



FILMTEC Membranes

FILMTEC Membrane Chemical Compatibility Testing Guidelines

Summary

Chemicals are usually added to membrane systems to prevent and remove biogrowth and to prevent membrane fouling and scaling. These chemicals must not, by themselves, negatively affect the membrane performance. The following describes some of the testing procedures that are used to identify whether or not these chemicals are compatible with thin film composite membranes. These test procedures, specifically, are designed to indicate whether or not the chemical either dissolves or alters the polyamide surface of the membrane or whether the flow of product water through the membrane is affected.

Test procedures involve either 1) the testing of membrane coupons or elements after soaking in the examined solution or 2) the continuous addition of the chemical to the membrane element during operation. Soak tests are useful in determining whether a chemical compound degrades the membrane. Meanwhile, the continuous addition of a chemical to the membrane element during operation is a means to simulate actual operating conditions using the test chemical. For example, in antiscalant compatibility determinations, a 1000-hour continuous operation test is recommended.

It is important to note that the following procedures examine only if the chemical appears to be compatible and whether detrimental effects are observed. These procedures do not determine efficacy or whether chemical has been proven useful. Also, even though the following tests are indication of compatibility, field observations and experience are, by far, the most reliable indication of compatibility and success.

It is important to note, that other test methods on compatibility determinations have been successful. Some of these methods developed by suppliers of membrane chemicals include such techniques as exposing the membrane to elevated levels of a particular chemical for a shorter period of time rather than at a normal use level for a longer period of time. Hence, the exposure in, for example, ppm-hours is the same. Other methods include examination of the membrane surface by microscopy and/or other analytical techniques that ascertain changes in or damage to the membrane. Such methods are often reliable when practiced by experienced personnel with a firm grasp of membrane technology and the chemistry of their products.

Even though a chemical may be determined to be compatible, it is no indication that problems will not occur. For example, gross overfeeding of a particular chemical can foul all types of membranes through the convective deposition of a large amount of chemical onto the membrane surface. This idea can be extended to the compatibility of a particular product at a low level which may cause catastrophic effects at higher levels through its inadvertent high level addition by such practices as its continuous addition independent of whether the membrane system is in operation or not. Also, a compatible chemical may be incompatible with other chemicals used in the system. For example, cationic flocculants often can foul a membrane by their reaction with negatively charged antiscalants. Hence, it is imperative that one consider the total membrane chemical addition system and the proper integration of the various chemical products in the membrane system. Also it is important to determine whether the chemical is compatible with the materials of construction used in storage and handling equipment.

The following discussions address testing procedures for chemical compatibility in each of the following five categories:

- coagulants and flocculants
- antiscalants
- cleaning chemicals
- biocides
- membrane preservatives

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Details – Test Equipment and Specific Test Procedures

