Toray Membrane America, Inc.
Cleaning Procedures for Composite Polyamide RO Membrane Elements

This bulletin provides general information about the most typical foulants which may affect the performance of Composite Polyamide Reverse Osmosis (RO) membrane elements, and procedures for the removal of these foulants. The information in this bulletin applies to both 4-inch and 8-inch diameter RO membrane elements.

The surface of the RO membrane is subject to fouling by foreign materials which may be present in the feed water. Examples are:

- Calcium carbonate scale
- Sulfate scale of calcium, barium or strontium
- hydrates of metal oxides (iron, manganese, copper, nickel, aluminum, etc.)
- Polymerized silica scale
- Inorganic colloidal deposits
- Mixed inorganic/organic colloidal deposits
- NOM organic material (Natural Organic Matter)
- Man-made organic compounds (e.g. antiscalant/dispersants, cationic polyelectrolytes)
- Biological (bacterial bioslime, algae, mold, or fungi)

The term fouling used here includes the build up/ deposition of all kinds of layers on the surface of the membrane, including scale formation.

Note: The Composite Polyamide type of RO membrane elements may not be exposed to chlorinated water under any circumstances. Any such exposure may cause irreparable damage to the membrane. Absolute care must be taken following any disinfection of piping or equipment or the preparation of cleaning or storage solutions to ensure that no trace of chlorine is present in the feedwater to the RO membrane elements. If there is any doubt about the presence of chlorine, perform chemical testing. Neutralize any chlorine residual with a sodium bisulfite solution, and ensure adequate mixing and contact time to accomplish complete dechlorination. Dosing rate is 1.8 to 3.0 ppm sodium bisulfite per 1.0 ppm of free chlorine.

Note: It is recommended that all RO membrane cleaning operations should be closely coordinated with Toray Membrane America during the RO membrane element warranty period. TMA field service personnel are available to be on site for cleaning assistance, should the need arise. Please contact TMA for current charges for this service.

Note: The use of cationic surfactant should be avoided in cleaning solutions, since irreversible fouling of the membrane elements may occur.

The nature and rapidity of fouling depends on a number of factors, including:

- quality of the feedwater
- system recovery rate
- element flux

Typically, fouling is progressive, and if not controlled early, will impair the RO membrane element performance in a relatively short time. Cleaning is recommended when

- RO shows evidence of fouling
- Prior to a long-term shutdown.

It is not recommended to clean the elements unless the data indicates there is fouling occurring. If there is no fouling occurring, do not clean!

Fouling characteristics that signal the need to clean are:

- A 10-15% decrease in normalized permeate flow.
- A 10-15% increase in normalized permeate quality.
- A 10-15% increase in normalized pressure drop, as measured between the feed and concentrate headers.

If your facility does not normalize operating data, the site measured values for flows and pressure can be applied instead of normalized values, providing there are no major changes in critical operating parameters. The operating parameters which must remain constant are: feed pressure, permeate back-pressure, recovery, temperature, and feed TDS.
If these operating parameters do fluctuate, it is highly recommended that data be normalized to determine if fouling is occurring or if the RO is actually operating normally based on the change in a critical operating parameter.

Monitoring overall plant performance on a regular basis is an essential step in recognizing when membrane elements are becoming fouled. Performance is affected progressively and in varying degrees, depending on the nature of the foulants. The following table provides a summary of the expected effects that common foulants have on membrane performance.

Cleaning Frequency

RO cleaning frequency due to fouling will vary by site. It may vary from every 6-12 weeks on a high fouling water to 6 –12 months (or longer) on low fouling waters. If cleaning is required more than once a month, then a re-evaluation of the pretreatment stage is justified, with a view to serious improvement and/or a re-design of the RO operation. If the cleaning frequency is every one to three months, you may want to focus on improving the operation of your existing equipment, fine tuning chemical dosage ect.

When to Clean.

It is important to clean the membranes before they become heavily fouled. Allowing the elements to become heavily fouled can impair the effectiveness of the cleaning chemical. Heavy fouling can prevent full penetration of the foulant layer by the cleaner, and impede flushing of the foulant from the elements. If normalized membrane performance drops more than 30 to 50% before cleaning, it may be impossible to fully restore the performance to baseline conditions.

