Tech Fact

FilmTec™ Membranes

Cleaning and Disinfection Procedures for FilmTec™ NF200 and NF270 Elements

Introduction

The following are general recommendations for cleaning FilmTec™ NF 200 and NF270 Elements. More detailed procedures for cleaning a nanofiltration (NF) system are typically included in the operating manual provided by the system supplier. It should be emphasized that frequent cleaning is not required for a properly designed and properly operated NF system, however because of the NF 200 and NF270 membrane's unique combination of pH range and temperature resistance, cleaning may be accomplished very effectively.

The cleaning procedure for the piperazine-based nanofiltration membranes FilmTec™ NF200 and FilmTec™ NF270 differs from the procedure proposed for the polyamide-based FilmTec™ FT30 Membranes (FilmTec™ BW30/TW30, FilmTec™ BW30LE, FilmTec™ XLE, FilmTec™ SW30 and FilmTec™ SW30HR).

There are two main reasons for the change:

- Alkaline cleaning at pH above 9 causes the membrane to swell. The net effect is an increase in flux (up to 40%) and a decrease in rejection. The effect disappears in normal operations, but can take up to 72 hours to disappear completely.
- Acid cleaning at pH below 4 causes the membrane to shrink. This becomes visible as an increase in rejection and a decrease in flux. The order of magnitude is less than with alkaline cleaners. Again this effect disappears during normal operation.

From an operations point of view, it is impractical to have to wait before the system stabilizes again. We have seen however, that the effect of the acid cleaner neutralizes the action of the alkaline cleaner (but not the other way around, as the alkaline effect is much stronger).

Cleaning Procedure

In normal operation, the membrane in nanofiltration elements can become fouled by mineral scale, biological matter, colloidal particles and insoluble organic constituents. Deposits build up on the membrane surfaces during operation until they cause loss in normalized permeate flow, loss of normalized salt rejection, or both.

Elements should be cleaned when one or more of the below mentioned parameters are applicable:

- The normalized permeate flow drops 10%
- The normalized salt passage increases 5 - 10%
- The normalized pressure drop (feed pressure minus concentrate pressure) increases 10 - 15%

Form No. 45-D01523-en, Rev. 2
January 2020

Cleaning Procedure (Cont.)

If you wait too long, cleaning may not restore the membrane element performance successfully. In addition, the time between cleanings becomes shorter as the membrane elements will foul or scale more rapidly.

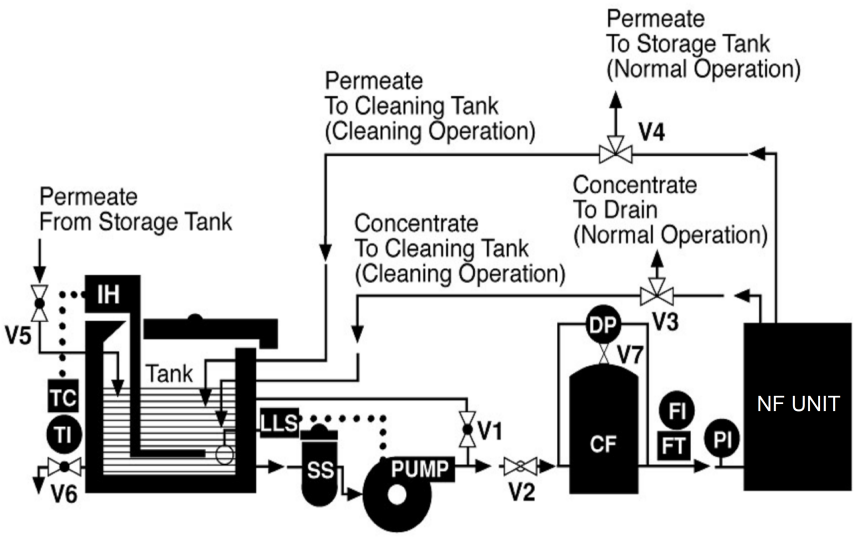
Differential Pressure (ΔP) should be measured and recorded across each stage of the array of pressure vessels. If the feed channels within the element become plugged, the ΔP will increase. It should be noted that the permeate flux will drop if feedwater temperature decreases. This is normal and does not indicate membrane fouling.