Test Equipment

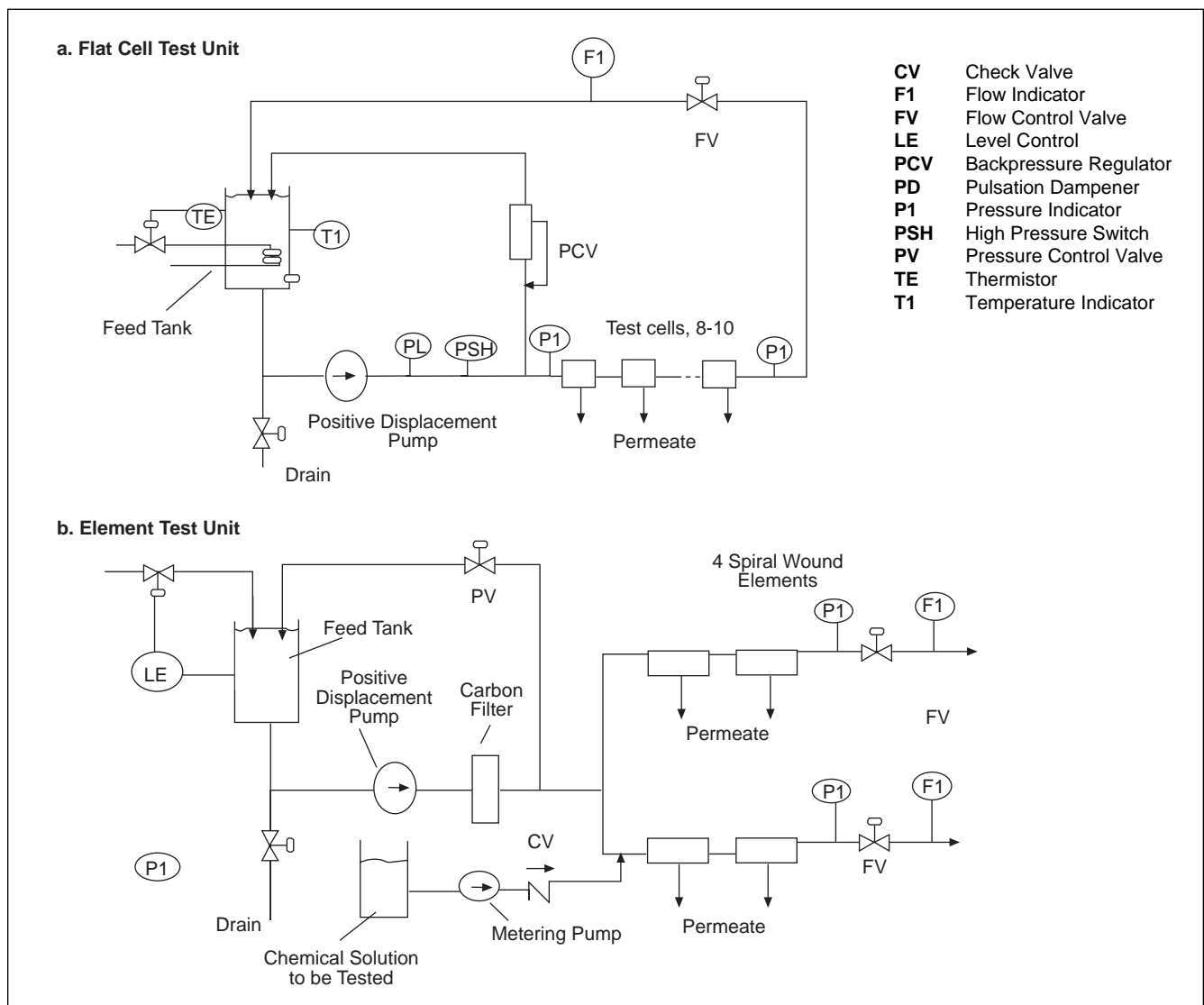
Flat Cell Unit. Two types of test loops have been used for laboratory chemical compatibility testing. The first one has many flat cells in series, 8-10, where flat sheet membrane coupons are tested. The flow schematic is shown in Fig. 1a. A test cell could be shut off by closing a ball valve on the permeate side. Testing could also be done on a stacked membrane plate and frame apparatus with a system design similar to the schematic in Fig. 1a.

Standard test conditions for the FILMTEC® membrane is 2000 ppm sodium chloride at 25°C with feed at about 1550 kPa (225 psi) gage pressure. Measurements are taken about two hours after start. The brine flow rate is will depend upon the specific test cells used and should conform to recommendations of the test cell supplier.

As shown in Fig. 1a, the concentrate is returned to the feed tank. The permeate is directed to a drain except for the 10-30 minutes, when it is collected in a beaker for measuring permeate flow rate.

A source for flat test cells is Osmonics at www.osmonics.com/products/Page489.htm.

Figure 1



Element Test Units. Fig. 1b shows the flow schematic of the second test loop. It contains two parallel lines, each consisting of two pressure vessels in series. Small elements, such as 2.5 inch diameter by 14 inches long are often used for these tests. A metering pump adds the chemical which is tested for membrane compatibility to one of two parallel lines. The concentrates and permeates from both lines go to drain. There are two elements per line. If something in the feed water is affecting the membrane performance, this should be noticeable for the elements in *both* lines. With this type of apparatus, one is better able to establish an effect level due to the presence of a “standard” line and a “test” line. This type of laboratory device can be expanded to, for example, a system using 8" FILMTEC membranes elements operated off a side stream in a full scale membrane water treatment unit. The same schematic as shown in Fig. 1b could be used.