Permeate Flush

One RO design feature that is commonly over-looked in reducing RO cleaning frequency is the use of RO permeate water for flushing foulants from the system. Soaking the RO elements during standby with permeate can help dissolve scale and loosen precipitates, thereby helping to reduce the frequency of chemical cleaning.

Nature of Foulants

The type of foulant present can and does vary from location to location. Frequently more than one foulant is present, necessitating both a low pH and high pH cleaning regimen. Table 1 shows the most usual foulants and types of membrane damage and their results on RO operation,

Type of Foulant/ Problem	Probable Location	Pressure Drop	Feed Pressure	Salt Passage
Metal Oxide Fouling (e.g. Fe,Mn,Cu,Ni,Zn)	1st stage lead elements	Rapid increase	Rapid increase	Rapid Increase
Colloidal Fouling (organic and/or inorganic complexes)	1st stage/ lead elements	Gradual increase	Gradual increase	Slight increase
Mineral Scaling (e.g. Ca, Mg, Ba, Sr)	Last stage/ tail elements	Moderate increase	Slight increase	Marked increase
Polymerized Silica	Last stage/ tail elements	Normal to increased	Increased	Normal to increased
Biological Fouling	Any stage, usually lead	Marked increase	Marked increase	Normal to increased
Organic Fouling (dissolved NOM)	All stages	Gradual Increase	Increased	Decreased
Antiscalant Fouling	2nd stage most severe	Normal to increased	Increased	Normal to increased
Oxidant damage (e.g Cl2, Ozone,KmnO4)	1st stage most severe	Normal to decreased	Decreased	Increased
Hydrolysis damage (out of range pH)	All stages	Normal to decreased	Decreased	Increased
Abrasion damage (carbon fines, etc)	1st stage most severe	Normal to decreased	Decreased	Increased
O-ring leaks (at interconnectors or adapters)	Random (typically at feed adapter)	Normal to decreased	Normal to decreased	Increased
Glue line leaks (due to perm pressure > feed pressure in service or standby)	1st stage most severe	Normal to decreased	Normal to decreased	Increassed
Glue line leaks (due to closed permeate valve while cleaning or flushing)	Tail element of a stage	Increased (based on prior fouling and high delta P	Increased (based on prior fouling and high delta P	Increased

Note: Pressure Drop is defined as the Feed pressure minus the Concentrate pressure

Table 1 Types of foulant, and their usual symptoms

Foulant types and effective cleaners

Calcium Carbonate Scale: Calcium carbonate is a mineral scale that may be deposited from almost any feedwater if there is a failure in the antiscalant/dispersant addition system or in the acid injection pH control system. An early detection of calcium carbonate scaling is essential to prevent damage caused by the crystals on the active membrane layers. Calcium carbonate scale detected early can be removed by lowering the feedwater pH to between 3.0 and 5.0 for one or two hours. Longer resident accumulations of calcium carbonate scale can be removed by a low pH cleaning with a citric acid solution.

Calcium, Barium & Strontium Sulfate Scale: Sulfate scale is a much “harder” mineral scale than calcium carbonate and is therefore more difficult to remove. Sulfate scale may be deposited if there is a failure in the antiscalant/dispersant feed system or if there is an over feed of sulfuric acid in pH adjustment. Early detection of the resulting sulfate scaling is essential to prevent damage caused by the crystals on the active membrane layers. Barium and strontium sulfate scales are particularly difficult to remove as they are insoluble in almost all cleaning solutions. Special care should be taken to prevent their formation.

Calcium Phosphate Scale: This scale is particularly common in municipal wastewaters and water supplies which may contain high levels of phosphate. This scale can generally be removed with acidic pH cleaners.

Metal Oxide/Hydroxide Foulants: Typical metal oxide and metal hydroxide foulants are iron, zinc, manganese, copper, aluminum, etc. They can be the result of corrosion products from unlined pipes and tanks; from oxidation of the soluble metal ion with air, chlorine, ozone, potassium permanganate; or from a pretreatment filter system upset that utilizes iron or aluminum based coagulant aids. Can generally be removed with low pH cleaners

Polymerized Silica Coating: A silica gel coating resulting from the super-saturation and polymerization of soluble silica can be very difficult to remove. It should be noted that this type of silica fouling is different from silica-based colloidal foulants, which may be associated with either metal hydroxides or organic matter. Polymerized silica scale can be very difficult to remove by traditional chemical cleaning methods.

