American Membrane Technology Association

America's Authority in Membrane Treatment

Ceramic Membranes

Membrane Filtration

Membrane filtration is becoming the technology of choice in liquid separations around the world for applications including desalination pretreatment, removal of suspended solids from water and wastewater, membrane bioreactors (MBR), as well as food and beverage processing. Most of the membranes produced today have a polymeric barrier layer but ceramic membranes are now available for many applications.

Ceramic Membranes

Ceramic membranes bring the porosity expected for microfiltration/ ultrafiltration (MF/UF) separation along with the added features of a durable material with high chemical, temperature and pressure tolerance. Ceramic membranes offer proven lifecycles up to 20 years or more and are used in potable water treatment, food and dairy industry, chemical industry and waste water treatment applications. In addition, there are a number of liquid separations that have very demanding conditions, and within those realms, ceramic membranes are being used extensively.

Membrane Material

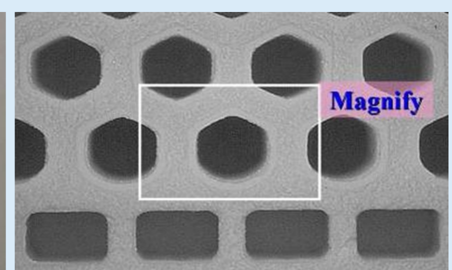
Ceramic membranes utilize a porous support such as alpha alumina or silicon carbide covered with a porous inorganic membrane layer of aluminum oxide, titanium oxide, zirconium oxide or silicon carbide rather than a polymeric barrier layer. The tubular, flat sheet, monolithic or hollow fiber support is made by extrusion, and then multiple layers of the ceramic membrane material are applied. Flat sheet membrane elements typically have the membrane coating on the outside and tubular membrane elements typically have several flow channels in the structure with the membrane coatings on the inside. Nitrides and carbides of similar metals may also be used as the barrier layer. The combined support structure and membrane layer is often referred to as a "membrane element" or ceramic element.

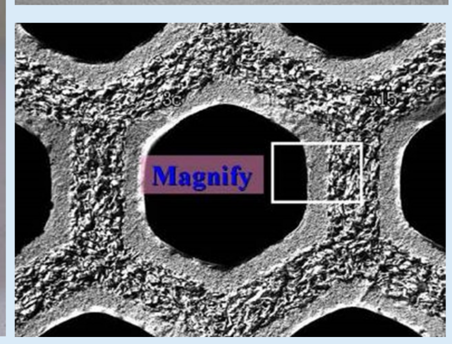
Pore Sizes, Channel Diameters and Active Area

The porous membrane layer will have distinct pores ranging from open microfiltration (1,4µm) to tight UF (1kD) and even nanofiltration (250D). Ceramic monolithic elements have multiple passageways or channels for the feed fluid to flow through the element or pass through the hollow fiber. Flat sheet ceramic membranes are submerged in the fluid and clean water is drawn through the membrane.

Ceramic elements come in different dimensions that can be beneficial for different applications. Some tubular types may be as long as 1,500 mm (5 feet) long. Diameters vary also and typically range from 20 to 200 mm. Filter channels can range from one very wide channel in an element to 100s of very narrow channels with inside diameters ranging from 1.0 - 25 mm (0.6 – 1.0 inches). Flat membranes can have up to 6 ft2 of surface area per sheet.

The diameter of the feed channels, its shape, the channel length and the number of channels per element will impact the membrane surface area of a ceramic element. Ceramic membrane elements of various shapes, diameters and lengths can have surface areas typically ranging from several ft 2 to nearly 300 ft 2. There can be one or up





to several thousand ceramic membrane elements in a membrane module.

Membrane & Process Variations

Ceramic membranes are available in flat sheet, monolithic, hollow fiber and multichannel tubular elements. Flat sheet ceramic membranes are typically outside-in flow; monolithic, hollow fiber and multichannel elements are typically inside-out in dead end or cross flow configuration. The filtrate is collected as it exits the exterior surface of the porous material (element). There are some models of ceramic membranes elements with slots built into the monolith that collect filtrate and direct it to the outside of the element. The channel diameter chosen is adapted to the viscosity or TSS of the liquid to be treated. A pressurized feed stream can run from the inlet end to an outlet face in a cross-flow arrangement. Ceramic membranes used for drinking water applications are both flat sheet, outside in, as well as multichannel inside-out running in either dead end and cross flow modes of operation. Flat sheet ceramic membranes have also been used for drinking water, MBR and sludge dewatering applications.