In laboratory tests, feed is softened tap water with typical anion concentrations of 300 mg/l bicarbonate, 15 mg/l chloride and 11 mg/l sulfate and conductivity 550 microS/cm. It also contains about 0.8 ppm free chlorine, which is removed by the carbon filter. Feed and permeate conductivities are measured and it is assumed that the conductivities are made up from sodium bicarbonate alone. Gage pressure is in the range of 350-400 kPa (50-80 psi), resulting in a fairly low permeate flux making it possible to operate with a fairly low water and chemical consumption. Typical feed flow rate per line has been about 0.2-0.4 l/minute. The feed water temperature is fairly constant, so there is no need for temperature control.

If the line gage pressure is above 350 kPa (50 psi) most of the time, there is no need for the feed tank or pump.

Antiscalants

A suitable antiscalant must pass two tests, a microbiological growth test and a membrane compatibility test.

Microbiological Growth Test. An antiscalant is typically transported in concentrated form. It is diluted in a tank from where it is added to the feed water to the membrane unit. It is important that there is no microbiological growth in the antiscalant solution entering the membrane unit. Typically there is no growth in the concentrated antiscalant solution, but there can be growth when it is diluted below a certain concentration. To determine minimum concentration of antiscalant in the dilution tank, a microbiological growth test is carried out. This is normally performed by the antiscalant manufacturer.

The antiscalant is diluted with chlorine-free water to different concentrations in beakers, which are stored for one month. Typical concentrations are 1, 6, 10 and 25 percent as supplied. A beaker with chlorine-free water is used as control. Either the solutions are inoculated with microorganisms or the beakers are open to the air for “natural” inoculations. Microbial plate counts are taken once weekly during the one-month storage time. The lowest concentration of antiscalant for which there is a decline in plate counts with time will be the lowest concentration in the dilution tank for which the antiscalant is approved.

Preferably, the microbiological test is carried out before the 1000-hour membrane compatibility test which is described below. The reason for this is that if there is a change in the biocide composition in the antiscalant, the membrane compatibility test has to be repeated.

Membrane Compatibility Test. For an antiscalant to be considered compatible for use, the antiscalant must be fed to spiral wound elements containing the membrane for 1000 hours without loss of performance. A setup as shown in Fig. 1b, or similar system, would be satisfactory for such a determination. Initially one must establish a baseline. This is achieved by operating the system for at least 12 hours without chemical addition. The test can not be considered valid if the permeate flow rate is more than 15 percent below the expected value for a clean membrane. The baseline for a membrane is established without antiscalant with a test using a 2000 ppm sodium chloride solution at 25°C and 130 psi (0.9 Mpa).

After the baseline is established, the antiscalant is then added continuously for at least 1000 hours. The normalized permeate flow and salt passage or rejection should remain relatively constant during this time for the chemical to be deemed compatible. The upper concentration limit for compatibility will be the maximum concentration of the chemical in the concentration stream.

Coagulants and Flocculants

Coagulants and flocculants have been tested in the setup shown in Fig. 1b. The elements are first operated with softened tap water for at least a day to ascertain that they are stabilized. Then the chemical to be compatibility tested is added to the feed water to one of the two parallel lines to make up about a 5 ppm solution. If chemical addition for one week does not significantly affect the element normalized permeate rate or salt passage, the chemical is considered satisfactory.

In general, coagulants and flocculants may interfere with membranes either directly or indirectly. Indirect interference occurs when the compound forms a precipitate which is deposited on the membrane. For example, channeling of the media filter may enable flocs to pass through and become deposited on the membrane. A precipitate can also be formed when concentrating the treated feedwater, such as when aluminum or ferric coagulants are added without subsequently lowering pH to avoid supersaturation in the system itself. Furthermore, a reaction with a compound added after the media filter can cause a precipitate to form. This is most noticeable with antiscalants. Nearly all antiscalants are negatively charged and will react with cationic coagulants or flocculants present in the water. Several systems have been heavily fouled by gel formed by the reaction between cationic polyelectrolytes and antiscalants. Therefore, it is important to test all coagulants and flocculants based on the possibility that some of these products will come into contact with the antiscalant.

Direct interference occurs when the compound itself affects the membrane resulting in a flux loss. The ionic strength of the water may have an effect on the interference of the coagulant or flocculant with the membrane. To minimize the risk of direct or indirect interference with the membrane, anionic or nonionic flocculants are preferred rather than cationic ones. Overdosing must be avoided.