Colloidal Foulants: Colloids are inorganic or mixed inorganic/organic based particles that are suspended in water and will not settle out due to gravity. Colloidal matter typically contains one or more of the following major components: iron, aluminum, silica, sulfur, or organic matter. High pH cleaners are generally more effective against this type of foulant

Dissolved NOM/ Organic Foulants: The sources of dissolved NOM (Natural Organic Matter) foulants are typically derived from the decomposition of vegetative material into surface waters or shallow wells. The chemistry of organic foulants is very complex, with the major organic components being either humic acid or fulvic acid. Dissolved NOMs can quickly foul RO membranes by being absorbed onto the membrane surface. Once absorption has occurred, then a slower fouling process of gel or cake formation begins. It should be noted that the mechanism of fouling with dissolved NOM should not be confused with the mechanism of fouling created by NOM organic material that is bound with colloidal particles. High pH cleaners are generally more effective against this type of foulant. Please note that wastewaters may contain a range of naturally occurring and man-made organic compounds. Should any of these compounds chemically bond to the membrane, cleaning regimes may be ineffective in removing the foulant.

Microbiological Deposits: Organic-based deposits resulting from bacterial slimes, fungi, molds, etc. can be difficult to remove, particularly if the feed path is plugged. Plugging of the feed path makes it difficult to introduce and distribute the cleaning solutions. To inhibit additional growth, it is important to clean and sanitize not only the RO system, but also the pretreatment, piping, dead-legs, etc. High pH cleaners in association with biocide treatments are most effective against this type of problem.

Selection and Use of Cleaning Chemicals

There are a number of factors involved in the selection of a suitable cleaning chemical (or chemicals) and proper cleaning protocol. At the time of the first cleaning, it is recommended to contact:

- Manufacturer of the equipment,
- RO element manufacturer,
- RO specialty chemical and service supplier.

Proper identification of the foulant is essential to prescibe the correct cleaners to most effectively remove the foulant.

Once the suspected foulant(s) are identified, one or more cleaning chemicals will be recommended.
These cleaning chemical(s) can be:

- Generic (typically technical grade, available from local chemical supply companies)
- Private-labeled proprietary chemicals.

Independent RO service companies are available who can determine the proper chemicals and cleaning protocol for your situation by testing a fouled element at their facility. For difficult situations, this is a recommended option.

It is not unusual to use a number of different cleaning chemicals in a specific sequence to achieve the optimum cleaning. As foulants may be laid down in discrete "layers", the sequence of cleaning can be important.

Typically, a low pH cleaning is first used to remove foulants (such as mineral scale), followed by a high pH cleaning to remove organic material. This is not always the case - there are instances where a high pH cleaning may used first to remove foulants like oil or biological matter, followed by a low pH cleaning. The optimum sequence can usually only be determined by conducting tests.

Some cleaning solutions are "combination" agents, and may have detergents added to aid in the removal of heavy biological and organic debris, while others have a chelating agent like EDTA added to aid in the removal of colloidal, organic and biological material, as well as sulfate scale. Advice on the best use of such cleaners is best obtained directly from the manufacturer of the speciality cleaners.

TMA has no objection to the use of speciality cleaners, providing it has been adequately demonstrated that the cleaner will not damage the TMA membrane.

General Precautions in Cleaning Chemical Selection and Usage

- If using a proprietary chemical, be sure the chemical has been qualified for use with the membrane by the chemical supplier. The chemical supplier's instructions should not be in conflict with TMA's recommended cleaning parameters and limits.
- Use the mildest cleaning regimen. This includes the cleaning parameters of pH, temperature, and contact time. This will optimize the useful life of the membrane.
- Clean at the recommended target temperatures to optimize cleaning efficiency and membrane life.
- Use the minimal amount of chemical contact time to optimize membrane life.
- Be prudent in the adjustment of pH at the low and high pH range to extend the useful life of the membrane. A "gentle" pH range is 4 to 10, while the harshest is 2 to 12.
- Typically, the most effective cleaning sequence is low pH followed by high pH solutions. One known exception is oil-fouled membranes should not use a low pH clean first as the oil will coagulate.
- Cleaning and flushing flows should be in the same direction as the normal feed flow to avoid potential telescoping and element damage.