Flow Patterns

In some dead end flow configurations, the membrane is run in an inside-out mode with the feed flowing inside the passageway and filtrate recovered on the outside of the membrane. As the solids accumulate at the membrane surface, the flow rate will drop off at constant pressure, or the transmembrane pressure will increase at constant flow, until a backwash with water or compressed air is required. A backwash drives the filter cake off the membrane surface and produces a concentrated stream of solids for disposal or recycling to the front of the process. Chemically enhanced backwash and even clean-in place efforts with acids, alkalis and bleach restore the membrane filter for repeated reuse. There are other ceramic systems that do not use backwash and have been in operation for over twenty years, employing alternatives like back pulse, air sparging and dynamic shock.

Flux rates of tens to thousands of gfd are being realized in operating systems. One manufacturer reports Marker based Direct Integrity Test (DIT) challenge tests for ceramic membranes used for surface water to potable and have run challenge tests at 2,000 gfd. Another has NSF419 approval for DIT Challenge similar to polymeric membranes. Ceramics are very hydrophilic and therefore have high water permeability.

Pretreatment

Some ceramic membrane systems may need some degree of pretreatment to reduce the load on the membrane plant or remove excess oil from the feed stream. High concentrations of small particulates, fibers and other items can block the feed channels and were found to erode the matrix when the wrong type or configuration of ceramic element was used. Some synthetic oils and grease may be difficult to remove from the matrix. Pretreatment methods might include centrifugation or coagulation/flocculation settlement to remove large particles or skim off free oil. Submerged flat-sheet ceramic membranes and tubular membranes tend to be usable with higher solids and oil concentrations. Similar to polymeric membranes, ceramic flat-sheet membranes used for MBR applications typically require a 2mm pre-screen.

Equipment and Skids

Additional equipment for a ceramic membrane process might include an air compressor to assist air scours (for submerged ceramic flat sheets) and backwashing, as well as chemical make-up tanks. Air scour for ceramic flat plates is not required in all cases and there are municipal systems in operation without air scour. Some ceramic membrane manufacturers have developed process designs so that they can operate like most other pressurized polymeric membranes and can fit into the open platform design concepts utilized by several equipment OEM's. There are now cases of a ceramic membrane module retrofitting into an existing polymeric membrane system and for the most part, utilizing the existing infrastructure of piping, controls, and backwash pumps.

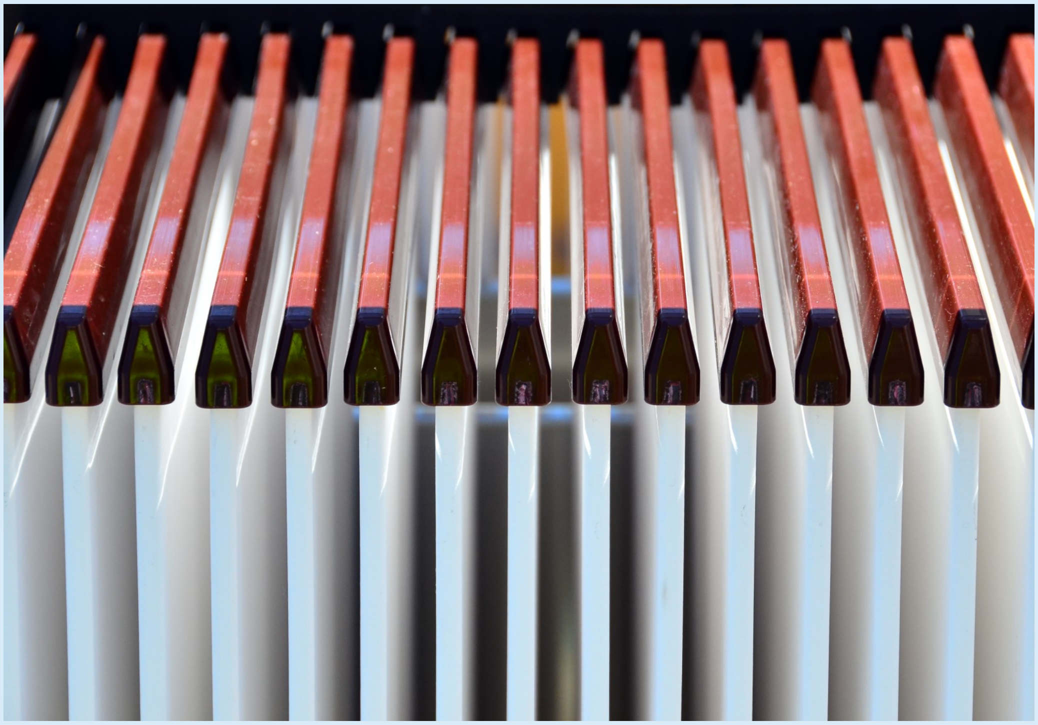
The ability to position more membrane elements in a module and more modules in a system can reduce the CAPEX required for a given system. There are modularized, skidded systems for ceramic membranes which provide a significant reduction in installed costs. Some of the manufacturers of ceramic membrane systems sell or rent pilot equipment.