Cleaning Chemicals

As one would expect, cleaning chemicals can be used at a wide range of conditions such as cleaning frequency, cleaning time and temperature. Due to this ambiguity, the discussions on cleaning chemicals will be based on a cleaning frequency in the order of once a month or less.

The flat cell test loop, as shown in Fig. 1a, with membrane coupons has been used for cleaning chemical compatibility tests.

A cleaning chemical that provides excellent cleaning performance may also degrade a membrane resulting in a decrease in the salt rejection of the membrane with time. This degradation might not be visible after only one cleaning. For determining cleaning chemical compatibility, membrane coupons (at least three) are soaked in the normal strength cleaning solution for two weeks and then tested at standard test conditions. Ideally, the temperature of the soak solution should be the maximum allowed cleaning temperature.

A cleaning chemical is considered compatible if a two-hour cleaning does not lower the membrane flux or salt rejection *and* a two-week soak test does not lower the salt rejection.

The salt used for performance testing of the FILMTEC membrane is 2000 ppm sodium chloride. The steps for the Two-Hour Cleaning Test and the Two-Week Soak Test in Cleaning Solution are listed as follows:

Two-Hour Cleaning Test

1. Test the membrane at standard test conditions (225 psi, 25°C, 2000 ppm sodium chloride).
2. Clean with double the normal strength of the cleaning solution by circulating the solution over the membrane at recommended cleaning temperatures and 50 psig for two hours.
3. Rinse out the cleaning solution. Use low conductivity water for this to be able to check that both permeate side and brine side of the membranes have been rinsed out effectively.
4. Retest at the standard test conditions. Flux loss shall be less than five percent and there should be no increase in salt passage compared to the initial test in item 1 above.

Two-Week Soak in Cleaning Solution

1. Test the membrane at standard test conditions (225 psi, 25°C, 2000 ppm sodium chloride).
2. Soak the membrane in normal strength cleaning solution at normal cleaning temperature for two weeks.
3. Rinse out the cleaning solution. Use low conductivity water for this to be able to check that both permeate side and brine side of the membranes have been rinsed out effectively.
4. Repeat at test conditions according to item 1 above. There shall be no increase in salt passage compared to the initial test in item 1 above.

Biocides

Like cleaning chemicals, biocides can cause the membrane to lose salt rejection and/or water permeability. Biocides possibly could be in contact with the membrane continuously for a long period, e.g., biocides used for membrane storage or continuous addition to feed water, or added intermittently, e.g., biocides used for periodical disinfection or “shock” treatments. A satisfactory biocide must not negatively affect the membrane performance during one-year contact. Like other compatibility tests, both “soak tests” and “continuous tests” are often completed to determine chemical compatibility and satisfactory performance.

An initial one-week test observing the effect of the continuous addition of a biocide on the water permeability of the membrane is often recommended. If the result is that the biocide has no negative effect on the water permeability of the membrane, a one-year soak test is then carried out.

An alternative, used more extensively in recent years, is a 1000-hour continuous compatibility test similar to that of antiscalant testing.

All biocide tests are generally carried out at 20-25°C. The solution pH might have an influence on how the biocide affects the membrane, especially when the molecular structure of the biocide changes with pH or when an oxidation reaction might take place.

Option 1

One-Week Continuous Operation Test. The continuous operation test is required when the water permeability of the membrane decreases during the soak test, which has been the case for almost all tested biocides. The test unit in Fig. 1b is used for the continuous operation test. The elements are operated for at least one day before the biocide is added to make certain that the elements are stabilized.

After the elements are stabilized, the biocide is added to the feed water to make up the maximum concentration for which the biocide will be approved. If there is no significant decrease in water permeability or salt rejection during one week of continuous biocide addition, the biocide is assumed to be a good candidate in not affecting the water permeability of the membrane and the longer term "soak test" can then be pursued.

