Ceramic Nanofiltration – Challenges Regarding Membrane Geometries and Materials

For certain applications the use of polymeric membranes is not a viable option due to material requirements and/or economical demands. As a result of high chemical and thermal resistance as well as their inert characteristics, ceramic membranes excel in these areas. Especially since the invention of ceramic membranes for nanofiltration, a wide range of applications for ceramic membranes have opened up. Further developments made the introduction of ceramic membranes into new, previously closed, markets possible – such as the field of drinking water treatment and wastewater technology.

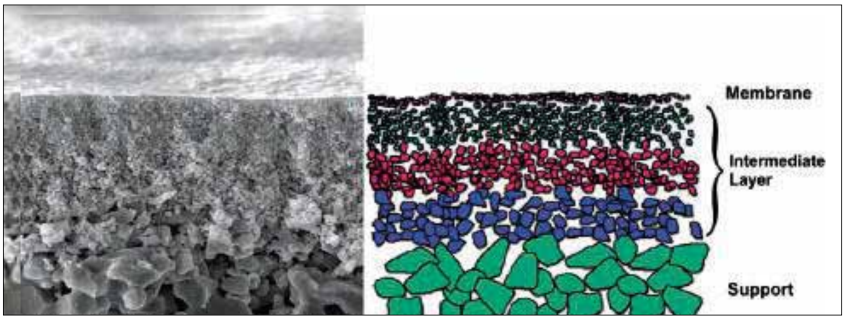

Fig. 1
Overview of support structure and interlayers of a ceramic membrane

First steps and developments
The first ceramic membranes were introduced in the 1940s, nearly a century ago, after being developed for the purpose of uranium enrichment. Soon after, they were manufactured and advertised at an industrial scale. During the last decades, the current membrane structure has been optimised through numerous research projects, establishing ceramic filtration as a real alternative wherever fluid streams are to be separated purely mechanically (without utilizing chemical or thermal properties). On top of a stabilizing, coarse-porous supporting structure (different geometries, e.g. tube, plate, disc etc.) multiple interlayers with decreasing pore sizes are applied (Fig. 1). The last layer embodies the active layer for the filtration process through which solid particles, bacteria and viruses are separated from the solution.

Polymeric membranes provide a cost advantage (specific price per membrane area) compared to ceramics but are limited by their relatively poor mechanical and chemical properties. For many years, they possessed unique selling points for both nanofiltration and reverse osmosis until the first ceramic nanofiltration membranes with a cut-off of 450 Da [g/mol] were developed at the Hermsdorfer Institute for Technical Ceramics (HITK), nowadays Fraunhofer IKTS [1, 2]). In cooperation with inopor®, a Rauschert brand, initial production capabilities were scaled up to allow for industrial scale production.

Keywords
nanofiltration, ceramic membrane, membrane design, hydrophobic membranes

State-of-the-art
Today, ceramic membranes can be found in the process chains of various industries, such as the food processing industry (e.g. dairy processing, fruit juice and wine preparation), the medical sector (cleaning of fluids, e.g. separation of bacteria and viruses) and sectors with highly toxic wastewaters (e.g. oil and gas, textile and chemical industry). Aside from high chemical and thermal resistances, their inert

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Tab. 1
The membrane portfolio of inopor®

	Membrane Material	Pore Size [nm]	Porosity [%]
Microfiltration inopor® micro	α-Al_2O_3	800	40–55
		600	
		400	
		200	
		100	
		70	
	TiO_2	800	
		400	
		250	
		200	
		100	
	ZrO_2	110	

	Membrane material	Pore Size [nm]	Cut-Off	Porosity [%]
Ultrafiltration inopor® ultra	γ-Al_2O_3	10	20 kDa	30–55
		5	7500 Da	
	TiO_2	30	100 kDa	
		10	20 kDa	
		5	8,5 kDa	
	ZrO_2	3	2 kDa	
Nanofiltration inopor® nano	TiO_2	1,0	750 Da	30–40
		0,9	450 Da	
		LC*	200 Da	

** These are the newest nanofiltration membranes and can only be manufactured currently on a laboratory scale*

properties are important, especially for food and pharma products.

As part of the Rauschert Distribution GmbH, inopor® offers a wide range of membranes with different geometries (from 1 to 163 channels), lengths (100–1200 mm) and pore sizes (0,9–800 nm) and thus covers the entire spectrum of ceramic filtration (Tab. 1). Membranes can be classified in three categories dependent on pore sizes: microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF).