Ceramic Membranes, Advantages, Disadvantages and Applications

Advantages

Like other ultrafiltration and microfiltration membrane products, ceramic membranes offer reliable operation with a positive barrier against water quality upsets. They are mechanically strong and can be used in applications where there is increased oil and suspended solids in the feed. They are also abrasion resistant. Ceramic membranes are durable with a resistance to degradation by a wide range of chemicals and chemical concentrations, which allows more aggressive chemical cleaning procedures to be used over a pH range of 0-14. Ceramic membranes have a high resistance to ozone and chlorine, which allows for their use for disinfecting raw water prior to membranes These membranes are thermally stable and can withstand temperatures up to several hundred ºF. Some of the limitations for ceramic membranes apply only to the gaskets and other module materials, and not necessarily to the ceramics. In all cases consideration should be given to the type of ceramic material used.

High flux rates can be achieved with ceramic membranes since they can tolerate higher cross flow, which allows for extended process runs, resulting in a lower TMP for a given flux. Ceramic membranes have very high thermal stability and pressure tolerances, with working conditions mostly limited by the sealing materials and vessel/module structures.



Ceramic membranes can have a high packing density like a hollow fiber module.

As with microfiltration and ultrafiltration operations, ceramic membranes will remove disinfection by-product (DBP) precursors from surface water supply sources with proper coagulation, and with or without flocculation. They can also remove suspended solids at a ≥ 98% filtrate water recovery rate. Ceramic membranes provide an absolute barrier against upsets or surges in fluctuating raw water quality, which is characterized by a rapid increase of suspended solids and oils. Reduction or elimination of filtrate losses is made possible by minimizing or eliminating some of the separation steps needed in conventional processes. Ceramic membranes do not need to stay wet like polymeric membranes; they can be drained, removed from use and then restarted after being out of service.

A feature mentioned for ceramic membranes is the possibility of reusing the membrane material itself. Due to the materials of construction, in some cases, used ceramic membranes could be recycled as raw ceramic material to make other products. This could reduce disposal costs and eliminate landfill issues

Energy requirements of ceramic membranes may be less than other membrane separations. Lifecycle costs and capital costs can be competitive, or better than, polymeric membranes. Advances in ceramic membrane technology and processes offer greater energy efficiency, reduction in cleaning requirements, minimization of chemical usage and elimination of filtrate losses, which contributes to lifecycle costs in favor of ceramic membranes.

There have been reports of ceramic membranes with 18 years of operation, with little loss in permeability. In some cases, manufacturers may offer a 20-year warranty.

In rare cases, if chemical cleaning does not work effectively, the ceramic elements can be heated in an external oven by the membrane manufacturer to burn off the contaminants.