A malfunction in the pretreatment, pressure control, or increase in recovery can result in reduced product water output or an increase in salt passage. If a problem is observed, these causes should be considered first. The element(s) may not require cleaning. A computer program called FTNORM is available from FilmTec™ for normalizing performance data of FilmTec™ RO and NF Membranes. This program can be used to assist in determining when to clean and can be downloaded from our web site's Download Software section (http://www.dupont.com/water/design-software.html).

Safety Precautions

1. When using any chemical indicated here in subsequent sections, follow accepted safety practices. Consult the chemical manufacturer for detailed information about safety, handling and disposal.
2. When preparing cleaning solutions, ensure that all chemicals are dissolved and well mixed before circulating the solutions through the elements.
3. It is recommended the elements be flushed with good-quality chlorine-free water (20°C minimum temperature) after cleaning. Permeate water or deionized water are recommended. Care should be taken to operate initially at reduced flow and pressure to flush the bulk of the cleaning solution from the elements before resuming normal operating pressures and flows. Despite this precaution, cleaning chemicals will be present on the permeate side following cleaning. Therefore, the permeate must be diverted to drain for at least 30 minutes or until the water is clear when starting up after cleaning.
4. During recirculation of cleaning solutions, the maximum temperature must not be exceeded. The maximum allowed temperature is dependent on pH and membrane type. Table 1 contains information on the maximum allowed temperatures.
5. For elements greater than six inches in diameter, the flow direction during cleaning must be the same as during normal operation to prevent element telescoping, because the vessel thrust ring is installed only on the reject end of the vessel. This is also recommended for smaller elements. Equipment for cleaning is illustrated below.

Cleaning System Flow Diagram



TANK	Chemical Mixing Tank, polypropylene or FRP	**DP**	Differential Pressure Gauge
IH	Immersion Heater (may be replaced by cooling coil for some site locations)	**FI**	Flow Indicator
		FT	Flow Transmitter (optional)
TI	Temperature Indicator	**PI**	Pressure Indicator
TC	Temperature Control	**V1**	Pump Recirculation Valve, CPVC
LLS	Lower Level Switch to shut off pump	**V2**	Flow Control Valve, CPVC
SS	Security Screen–100 mesh	**V3**	Concentrate Valve, CPVC 3-way valve
PUMP	Low-Pressure Pump, 316 SS or non-metallic composite	**V4**	Permeate Valve, CPVC 3-way valve
		V5	Permeate Inlet Valve, CPVC
CF	Cartridge Filter, 5-10 micron polypropylene with PVC, FRP, or SS housing	**V6**	Tank Drain Valve, PVC, or CPVC
		V7	Purge Valve, SS, PVC, or CPVC

Suggested Equipment

The equipment for cleaning is shown in the Cleaning System Flow Diagram. The pH of cleaning solutions used with FilmTec™ NF 200 and NF 270 Elements can be in the range of 1 to 11 (see Table 1), and therefore non-corroding materials should be used in the cleaning system.

1. The mixing tank should be constructed of polypropylene or fiberglass-reinforced plastic (FRP). The tank should be provided with a removable cover and a temperature gauge. The cleaning procedure is more effective when performed at a warm temperature, and it is recommended that the solution be maintained according to the pH and temperature guidelines listed in Table 1. It is not recommended to use a cleaning temperature below 20°C because of the very slow chemical kinetics at low temperatures. In addition, chemicals such as sodium lauryl sulfate might precipitate at low temperatures. Cooling may also be required in certain geographic regions, so both heating/cooling requirements must be considered during the design. A rough rule of thumb in sizing a cleaning tank is to use approximately the empty pressure vessels volume and then add the volume of the feed and return hoses or pipes. For example, to clean ten 8-inch diameter pressure vessels with six elements per vessel, the following calculations would apply:

    a. Volume in Vessels

    $V1 = \pi r^2 L$

    $= 3.14\ (4\ in)^2\ (20\ ft)\ (7.48\ gal/ft^3) / (144\ in^2/ft^2)$

    $V1 = 52\ gal/vessel\ (0.2\ m^3)$

    $V10 = 52 \times 10 = 520\ gal\ (1.97\ m^3)$

    b. Volume in Pipes, assume 50 ft. length total 4" Sch 80 pipe

    $Vp = \pi r^2 L$

    $= 3.14\ (1.91\ in)^2\ (50\ ft)\ (7.48\ gal/ft^3) / (144\ in^2/ft^2)$

    $= 30\ gals\ (0.11\ m^3)$

    $Vct = V_{10} + Vp = 520 + 30 = 550\ gal.$

    Therefore, the cleaning tank should be about 550 gals ($2.1\ m^3$).