The active layer of a ceramic membrane is generally described as a porous layer through which particles are filtrated purely mechanically due to the size exclusion principle. No additional substances are needed for a successful filtration. Diluted acids, alkaline solutions or ready-made cleaning solutions are merely used to keep the membranes clean and ensure a cost-efficient filtration process over time.

Since the development and commercial launch in 2000, Fraunhofer IKTS and inopor® have consistently improved material properties and filtration efficiency and still remain the only supplier of membranes with pore sizes below 1 nm.

The Rauschert Distribution GmbH sells ceramic membranes in tubular geometries for cross-flow filtration. Many steps are necessary for their production: at first, the ceramic powder is mixed with additives and formed through an extrusion process (Fig. 2). After a defined drying and firing cycle to create the support structure, the respective interlayers are applied and burned in (each with their separate drying and firing cycle) with the active layer as the final one.

The finished membrane elements are integrated in stainless steel modules/housings as portrayed by Fig. 4. The number of elements required for a specific application depends on the surface area needed for filtration. The module can then be fitted accordingly. Depending on the type of separation and process parameters, membranes can be arranged parallel or in series. O-ring seals on both sides of the tubes seal them off towards the steel

Fig. 2
Extrusion process of a membrane element

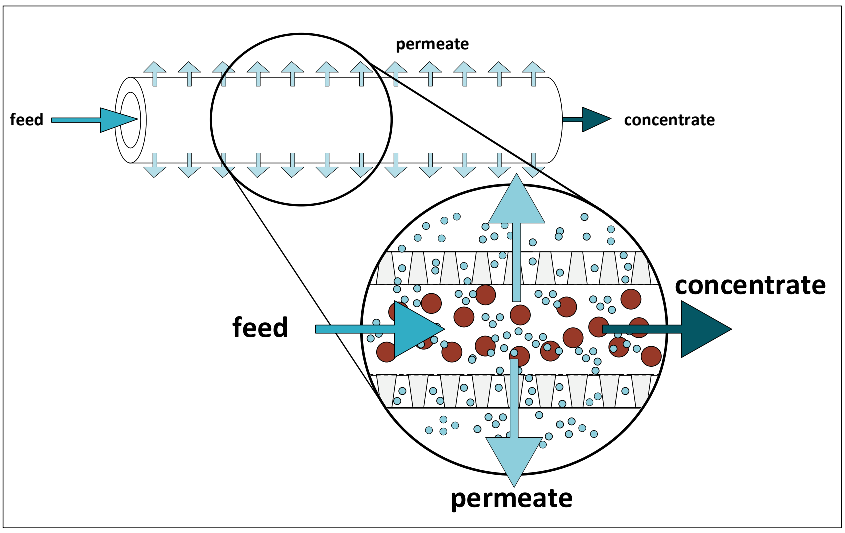

Fig. 3
Illustration of the filtration principle and corresponding mass flows

Fig. 4
Example of a stainless steel housing with 55 ceramic elements (Photo: Della Toffola S.p.A.)

housing (permeate side), thus forcing the flow of the incoming medium (feed) through the membrane channels. The filtrated medium (passed through the active layer) is called permeate. The part of the feed that is leaving the channel is called concentrate or retentate (Tab. 1).
Short circuit flows, i.e. a direct connection between feed and permeate are thus prohibited. The retentate is usually returned to the feed vessel – it is recirculated until a target concentration (volume concentration factor) is reached. The permeate gets collected separately.
The driving force for the filtration process is a transmembrane pressure difference – the pressure difference between the feed and permeate side of the membrane. Each layer of the ceramic membrane creates a certain flow resistance which has to be overcome to create a flow through the membrane itself.

Advanced engineering
Recent developments show the increasing significance of ceramic membranes for the separation of dissolved substances, respectively a partial desalination and softening of water streams. In 2013, as part of the project Nanomembrane (FKZ 03X0080, funded by the German Federal Ministry of Education and Research), it was possible to even further decrease the cut-off to 200 Da [g/mol] [3]. Initial systematic studies of flow behaviour, detention and chemical stability have shown satisfying results, opening the door to test the membranes in various possible applications.
In addition a ceramic membrane type with hydrophobic characteristics was developed to improve the possibility to treat even organic solvents in a proper way. Using a polystyrene mix, the cut-off of this membrane was measured with 350 Da [g/mol] (solvent: tetrahydrofuran, transmembrane pressure: 20 bar). However, tests with different organic solvents lead to widely different values in the (pure) solvent flux and cut-off, depending on the solvent and solute combination. For a first series of tests membrane elements were produced on a laboratory scale but meanwhile possibilities for a large scale production of membranes with 7, 19 or 61 channels per element respectively exist. The surface area of a single 61 channel element, for example, average 0,51 m^2 for 1200 mm in length.