Disadvantages

Ceramic membranes have many useful properties, but the economics due to historically higher capital costs for the membranes and their system type must be considered and compared against recent advancements in cost reduction. There are a limited number of full-scale installations for potable water treatment and municipal MBR. Ceramic systems that can operate at half the CAPEX and OPEX of polymeric membrane processes are being promoted in the industry and deserve attention.

Claims of extended life cycles are inviting, but there are some possible methods for ceramic membrane degradation, including the possibility of chemical attack (very limited and mainly by fluoric acid), and thermal shock of the matrix. An advantage of ceramic membranes is the ability to heat the matrix to restore flow. However, too rapid a change in temperature, such as the introduction of a cold liquid, can result in thermal shattering of some of the ceramic materials and destruction of the element. Limits of no more than a 30ºC temperature differential and controlled heating or cooling rates are to be followed as recommended by certain manufacturers. Careful operating controls can minimize this risk. Generally, ceramic membranes are not to be frozen, although there are some exceptions with some specific designs.

Certain ceramic membranes can be subject to erosion from particulates in the feed stream, colliding with the membrane surface due to their materials of construction and manufacturing method. Fortunately, more durable ceramic membranes with abrasion resistance exist as seen in other applications, where ceramics are specifically used for their abrasion resistance quality in applications like powdered activated carbon and ceramic bearings.

Applications

Potable Water Applications

The use of ceramic membranes to produce potable water in the United States is limited to a half dozen installations as of 2017. In Japan, there are over 130 potable water facilities using ceramic membranes dating back to 1998, where the facility is still using the original membranes. A drinking water plant in Japan rated at 46 MGD, treating surface water was commissioned in April 2014. Several 1 MGD drinking water plants have been installed in Delaware, Texas and Mississippi and have been in operation in the USA since 2014. A 10 MGD plant treating reclaimed secondary effluent and surface water from a reservoir for indirect potable reuse stated up in January 2015 in Parker, Colorado

Food and Dairy Industry

The food and dairy industry has embraced ceramic membranes for their unique properties. There are a number of installations around the world using these products for their sanitization properties and durability. The majority of ceramic membrane applications in the dairy industry are for Extended Shelf Life (ESL) milk where polymeric membranes simply will not work. In addition, there are systems operating that are used to defat whey, curd cheese and other dairy products. Another application that has been using ceramic membranes is the fractionation of whey proteins in the cheese making process.

Additional applications of ceramic membranes in food industry is in for beverage applications, such as juice clarification, s and beer production that require daily cleanings and, in many cases, thermal and chemical sanitization. Other applications include cell separation in amino acid production, lactic acid production, fermentation broth treatment, oil/water separations and sugar syrup production.

Chemical Industry Applications

Ceramic membranes are used in industrial applications that include oil/water separations, catalyst recovery, textile needs, waste water and even alkaline cleaning solution recovery. Applications to treat produced water that might be high in oil and grease, which are problematic for polymeric membranes are using ceramic membranes. Facilities in Colorado, Texas and Alberta have been installed to treat oil laden waters. Additionally, there are gas phase separations that use ceramic membranes, including separation of hydrogen from the waste steam of refinery and gasification plants, as well as separation of carbon dioxide from natural gas to a concentration of less than 2% for pipelines of natural gas.

Sanitary Waste Water Treatment

Ceramic MBRs are now being considered in the United State but may find market share in industrial MBR and smaller municipal MBR applications. Ceramic membranes can be an effective integrity barrier for pathogens and this will be a key consideration for log removal credits in potable reuse applications including their use in MBRs

