

# Back to Ceramics

Centuries old material proves its mettle in maximizing financial and operational performance

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**F**or almost 25 years, managers and owners of municipal drinking water facilities have relied on polymeric ultrafiltration membrane systems to address the risk of microbial contamination. These membrane systems have their merits. However, operators also have experienced

shortcomings, such as short membrane life and an inability to handle variable feedwaters or recover from upset conditions. Ceramic membranes, on the other hand, have shown to be especially effective at handling upsets partially due to their ability to be cleaned more aggressively particularly in challenging water

**Lake Dunlap Water Treatment Plant in New Braunfels, Texas, is the largest drinking water ceramic membrane facility in North America.**

Nanostone Water

systems. These factors have made the technology a viable alternative to polymeric membranes.

Ceramic-membrane technology has existed for centuries — in various forms. (See “Ceramic Membranes Through History” on p. 46.) Today, any membrane that has at least one layer made of ceramic material is classified as a ceramic membrane. Inorganic membranes on a metal or glass support and hybrid membranes with an organic template or top layer are both examples of today’s ceramic membrane.

The most common materials used to manufacture ceramic membranes are alumina, silica, titania, and zirconia (zirconium dioxide  $ZrO_2$ ). Silicon carbide (SiC) membranes are a more recent development and have demonstrated very high permeability in water treatment applications but are more expensive to produce. Therefore, they have much higher capital costs.

## Configuration Evolution

The first ceramic membranes for liquid separation were tubular. These were single or multichannel cylinders of ceramic with a membrane made of the same raw material in a different structure on the inner surface. Tubular ceramic membranes are still used for many industrial applications, but they are not feasible for use in relatively large-scale drinking water or wastewater facilities because of high footprint requirements, as well as high operating and capital costs. There are, however, three ceramic membrane configurations that have been successfully used in large-scale drinking water and wastewater facilities.

**Flat sheet membranes.** In the flat sheet ceramic membrane configuration, a flat sheet of ceramic is cast with channels inside it. The flow of filtration is outside-in. The sheets are packaged in a module, which can be submerged in a tank of fluid for filtration. Vacuum is applied to the permeate side and clean water is pulled through. Flat sheet ceramic membranes can be physically cleaned by air scrubbing from the bottom or spraying water under high pressure from the top, as well as disassembling the module and scrubbing the plates manually or with a high-pressure water gun. Flat sheet ceramic membranes can be used on sources with total suspended solids concentrations up to 20,000 mg/L. This configuration is well-suited to sources that can be very challenging like membrane bioreactors.

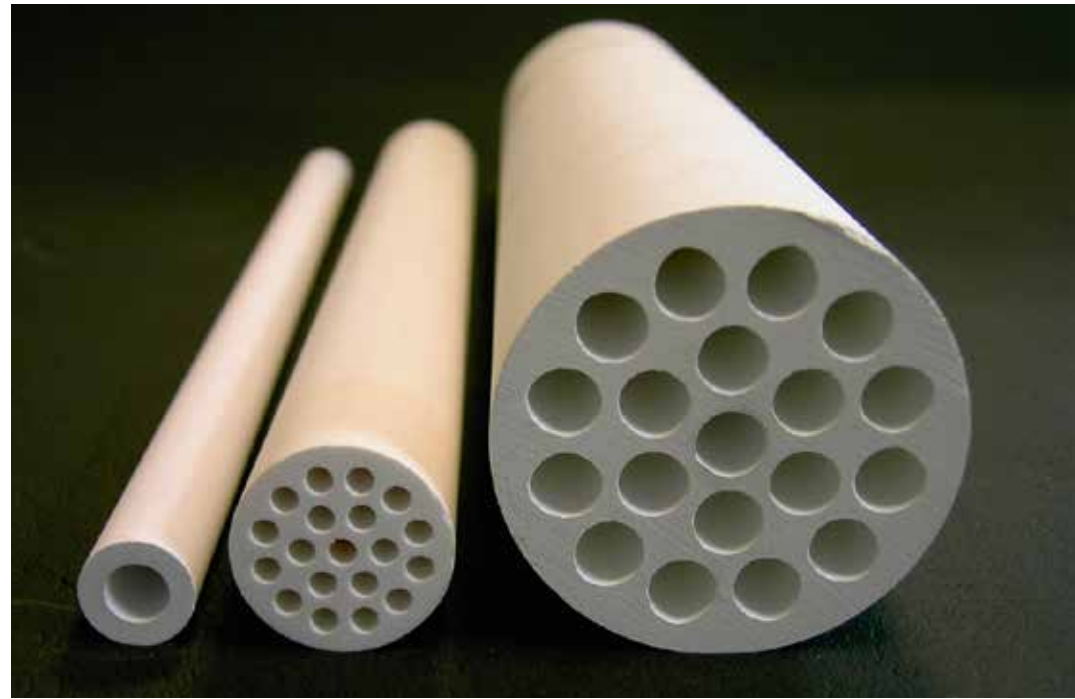
**Monolith membranes.** The monolith membrane configuration also can be used in both drinking water and wastewater facilities. This configuration was developed to address issues of packing density and cost. In this configuration, a cylinder is extruded with internal flow channels on which additional layers of ceramic particles are coated. This creates a very high membrane packing density, which addresses the footprint issues of tubular products and adds mechanical robustness. Although lower in cost per unit of membrane area than flat plate membranes, the monolith can still be a relatively expensive configuration because of manufacturing challenges, such as the consistent extrusion of the cylinder and the subsequent yield losses associated with the complex production process. The monolith configuration did, however, make it more feasible for large-scale applications. This configuration reduces the capital costs and footprint compared to tubular and flat sheet configurations. This results in an increase in installed capacity at utilities.