2. The cleaning pump should be sized for the flows and pressures given in Table 2, making allowances for pressure loss in the piping and across the cartridge filter. The pump should be constructed of 316 SS or nonmetallic composite polyesters.

3. Appropriate valves, flow meters, and pressure gauges should be installed to adequately control the flow. Service lines may be either hard piped or hoses. In either case, the flow rate should be a moderate 10 ft/sec (3 m/sec) or less.

Cleaning Elements In Situ

There are six steps in the cleaning of elements:

1. Prepare and mix the appropriate cleaning solution, and check pH of the solution. Ensure that all chemicals are dissolved and well mixed before circulating the solution to the elements. Any cleaning solution must be clear.

2. Low-flow pumping. Pump mixed, preheated cleaning solution to the vessel at conditions of low flow rate (about half of that shown in Table 1) and low pressure to displace the process water. Use only enough pressure to compensate for the pressure drop from feed to concentrate. The pressure should be low enough that essentially no or little permeate is produced. A low pressure minimizes redeposition of dirt on the membrane. Dump the concentrate, as necessary, to prevent dilution of the cleaning solution.

3. Recycle. After the process water is displaced, cleaning solution will be present in the concentrate stream. Then recycle the concentrate and permeate to the cleaning solution tank and allow the temperature to stabilize. Measure the pH of the solution and adjust the pH if needed.

Cleaning Elements In Situ (Cont.)

4. **Soak.** Turn the pump off and allow the elements to soak. Sometimes a soak period of about 1 hour is sufficient. For difficult fouling an extended soak period is beneficial; soak the elements overnight for 10-15 hours. To maintain a high temperature during an extended soak period, use a slow re-circulation rate (about 10% of that shown in Table 1).

Table 1: Recommended feed flow rate per pressure vessel during high flow rate recirculation

Feed Pressure[1] (psig)	(bar)	Element Diameter (inches)	Feed Flow Rate per Pressure Vessel (gpm)	(m^3/hr)
20 - 60	1.5 - 4.0	2.5	3 - 5	0.7 - 1.2
20 - 60	1.5 - 4.0	4	8 - 10	1.8 - 2.3
20 - 60	1.5 - 4.0	8	30 - 40	6. - 9.1

Dependent on number of elements in pressure vessel.

Table 2: pH range and temperature limits during cleaning

	Max. temp 25°C (77°F) pH range	Max. temp 35°C (95°F) pH range	Max. temp 45°C (113°F) pH range
FilmTec™ NF200/NF270	1 - 12	1 - 11	3 - 10

Cleaning Elements In Situ (Cont.)

5. High flow pumping. Feed the cleaning solution at the rates shown in Table 1 for 30-60 minutes. The high flow rate flushes out the foulants removed from the membrane surface by the cleaning. If the elements are heavily fouled, which should never happen, a flow rate ~50% higher than shown in Table 1 may aid cleaning. At higher flow rates excessive pressure drop may be a problem. The maximum recommended pressure drops are 1.0 bar (15 psi) per element or 3.4 bar (50 psi) per multi-element vessel, whichever value is more limiting. For 8" elements, the direction of flow during cleaning must be the same as during normal operation to avoid telescoping of the elements.

6. Flush out. NF permeate or deionized water are recommended for flushing out the cleaning solution. Prefiltered raw water or feed water should be avoided as its components may react with the cleaning solution: precipitation of foulants may occur in the membrane elements. The minimum flush out temperature is 20°C (68°F).

Cleaning Tips

1. It is strongly recommended to clean the stages of the NF system separately. This is to avoid having the removed foulant from stage 1 pushed into the 2nd stage resulting in minimal performance improvement from the cleaning. If the system consists of 3 stages, stage 2 and stage 3 should also be cleaned separately.