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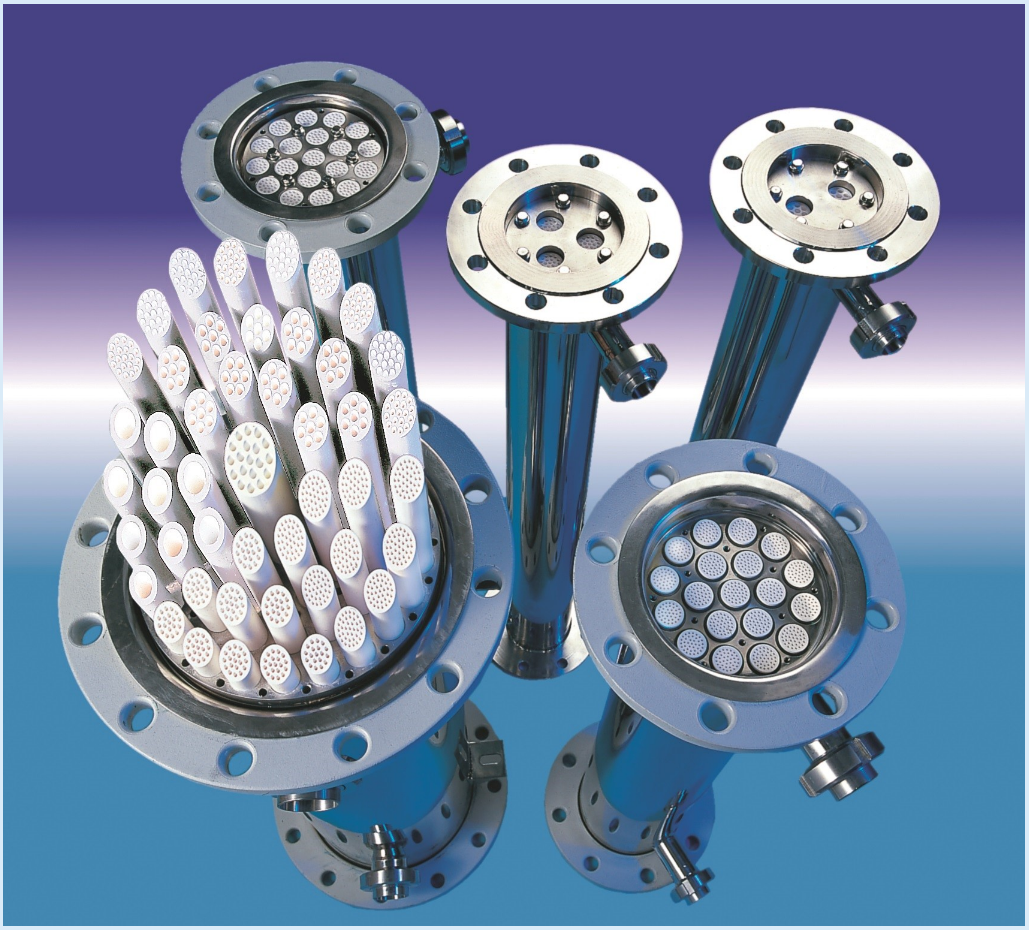
Other Applications and Considerations

Ceramic membrane's durability, wide range of thermal and chemical stability and long lifecycles make them ideal candidates for difficult applications that would otherwise foul polymeric membranes and limit their useful life. Although ceramic membranes have traditionally been more costly than polymeric membranes, recent innovations such as; increasing surface area, reducing cleaning complexity and reducing manufacturing costs have made them more competitive. As their volume grows, especially where lifecycle costs and value are considered, ceramics will find increased use in water treatment and other applications due to these advantages.

Ceramic membranes do not remove dissolved components like reverse osmosis membrane, but do a very effective job of removing very fine solids and larger molecules and coagulated dissolved organic carbon (DOC) from solution. However, some ceramic membranes entering the market are in the nanofiltration range and may exhibit some salt rejection. Ceramic membrane systems have also been used as a pretreatment prior to ion exchange and reverse osmosis systems.

Conclusion

Ceramic membranes have many desirable properties and are being used extensively in water purification, food and dairy applications as well as for industrial needs. These market uses of ceramics will continue to increase. As ceramic membrane production volume grows and product innovations reduce the capital cost, use of ceramic membranes will increase. They will be more prominent as they are better understood for use in potable water, waste water recycling, reuse, and even produced water in the oil field.



This material has been prepared as an educational tool by the American Membrane Technology Association (AMTA). It is designed for dissemination to the public to further the understanding of the contribution that membrane water treatment technologies can make toward improving the quality of water supplies in the US and throughout the world.

For more information, please contact:

American Membrane Technology Association (AMTA)
2409 SE Dixie Highway
Stuart, Florida 34996
Phone: (772) 463-0820
Fax: (772) 463-0860
Email: admin@amtaorg.com

or visit our website at:
www.amtaorg.com