- When cleaning a multi-stage RO, the most effective cleaning plan is to clean one bank/stage at a time so cleaning flow velocities can be optimized and foulants from upstream stages will not pass through to downstream stages.
- Flushing detergents with higher pH permeate can reduce any foaming problems.
- Verify that proper disposal requirements for the cleaning solution are followed.
- If the system has been fouled biologically, consider the extra step of introducing a sanitizing biocide chemical after a successful cleaning. Biocides can be introduced
    - immediately after cleaning,
    - periodically (e.g. once a week),
    - continuously during service.
- Ensure that the biocide is compatible with the membrane, does not create any health risks, is effective in controlling biological activity, and is not cost prohibitive before going this route.
- Safety Considerations
    - Be sure all hoses and piping can handle the temperatures, pressures and pH which will be encountered during a cleaning.
    - Always add chemicals slowly to an agitated batch of make-up water.
    - Always wear safety glasses and appropriate protective gear when working with chemicals.
    - Don't mix concentrated acids with caustic solutions.
    - Thoroughly rinse the 1st cleaning solution from the RO system before introducing the next solution.

pH and Temperature Limits for Cleaning TMA

Membrane Type	**45 C (113 F)**	**35 C (95 F)**	**30 C (86 F)**
Brackish ("7 "and "L")	2-10	2-11.5	2-12
Low Pressure Brackish ("G" And "H")	2-10	2-11.5	2-12
Seawater	2-10	2-11	2-12

Note: The above cleaning parameters denote the maximum temperature limits for a corresponding range of pH. Cleaning operations performed at the extremes may result in a more effective cleaning, but can shorten the useful life of the membrane due to hydrolysis.effects. To optimize the useful life of a membrane, it is recommended to use the least harsh cleaning solutions necessary and to minimize the contact time whenever possible.

Cleaning and Flushing Flow Rates per RO Pressure Tube
(differential Pressures are not to exceed 60 psi (4 bar) across any tube.)

Element Diameter	GPM	LPM
4-inches	6 to 10	23 to 38
8-inches	24 to 40	91 to 151

Elements should be cleaned at the highest flow rate possible without exceeding 60 psi differential pressure limit. Exceeding the limit can result in mechanical damage to the elements.

Cleaning Solution Volume Requirement per RO Element
(This volume does not include additional volumes required for piping, filters, etc. or the initial 20% of volume dumped to drain.)

Element Size	Normal Fouling (Gallons)	Heavy Fouling (Gallons)	Normal Fouling (Liters)	Heavy Fouling (Liters)
4 x 40 inches	2.5	5	9.5	19
8 x 40 inches	9	18	34	68

Cleaning Tank sizing

Required volume of cleaning solution can be estimated as follows:

1. Cleaning solution requirement per element (see above) x number of elements to be cleaned

Plus

2. Swept volume of connecting pipework to and from cleaning skid

Plus

3. Extra 20% of (1+2) above for first part of cleaning solution sent to drain

RO Cleaning Skid

The successful cleaning of an RO on-site requires a well designed RO cleaning skid. See Figure 1 for a typical arrangement. The skid may or may not be hard piped to the RO skid and may use flexible hose for connections to the RO skid. For a multi-stage RO, it is recommended that each bank/array be cleaned one stage at a time to optimize cross-flow cleaning velocity.

The source water for chemical solution make-up and rinsing should be clean RO permeate or DI water and be free of hardness, transition metals (e.g. iron), and chlorine..

RO Cleaning Tank:
This tank needs to be sized properly to accommodate the displacement of water in the hose, piping, and RO elements. (see above).The tank should be designed to:

- Allow 100 % drainage
- easy access for chemical introduction and mixing
- recirculation line from the RO Cleaning Pump,
- proper venting,
- overflow,
- return line located near the bottom to minimize foam formation when using a surfactant.

RO Cleaning Pump:
This pump needs to be sized to develop the proper cross-flow velocity to scrub the membrane clean. The maximum recommended pressure is 60 psi (4 bar) at the inlet to the pressure vessels to minimize the production of permeate during cleaning and so reduce the convective re-deposition of foulant back on the membrane surface. The table above gives the recommended flow rate ranges for each pressure tube.

RO Cleaning Cartridge Filter:
Normally 5 to 10-micron and is designed to remove foulants that have been displaced from the cleaning process. Filter must be located upstream of the RO elements.