Soak Test. The biocide solutions to be tested are placed into glass jars with lids. The concentration of the biocide is the maximum approval concentration. As controls, a jar with standard storage solution (1 percent sodium bisulfite solution) and an empty jar are used. About 20 coupons of each membrane type, to be tested, are placed in each jar. Two coupons of each type membrane from each jar are tested after a soak time of:

1. 1 week
2. 2 weeks
3. 4 weeks
4. 2 months
5. 4 months
6. 6 months
7. 1 year

The coupons are used only once and are discarded after the test. Some biocide solutions have a shorter lifetime than one year and these must be replaced with fresh biocide solution at suitable interim intervals.

If the salt passage of the membrane soaked in the biocide solution for one year has not increased significantly, the biocide is assumed not to degrade the membrane.

The combined data from the one year soak test and one week continuous operation test often is enough for a decision whether to determine if a biocide is compatible. However, if one or the other test indicates questionable results, a long term continuous operation test is required, either in the laboratory or in the field.

In cases where the biocide will only be used intermittently, for example, once a week for a few hours such as in a "shock treatment", it may *not* be necessary to do the one-year soak test. The continuous test hours of exposure for the expected life of the membrane at the biocide dosage level may be sufficient. For example, if a biocide is used for 30 minutes per week at 400 ppm, a continuous test at 400 ppm for 130 hours (30 min/week x 52 weeks /yr. x 5 years) may be sufficient.

Option II

1000-Hour Continuous Operation Test. Similar to the test for antiscalants, for a biocide can to be considered compatible, the biocide must be fed to spiral wound elements containing the membrane for 1000 hours without loss of performance. Based upon recent experience, this test appears to be preferred despite its greater time requirement. A setup as shown in Fig. 1b is satisfactory for such a determination. Initially one must establish a baseline. This is achieved by operating the system for at least 12 hours without chemical addition. Normally, the test can not be considered valid if the permeate flow rate is more than 15 percent below the expected value for a clean membrane. For the FILMTEC membrane, this permeate flow rate is 24 gfd +/-15 percent using a 2000 ppm sodium chloride solution at 25°C and 225 psi (0.9 Mpa)

After the baseline is established, the biocide is then added continuously for at least 1000 hours. The normalized permeate flow and salt passage should remain relatively constant during this time for the chemical to be deemed compatible. The upper concentration limit for compatibility will be the maximum concentration of the chemical in the concentration stream.

FILMTEC Membranes

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Membrane Preservatives

Membrane preservatives are biocide solutions used to prevent biogrowth and change in membrane performance during extended storage times. Thus, the biocide used must have a long lifetime. Surfactants and/or humectants are often present in the solution to keep the membrane wet. Consequently, any of those compounds could affect the membrane negatively either in directly or indirectly by interacting with other parts of the element and the formation of compounds harmful to the membrane.

A compatible membrane preservative should not exhibit any significant decrease in water permeability or salt rejection properties of the membrane element during one year storage. A means to perform the test is to store five tested elements fully immersed in the storage solution and test one of them after 2, 4, 6 and 12 months storage. A new element is tested each time and is returned to the storage solution following the test. The fifth element is included in the test as a spare to use if the test data of any of the other elements is in doubt. Two elements stored in the present storage solution, one percent sodium bisulfite, should be used as controls. These are tested at the same time as any one of the other five elements. If the membrane performance in the preservative solution is maintained, the same test should continue for years with element test once or twice yearly to learn about the lifetime of the storage solution.

Before wet elements are stored, the elements are initially soaked in the storage solution for about one hour and then drained and bagged. There should not be any biological growth in the bag or deterioration of the bagged elements performance during the shelf life of the storage solution. To examine whether another membrane preservative solution can be used for bagged element storage, elements are tested and then soaked for 1, 2 or 20 hours in the membrane preservative solution. Then the elements are drained and bagged. After 2, 6, 12, 18, 24, 36 and 48 months storage, two elements from each soak time are taken out from their bags. Microbial plate counts are taken of the storage solution in the bag, and the elements are tested. The element performance is measured both before and after permeate pressure is applied to determine whether the membrane dries when stored. Permeate pressure is most easily applied by shutting the permeate port at a feed pressure of at least 1000 kPa (150 psi) pressure above the osmotic pressure of the feed solution. Three soak times, seven test times, and duplicate elements, result in 42 elements per storage solution to test. To save storage space, small elements are often used. Again, the one percent sodium bisulfite solution is used as a control. Since one-hour soak time is sufficient for the control, only 14 control elements are required.

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