**Segmented monolith membranes.** The fourth type of ceramic membrane configuration that can bring value to drinking water and wastewater facilities is the segmented monolith configuration. Segmented monolith membranes were developed to lower the cost per unit of membrane area in relation to both flat sheet and monolith membranes. In this configuration, flat sheets are extruded and assembled to make a monolith. The extrusion process is simpler than a monolith because losses and risk of deformation in production are reduced, leading to overall yield improvement in the finished product.

## Polymeric Membranes

Microfiltration and ultrafiltration polymeric membranes were first installed in large-scale municipal drinking water facilities in the 1990s, driven by the need for utilities to provide absolute barriers against suspended solids and microorganisms — particularly chlorine-resistant *Cryptosporidium* and *Giardia* — in the drinking water supply.

Polymeric membranes — typically hollow fiber modules — were used for these applications because they offered a complete barrier against contaminants. The first hollow fiber membranes initially were made from cellulose acetate. Those rapidly were followed by new polymers based on polysulfone (PS), polyethersulfone (PES), polypropylene (PP), and polyvinylidene fluoride (PVDF) chemistries. They initially were used by utilities in North America and Europe and gradually expanded for global use.



**In the evolution of ceramic membrane configuration, the first ceramic membranes for liquid separation were tubular.** Nanostone

Polymeric membranes work well, but struggled to achieve the promised capacity, particularly when dealing with variable water quality. When water quality changed — for example, seasonal lake inversions, algal blooms,

chemical exposure meant installed membrane life was shortened beyond original expectations and fiber integrity issues occurred with regularity in the field, requiring an excessive amount of labor to maintain the systems.

**Over the last decade, several ceramic membrane suppliers have entered the market.**

high turbidity events caused by snowmelt — polymeric membranes fouled more quickly than they did under normal conditions. This led to more frequent cleanings being needed to maintain facility performance. The additional

**Competitive Advantages**

Over the last decade, several ceramic membrane suppliers have entered the market. They aggressively began to pursue municipal water projects based on the technical and economic competitive advantages of advanced flat sheet, monolith, and segmented monolith ceramic membranes over polymeric membranes. The manufacturers promote the following as distinct competitive advantages when using ceramic membranes.

**Longer life expectancy.** Building a new water facility is a significant expense for a community, and it is generally expected that these facilities should last for decades — including the core technology components. With polymeric membranes, depending on the type of polymer and the chemical and hydraulic stress, lifetime varies between 1 and 8 years, with an average of 5 years. The typical warranty for polymeric membranes is 5 to 7 years.

In contrast, ceramic membranes can last as long as bricks, pipes, and tanks in a facility. For example, the original ceramic membranes installed in 1997 at the Shin-Yamashina Purification Plant in Kyoto, Japan, are still operating efficiently and

effectively today. In addition, most suppliers of ceramic membranes offer a 20-year warranty on their products when they are used in drinking water treatment applications.

**No fiber breakage.** Among the most significant disadvantages of polymeric hollow fiber membranes for drinking water facilities is fiber breakage, which allows potentially harmful contaminants to pass through the membrane to the clean water side. Polymeric membranes, when exposed to high temperatures, hydraulic stress, and chemical cleaning, develop integrity failures over time. This degradation is measured regularly via integrity tests. In some documented cases, the polymers are pierced by small, sharp objects in the incoming water, such as diatomites.