   For multi-stage systems, while each stage should be cleaned separately, the flushing and soaking operations may be done simultaneously in all stages. Fresh cleaning solution needs to be prepared when the cleaning solution becomes turbid and/or discolored. High-flow recirculation, however, should be carried out separately for each stage, so the flow rate is not too low in the first stage or too high in the last. This can be accomplished either by using one cleaning pump and operating one stage at a time, or by using a separate cleaning pump for each stage.

Cleaning Tips (Cont.)

2. The fouling or scaling of elements typically consists of a combination of foulants and scalants, for instance a mixture of organic fouling, colloidal fouling and biofouling. Therefore, it is very critical that the first cleaning step is wisely chosen. FilmTec™ strongly recommends alkaline cleaning as the first cleaning step.

   Acid cleaners typically react with silica, organics (for instance humic acids) and biofilm present on the membrane surface which may cause a further decline of the membrane performance. Sometimes, an alkaline cleaning may restore this decline that was caused by the acid cleaner, but often an extreme cleaning will be necessary. An extreme cleaning is carried out at pH and temperature conditions that are outside the membrane manufacturer's guidelines or by using cleaning chemicals that are not compatible with the membrane elements. An extreme cleaning should only be carried out as a last resort as it can result in membrane damage.

   If the NF system suffers from colloidal, organic fouling or biofouling in combination with calcium carbonate, then a two- step cleaning program will be needed: alkaline cleaning followed by an acid cleaning. The acid cleaning may be performed when the alkaline cleaning has effectively removed the organic fouling, colloidal fouling and biofouling.

3. Always measure the pH during cleaning. If the pH increases more than 0.5 pH units during acid cleaning, more acid needs to be added. If the pH decreases more than 0.5 pH units during alkaline cleaning, more caustic needs to be added.

4. Long soak times. It is possible for the solution to be fully saturated and the foulants can precipitate back onto the membrane surface. In addition, the temperature will drop during this period, therefore the soaking becomes less effective. It is recommended to circulate the solution regularly in order to maintain the temperature (temperature should not drop more than 5°C) and add chemicals if the pH needs to be adjusted.

5. Turbid or strong colored cleaning solutions should be replaced. The cleaning is repeated with a fresh cleaning solution.

6. If the system has to be shutdown for more than 24 hours, the elements should be stored in 1% w/w sodium metabisulfite solution.

In addition to applying the correct cleaning sequence (alkaline cleaning step first), selecting the correct pH is very critical for optimum foulant removal. If foulant is not successfully removed, the membrane system performance will decline faster as it is easier for the foulant to deposit on the membrane surface area. The time between cleanings will become shorter, resulting in shorter membrane element life and higher operating and maintenance costs.

Most effective cleaning allows longer system operating time between cleanings and results in the lowest operating costs.

Cleaning Chemicals

Table 3 lists suitable cleaning chemicals. Acid cleaners and alkaline cleaners are the standard cleaning chemicals. The acid cleaners are used to remove inorganic precipitates including iron, while the alkaline cleaners are used to remove organic fouling including biological matter. Sulfuric acid should never be used for cleaning because of the risk of calcium sulfate precipitation. Permeate or deionized water should be used for the preparation of the cleaning solutions.

Table 3: Simple cleaning solutions for FilmTec™ NF200/270 Membrane

Cleaner Foulant	0.1% (W) NaOH and pH 11, 30°C max. or 1% (W) Na_4EDTA and pH 11, 30°C max.	0.1% (W) NaOH and pH 11, 30°C max. or 0.025 Na-DDS, pH 11, 30°C max.	0.1% STP and 1% Na_4EDTA or 0.1% TSP and 1% Na_4EDTA	0.1% (W) HCl	0.5% (W) H_2PO_4	2% (W) citric acid	0.2% (W) NH_2SO_3H	1% (W) $Na_2S_2O_4$
Inorganic salts (e.g. $CaCO_3$)				Preferred	Alternative	Alternative		Alternative
Sulfate scales ($CaSO_4$, $BaSO_4$)	Preferred	Alternative						
Metal oxides (e.g. iron)					Alternative	Alternative	Alternative	Preferred
Inorganic colloids (silt)		Preferred						
Silica	Alternative	Preferred						
Biofilms	Alternative	Preferred						
Organics	Alternative step 1	Preferred step 1	Preferred step 2					