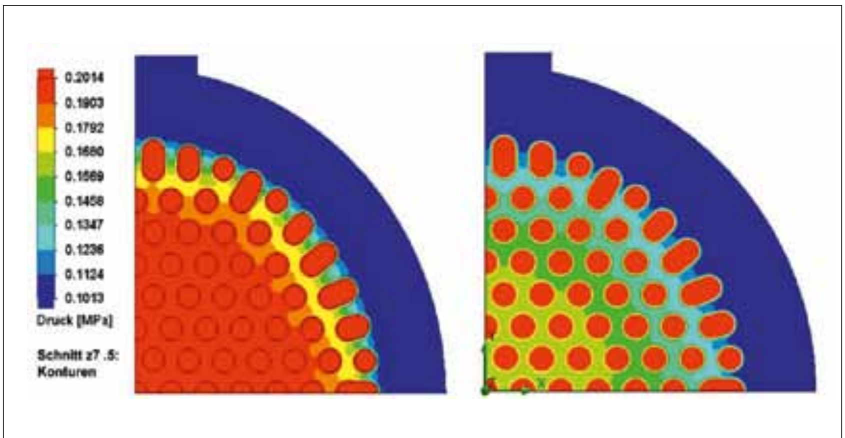

Fig. 5
Pressure distribution of 163 channel membrane elements with different active layers: UF (l.), and NF (r.)

To increase the competitiveness of ceramic membranes over polymeric alternatives, compactness (filtration area per element) has to be increased and overall costs (lower price per membrane area) decreased. One option for a more cost-effective production involves the manufacture of membrane elements with higher filtration areas. This can be achieved through the increase of tube diameters and the amount of channels at the same time. Currently, inopor® membranes have a maximum outer diameter of 41 mm. Compared to smaller variations (e.g. DA = 25 mm), the inner membrane channels of these elements become more and more ineffective for the filtration as diameter (and the amount of channels associated with it) increases. This observation is in accordance with flow simulations (CFD, Computational Fluid Dynamics) and extensive flux measurements. The permeate that passes through the entire membrane/support structure creates a stagnation pressure within it. This pressure is detrimental to the main driving force of the filtration process (transmembrane pressure difference) and hence results in loss of performance. The more permeate is discharged per membrane area, the more pronounced the effect. Thus microfiltration membranes (usually with higher flow rates) are more problematic than membranes for ultra- and nanofiltration (Fig. 5).
It is pivotal to find the right balance between the amount of channels and the efficiency of the membrane area relevant for filtration.
Taking these issues into consideration, an increase of the individual surface area per element during membrane development was deduced as the most sensible approach since this step is also the most cost-intensive during production. Based on these findings, which were in part established within the framework of a research project funded by the European Union [4], different solution have emerged.
For one, a new support material showing 15 – 20 % higher permeate flow rates (—>decrease of stagnation pressure) in initial clear water flux is being researched. On the other hand a geometrical change of the supporting structure towards newly developed circular segments is used to counteract negative pressure effects. As

a first result tubular membrane elements with 75 mm outer diameter and 563 channels were produced. For this industry-driven development project first screenings of membrane elements for process water recycling have been started. Previously unattractive market segments (from the user's point of view), e.g. drink water preparation and communal/industrial waste water purification, could be tapped with these innovative and durable new membrane elements.
Especially process water intensive branches, e.g. textile inward processing, textile production or the paper and pulp industry can benefit from these advancements of the ceramic membranes. Exemplary, Fig. 6 portrays both feed and permeate for different textile process waters. The first permeate shows some residues since particles are smaller than the 450 Da cut-off of the active layer used.

Ceramic applications

With the invention of ceramic nanofiltration membranes, a wide range of markets for ceramic membranes was opened. Different applications for ceramic membranes are presented in Tab 2.

Tab. 2
Fields of applications for ceramic filtration membranes

Separation Process	Application
Microfiltration	milk fractioning
	bio-mass separating
	pre- and clear-filtration of liquids
	oil-water-separation
Ultrafiltration	germs and virus retention
	milk fractioning
	oil-water separation
	acids and alcalis recycling
Nanofiltration	demineralisation/softening (retention of mono and divalent ions)
	pharmaceutical separation
	decolorisation
	removing dissolved organic

Fig. 6
Visual differences between feed and filtrated permeate

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