RO Tank Heater or Cooler:
The maximum design temperature for cleaning is 113° F (45° C). It should be noted that heat is generated and imparted by the RO Cleaning Pump during recirculation which can act as a heater,

RO Tank Mixer: This component is recommended for optimal mixing of chemical, though some designers rely solely on the slow introduction of chemical while maintaining a recirculation through the RO Cleaning Pump back to the tank.

Instrumentation: Cleaning system instrumentation should be included to monitor flow, temperature, pressure, and tank level.

Sample Points:
Sample valves should be located to allow pH and TDS measurements off the RO Cleaning Pump discharge and the concentrate side recirculation return line.

Permeate Return Line:
A small amount of the cleaning solution can permeate through the membranes, therefore a permeate-side return line back to the RO Cleaning Tank is required. Important: The permeate line and any permeate valves must always be open to atmospheric pressure during the cleaning and flushing steps or damage to RO elements can occur. If the permeate line is closed, the permeate pressure can build up and become higher than the feed-side pressure of the tail elements. This can result in excessive permeate back-pressure which can damage the membrane glue lines in the tail elements.

RO Membrane Element Cleaning and Flushing Procedures

The RO membrane elements can be cleaned in place in the pressure tubes by recirculating the cleaning solution across the high-pressure side of the membrane at low pressure and relatively high flow. A cleaning unit is needed to accomplish this task. See fig 1 for general arrangement.

RO cleaning procedures may vary dependent on the situation. The time required to clean a stage is from 4 to 8 hours. A general procedure for cleaning the RO membrane elements is as follows:

1. Perform a low pressure flush at 60 psi (4 bar) or less of the pressure tubes by pumping clean water from the cleaning tank (or equivalent source) through the pressure tubes to drain for several minutes. Flush water should be clean water of RO permeate or DI quality and be free of hardness, transition metals, and chlorine.
2. Mix a fresh batch of the selected cleaning solution in the cleaning tank. The dilution water should be clean water of RO permeate or DI quality and be free of hardness, transition metals, and chlorine. The temperature and pH should be adjusted to their target levels.
3. Start recirculation. Initially send the displaced water from the system to drain so y cleaning chemical is not diluted. Then divert the first 20%of the returned cleaning solution (the most highly fouled cleaning solution) to drain before allowing the remaining cleaning solution to recirculate back into the RO Cleaning Tank. For the first 5 minutes, slowly throttle the flow rate to 1/3 of the maximum design flow rate. This is to minimize the potential plugging of the feed path with a large amount of dislodged foulant.. For the second 5 minutes, increase the flow rate to 2/3 of the maximum design flow rate, and then increase the flow rate to the maximum design flow rate. If required, readjust the pH back to the target when it changes more than 0.5 pH units. Circulate the cleaning solution through the pressure tubes for approximately one hour or as required.
4. An optional soak and recirculation sequence can be used, if required. The soak time can be from 1 to 8 hours depending on the manufacturer's

recommendations. Caution should be used to maintain the proper temperature and pH.

5. Upon completion of the chemical cleaning step, a low pressure cleaning rinse with clean water (RO permeate or DI quality and free of hardness, transition metals, and chlorine) is required to remove all traces of chemical from the Cleaning Skid and the RO Skid. Drain and flush the cleaning tank; then completely refill the Cleaning Tank with clean water for the Cleaning Rinse. Rinse the pressure tubes by pumping all of the rinse water from the Cleaning Tank through the pressure tubes to drain. A second cleaning can be started at this point, if required.
6. Once the RO system is fully rinsed of cleaning chemical with clean water from the Cleaning Tank, a final low pressure clean-up flush can be performed using pretreated feedwater.The permeate line should remain open to drain. Feed pressure should be less than 60 psi (4bar). This final flush continues until the flush water flows clean and is free of any foam or residues of cleaning agents. This usually takes 15 to 60 minutes. The operator should sample the flush water going to the drain for detergent removal and lack of foaming by using a clear flask and shaking it. A conductivity meter can be used to test for removal of cleaning chemicals. The flush water to drain should be within 10-20% of the feedwater conductivity.A pH meter can also be used to compare the flush water to drain to the feed pH.
7. Once all the stages of a train are cleaned and the chemicals flushed out, the RO can be restarted and placed into a Service Rinse. The RO permeate should be diverted to drain until it meets the quality requirements of the process (e.g. conductivity, pH, etc.). It is not unusual to take a period from a few hours to a few days for the RO permeate quality to fully stabilize, especially after high pH or very low pH cleanings..