1. (W) denotes weight percent of active ingredient.
2. Foulant chamical symbols in order used: $CaCO_3$ is calcium carbonate; $CaSO_4$ is calcium sulfate; $BaSO_4$ is barium sulfate.
3. Cleaning chemical symbols in order used: NaOH is sodium hydroxide; Na_4EDTA is the tetra-sodium salt of ethylene diamine tetraacetic acid and is available from DuPont de Nemours Inc. under the trademark VERSENE™ 100 and VERSENE 220 crystals; Na-DDS is sodium salt of dodecylsulfate; STP is sodium triphosphate; TSP is trisodium phosphate; HCl is hydrochloric acid (Muriatic Acid); H_3PO_4 is phosphoric acid; NH_2SO_3H is sulfamic acid; $Na_2S_2O_4$ is sodium hydrosulfite.
4. For effective sulfate scale cleaning, the condition must be caught and treated early. Adding NaCl to the cleaning solution of NaOH and Na_4EDTA may help as sulfate solubility increases with increasing salinity. Successful cleaning of sulfate scales older than 1 week is doubtful.

Disinfecting NF Systems

If the plant has been infected by bacteria or mold, a disinfection must be carried out after the cleaning. The procedure is the same as for cleaning, except that the high flow pumping step can be skipped.

Hydrogen peroxide or hydrogen peroxide/peracetic acid solutions can be used at concentrations up to 0.2%. The biocidal efficacy of peracetic acid is much higher than that of hydrogen peroxide, but as most peracetic acid solutions also contain hydrogen peroxide, care must be exercised not to exceed the 0.2% concentration as a sum of both compounds. Continuous exposure at this concentration may eventually damage the membrane. Instead, periodic use is recommended.

When hydrogen peroxide is applied, the pH of the solution must be lower than 4. A pH of 3 is recommended. This will ensure optimal biocidal results and longer membrane lifetime. If no acid is added to the hydrogen peroxide solution, the chemical attack on the membrane will be much faster. When a mixture with peracetic acid is used, pH adjustment is usually not required.

Disinfecting NF Systems (Cont.)

If an alkaline cleaning has preceded disinfection, the alkalinity has to be carefully rinsed out also from the permeate side (check pH!) before peroxide/peracetic acid is applied. Otherwise, the membrane might become oxidized.

Two other factors greatly influence the rate of hydrogen peroxide attack on the membrane: temperature and iron.

The disinfecting solution must not exceed 25°C (77°F). FilmTec™ NF200/NF270 Membrane samples tested with 0.5% hydrogen peroxide at 34°C (93°F) showed a very high salt passage after several hours. At 24°C (75°F) however, membrane samples demonstrated compatibility with 0.5% hydrogen peroxide after 96 hours.

Iron or other transition metals must not be present, because they catalyze membrane degradation in the presence of hydrogen peroxide solutions. NF200/NF270 samples were tested using a 0.15% solution of hydrogen peroxide and tap water containing iron. After 150 hours, the salt passage of the membrane began to increase dramatically.

For NF200/NF270 Membrane systems, DuPont recommends the following procedure for disinfection with hydrogen peroxide solutions:

1. Any type of deposit on the membrane or other parts of the system should be removed with an alkaline cleaner before disinfecting. Removal of these deposits, which harbor microorganisms, will maximize the degree of disinfection. After alkaline cleaning, flush the system with NF permeate.
2. Clean the NF system with acid, e.g. 0.1% by volume hydrochloric acid or 0.4% by volume phosphoric acid, to remove any iron from the membrane surface. Flush the unit with NF permeate.
3. Circulate a solution of 0.2% hydrogen peroxide (preferably containing peracetic acid) diluted with NF permeate and pH adjusted to 3-4 with HCl at a temperature below 25°C (77°F) for 20 minutes.
4. Flush out the disinfecting solution. Rinse the system.
5. Allow the elements to soak in the disinfecting solution for 2 hours.
6. Flush out the disinfecting solution. Rinse the system.

Other disinfectants iodine, quaternary germicides and phenolic compounds cause flux losses and are not recommended for use as disinfectants.

70% ethanol can be used for disinfection. **Brand name biocides** have also been tested for effects on the membrane performance. There are fully compatible and limited compatible biocides.

Have a question? Contact us at:

www.dupont.com/water/contact-us

Form No. 45-D01523-en, Rev. 2
January 2020