Failed membranes must be isolated from the skid, removed, and manually repaired in the field. This is a time-consuming and labor-intensive process, which is carried out by costly full-time dedicated fiber repair teams in some water treatment plants. As more and more fibers are damaged, the capacity of the membrane to filter water is reduced, putting even more stress on the system and accelerating the rate of fiber failures.

In contrast, ceramic membranes do not contain any fibers that can be damaged in this manner. Ceramic membranes simply do not have a fiber integrity issue.

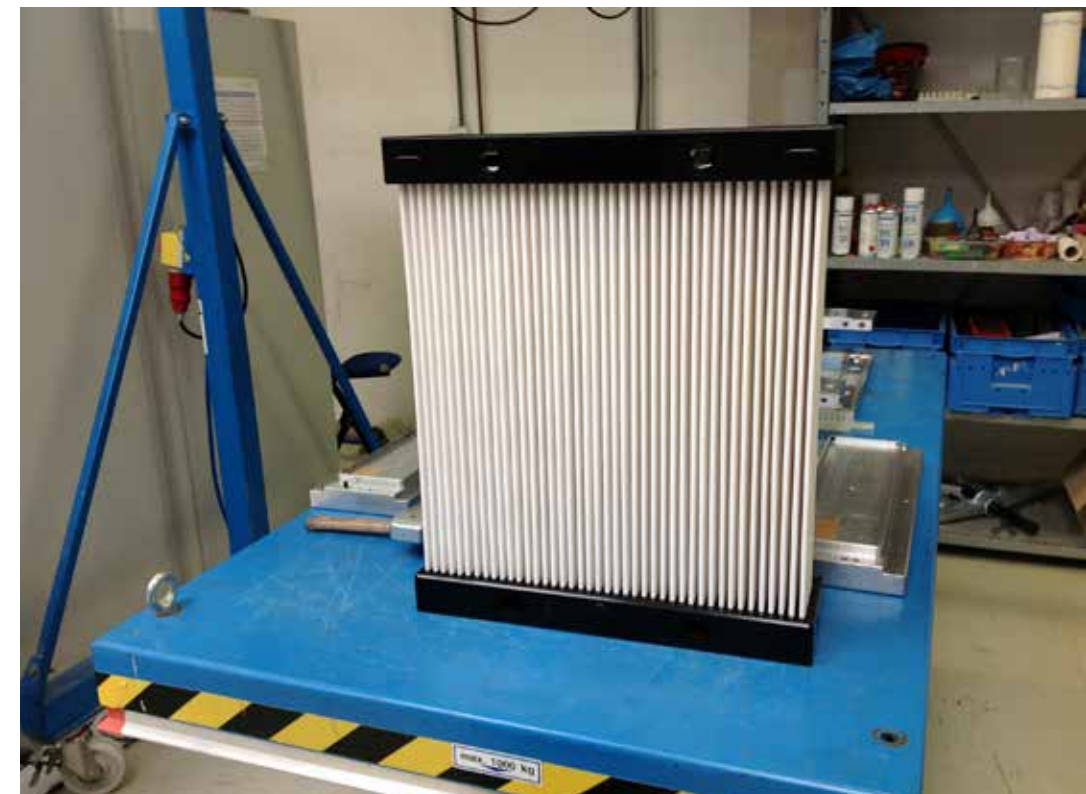
**Easy cleaning and disinfecting.** Polymeric membranes are organic compounds and deteriorate with exposure to high and low pH. They can also be attacked and destroyed by such oxidants as peroxide, ozone, and hypochlorite. This limits the ability of drinking water facilities to clean and disinfect, because operators can only expose polymeric membranes to limited doses of oxidants.

Polymeric membranes also are limited in their ability to resist high temperatures. Most hollow fiber polymeric membranes for water treatment are limited to a maximum temperature of 40°C (104°F).

Conversely, ceramic membranes are inorganic and, as a result, can withstand continuous exposure to oxidants. In addition, ceramics can handle both high and low pH.

Ceramic membrane systems also have much higher temperature limits than polymeric membranes. Temperature limits for a ceramic system are determined, not by the ceramic elements, but by other components of the skid. These higher temperature limits — up to 55°C (131°F) — combined with the chemical resistance of ceramic membranes, give operators flexibility in cleaning their fouled ceramic membranes, which ultimately leads to lower life-cycle costs.