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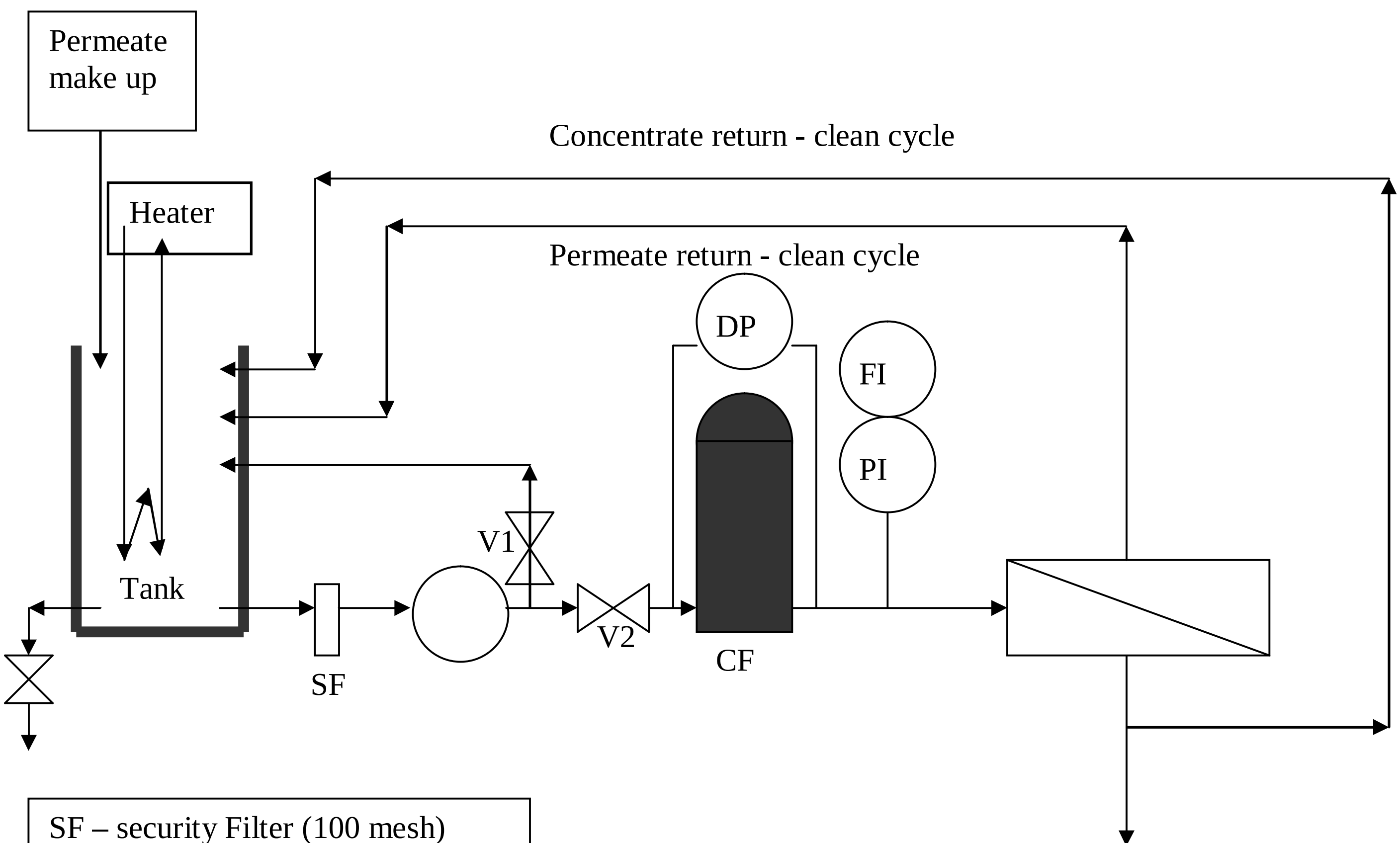

SF – security Filter (100 mesh)
CF – cartridge filter 5-10 um
V1 – Pump recirc valve
V2 – Flow Control valve
PI – Pressure indicator
FI – Flow indicator
DP – Differential pressure indicator

Figure 1: Typical Cleaning skid arrangement