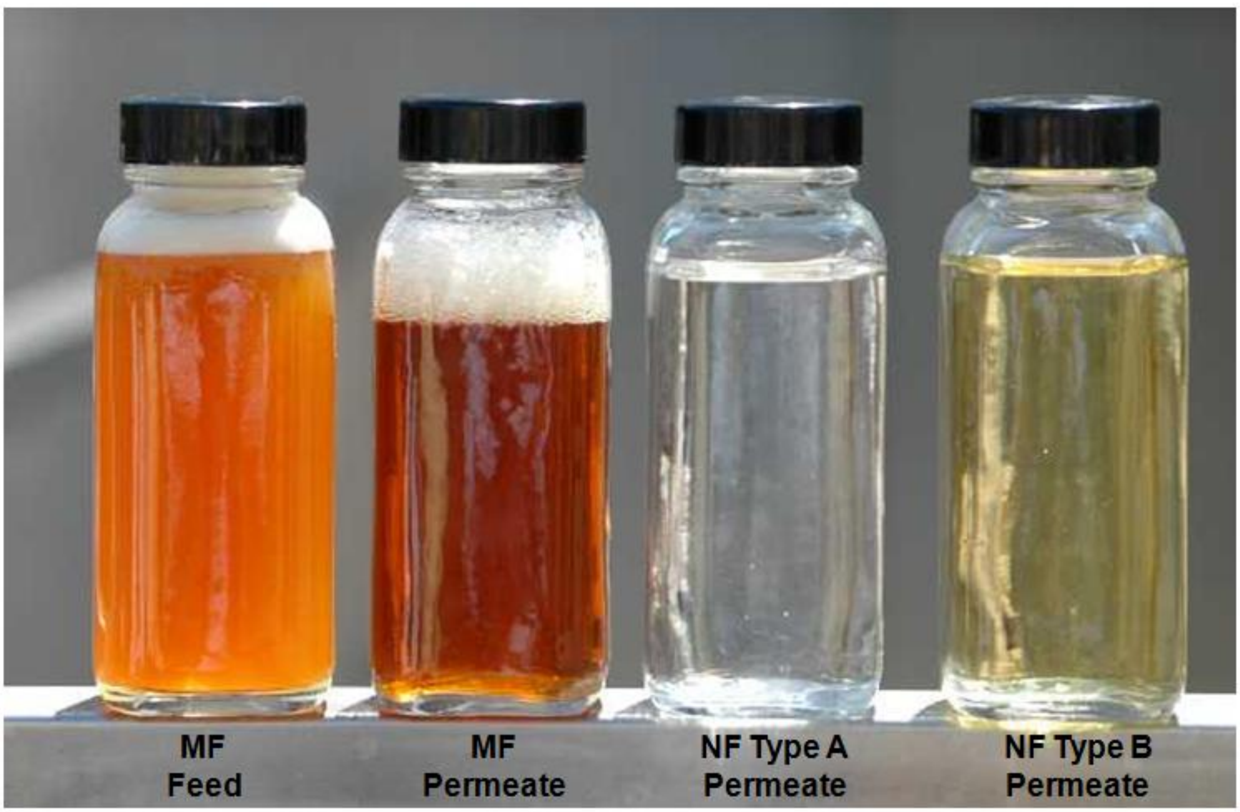
SUMMARY

Membrane filtration provides proven process solutions for point-source, waste stream applications. Specifically membrane filtration systems have been operating for more than a decade clarifying and purifying spent caustic solutions for reuse. The citrus processing plant has the choice of either a clarified caustic for reuse or a purified caustic for reuse (with significantly reduced dissolved contaminants). While the end-user's specific process and cost parameters will vary (and require pilot testing and process design work to define), enough information exists to generate "typical" parameters which can be used as a starting point in any evaluation. These parameters are presented in this paper.

The visual differences in the caustic at various points in the process can be seen in Photograph 1:



Photograph 1: Caustic MF and NF Samples

This paper was submitted and accepted for the 55th Annual Citrus Engineering Conference, March 19th, 2009. Please contact GEA Filtration for more information.