**Higher permeability.** Ceramic membranes are three to four times more permeable than polymeric membranes. This means ceramic



**Flat sheet ceramic membranes contain a flat sheet of ceramic cast with channels inside it.** Nanostone

## Ceramic Membranes Through History

Ceramic membranes for water treatment have a long history. The original ceramic membranes were unglazed terra cotta pots used in ancient times all over the world. They have been found in ancient Roman sites, as well as archaeological sites in Asia. Functioning much as today's sand filters, they were used to remove particulate matter from water prior to use for drinking or other needs.

The modern history of ceramic membranes begins with the Manhattan Project, the American effort to develop nuclear weapons. While many aspects of that work are still classified, we know that researchers needed to develop a method to separate U-238 and U-235 isotopes. This process

required feeding highly corrosive UF<sub>6</sub> through semi-permeable membranes at high temperatures. The only materials feasible for this were oxides, such as alumina (Al<sub>2</sub>O<sub>3</sub>), titania (TiO<sub>2</sub>), and zirconia (ZrO<sub>2</sub>). This gas diffusion process for uranium enrichment was developed in the 1940s and refined through the 1950s to continue to improve efficiency and cost.

Initially, applications of these membranes for liquid separations were not successful due to low flux. However, in the 1970s and 1980s, researchers developed the first functional ceramic membranes for liquid separation. This was based on a multi-layer structure that gives the membrane its physical strength and is highly permeable.



Original ceramic membranes were unglazed terra cotta pots, such as these from a Roman groundwater treatment at Emporion, Spain, that operated circa 300 BC. Mary Harrsch/Wikimedia Commons

membrane systems consume less energy than polymeric membrane systems. This is because the extremely porous and hydrophilic nature of ceramic membranes, particularly when compared to oleophilic polymeric membranes. Higher permeability means lower pressure for the systems, which translate into lower energy consumption for the facility.

### Market Share Increases

Installations of ceramic membranes have dramatically increased during the past 6 years. In fact, total installed capacity of ceramic membranes for drinking water now exceeds 2.2 million m<sup>3</sup>/d (500 mgd). While this is a fraction of the total installed capacity of polymeric membranes today, market share for ceramic membranes is increasing rapidly, including both greenfield and retrofit applications.

Among the growing number of water facilities that have opted to use ceramic membranes is the Chao Chu Kang Water Works (CCK) in Singapore, the largest ceramic membrane drinking water facility in the world.

Commissioned by the Public Utilities Board (PUB) in 2019, the facility installed the PWNT Water Technology (Velsorbroek, Netherlands) Ceramac design with ceramic membranes supplied by membrane producer Metawater (Tokyo, Japan). Using this module configuration, the facility is extremely compact. It is also the first large-scale application of ceramic membranes with ozone. Operating with residual ozone on the membrane surface, the 181.7 million m<sup>3</sup>/d (48 mgd) facility operates at a flux of 240 to 315 L/m<sup>2</sup>•h.

This greenfield facility was designed from the beginning to use ceramic membranes. This permitted all systems, including pretreatment and backwash, to be optimized for operation of the ceramic membranes, delivering the lowest overall lifecycle cost and maximizing the volume of product water for the facility.

### Focus on Retrofits

While most of the facilities employing ceramic membranes have been greenfield facilities, Nanostone Water (Waltham, Massachusetts) has focused on retrofitting struggling polymeric membrane facilities. Over 2 years, Nanostone Water completed four drinking water facility retrofits in the U.S., using as much of the existing infrastructure as possible.

The largest of these facilities is the Lake Dunlap Water Treatment Plant in New Braunfels, Texas, which had struggled to meet capacity targets as source water quality deteriorated.



The segmented monolith contains flat sheets that are extruded and assembled to make a monolith. Nanostone Water

The facility was originally designed to produce 54.5 million m<sup>3</sup>/d (14.4 mgd) with polymeric membranes installed in the early 2000s. Within a year of switching to the ceramic membrane installation, the facility successfully conducted a 30-day run to demonstrate its ability to achieve the 54.5-million m<sup>3</sup>/d (14.4-mgd) capacity. This equates to a flux of 220 gal/ft<sup>2</sup>•d and recovery of more than 97%. This is the largest drinking water ceramic membrane facility in North America.

### Technologically Efficient, Cost Effective

The technical advantages of ceramic membranes have long been recognized in a variety of water treatment conditions. They continue to gain traction in the marketplace because — among other things — they meet the need of utilities relying more on difficult feed water sources.

Now, thanks to advanced manufacturing techniques and optimized application designs, ceramic technology is becoming increasingly cost-effective as well. The longer life cycles and lower operating costs of ceramic membranes, coupled with their technical advantages, have contributed to their adoption by a growing number of large-scale drinking water facilities around the world. ↘

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